Geo-Mar Lett (2005) 25: 265–271
DOI 10.1007/s00367-005-0211-8

ORIGINAL

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Close correlation between Sr/Ca ratios in bulk sediments from the southern Cape Basin and the SPECMAP record

Received: 17 November 2003 / Accepted: 24 January 2005 / Published online: 17 March 2005

Abstract High-resolution records of Ca and Sr were obtained from shipboard XRF analyses of bulk sediments in five gravity cores from the southern Cape Basin, South Atlantic Ocean. Sr/Ca ratios display regular glacial/interglacial variations of 14–40% and reveal a close correlation with the SPECMAP record, minimum Sr/Ca ratios appearing during glacial (δ^{18} O) maxima, distinct increases during periods of deglaciation, and highest ratios in interstadials. Shifts in carbonate-producing phytoplankton and/or zooplankton assemblages over glacial/interglacial cycles are suggested to be the main cause for the observed variations in Sr/Ca patterns. Quick assessment of the relationship between Sr/Ca ratios and the SPECMAP record made it possible to easily transfer an age model to the newly collected cores already during the cruise.

Introduction

The oxygen isotope composition (δ^{18} O) of ocean water is determined by variations in the global ice volume, local temperature and salinity (Emiliani 1955; Shackleton and Opdyke 1973). Stacked foraminiferal δ^{18} O records from low-latitudinal and mid-latitudinal open ocean sites reveal strong coherency with orbital variations in precession (19 and 23 ka), obliquity (41 ka) and eccentricity (100 ka), and thus monitor oceanic responses to major changes in the global climate (Imbrie et al. 1984; Pisias et al. 1984; Martinson et al. 1987). These δ^{18} O records have been compiled into the SPECMAP (Mapping Spectral Variability in Global Climate Project) datasets (Imbrie et al. 1984; Martinson et al. 1987), which are widely used to correlate the oxygen isotope profiles of marine sediment cores worldwide and to assign ages to these cores.

In addition to being reflected in Foraminifera δ^{18} O records, glacial/interglacial sea-level cycles also influence the Sr budget of the ocean (Stoll and Schrag 1996). The amplitude of Sr/Ca variation in modern surface ocean water is less than 2% (de Villiers et al. 1994; de Villiers 1999). By contrast, Sr/Ca variation over Quaternary glacial/interglacial cycles has been reported to be in the range of 1–3% (Stoll and Schrag 1998), and is attributed mainly to the recrystallisation of shelf aragonite into calcite, resulting in increased Sr/Ca ratios during glacial maxima (Schlanger 1988; Stoll and Schrag 1998). Variable incorporation of Sr by carbonate-producing marine organisms is, however, controlled by diverse factors other than only seawater Sr levels. For instance, Sr incorporation by foraminifers and coccolithophores (gold-brown algae) has been suggested to vary on a species-to-species basis (e.g. Elderfield et al. 2000), or with changes in growth and calcification rates (e.g. Stoll and Schrag 2000), respectively. Thus, marine carbonate production, composition and amount of terrigenous components, and recrystallisation and dissolution of carbonate are all important in this context, making it difficult to unambiguously trace any single key cause of Sr/Ca variations in bulk sediments. Nevertheless, Sr/Ca patterns can give valuable insight into biogenic/hydrographic conditions in the geological past.

The southern Cape Basin, South Atlantic Ocean, lends itself well to investigating such aspects. The unique character of this basin results from its location at the southern extremity of the Benguela upwelling system, which is influenced by the intersection of several important water masses and current systems and, therefore, highly variable hydrographic conditions (e.g. Lutjeharms 1996; Shannon and Nelson 1996; Gordon 2003). The complexity of the Benguela system, which interacts at its southern and northern boundaries with the warm water regimes of the Agulhas Current and the Angola Current, respectively (e.g. Shannon and Nelson

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1996), renders it highly susceptible to shifts in species ranges. Previous studies in this region indicate sometimes subtle responses of various nanofossil and microfossil groups to changes in productivity, water temperature and water circulation (e.g. Giraudeau 1993; Giraudeau and Rogers 1994; Schmiedl and Mackensen 1997; Gingele and Schmiedl 1999; Abrantes 2000). Since 1981, the interdisciplinary Benguela Ecology Programme (BEP) has been concerned with the shelf and adjacent offshore waters off southern Africa (e.g. Lutjeharms et al. 1995; Boyd and Nelson 1998; Gammelsrød et al. 1998; Nelson et al. 1998; Skogen 1999; Steinke and Ward 2003; Demarcq et al. 2003), and the impacts of physicochemical variability on the shelf environment and its living resources (e.g. Crawford 1998; Mitchell-Innes et al. 1999; Griffiths 2003; Skogen et al. 2003).

RV Meteor cruise M 57-1 to the eastern South Atlantic Ocean was dedicated to the reconstruction of the Late Quaternary climate history of the southern Benguela system, and the influence of Agulhas warm water entrainment from the Indian Ocean into the South Atlantic Ocean (Schneider and Cruise Participants 2003). The primary objective of the present study was to assess any correspondence of Sr/Ca ratios in bulk sediments in the southern Cape Basin with the SPECMAP record (Imbrie et al. 1984, 1989; McIntyre et al. 1989). By correlating these data with a dated reference core, we also aimed to assign an age model to newly collected gravity cores, and this already during the cruise. Within this context, we performed shipboard XRF analyses on bulk sediments from the cores, using the new portable Spectro Xepos analyser (cf. Wien et al. 2005, this issue).

Materials and methods

During RV Meteor cruise M 57-1 in January/February 2003, altogether 19 gravity cores were recovered from the southern (and central) Cape Basin in the southern Benguela upwelling system (Schneider and Cruise Participants 2003). Onboard descriptions of cores from the southern Cape Basin provide evidence of the occurrence of foraminifer-bearing nanofossil ooze in several cases (cores GeoB 8303-6, GeoB 8307-6 and GeoB 8308-1) and, in one core (GeoB 8306-2), the sediment is described as foraminifer-bearing and coccolith-bearing mud (Schneider and Cruise Participants 2003).

The present study is based on data from four of these cores (Table 1, Fig. 1). Core GeoB 8301-6 is composed largely of mud and sand, core GeoB 8307-6 of foraminifer-bearing nanofossil ooze, core GeoB 8310-2 of mud and foraminifer-bearing sandy mud, and core GeoB 8315-6 of foraminifer-bearing mud.

The gravity cores were sampled at regular depth intervals of 4 cm, and the aliquots dried at 200°C in a laboratory oven and ground manually. For the shipboard elemental analyses, approximately 4 g of this material was poured into sample cups, firmly pressed to remove air from the interstices, and analysed using the compact benchtop energy-dispersive polarisation X-ray fluorescence (EDPXRF) analysis system Spectro Xepos (Wien et al. 2005, this issue). In all, 18 elements were measured (Si, Ti, Al, Fe, Mn, Mg, Ca, K, Sr, Ba, Rb, Cu, Ni, Zn, P, S, Cl and Br), only the Sr and Ca data being reported in the present study. Sr/Ca ratios were calculated as Sr (mg)/Ca (g). All XRF datasets presented here are available on the Pangaea database homepage http://www.wdc-mare.org/PangaVista?query=@Ref25740.

Table 1 Core number, geographic position, water depth and recovery of the gravity cores in the southern Cape Basin

Core no.	Latitude	Longitude	Water depth (m)	Recovery (cm)
GeoB 8301-6	34°46.00′S	17°41.54′E	1,952	879
GeoB 8307-6	33°50.43′S	16°31.99′E	2,667	843
GeoB 8310-2	32°54.57′S	16°22.92′E	1,993	833
GeoB 8315-6	32°53.30S	15°41.70′E	2,995	851
GeoB 2004-3	30°52.10′S	14°20.50′E	2,572	950

Gravity core GeoB 2004-3, collected in the northern part of the southern Cape Basin in February 1993 during RV Meteor cruise M 23-1 (Spieß and Cruise Participants 1993), had been analysed earlier in the laboratory at Bremen University, using the same analytical method as that aboard ship. In order to use this core as reference during the cruise, it was correlated with the giant piston core MD 962085 collected on the lower slope off Namibia during RV Marion Dufresne cruise NAUSICAA-IMAGES II in October/November 1996 (Bertrand and Cruise Participants 1997). This piston core has been dated based on Foraminifera δ^{18} O records (Chen et al. 2002). The age model was fitted by comparing colour reflectance data (700 nm) of MD 962085 (Bertrand and Cruise Participants 1997) with XRF Ca data of GeoB 2004-3. Any correlations between the cores were assessed on the basis of linear interpolation between tie points, using the software AnalySeries, Version 1.1 (Paillard et al. 1996).

Results

For the combined dataset comprising the five cores GeoB 8301-6, GeoB 8307-6, GeoB 8310-2, GeoB 8315-6 and GeoB 2004-3, average Sr/Ca ratios vary between 3.633 and 3.886 (Table 2). Core-specific variations in Sr/Ca range from 14% to 40%.

The data also suggest a latitudinal gradient in Sr/Ca variations within the southern Cape Basin. Thus, the largest ranges in Sr/Ca ratios were documented in the SE of the study area, the smallest in the NW (cf. Fig. 1, Table 2). Additionally, these variations seem to decrease with increasing water depth (range 1,952–2,995 m for the five cores; Table 1).

The Sr/Ca profiles show a close correlation between all analysed cores (Fig. 2). A comparison of these profiles with the SPECMAP record (Imbrie et al. 1984, 1989;

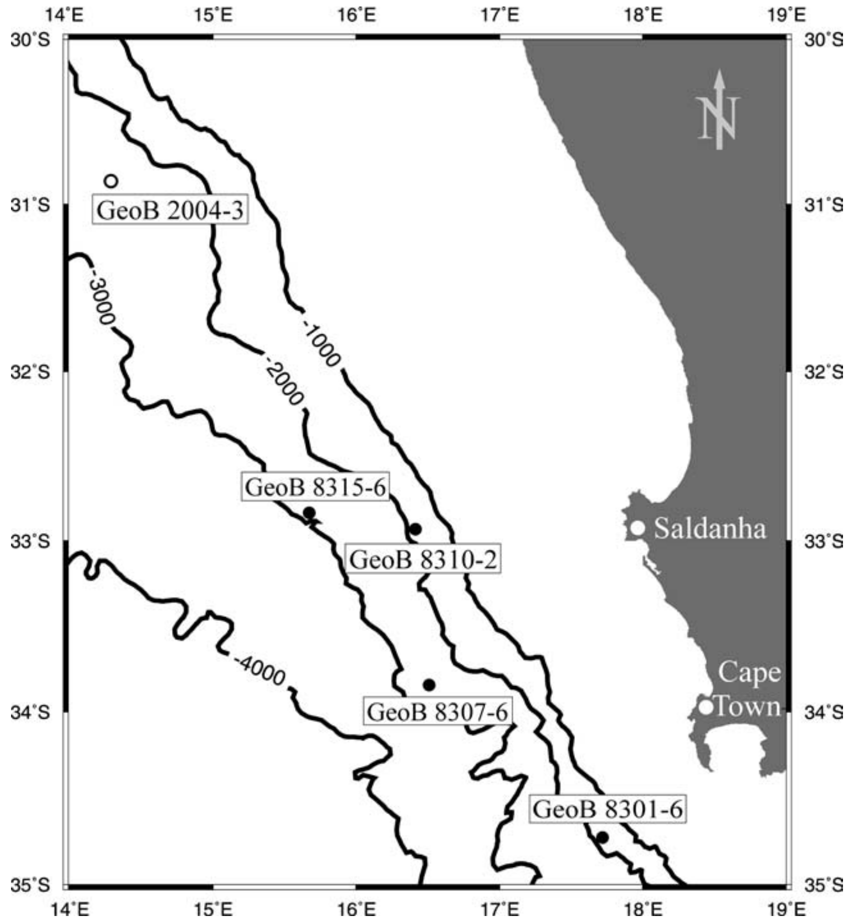

Fig. 1 Locations of the gravity cores in the southern Cape Basin. *Closed circles* selected core positions during RV Meteor cruise M 57-1 (present study), *open circle* position of reference core GeoB 2004-3 (RV Meteor cruise M 23-1)

McIntyre et al. 1989) reveals good correspondence between the datasets. Thus, the Sr/Ca ratios of all cores correlate inversely with the δ^{18} O values, this being most visible in core GeoB 8307-6 which goes furthest back in stratigraphy, postdating to approximately 450 ka. Minimum Sr/Ca ratios appear during glacial (δ^{18} O) maxima—for example, a Sr/Ca ratio of 3.2 during oxygen isotope stage (OIS) 2. By contrast, periods of deglaciation are characterised by distinct increases in Sr/Ca ratios, followed by interstadials, which show the highest Sr/Ca values (e.g. Sr/Ca ratios of 3.9 during OISs 1, 5 and 7). In core GeoB 8307-6 at ~50, 270–330, ~480 and ~650 cm, low Sr/Ca ratios correspond to maximum values in the stacked δ^{18} O record of the SPECMAP profile at 19, 140–150, 250 and 340 ka, respectively.

Table 2 Bulk sediment Sr/Ca data of all analysed gravity cores in the southern Cape Basin

Core no.	GeoB 8301-6	GeoB 8307-6	GeoB 8310-2	GeoB 8315-6	GeoB 2004-3
Average Sr/Ca (mg/g)	3.633	3.716	3.688	3.751	3.886
Minimum Sr/Ca (mg/g)	2.770	3.078	3.143	3.363	3.599
Maximum Sr/Ca (mg/g)	4.227	4.350	4.128	4.084	4.148
Range (%)	40	34	27	19	14

Average sedimentation rates were hindcast to 190 ka, this being the oldest age identified in all five cores combined (Table 3). The values vary between 1.9 and 4.3 cm/10^3 year at the water depths investigated in the present study (cf. Fig. 1, Table 1), and decrease both downslope from the NE to the SW and alongslope from the NW to the SE at the study site. Sedimentation is slower at the deeper sites on the lower slope (1.9–2.7 cm/10^3 year; GeoB8307-6 and GeoB8315-6, water depths 2,667 and 2,995 m, respectively) than at the shallower sites (3.6–4.3 cm/10^3 year; GeoB 8301-6, GeoB 8310-2 and GeoB 2004-3, water depths 1,952, 1,993 and 2,572 m, respectively). A south-eastward decrease of sedimentation rates is obvious when comparing cores from similar water depths but different latitudes alongslope. At water depths of 2,500–3,000 m, values decrease south-eastwards from 3.6 (GeoB 2004-3) through 2.7 (GeoB 8315-6) to 1.9 cm/10^3 year (GeoB 8307-6), and at water depths of 1,950–2,000 m from 4.3 (GeoB 8310-2) to 3.6 cm/10^3 year (GeoB 8301-6).

Discussion and conclusions

The findings of the present study convincingly demonstrate inverse relationships between bulk sediment Sr/Ca ratios and δ^{18} O values of the SPECMAP record

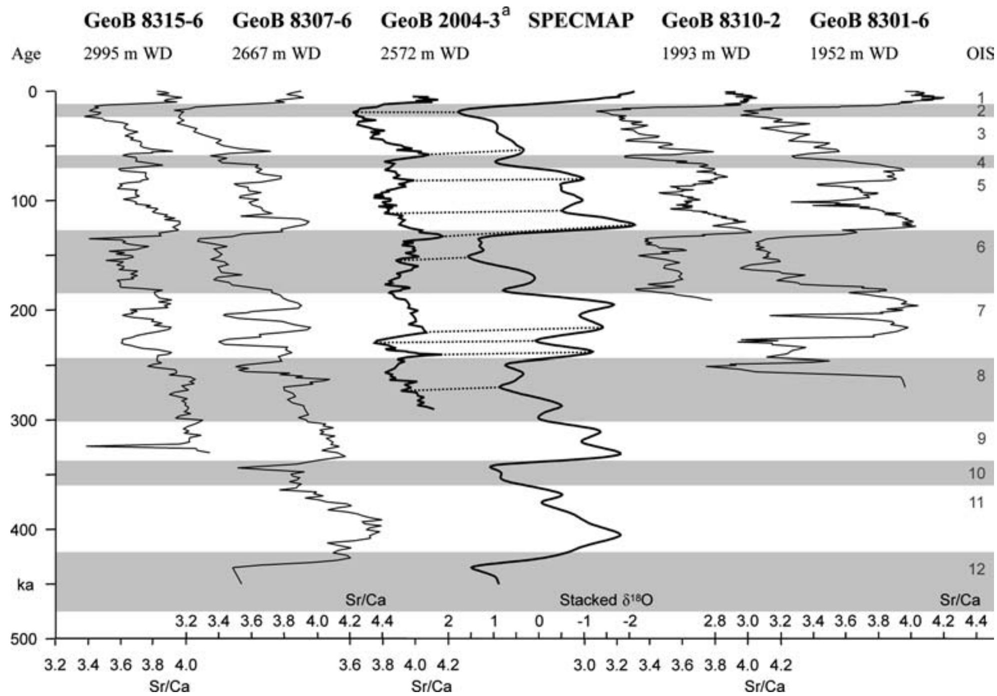

Fig. 2 Correspondence of Sr/Ca ratios (mg/g) in bulk sediments with the SPECMAP record. *a* Core GeoB 2004-3 was recovered during RV Meteor cruise M 23-1 (Spieß and Cruise Participants 1993); the age model is by correlation with core MD 962085 (Chen et al. 2002). The profile for reference core GeoB 2004-3 shows the correspondence of the age model with the SPECMAP record. *Dotted lines* indicate well-correlated peaks. *WD* water depth, *OIS* oxygen isotope stage

documented in all study cores from the southern Cape Basin. As pointed out above, the main causes of Sr/Ca variations over glacial/interglacial cycles are (1) fluctuations in the input and burial of biogenic carbonate particles of different Sr/Ca ratios, due either to shifts in species assemblages or to changes in growth and calcification rates; (2) selective dissolution of carbonate. Thus, Sr/Ca ratios ultimately preserved in bulk sediments represent a composite signature integrating all these effects.

Variations in species assemblages of biogenic carbonate producers

The location of the southern Cape Basin in an oceanographically complex area (e.g. Shannon and Nelson 1996; Gordon 2003) is associated with biotic responses to surface hydrological variations which reflect global glacial/interglacial cycles (Flores et al. 1999; Rau et al. 2002; Peeters et al. 2004) and additional pulses due to local (Agulhas Current) and regional (Subtropical Convergence and associated subantarctic water masses) ocean dynamics (Rau et al. 2002). Bulk carbonate in the modern ocean is sequestered mainly in coccoliths, foraminifers and, at shallower sites, aragonitic pteropods (e.g. Schiebel 2002). According to onboard descriptions, the dominant carbonate producers in the study cores are coccoliths and foraminifers (Schneider and Cruise Participants 2003).

Former studies on cores recovered from the continental margin off Cape Town, South Africa, report fluctuations in bulk coccolith abundances over glacial/interglacial cycles, with higher values during interglacial OISs 1, 5 and 7, and lower values during glacial OISs 2–4 and 6 (Flores et al. 1999; Boeckel 2003). Among the planktonic Foraminifera, especially the tropical–subtropical Agulhas fauna shows a distinct glacial/interglacial periodicity, higher abundances having been recorded during interglacial periods (Peeters et al. 2004). These fluctuations are in general agreement with the patterns in Sr/Ca variations documented in the bulk sediments of our cores from the southern Cape Basin.

Table 3 Sedimentation rates for all gravity cores, estimated back to 190 ka

Core no.	Sedimentation rate (cm/10^3 year)
GeoB 8301-6	3.6
GeoB 8307-6	1.9
GeoB 8310-2	4.3
GeoB 8315-6	2.7
GeoB 2004-3	3.6

Variations in growth and calcification rates of biogenic carbonate producers

For many carbonate producers, Sr/Ca variations of shells and skeletons considerably exceed the 1–3% global range proposed for ocean water over the last 100,000s of years (Stoll and Schrag 1998). This results partially from changes in the growth and calcification rates of the different species. Generally, Sr/Ca ratios of coccolith carbonate significantly exceed those for most Foraminifera (Stoll et al. 1999; Stoll and Schrag 2000), nearly by factor 2 (Stoll et al. 2002). Moreover, in various time-series records Foraminifera show less Sr/Ca variability than do coccoliths (e.g. Martin et al. 1999; Stoll et al. 1999; Elderfield et al. 2000; Stoll and Schrag 2000; Shen et al. 2001).

For our study cores, there is some independent evidence that the Sr/Ca signal is affected by fluctuations in coccolith assemblages. Stoll and Schrag (2000) report Sr/Ca variations of nearly 20% over the last 250 ka in the downcore fine "coccolith" fraction from the equatorial Pacific, with minimum Sr/Ca values corresponding to glacial (δ^{18} O) maxima in the composite benthic δ^{18} O curve of Martinson et al. (1987). These data agree with our findings, in terms of both the range (15–40%) as well as the general trend of Sr/Ca variations (cf. Sr/Ca minima during glacial maxima) in bulk sediments from the southern Cape Basin.

Carbonate dissolution

Species-dependent dissolution of carbonate particles in the water column and on the seafloor (Berger 1970; Berger et al. 1982; Berger and Wefer 1996) may also bias the Sr/Ca ratios of sediments, as does selective dissolution due to different within-species reactivites (e.g. Lohmann 1995; Brown and Elderfield 1996; Stoll et al. 1999). Hence, dissolution may cause sediments to become enriched with resistant species at the expense of more susceptible ones (Berger 1970). Carbonate dissolution is controlled mainly by the positions of the aragonite and calcite lysoclines, both of which varied over glacial/interglacial cycles (e.g. Berger 1977). However, since all our study sites are located in relatively shallow water at ca. 2,000–3,000 m water depth, preservation of coccolith and foraminifer calcite is assumed to be generally good in this case (see also Flores et al. 1999; Boeckel 2003). Pteropods, on the other hand, are known to be only rarely preserved in deep-sea sediments, and may only sporadically be present in deglaciation preservation spikes. In our study area in the southern Cape Basin, it is only during the intense carbonate dissolution event in the early OIS 6 (Bertrand et al. 2002) that the deeper sites GeoB 2004, GeoB 8307 and GeoB 8315 may possibly have been positioned at or below the calcite lysocline and, therefore, have been affected by enhanced carbonate dissolution.

Compared to the highly productive Benguela upwelling system off Namibia, upwelling in the southern Cape Basin is subdued and the region is subjected to incursions from the South Atlantic Current and eddies from the Agulhas retroflection. Moreover, nutrient concentrations decrease southwards in these thermocline waters (Berger et al. 2002). This is consistent with the results of the present study, which show that sedimentation rates decrease from the NW to the SE in the study area. By contrast, Sr/Ca variations are highest in the south-eastern part of the southern Cape Basin, and decrease both north-westwards and with increasing water depth. This may reflect a changing influence especially of warm water entrainment from the Indian Ocean at the Agulhas retroflection, coupled with shifts in species assemblages over glacial/interglacial cycles caused by extensions of species distributions beyond present-day warmer regions in the Indian Ocean off south-eastern Africa.

In conclusion, the diversity of factors controlling Sr/Ca variations in bulk sediments in the southern Cape Basin is too complex to be fully deciphered by the data available to date. Further studies need to focus on the complete assemblage of calcareous organisms in this region, and to unravel individual Sr/Ca signals. The most obvious use of the preserved Sr/Ca signal is for correlating and age dating of cores from this region.

Acknowledgements Karsten Enneking, Silvana Hessler, Luzie Schnieders and Rainer Zahn are gratefully acknowledged for helping with the laboratory work during RV Meteor cruise M 57-1. We thank the captain and crew members of this expedition, and Ralph Schneider who, as chief scientist of this leg, took care of organisation and the selection of sites. This research has benefited greatly from discussions with Syee Weldeab and from many helpful suggestions by W.H. Berger. Funded by the Deutsche Forschungsgemeinschaft as part of the DFG-Research Center "Ocean Margins" of the University of Bremen Project No. RCOM0207.

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