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## Deep-Sea Research II

journal homepage: [www.elsevier.com/locate/dsr2](http://www.elsevier.com/locate/dsr2)

# Shifting frontal regimes and its influence on bioproductivity variations during the Late Quaternary in the Indian sector of Southern Ocean

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## ARTICLE INFO

Available online 28 March 2015

## Keywords:

Opal; carbonate; productivity; Palaeoceanography; Antarctic front; Late Quaternary; Southern Ocean

## ABSTRACT

Reconstruction of palaeoproductivity from Southern Ocean is crucial for understanding the functioning of the Southern Ocean biological pump in the past. High resolution records of multi-proxy parameters (calcium carbonate, opal, total organic carbon biogenic barium and planktonic carbon isotope ratios ( $\delta^{13}\text{C}$ )) were investigated in two well-dated sediment cores (SK200/22a and SK200/27) from the Indian sector of Southern Ocean situated to the north and south of Antarctic Polar front (APF), respectively. The palaeoproductivity records extending ~95 ka BP (SK200/22a) and 75 ka BP (SK200/27) revealed inverse relationships between the calcite and opal productivity, indicating the influence of shifting nutrient regimes. At core SK200/22a, reduced calcite productivity during marine isotope stage (MIS) 2, 4, and part of MIS 3 suggest an equatorward migration of the frontal regimes during glacial intervals. Compared to this, the region south of the APF (core SK200/27) was characterized by the near absence of calcite content during the last glacial period and increased opal productivity during MIS 1 and MIS 3, supporting a southward migration of APF during warmer intervals.  $\text{Ba}_{(\text{bio})}$  records exhibit good correlation with opal records in both the cores and also correlate with that of calcite record at SK200/22a, indicating that Ba is influenced by the combined opal and calcite productivity. The enhanced opal productivity during the glacial periods north of the APF is attributed to the northward shifting of oceanic fronts and associated transfer of nutrients. Diatom productivity records of SK200/22a reveal significant similarities with the dust records from the Antarctic and Southern Ocean, but showed no significant relationships with the diatom record of SK200/27. It is proposed that the dust-derived Fe input had apparently influenced the palaeoproductivity north of the modern APF, but had a minor influence on opal productivity south of the APF. Comparison with the ice core climate records from Antarctica and Greenland revealed that bioproductivity peaks in the study region are nearly synchronous with the millennial Antarctic warming events. Remarkably, the calcite and opal productivity records at SK200/22a responded differently to the Antarctic warming events, with opal productivity lagging behind the calcite productivity peaks by ~1–2 ka.

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## 1. Introduction

The Southern Ocean is considered as a key region in understanding the role of biogeochemical cycling on global climate change (Marinov et al., 2006). Southern Ocean sediments are a significant sink for some bioactive elements (DeMaster, 2002) and are potential sources of many other essential micronutrients (Pollard et al., 2002). The magnitude of the biogeochemical fluxes to the sea-floor sediment depends on the vertical fluxes of material from the upper ocean as well as on the preservation

efficiency of each component in the sediments. Biological productivity in the Southern Ocean is primarily controlled by the upwelling of the old, cold, and nutrient-rich water to the surface, the extent of sea ice coverage, light and micronutrients (Dezileau et al., 2003; Stenni et al., 2010). These wind driven upwelled waters subsequently subduct into the subsurface waters and flow northward and circulate to the lower latitudes (Toggweiler et al., 1991). Studies have shown that the processes determining the properties of Subantarctic Mode Water (SAMW), and the mechanisms leading to its formation in the Subantarctic Zone, are crucial in determining the supply of nutrients to the subtropical thermocline and low latitude productivity (Sarmiento et al., 2004). Biological utilization of nutrients is thus important in the

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Southern Ocean, which regulates the global efficiency of the biological pump (Sigman and Boyle, 2000; Marinov et al., 2006).

Proxy records from the Southern Ocean are important for reconstructing the palaeoclimatic and palaeoceanographic history and improve our understanding of the role of biogeochemical cycling in influencing climate and ocean-atmosphere carbon exchange over longer timescale (Francois et al., 1997; Anderson et al., 2009; Yu et al., 2014) and CO<sub>2</sub> degassing. Previous workers have used several proxy records like accumulation rates of biogenic detritus, carbon isotopic composition of foraminiferal calcite, and trace elemental concentrations, have been used to infer the Southern Ocean palaeoproductivity (Labeyrie and Duplessy, 1985; Mortlock et al., 1991; Francois et al., 1997; Anderson et al., 1998, 2002, 2014; Bareille et al., 1998; Latimer and Filippelli, 2001, 2007; Tomczak and Liefbrink, 2005; Filippelli et al., 2007; Sruthi et al., 2012). In this region of high nutrients low chlorophyll (HNLC), Fe is considered to be an important limiting factor for the biological productivity that could directly influence the atmospheric CO<sub>2</sub> concentration (Martin, 1990; Kumar et al., 1995; Wolff et al., 2006; Martínez-García et al., 2009, 2014). Tagliabue et al. (2014) reported that winter mixing and surface-water iron recycling are also important drivers of temporal variations in Southern Ocean primary production. The glacial-interglacial difference in atmospheric CO<sub>2</sub> was attributed to increased dust fluxes during the glacial intervals leading to increased Fe fertilization of surface waters and subsequent increased export production in the Southern Ocean (Martínez-García et al., 2014; Anderson et al., 2014), contributing to the reduction of atmospheric CO<sub>2</sub> concentrations.

The Subantarctic Zone (SAZ) and the Polar Frontal Zone (PFZ) represents the largest High-Nutrient, Low-Chlorophyll (HNLC) regions of the world. At present, high productivity (dominated by diatoms) occurs south of 50°S between the Antarctic Polar Front and the winter sea ice edge due to the upwelling of deep waters that brings high concentrations of nitrate and silicate to the surface waters (DeMaster, 1981; Smith and Nelson, 1986; Leynaert et al., 1991). Proxy based reconstruction of biological productivity in this region would help in deciphering the past shifts in frontal regimes, associated changes in macro and micro nutrient uptake and functioning of the biological pump. Biogenic constituents, such as calcite (CaCO<sub>3</sub>), total organic carbon (TOC), opal (SiO<sub>2</sub>·2H<sub>2</sub>O) and barium (Ba) profiles of the sediment records have previously been used to reconstruct changes in past oceanic biological productivity (e.g. Charles et al., 1991; Mortlock et al., 1991; Samthein et al., 1992; van Kreveld et al., 1996; Anderson and Delaney, 2005; Anderson et al., 2009; Jaccard et al., 2013; Hendry and Brzezinski, 2014). However, some of the individual proxy records are unreliable as sediments are affected by diagenesis, burial, preservation and other environmental factors (Bloemendal et al., 1992; McManus et al., 1998; Schnetger et al., 2000; Burdige, 2007). While, there are some paleoproductivity records from the Southern Ocean, high resolution multi-proxy records are lacking from the Indian sector of the Southern Ocean. In this study, we have employed a suite of paleoproductivity proxy records (profiles of sedimentary calcite, TOC, opal, Ba<sub>(bio)</sub> and planktonic foraminiferal δ<sup>13</sup>C records) to understand the palaeoproductivity variability in the Indian sector of the Southern Ocean and compare the results with other regional and global records to better understand the climatic and oceanographic implications during the late Quaternary.

## 2. Materials and methods

Two sediment cores, SK200/22a (43° 42'S/45° 04'E; water depth – 2730 m) and SK200/27 (49° 00'S/45° 13'E; water depth – 4390 m) were collected in the year 2004 from the Indian sector of Southern Ocean (Fig. 1). The core SK200/22a was collected close to

the sub-Antarctic Front (SAF) and core SK200/27 close to the Antarctic Polar Front (APF) region. Age models are mainly based on Accelerator Mass Spectrometry (AMS) radiocarbon (<sup>14</sup>C) dates measured on the planktonic foraminifers, complementing the stable isotope and geochemical profiles of the cores with the stacked oceanic and ice core records from Southern Hemisphere (Manoj, 2014). In the absence of calcitic foraminiferal tests below 75 cm in the core SK200/27, additional chronological constraints were obtained using AMS <sup>14</sup>C dating of the total organic carbon in the sediments. All radiocarbon ages were calibrated to calendar ages, using the Calib 6 (Stuiver et al., 2005) with a ΔR value of 850 years (Bard, 1988; Berkman and Forman, 1996; Dutta, 2008) and all dates cited in the text are in calendar years BP. While there are spatial and temporal differences in the reservoir ages within the different sectors and frontal regimes of the Southern Ocean, it is well within the chronological uncertainties of the cores. Chronological controls beyond the limits of conventional radiocarbon dating technique were achieved by correlating the planktonic and benthic δ<sup>18</sup>O data with the established Antarctic ice core records (Byrd and EDML) (Blunier and Brook, 2001; EPICA Community Members, 2006), and LR04 δ<sup>18</sup>O Stack (Lisiecki and Raymo, 2005) as well as records from the Drake Passage in the Southern Ocean (Bae et al., 2003) (Fig. 2). The final age model is based on a linear interpolation between the control points, assuming that the signals documented in the Southern Ocean sediment cores and Antarctic ice cores are closely related to the climate variability in the rest of the Southern Hemisphere. Accordingly, the 7.54 m of the sediment core SK200/22a represents the past ~95 ka BP (95,000 years before present) and SK200/27 represents the past ~75 ka BP (75,000 years before present) (Fig. 3).

The present study investigates the down core profiles of calcite (CaCO<sub>3</sub>), total organic carbon (TOC), opal (SiO<sub>2</sub>·2H<sub>2</sub>O) and barium (Ba) concentration and planktonic foraminiferal δ<sup>13</sup>C records to better understand the past changes in biological productivity and the processes involved in their variability. All geochemical and stable isotope analyses were carried out at the National Centre for Antarctic and Ocean Research (NCAOR), Goa. The total organic carbon (TOC) and inorganic carbon (IC) concentration was measured using a Total Organic Carbon analyzer (TOC-V series SSM-5000A from Shimadzu). The analytical precision of the TOC measurements was ± 5%. The CaCO<sub>3</sub> content (wt%) was estimated from the inorganic carbon content, after Manoj et al. (2012). The biogenic silica (opal) content of the bulk sediment samples was measured using the base dissolution technique described by Mortlock and Froelich (1989). Biogenic silica was extracted from the bulk sediment by using 2 M Na<sub>2</sub>CO<sub>3</sub> and then measured by molybdate-blue spectrophotometry, using a BioTek® Synergy 2 Spectrophotometer. The analytical precision of the biogenic silica measurements was better than ± 1%. For the determination of Ba content, the dried and powdered sediment samples were dissolved by acid digestion and analyzed by inductively coupled plasma-mass spectrometry (ICP-MS- Thermo X-series with CCT). The standard deviation based on repeated analyses of the NIST standard (NIST 2702) for Ba was better than ± 5%. Oxygen and carbon isotope measurements were performed at selected depths on clean *Neogloboquadrina pachyderma* tests using an Isotope Ratio Mass Spectrometer (Isoprime, GV Instruments). The estimated external precision using a laboratory standard (Z-Carrara marble) for δ<sup>18</sup>O and δ<sup>13</sup>C are 0.10‰ for and 0.05‰, respectively.

## 3. Results

The down core variation of CaCO<sub>3</sub> (calcite), opal, organic carbon and Ba<sub>(bio)</sub> records of the sediment cores SK200/22a and SK200/27 are depicted in Fig. 4. The CaCO<sub>3</sub> content of the sediments varies

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