Sr isotope evidence for sources of terrigenous sediment in the southeast Atlantic Ocean: Is there increased available Fe for enhanced glacial productivity?

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[1] Sr isotope ratios of the terrigenous sediments from the Cape Basin (southeast Atlantic Ocean) exhibit a systematic pattern of climate-related variability from the Holocene through the last glacial period. Values are high during warm climate intervals (marine isotope stages (MISs) 1 and 3) and lower during full glacial periods (MISs 2 and 4). The variability is large ($^{87}Sr/^{86}Sr = 0.717-0.723$), and the rapid changes correspond temporally to abrupt climate change during the MIS 5a/4 and 2/1 transitions and through MIS 3. The Sr isotope variability corresponds to changes in $\delta^{13}C$ of benthic foraminifera at orbital frequencies and within periods of rapid variability. Prior studies have suggested that benthic $\delta^{13}C$ records from the Cape Basin follow Greenland ice core variability and thus global overturning circulation. Other studies suggest that these benthic $\delta^{13}C$ records contain a strong overprint from isotopically light carbon, possibly associated with high fluxes of organic matter to the seabed. We explore the scenario that the relationship between lower terrigenous $^{87}Sr/^{86}Sr$ and lighter benthic $\delta^{13}C$ may reflect high productivity during cold climatic intervals as a result of iron fertilization of the southern Atlantic Ocean. Increased supply of iron during cold periods may be associated with greater terrigenous sediment fluxes from South America, characterized by a less-radiogenic Sr isotopic signature.

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1. Introduction

[2] Marine terrigenous sediments are the weathering products of continental rocks that have a wide range of Sr isotope ratios. Radiogenic isotope ratios of deep-sea sediments reflect the compositions of their continental sources, and thus the Sr isotope compositions of terrigenous sediments provide a way to trace changes in their continental provenance. The ⁸⁷Sr/⁸⁶Sr of continental source rocks depend on Rb/Sr ratio, age, and geological history. Any change in the continental sources of terrigenous sediment to the oceans would be reflected in the down-core records of isotopic compositions of the sediments at different locations in the oceans.

[3] The earliest studies in the South Atlantic showed systematic geographical variations in the ⁸⁷Sr/⁸⁶Sr of surface sediments, with lowest values in the circum-Antarctic region and near South America [Biscaye and Dasch. 1971; Dasch. 1969]. Recent Sr. Nd, and Pb isotopic studies of terrigenous sediments in the tropical and south Atlantic Ocean and its adjacent sector of the Antarctic Ocean have

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documented variability on glacial-interglacial timescales. generally showing lower Sr and Pb and higher Nd isotope ratios during cold climate intervals [Abouchami and Zabel, 2003; Walter et al., 2000]. Until now, there have been few radiogenic isotope studies that address relationships between millennial climate variability and sediment provenance changes, and these have focused on the North Atlantic [Eisenhauer et al., 1999; Fagel et al., 2002; Grousset et al., 1988; Innocent et al., 1997], and the Indian ocean [Burton and Vance, 2000; Jung et al., 2004]. Here we report a high resolution (63 samples over ~70 kyr) Sr isotopic investigation of the terrigenous sediments from the well-studied Cape Basin core RC11-83 [Charles and Fairbanks, 1992; Charles et al., 1996; Piotrowski et al., 2004; Rutberg et al., 2000]. Large R7Sr/R6Sr variations are found through the last glacial cycle, providing a systematic pattern of variability that can be compared with other climate proxies on Milankovich to millennial timescales. The down-core time resolution is high enough to show that changes are abrupt, especially during major climate transitions, where they are synchronous with changes in ξ^{13} C of benthic foraminifera. The correlation between the ⁸⁷Sr/⁸⁶Sr of terrigenous sediments and δ¹³C of benthic foraminifera leads us to suggest that climate-related changes in the terrigenous ⁸⁷Sr/⁸⁶Sr ratio of Cape Basin sediments may be related to variability in the supply of terrigenous sediment, such that the terrigenous sediment

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Table 1. Location and Average Sediment Accumulation Rate of Cores Discussed in the Text^a

Core	Latitude	Longitude	Water Depth, m	Approximate sedimentation Rate, cm/kyr
RC11-83	40°36′S	9°48′E	4718	20
TNO57-21	41°08′S	7°49′E	4981	15
ODP Site 1089	40°57′S	9°53′E	4575	22

*The sedimentation rate for core RC11-83 was derived from the age model of *Charles et al.* [1996]. The sedimentation rate for TNO57-21 was derived from the age model in the work of *Stoner et al.* [2000]. Sedimentation rate for ODP Site 1089 was derived from the age model given in the work of *Cortese and Ablemann* [2002].

served as an important source of biologically available iron for the Subantarctic South Atlantic Ocean.

2. Study Area

[4] 87Sr/86Sr ratios were measured in the terrigenous detritus fraction of samples from RC11-83 (Table 1) recovered from a drift deposit in the southern Cape Basin, southeast Atlantic Ocean (Figure 1). Within the Cape Basin, deep water circulates in a clockwise gyre [Tucholke and Embley, 1984], and sediments are focused into drifts along the southern boundary [Shipboard Scientific Party, 1999]. High-resolution stable isotope records from RC11-83 have been interpreted to reflect changing composition of surface and deep waters in the Cape Basin [Charles and Fairbanks, 1992; Charles et al., 1996]. The data available from this core, together with published results from other nearby cores (Table 1), allow the interpretation of the terrigenous 87Sr/86Sr ratios to be made in the context of a wealth of complementary paleoceanographic data.

3. Analytical Procedures

[5] RC11-83 samples typically weighing ~50 mg were leached with a series of solutions to remove CaCO3 and Fe-Mn oxides. Carbonate was removed by leaching each sample for two 2-hour periods with a 0.45 molar acetic acid leach solution. This solution was buffered to pH = 5 with NaCO₃ to dissolve the CaCO₃ without attacking the clays [Biscaye, 1964, 1965]. The buffered acetic acid was made with distilled water, reagent grade acetic acid (27 mL/L solution) and reagent grade sodium acetate (82 g/L). After the CaCO3 was removed, the samples were rinsed three times with quartz-distilled water. A 0.02 molar hydroxylamine hydrochloride/25% acetic acid solution was used to dissolve the dispersed Fe-Mn oxides in a procedure modified from Chester and Hughes [1967] [cf. Rutberg et ul., 2000]. After leaching, the samples selected for Sr isotope analyses were rinsed thoroughly three times with quartz distilled water and were then transferred to Savillex. for dissolution. Samples were dissolved on a hotplate using a 3:1 mixture of HNO3 and HF. A small amount of HClO4 was used to oxidize any organic matter and to dissolve any CaF2 present. After drying down, they were re-dissolved in 3N of HNO3 and loaded onto 30 µL Teflon columns containing Eichrom Sr Spec ** resin that had been cleaned with water and equilibrated with 3N HNO₃. Seven hundred microliters of 3N HNO₁ were passed through the

resin to remove matrix elements, and subsequently Sr was eluted with 500 µL of quartz-distilled water.

[6] Sr isotope ratios were measured on a VG Sector 54 thermal ionization mass spectrometer at the Lamont-Doherty Earth Observatory in multidynamic mode. The Sr was loaded onto tungsten filaments with TaCl₅ solution [Birck, 1986]. ⁸⁷Sr/⁸⁶Sr ratios were measured by dynamic multicollection and corrected for mass discrimination assuming ⁸⁶Sr/⁸⁸Sr = 0.1194. Typical beam intensities were $2.0-4.0 \times 10^{-11}$ amps on mass 88. External reproducibility was monitored using strontium standard SRM 987. One of our goals was to analyze samples rapidly. Because there is a large range in Sr isotope ratios (0.717-0.723), we decided that a larger number of samples were preferable to high precision. As a result, 2 samples were run per hour, typically with 40 ratios in 2 blocks of 20 measurements per sample. Nevertheless, the 2σ reproducibility of SRM987, even with these rapid measurements, was about ±0.00004 (Table 2). This method makes collection of Sr isotopic data very efficient with short analysis times of 20-40 min.

4. Results

[7] The age model used for RC11-83 is that of Charles et al. [1996] based on ¹⁴C dates and oxygen isotope stratigraphy. The terrigenous ⁸⁷Sr/⁸⁶Sr varies from low values of \sim 0.717 during MIS 2 and 4 to high values of \sim 0.723 during the Holocene and MIS 3 (Table 2; Figure 2). The variability is much smaller within individual stages, with MIS 3 showing significantly more variability than the other stages. The terrigenous ⁸⁷Sr/⁸⁶Sr record in RC11-83 varies in tandem with the δ^{13} C of benthic foraminifera (Figure 3). The covariability between these two proxies allows for a common cause, and the hypothesis proposed here follows the assumption that the correlation suggests related causes.

5. Discussion

[8] The down-core Sr isotope variability and the systematic relationship to climate changes shows that the average source has lower ⁸⁷Sr/⁸⁶Sr during cold climate intervals. The regional distribution of terrigenous ⁸⁷Sr/⁸⁶Sr in Holocene sediments helps constrain possible changes of source in the past [Goldstein et al., 1999a, 1999b]. High ⁸⁷Sr/⁸⁶Sr (>0.720) are observed in a narrow band along the coast of southeast Africa, along the path of the southwest flowing Agulhas Current, which brings warm and salty water from the tropical and subtropical Indian Ocean to the Atlantic Ocean. The band of high ⁸⁷Sr/⁸⁶Sr ratios extends into the Cape Basin, where there is a sharp gradient to lower values to the south, west, and north [Dasch, 1969; Goldstein et al., 1999a, 1999b]. Thus the high ⁸⁷Sr/⁸⁶Sr Holocene Signal in the Cape Basin is from detritus from southeast Africa,

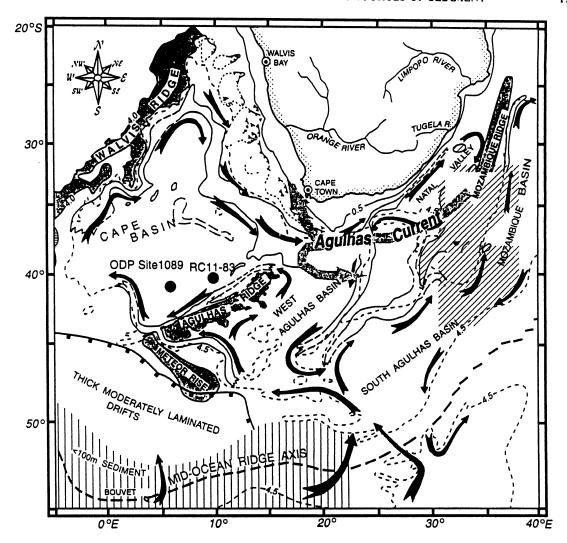


Figure 1. Bathymetric map showing bottom currents, the Agulhas Current, and core locations. The black arrows represent deep currents [after *Tucholke and Embley*, 1984].

transported to the Cape Basin by the Agulhas Current. Accordingly, the down-core Sr isotope variations in RC11-83 may reflect variability in the strength of the Agulhas contribution to the Cape Basin, or increases in the contributions of sources with lower Sr isotope ratios, or some combination thereof.

6. Sea Surface Temperature and Terrigenous ⁸⁷Sr/⁸⁶Sr

[9] One means of evaluating the temporal changes in the Agulhas flux to the southeast Atlantic is through sea surface temperature proxies because a strong Agulhas flux should be associated with higher sea surface temperatures. In the modern ocean, leakage of Agulhas water into the southeast Atlantic Ocean transports 2.3-47 × 10¹³ Watts [Gordon, 1985]. A 2°C temperature anomaly was associated with an unusual westward penetration of the Agulhas Current into

the Atlantic Ocean in 1986, and this demonstrates that surface temperatures of the southeast Atlantic Ocean are sensitive to changes in interocean exchange on annual timescales [Shannon et al., 1990]. On the basis of the modern link between the westward penetration of Agulhas water and SST in the southeast Atlantic Ocean, we might expect a correspondence between sea surface temperature and Sr isotopes, if this is the primary control on the provenance variation.

[10] Summer sea surface temperatures (SSST) based on radiolarian assemblages at ODP Site 1089, located near RC11-83, (Table 1) vary over the last glacial cycle [Cortese and Abelmann, 2002], but covary with the \$^7\$Sr/^{86}\$Sr record from RC11-83 only during the LGM and the Holocene, not during MIS 3 and MIS 4 (Figure 4). The SSSTs show strong short-term variability on the order of 3-4°C from MIS 5 through MIS 2, and an abrupt change of \sim 6°C to warmer Holocene values. This is in contrast to the 87 Sr/^{86}\$Sr record that shows distinctly higher values in MIS 3 than in MIS 4.

Table 2. Detrital Sr Isotope Ratios are Reported for Core RC11- Table 2. (continued)

83°				
Depth. cm	Age, kyr	⁸⁷ Sr ^{,86} Sr		
84	6.62	0.72259		
100	7.53	0.72174		
100 ⁶		0.72177		
117	8.49	0.72219		
125	8.95	0.72217		
132	9.29	0.7227		
148 150	10.06 10.15	0.72228		
164	10.13	0.7227 0.72284		
180	11.48	0.72287		
196	12.12	0.72285		
212	12.72	0.72196		
228	13.27	0.72228		
• 244	14.03	0.72158		
250 250 ⁶	14.35	0.72066		
250 ^b		0.72037 0.72039		
260	14.84	0.72039 0.71951		
270	15.26	0.71865		
276	15.46	0.72175		
276	15.46	0.72175		
286	15.81	0.71815		
292	16.02	0.71812		
292 ^h		0.71806		
292 ⁶	14.45	0.71808		
308 324	16.65 17.33	0.71789 0.71738		
338	17.88	0.71753		
360	18.61	0.71757		
372	18.88	0.7176		
388	19.55	0.71781		
400	19.75	0.717		
418	20.28	0.71763		
432	20.89 21.58	0.71759 0.7178		
448 541	23.83	0.71762		
600	25.41	0.71714		
670	31.41	0.71811		
. 743	28.08	0.71825		
760	32.16	0.71858		
780	33.08	0.71908		
780°	22.07	0.71911		
800 840	33.97 35.82	0.72069 0.72134		
860	36.78	0.72105		
887	50.76	0.72023		
919	39.75	0.72067		
919h		0.72062		
960	41.9	0.72178		
999	44.01	0.72275		
999 ⁶	44.05	0.72279 0.72306		
1000	44.05 46.76	0.72261		
1047 1060	47.51	0.72282		
1070	48.01	0.72288		
1071	48.14	0.72287		
1080	48.64	0.72136		
1090	49.24	0.72299 0.72323		
1100	49.82 52.2	0.72189		
1141 1151	52.78	0.72108		
1163	53.48	0.72048		
1195	55.52	0.71924		
, 1210	56.62	0.71949		
1230	58.13	0.72001 0.7191		
1250	59.64 62.14	0.71995		
1285	02.14			
1285b		0.72002		
	/4 //	18418 4		
1311	63.18	0.71971		
1380	67.34	0.72065		
1'790	(17.34	0.12003		

Depth, cm	Age, kyr	8 ⁷ Sr ⁸⁶ Sr
1415	68.2	0.72139
1450	69.66	0.72188
1485	71.87	0.72266

The average 87Sr/86Sr values and external reproducibility measured for SRM 987 over three intervals during which samples were measured are: 0.71031 ± 3 (2 s external reproducibility, n = 8), 0.71026 ± 4 (2 s external reproducibility, n = 38), 0.71023 ± 3 (2 s external reproducibility, n = 16). These errors are far less than the isotopic difference among samples. Because our samples had a wide range in composition, higher precision data was not required, allowing us to minimize analytical time which greatly contributed to the efficiency of this method. The external error is taken to be the best estimate of the analytical uncertainty. The procedural blank is ~500 pg, which comprises less than 0.05% of sample Sr. The RC11-83 ages are derived from the age model of Charles et al. [1996]. ^bDuplicate analysis.

[11] Oxygen isotope ratios in planktonic foraminifera (planktonic δ^{18} O) have been interpreted as a proxy for sea surface temperature (SST) in southeast Atlantic cores [Charles et al., 1996; Ninnemann et al., 1999]. Planktonic δ¹⁸O is also sensitive to a variety of factors, including water mass distribution (salinity), ice volume, and meltwater. Planktonic δ¹⁸O in nearby core TNO57-21 (the stratigraphy of which has been correlated with RC11-83 on the basis of excellent correspondence of the benthic $\delta^{13}C$ records [Ninnemann et al., 1999]), shows warm stage to cold stage differences, but there is no clear covariability between the planktonic δ¹⁸O and terrigenous ⁸⁷Sr/⁸⁶Sr records (Figure 4). The two records show concurrent SST change between MIS 2 and the Holocene but little covariability deeper in the core.

[12] Alkenone-based sea surface temperatures at site TNO57-21 [Sachs et al., 2001] vary over the last glacial cycle but do not show a strong covariation with the terrigenous 87Sr/86Sr in RC11-83 (Figure 4). Both records have low values in MISs 2 and 4 as compared to MISs 1 and 3, but they deviate substantially over the MIS 3-2 transition and during MIS 4, during which time terrigenous 87Sr/86Sr values are low and alkenone-derived paleotemperatures are relatively high.

[13] The three temperature proxies record dissimilar patterns and values in the Cape Basin. This may reflect a dominant signal during different seasons among the different proxies or other problems, and it may reflect transport over longer distances in the case of alkenone-derived SST values. In addition to disagreements among themselves, none of the SST records closely follows the terrigenous ⁸⁷Sr/⁸⁶Sr variability over the last glacial cycle. Assuming that the modern relationship between the input of Agulhas Current waters to the southeast Atlantic Ocean and southeast Atlantic (S)SSTs should apply throughout the last glacial cycle, these comparisons imply that terrigenous ${}^{87}\mathrm{Sr}/{}^{86}\mathrm{Sr}$ is not (simply) recording changes in the amount of Agulhas water exported to the southeast Atlantic Ocean.

7. Benthic δ¹³C and Terrigenous ⁸⁷Sr/⁸⁶Sr

[14] The strong correlation in RCII-83 between the terrigenous 87 Sr/ 86 Sr and benthic δ^{13} C contrasts with the

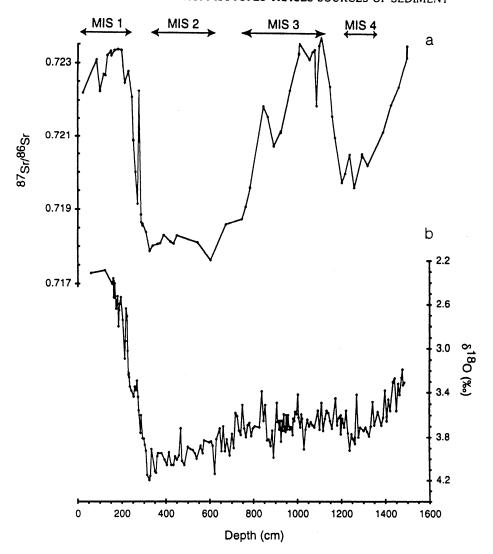


Figure 2. (a) Detrital ${}^{87}\text{Sr}/{}^{86}\text{Sr}$ ratios in RC11-83. (b) Benthic ${}^{618}\text{O}$ in RC11-83. Benthic ${}^{618}\text{O}$ (C. wuellerstorfi) data are from Charles et al. [1996]. All data are plotted against depth in core. Approximate depths of marine isotope stages are noted by the horizontal arrows at top of figure.

disagreement between terrigenous 87 Sr/ 86 Sr and SST records and among the SST records themselves. Cold marine isotope stages are characterized by low benthic δ^{13} C, and the terrigenous 87 Sr/ 86 Sr ratios are also low, and during warm stages, both benthic δ^{13} C and 87 Sr/ 86 Sr ratios are high (Figure 3).

[15] A visual examination of the fine-scale features suggests covariability on shorter timescales as well (Figure 3). For example, during the LGM to Holocene transition both proxies jump briefly to nearly Holocene values. This benthic k¹³C excursion was noted by *Charles and Fairbanks* [1992], and they suggested that it reflects a "false start" of NADW prior to the full transition to Holocene conditions. The proxies then return abruptly to glacial-like values before making the final transition to values that characterize the Holocene (see inset of Figure 3). These proxies change

concurrently during several abrupt excursions in the Holo-

cene and MISs 3 and 4 (Figure 3). The coherence of the benthic $\delta^{13}C$ and terrigenous $^{87}Sr/^{86}Sr$, in contrast with the absence of such clear coherence with SST proxies, is taken to suggest that a common process could be affecting the benthic $\delta^{13}C$ and terrigenous $^{87}Sr/^{86}Sr$ variability. In the following discussion we explore paleoproductivity variations, driven by variations in Fc fertilization, as a plausible common process to explain both.

8. Origin of the Benthic δ^{13} C Signal

[16] The benthic 8¹³C record in RC11-83 has been interpreted as evidence for shallowing or shutting down of North Atlantic Deep Water (NADW) during the cold stages of the last glacial cycle [Charles and Fairbanks, 1992; Charles et al., 1996]. Neodymium isotopes in the Fe-Mn oxide fraction of RC11-83 sediments have also

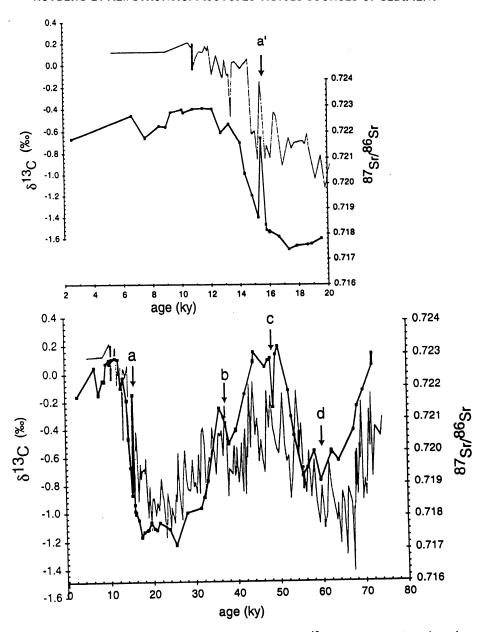


Figure 3. Detrital ${}^{87}\text{Sr}/{}^{86}\text{Sr}$ ratios (black line) and benthic $\delta^{13}\text{C}$ (gray line) plotted against age in RC11-83. The benthic $\delta^{13}\text{C}$ was measured in *C. wuellerstorfi* [Charles et al., 1996]. Ages were calculated by linearly interpolating between ${}^{14}\text{C}$ dates and $\delta^{18}\text{O}$ tie points presented in the work of Charles et al. [1996]. The arrows point to excursions in the ${}^{87}\text{Sr}/{}^{86}\text{Sr}$ (a-d) that visually correlate with excursions in the benthic $\delta^{13}\text{C}$ record. Features "a" and "a" (inset) represents the abrupt, synchronous, excursion in both records that immediately precedes termination 1.

been interpreted to indicate a decreased NADW flux to the southeast Atlantic Ocean during colds stages [Piotrowski et al., 2004: Rutherg et al., 2000]. However, the extremely low benthic δ¹³C must indicate significant additional oceanographic processes unrelated to NADW variability. For example, the glacial benthic δ¹³C values recorded in Southern Ocean cores are significantly lower (~0.5‰) than glacial deep Pacific values [Mackensen et al., 1993]. In addition, Cd/Ca and Ba/Ca ratios in the shells of benthic foraminifera do not show a substantial change during the last

glacial cycle [Boyle, 1988; Lea, 1995; Oppo, 1994]. We propose that a portion of the glacial benthic δ^{13} C signal in the southern Cape Basin reflects a phytodetrital effect [Mackensen et al., 1993], i.e., a negative overprint on the benthic δ^{13} C record due to the decay of low δ^{13} C organic material at the sediment water interface. Mackensen et al. [2001] concluded that an upper limit for the phytodetrital effect on the δ^{13} C of epibenthic foraminifera to be 0.4‰. However, Bickert and Wefer [1999] have found that C. wuellerstorfi, living during glacial periods within the

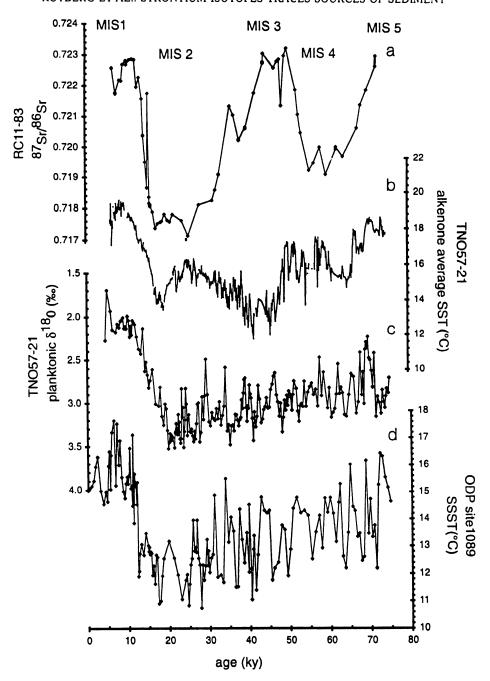


Figure 4. The first graph shows detrital ⁸⁷Sr/⁸⁶Sr ratios, and the second, third, and fourth graphs show southeast Atlantic sea surface temperature records plotted against age. The second graph shows average SST derived from the alkenone paleotemperature technique [Sachs et al., 2001] from sediment core TNO57-21. The age model for the second graph is from Stoner et al. [2000]. The third graph shows planktonic δ¹⁸O (G. bulloides) record from core TNO57-21 [Mortyn et al., 2003]. The fourth graph shows summer sea surface temperature (SSST) derived from radiolarian assemblages at ODP Site 1089 [Cortese and Abelmann, 2002]. Marine isotope stages are noted. Warm stages are highlighted in gray.

upwelling region off Namibia, had δ^{13} C values about 0.6% lower than contemporary *C. wuellerstorfi* living at comparable depths a short distance offshore. They argued that the δ^{13} C of the dissolved inorganic carbon (DIC) could not

have been very different at the two sites, so the difference in $\delta^{13}C$ of *C. wuellerstorfi* must have been created by a phytodetritus effect in the productive upwelling region off Namibia.

[17] A similar argument can be applied to the benthic $\delta^{13}C$ records from the Southern Cape Basin. Benthic $\delta^{13}C$ values from sites in the southern Cape Basin, including our core (RC11-83), are about 0.6% lower than contemporary ε¹³C values of C. wuellerstorfi living at 4084 m in the northern Cape Basin (Bickert and Wefer [1999]; Site GeoB1211). Therefore, following reasoning similar to that of Bickert and Wefer [1999]. we conclude that about 0.6% of the benthic 813C signal in deep southern Cape Basin sediments was created by phytodetritus effects. Changes in deep circulation [e.g., Charles and Fairbanks, 1992; Charles et al., 1996; Rutberg et al., 2000, Piotrowski et al., 2004], as well as changes in the global average δ^{13} C of dissolved organic carbon (DIC) [Duplessy et al., 1988], also influenced Cape Basin records, but these effects do not account fully for the glacial benthic $\delta^{13}C$ at the site of RC11-83.

[18] Enhanced export of organic carbon in the Subantarctic Atlantic Ocean during cold periods has been suggested previously [Anderson et al., 1998, 2002; Chase and Anderson, 2001; Francois et al., 1997; Kumar et al., 1995; Suchs and Anderson, 2003]. Increased supply of organic material at the sediment water interface would stimulate rapid chamber building and reproduction in benthic foraminifera [Mackensen et al., 1993], and the respiration of this organic matter would create a pool of isotopically light DIC near the sediment water interface [Mackensen et al., 1993]. Both factors would have driven the ξ^{13} C recorded in benthic foraminifera toward values lower than the ξ^{13} C of DIC in the surrounding seawater.

9. Sr Isotopes Constrain Sources of Terrigenous Iron for Fertilization

[14] Accepting that most of the benthic δ^{13} C variability in RC11-83 was caused by a phytodetritus overprint, we consider a mechanism involving iron fertilization of South Atlantic phytoplankton that could have generated the strong correlation between terrigenous 87Sr/86Sr and the surface origin of the δ^{13} C signal. On the basis of Nd concentrations and isotope compositions of terrigenous sediment in the Cape Basin, Bayon et al. [2003] suggested that the supply of terrigenous material derived from the southwest Atlantic region was greater during glacial periods than during interglacials. They suggested that the increase in flux of clays from the southwest Atlantic region was caused by increased transport into the Cape Basin by Circumpolar Deep Water (CDW). However, rather than interpreting the Nd data to reflect an increased transport by deep currents, we invoke a glacial increase in the source of Patagonian terrigenous material [Diekmann et al., 2000; Walter et al., 2000] to explain the results of this study and Bayon et al. [2003] from the Cape Basin. This suggestion is consistent with published flux estimates from Kumar et al. [1995] of up to five times greater terrigenous flux during the LGM in the Southern Ocean west of the Cape Basin.

[20] Clay mineralogy records from Cape Basin sediments at ODP 1089 show systematic climate-related changes that are also consistent with increased proportion of terrigenous sediment from the west and/or south during cold periods.

Kuhn and Diekmann [2002] showed that kaolinite/chlorite ratios varied by more than a factor of two, with low values during glacial periods. They further suggested the principal source of chlorite to Cape Basin sediments to be Patagonia. The clay mineralogy and Nd isotope evidence for provenance [Bayon et al., 2003; Kuhn and Diekmann, 2002] are consistent with the evidence of higher fluxes [Kumar et al., 1995] and suggest a greater contribution from South America or other western sources during the LGM.

[21] Diekmann et al. [2000] reported increased supply of glaciogenic material derived from the Chilean Archipelago to the northern Scotia Sea during cold periods. The conclusions of Diekmann et al. [2000] were based largely on the mineralogical composition of the sediments. Walter et al. [2000] reached similar conclusions based on Nd and Sr isotope evidence; for example, they found 87 Sr/86 Sr of 0.710 for the terrigenous fraction of sediments deposited on the Mid-Atlantic Ridge at 41°S during the LGM. An increase during cold periods in the supply to the Cape Basin of clays having this 87 Sr/86 Sr might explain the down-core variability.

[22] Terrigenous sediments derived from the western South Atlantic are transported eastward by the Antarctic Circumpolar Current (ACC) and the South Atlantic Current (SAC), and it is possible that the increased flux of terrigenous material could have provided labile iron to fertilize biological productivity [Bishop et al., 2002; Blain et al., 2001]. Experimental evidence has demonstrated that the addition of iron to Southern Ocean surface waters can stimulate productivity [Boyd et al., 2000; Coale et al., 2004]. Iron fertilization via the release of iron from the increased supply of terrigenous sediment during cold periods might have led to an increased flux of organic carbon to the seafloor. Therefore we suggest that an enhanced flux of terrigenous material from Patagonia fertilized Subantarctic surface waters with iron during cold periods, stimulating export productivity. This would have driven benthic δ^{13} C toward the low values that characterize the glacial southern Atlantic Ocean, and the terrigenous 87 Sr/86 Sr toward the low values that characterize sediments derived from South America. This scenario is consistent with the earlier findings of Kumar et al. [1995].

[23] Although much of the terrigenous material from South America was probably eroded by ice and transported by the ACC or by the SAC, we cannot rule out a contribution by dust as well to the increased supply of iron during cold periods. Grousset et al. [1992] and Basile et al. [1997] have made a strong case that Patagonia was the source of the increased fluxes of dust to the site of the Vostok ice core during glacial periods. Consequently, there must have been a glacial increase in flux of Patagonian dust to the Subantarctic South Atlantic Ocean as well. However, at this time there is no reliable method to evaluate the dust contribution to the increased flux of Patagonian terrigenous material to Cape Basin sediments during cold periods.

10. Conclusions

[24] ⁸⁷Sr/⁸⁶Sr ratios of terrigenous detritus in core RC11-83 vary with climate over the last glacial cycle,

from 0.723 during marine isotope stages (MISs) 1 and 3 to 0.717 during MISs 2 and 4. The Holocene distribution of terrigenous ⁸⁷Sr/⁸⁶Sr indicates a southeast African source for the high ⁸⁷Sr/⁸⁶Sr ratios observed during the Holocene, transported to the Cape Basin by the Agulhas Current. This means that the temporal pattern through the last glacial cycle reflects either reduced supply from the Agulhas Current or a relative increase in the supply from other sources. SST proxies in the Cape Basin do not covary with ⁸⁷Sr/⁸⁶Sr as would be expected if the variability were controlled by the supply of warm Agulhas Current water. However, the close correlation between terrigenous ⁸⁷Sr/⁸⁶Sr ratios and the δ^{13} C of benthic foraminifera in Cape Basin sediments strongly suggests that these two proxies are related.

[25] Increased dust fluxes to Antarctic ice have been documented during MISs 2 and 4, and there was also a general increase in the supply of terrigenous sediment in the South Atlantic. These sources have low ⁸⁷Sr/⁸⁶Sr and might have supplied labile iron that stimulated productivity and the flux of particulate organic material to the seafloor. We

suggest that the exported organic matter provided a pool of isotopically light carbon from which benthic foraminifera calcified, thereby accounting for the anomalously low δ^{13} C values of benthic foraminifera in the glacial South Atlantic Ocean as well as the strong correlation between benthic δ^{13} C and terrigenous 87 Sr/ 86 Sr ratios.

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References

- Abouchami, W., and M. Zabel (2003), Climate forcing of the Pb isotope record of terrigenous input into the equatorial Atlantic, *Earth Planet. Sci. Lett.*, 213, 221-234.
- Anderson, R. F., N. Kumar, R. A. Mortlock, P. N. Froelich, P. Kubik, B. Dittrich-Hannen, and M. Suter (1998), Late Quaternary changes in productivity of the Southern Ocean, J. Marine Syst., 17, 497 514.
- Anderson, R. F., Z. Chase, M. Q. Fleischer, and J. Sachs (2002). The Southern Ocean's biological pump during the Last Glacial Maximum, Deep Sea Res. Part II, 49, 1909-1938.
- Basile, I., F. E. Grousset, M. Revel, J. R. Petit, P. E. Biscaye, and I. Barkov-Nartssis (1997). Patagonian origin of glacial dust deposited in east Antarctica (Vostok and Dome C) during glacial stages 2, 4, and 6, Earth Planetary Sci Lett., 146, 573-589.
- Bayon, G., C. R. German, R. W. Nesbitt, P. Bertrand, and R. R. Schneider (2003), Increased input of circumpolar deep water-borne detritus to the glacial SE Atlantic Ocean. Geochem. Geophys. Geosyst., 4(3), 1025, doi:10.1029/2002GC000371.
- Bickert, T., and G. Wefer (1999), South Atlantic, and benthic foraminfer 8¹³C deviations: implications for reconstructing the late Quaternary deep-water circulation. *Deep Sea Res. Part II*, 46, 437–452.
- Birck, J. L. (1986). Precision K-Rb-Sr isotopic analysis, application to Rb-Sr chronology. *Chem. Geol.*, 56, 73-83.
- Biscaye, P. E. (1964). Mineralogy and sedimentation of the deep-sea sediment fine fraction in the Atlantic Ocean and adjacent seas and ocean. Ph.D. thesis, Yale Univ., New Haven, Ci.
- Biscaye, P. E. (1965). Mineralogy and sedimentation of recent deep-sea clay in the Atlantic Ocean and adjacent seas and oceans, *Geol. Soc. Am. Bull.*, 76, 803-832.
- Biscaye, P. E., and J. Dasch (1971), The rubidium, strontium, strontium-isotope system in deep-sea sediments: Argentine Basin, J. Geophys. Res., 76, 5087-5096.

- Bishop, J. K. B., R. E. Davis, and J. T. Sherman (2002). Robotic observations of dust storm enhancement of carbon biomass in the North Pacific, *Science*, 298, 817-821.
- Blain, S., et al. (2001), A biochemical study of the island mass effect in the context of the iron hypothesis: Kerguelen Islands, Southern Ocean, Deep Sea Res. Part 1, 48, 163-187.
- Boyd, P. W., et al. (2000), A mesoscale phytoplankton bloom in the polar Southern Ocean stimulated by iron fertilization, *Nature*, 407, 695-702.
- Boyle, E. A. (1988), Cadmium: Chemical tracer of deepwater paleoceanography, *Paleoceano-graphy*, 3, 471-489.
- Burton, K., and D. Vance (2000), Glacialinterglacial variations in the neodymium isotope composition of seawater in the Bay of Bengal recorded by planktonic foraminifera, Earth Planer. Sci. Lett., 176, 425-441.
- Charles, C. D., and R. G. Fairbanks (1992), Evidence from Southern Ocean sediments for the effect of North Atlantic deep-water flux on climate. *Nature*, 355, 416-419.
- Charles, C. D., J. Lynch-Stieglitz, U. S. Ninnemann, and R. G. Fairbanks (1996), Climate connections between the hemisphere revealed by deep sea sediment core/ice core correlations, Earth Planet. Sci. Lett., 142, 19-27
- Chase, Z., and R. F. Anderson (2001), Evidence from authigenic uranium for increased productivity of the glacial Subantarctic Ocean, *Paleo*ceanography, 16, 468-478.
- Chester, R., and M. J. Hughes (1967), A chemical technique for the separation of ferromanganese minerals, carbonate minerals and adsorbed trace elements from pelagic sediments, Chem. Geol., 2, 249-262.
- Coale, K. H., et al. (2004), Southern Ocean iron enrichment experiment: Carbon cycling in high- and low-Si waters, *Science*, 304, 408-414.
- Cortese, G., and A. Abelmann (2002), Radiolarian-based paleotemperatures during the last

- 160 kyr at ODP Site 1089 (Southern Ocean, Atlantic Sector), Palaeogeogr. Palaeoclimatol Palaeoecol., 182, 259-286.
- Dasch, E. J. (1969), Strontium isotopes in weathering profiles, deep-sea sediments, and sedimentary rocks, Geochim. Cosmochim. Acta. 33, 1521-1552.
- Diekmann, B., G. Kuhn, V. Rachold, A. Abelmann, U. Brathauer, D. K. Futterer, R. Gersonde, and H. Grobe (2000), Terrigenous sediment supply in the Scotia Sea (Southern Ocean): Response to late Quaternary ice dynamics in Patagonia and on the Antarctic Peninsula, Palaeogeogr. Palaeoclimatol. Palaeogeol., 162, 357-387.
- Duplessy, J. C., N. J. Shackleton, R. G. Fairbanks, L. Labeyrie, D. Oppo, and N. Kallel (1988). Deepwater source variations during the last climatic cycle and their impact on the global deepwater circulation. *Paleoceanography*, 3, 343-360.
- Eisenhauer, A., H. Meyer, V. Rachold, T. Tutken, B. Wiegand, B. Hansen, R. Spielhagen, F. Lindemann, and H. Kassens (1999), Grain size separation and sediment mixing in Arctic Ocean sediments: Evidence from the strontium isotope sysematic, Chem. Geol., 158, 173-188.
- Fagel, N., C. Innocent, C. Gariepy, and C. Hillaire-Marcel (2002). Sources of Labrador Sea sediments since the last glacial maximum inferred from Nd-Pb isotopes, Geochim. Cosmochim. Acta. 66, 2569-2581.
- Francois, R., M. A. Altabet, E.-F. Yu, D. M. Sigman, M. P. Bacon, M. Frank, G. Bohrmann, G. Bareille, and L. D. Labeyrie (1997). Contribution of Southern Ocean surface-water stratification to low atmospheric CO₂ concentrations during the last glacial period. *Nature*, 389, 929-935.
- Goldstein, S. L., S. R. Hemming, S. Kish, and R. L. Rutberg (1999a), Sr isotopes in South Atlantic detritus as a tracer of the Agulhas Leakage, *Eox Trans. AGU*, 80(46), Fall Meet. Suppl., Abstract OS32C-08.

- Goldstein, S. L., S. R. Hennning, S. Kish, and R. L. Rutberg (1999b), Strontium isotopes in South Atlantic detritus: A surface current proxy and tracer of Agulhas Leakage, paper presented at Ninth Annual V. M. Goldschnidt Conference, Geochem. Soc., Cambridge, Mass.
- Gordon, A. L. (1985). Indian-Atlantic transfer of thermocline water at the Agulhas Retroflection, Science, 227, 1030-1033.
- Grousset, F. E., P. E. Biscaye, A. Zindler, J. Prospero, and R. Chester (1988), Neodymium isotopes as tracers in marine sediments and acrosols: North Atlantic. Earth Planet. Sci. Lett., 87, 367-378.
- Grousset, F. E., P. E. Biscaye, M. Revel, J. R. Petit, K. Pye, S. Joussaume, and J. Jouzel (1992). Antarctic (Dome C) ice-core dust at 18 k.y. B.P.: Isotopic constraints on origins, Earth Planet. Sci. Lett., 111, 175-182.
- Innocent, C., N. Fagel, R. K. Stevenson, and C. Hillaire-Marcel (1997), Sm-Nd signature of modern and late Quaternary sediments from the northwest North Atlantic: Implications for deep current changes since the Last Glacial Maximum. Earth Planet. Sci. Lett., 146, 607-625.
- Jung, S. J. A., et al. (2004), Stepwise Holocene aridification in NE Africa deduced from dustborne radiogenic isotope records, Earth Planet. Sci. Lett., 221, 27-37.
- Kuhn, G., and B. Dickmann (2002), Late Quaternary variability of ocean circulation in the southeastern South Atlantic inferred from the terrigenous sediment record of a drift deposit in the southern Cape Basin (ODP Site 1089). Palaeogeogr. Palaeoclimatol. Palaeoecol., 182, 287–303.
- Kumar, N., R. F. Anderson, R. A. Mortlock, P. N. Froelich, P. Kubik, B. Dittrich-Hannen, and M. Suter (1995), Increased biological productivity and export production in the glacial Southern Ocean. *Nature*, 378, 675– 679.
- Lea, D. W. (1995). A trace metal perspective on the evolution of Antarctic Circumpolar Deep

- Water chemistry, Paleoceanography, 4, 733-747
- Mackensen, A., H. W. Hubberten, T. Bickert, G. Fischer, and D. K. Futterer (1993), The δ¹³C in benthic foraminiferal tests of Fontbiotia Wuellerstorfi (Schwager) relative to the δ¹³C of dissolved inorganic carbon in Southern Ocean Deep Water: Implications for glacial ocean circulation models, *Paleoceanography*, 8, 587-610.
- Mackensen, A., M. Rudolph, and G. Kuhn (2001), Late Pleistocene deep-water circulation in the sub-Antarctic eastern Atlantic. Global Planet. Change, 30, 197-229.
- Global Planet. Change. 30. 197-229.

 Mortyn, P. G., C. D. Charles, U. S. Ninnemann, K. Ludwig, and D. A. Hodell (2003). Deep sea sedimentary analogs for the Vostok ice core, Geochem. Geophys. Geosyst., 4(8), 8405, doi:10.1029/2002GC000475.
- Ninnemann, U. S., C. D. Charles, and D. A. Hodell (1999), Origin of global millennial scale climate events: Constraints from the Southern Ocean deep sea sedimentary record, in Mechanisms of Global Climate Change at Millennial Time Scales. Geophys. Monogr. Ser., vol. 112, edited by P. U. Clark, R. S. Webb, and L. D. Keigwin, pp. 99–111, AGU, Washington, D. C.
- Oppo, D. W. (1994), Cd/Ca Changes in a deep Cape Basin core over the past 730,000 years: Response of circumpolar deepwater variability to Northern Hemisphere ice sheet melting, Paleoceanography, 9, 661-675.
- Piotrowski, A. M., S. L. Goldstein, S. R. Hemming, and R. G. Fairbanks (2004). Intensity and variability of ocean thermohaline circulation during the last deglaciation, Earth Planet. Sci. Lett., 224, 205-220.
- Rutberg, R. L., S. R. Heinming, and S. L. Goldstein (2000). Reduced North Atlantic Deep Water flux to the glacial Southern Ocean inferred from neodymium isotope ratios. *Nature*. 405, 935–938.
- Sachs, J. P., R. F. Anderson, and S. J. Lehman (2001), Glacial surface temperatures of the southeast Atlantic Ocean, *Science*, 293, 2077-2079.

- Sachs, J. P., and R. F. Anderson (2003). Fidelity of alkenone paleotemperatures in southern Cape Basin sediment drifts. *Paleoceanogra*phy, 18(4), 1082, doi:10.1029/2002PA000862.
- Shannon, L. V., J. J. Agenbag, N. D. Walker, and J. R. E. Lutjeharms (1990), A major perturbation in the Agulhas Retroflection area in 1986, Deep Sea Res., 37, 493-512.
- Shipboard Scientific Party (1999), Site 1088, Proc. Ocean Drill. Program, Initial Rep., 177. (Available at http://www-odp.tamu.edu/ publications/177_IR/CHAP_04/Outputchap_04.htm.)
- Stoner, J. S., J. E. T. Channell, C. Hillaire-Marcel, and C. Kissel (2000). Geomagnetic paleointensity and environmental record from Labrador Sea core MD95-2024: Global marine sediment and ice core chronostratigraphy for the last 110 kyr, Earth Planet. Sci. Lett., 183, 161-177.
- Tucholke, B. E., and R. W. Embley (1984), Cenozoic regional crosion of the abyssal sea floor off South Africa, in Interregional Unconformities and Hydrocarbon Accumulation, edited by J. S. Schlee, pp. 145-164, Am. Assoc. of Petrol. Geol., Tulsa, Okla.
- Walter, H. J., E. Hegner, B. Diekmann, G. Kuhn, and M. M. Rutgers Van Der Loeff (2000). Provenance and transport of terrigenous sediment in the South Atlantic Ocean and their relations to glacial and interglacial cycles: Nd and Sr isotopic evidence. Geochim. Cosmochim. Acta, 64, 3813-3827.

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