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Late Pleistocene evolution of the ocean's carbonate system

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Abstract

We demonstrate that the carbonate record from a single site (Ocean Drilling Program Site 1089) in the deep South Atlantic represents a qualitative, high-resolution record of the temporal evolution of the carbonate saturation state of the deep sea. The record is especially notable because it is free from many of the complications that limit other records (low sedimentation rates, blurring by chemical erosion, bioturbation, etc.). The pattern of carbonate variability is characteristic of Indo–Pacific cores with high-carbonate glacials and low-carbonate interglacials. Wt% carbonate lags changes in benthic $\delta^{18}O$ by an average of ~7.6 kyr, and carbonate variations are in-phase with the rate of change (first derivative) of benthic $\delta^{18}O$. Intense dissolution occurs at the transition from interglacial to glacial periods and increased preservation occurs during deglaciations. These observations represent two fundamentally different responses of the marine carbonate system. The lagged response of carbonate to $\delta^{18}O$ reflects a steady-state mass balance process whereby the lysocline adjusts to maintain alkalinity balance between riverine input and marine burial. The Site 1089 carbonate signal is remarkably similar to inferred changes in the Sr/Ca of seawater for the past 250 kyr, which implies that both carbonate dissolution and seawater Sr/Ca may be controlled by sea level-induced changes in the location of carbonate deposition (shelf-basin fractionation) during glacial to interglacial cycles. The transient change in preservation during the transitions into and out of glacial stages reflects a response of the carbonate system to a redistribution of alkalinity and DIC in the ocean (i.e. carbonate compensation). Comparison of the Site 1089 carbonate and Vostok pCO_2 records suggests a role of deep-sea $[CO_3^{2-}]$ variations for governing at least some second-order features of the atmospheric pCO_2 signal. In order to quantify this role, however, measurement of indices of dissolution along a true depth transect will be required to estimate the magnitudes of changes in deep-sea $[CO_3^{2-}]$.

Keywords: carbonate compensation depth; solution; sea-level changes; stable isotopes; ocean circulation; upper Pleistocene

1. Introduction

The inverse relationship between the carbonate ion content of the deep ocean and atmospheric pCO_2 [3] has led many paleoceanographers to search for proxies that might monitor changes in deep-water carbonate chemistry. Of course, the actual carbonate content of deep-sea sediments is controlled by a complex interplay among production in overlying surface waters, dilution by non-carbonate phases, and dissolution in the

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water column, at the sea floor, and in sediment pore waters. As a result, it is often difficult to uniquely isolate changes due to the carbonate saturation state of deep water from other controlling factors. Proxies that might be sensitive to dissolution alone have been employed, such as foraminiferal fragmentation, wt% >150 μm, ratios of planktic and benthic foraminifera and, most recently, shell thinning of planktic foraminifera [4] and the carbonate content of the >63 mm size fraction [5]. Also, past changes in deep-water pH and alkalinity have also been reconstructed using boron isotopes and Ba/Ca in benthic foraminifera, respectively [6–9].

Yet what has been lacking is any kind of high-resolution, continuous record of the timing of these changes in dissolution and carbonate saturation. Existing records from low sedimentation rate cores in the Indian and Pacific Oceans represent a damped response of sedimentary carbonate to changes in $[CO_3^{2-}]$ because of bioturbation and chemical erosion [10–12]. For example, the reason why the depth of 0–20% carbonate contour does not change in Farrell and Prell's [13] reconstruction is that chemical erosion and exhumation reduce the actual amplitude of the fluctuations [14]. Similar arguments about truncation can be made about even shallower cores in the Pacific [15]. Ideally what is needed is a core with high and relatively constant sedimentation rates where the 'apparent age' (average age of sediment particles in the bioturbated layer) is short [10,11], thereby minimizing the effects of bioturbation and chemical erosion.

During Leg 177 of the Ocean Drilling Program (ODP), we recovered an expanded late Pleistocene section from a water depth of 4621 m at Site 1089 in the southern Cape Basin, just north of the Agulhas Fracture Zone Ridge in the South Atlantic Ocean. We used diffuse color reflectance of the sediments while aboard ship as a proxy of carbonate content and predicted the position of marine isotope stages (MIS) 1 through 19 assuming that carbonate peaks coincided with interglacial periods [16], a relationship typical of 'Atlantic-type' carbonate stratigraphy. However, to our surprise, when oxygen isotope measurements were made post-cruise, we found the opposite, Indo–Pacific-type pattern, i.e. high reflectivity and high carbonate content generally occurred during glacial stages, whereas interglacial periods were marked by lower carbonate concentrations [13,17,18]. This pattern was unexpected because cores shallower than $\sim$4200 m in the Cape Basin all exhibit the 'Atlantic-type' carbonate pattern.

Here we address several questions raised by these somewhat puzzling observations: why do cores >4600 m in the Cape Basin exhibit a 'Pacific-type' carbonate stratigraphy, whereas those <4200 m exhibit an 'Atlantic-type' pattern? What is controlling carbonate variations in the deep Cape Basin? What are the implications for changes in the ocean's carbonate system, deep-water circulation, and atmospheric pCO$_2$? We conclude that the carbonate signal at Site 1089 (4620 m) in the Cape Basin represent a high-resolution record of temporal variability in the carbonate ion concentration of deep waters in the Indo–Pacific. Increased production of North Atlantic Deep Water (NADW) during interglacial periods influenced carbonate ion concentrations in water depths <4200 m, and accounts for the out of phase dissolution pattern above and below $\sim$4300 m. We further suggest that the carbonate dissolution changes observed may play a role in at least the second-order features of the atmospheric CO$_2$ curve from ice cores.

2. Site locations

The cores used in this study are from the Cape Basin off southwest Africa (Table 1). ODP Site 1089 was recovered in the southern Cape Basin close to the northern flank of the Agulhas Ridge. The site is located on a sediment drift and, consequently, sedimentation rates are high averaging 13.2 cm/kyr during the Brunhes Chron [16]. Piston core TTN057-6 and ODP Site 1090 were recovered 235 km to the southwest of Site 1089 on the northern flank of the Agulhas Ridge in $\sim$3751 m and 3702 m of water, respectively (Table 1). In these cores, sedimentation rates averaged $\sim$3.5 cm/kyr during the Pleistocene [16]. Our results from the southern Cape Basin are compared with two piston cores, RC13-229

Table 1
Cores from the Cape Basin in order of increasing water depth

	Latitude	Longitude	Water depth
RC13-228	22°20′S	11°12′E	3204
Site 1090	42°55′S	8°54′E	3702
TTN057-6-PC4	42°53′S	8°58′E	3751
RC13-229	25°30′S	11°19′E	4191
Site 1089	47°56′S	9°54′E	4621

(4191 m) and RC13-228 (3204 m), from the northern Cape Basin. Isotopic and carbonate records of these northern cores have been reported previously [19–23].

3. Modern hydrography

The abyssal Cape Basin is largely filled by lower Circumpolar Deep Water (CDW) that enters the basin from the south. Waters below 4500 m have nearly the same values of potential temperature (0.7°C), salinity (34.68), oxygen (4.2 ml/l), and silica (110 μM) as deep waters entering the South Atlantic through the Drake Passage [24]. Silicate concentrations in the South Atlantic are useful for estimating the proportion of northern and southern source waters because NADW has low dissolved silicate (12 μM), whereas southern source waters have high silicate values (125 μM) [25]. The origin of the high silica concentrations of CDW can be traced to the dense waters of the abyssal Southeast Pacific Basin [26]. The rapid increase of dissolved silica between 3500 and 4500 m in the Cape Basin represents a mixing line between northern and southern source waters (Fig. 1). ODP Site 1089 is bathed by nearly pure lower CDW ($t = 0.62$°C, $S = 34.65$). Site 1090/TTN057-6 is positioned in a mixing zone and waters are composed of ~60% CDW and 40% NADW.

Carbonate saturation in the southern Cape Basin decreases with depth and mirrors the dissolved silica profile. The saturation horizon is located at a depth of ~4000 m near the top of lower CDW (Fig. 1). Site 1089 is located below the modern saturation horizon, whereas Site 1090/TTN057-6 is located above. The carbonate ion concentration of CDW is nearly constant at 85 ± 5 μmol/kg [27], which is about the same as values found in the southern Cape Basin below ~4100 m.

4. Methods

Site 1089 was sampled at a constant 5 cm interval resulting in a temporal resolution of approximately one sample every 350 yr. Piston core TTN057-6-PC4 was sampled at 3 cm intervals and Site 1090 was sampled at 5 cm intervals, corresponding to a temporal spacing of approximately 1 and 1.7 kyr, respectively. Calcite tests of the benthic foraminifera *Cibicidoides wuellerstorfi*

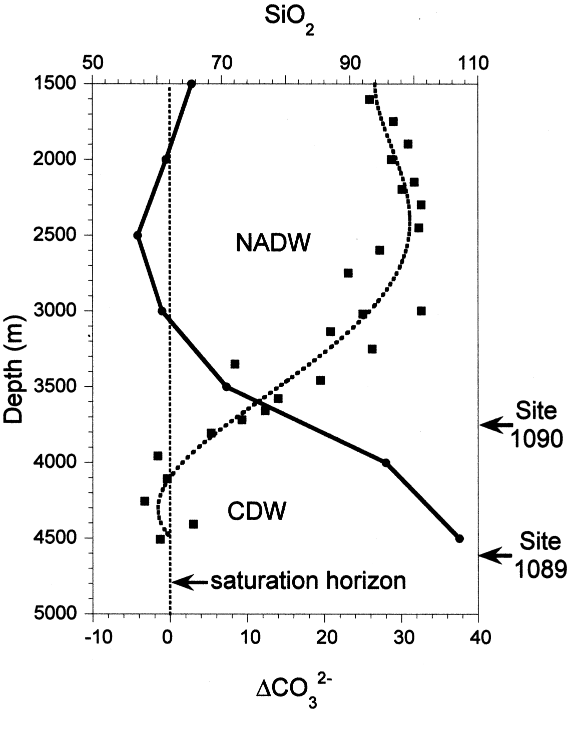

Fig. 1. Position of cores studied relative to dissolved silica (squares) at Site 1089 and ΔCO_3^{2-} (dots) from nearby GEOSECS Stations 93 (41°46′S, 18°27′E). ΔCO_3^{2-} indicates the degree of calcite saturation in seawater at in situ temperature and pressure conditions. Zero represents the saturation horizon. Positive values represent supersaturation, whereas negative values represent undersaturation. The saturation horizon is at ~4100 m. Increase in dissolved silica between ~3500 and 4500 m represents mixing of northern (NADW) and southern source waters (CDW).

and *Cibicidoides kullenbergi* were selected from the > 150 μm fraction and analyzed for their oxygen and carbon isotopic ratios. Samples from the upper 37.5 mcd of Site 1089 were analyzed at Scripps Institution of Oceanography using a Carousel-48 automatic carbonate preparation device coupled to a Finnigan MAT 252 mass spectrometer. Samples from Site 1090 [28] and below 37.5 mcd in Site 1089 were analyzed at the University of Florida using a Kiel III carbonate preparation device interfaced with a Finnigan MAT 252 mass spectrometer. Isotope analyses from piston core TTN057-6 were made using an Isocarb preparation device and Micromass PRISM Series II mass spectrometer [29]. All isotope results in this study are reported in standard delta notation relative to V-PDB and analytical precision was better than ± 0.1 ‰ for all analyses.

Percent $CaCO_3$ was determined by coulometric titration in piston core TTN057-6 and from the composite section of ODP Sites 1089 and 1090. Analytical precision is estimated to be ± 1% based on repeated analysis of reagent-grade (100%) $CaCO_3$. Samples from piston core TTN057-6 and Site 1089 were also analyzed for percent fragmentation of planktic foraminifera, which is sensitive to dissolution. Samples were split until approximately 300 specimens of foraminifera remained and the percentage of fragmented to whole foraminifera was determined.

The piston core record of TTN057-6 was spliced to Site 1090 at 345 kyr by matching the oxygen isotope and carbonate records. The chronology for each core was constructed by correlating the benthic oxygen isotope signal to the SPECMAP reference curve [30,31] (Fig. 2). In Site 1089, intense carbonate dissolution and scarcity of benthic foraminifera during MIS7 prevented us from obtaining a continuous benthic oxygen isotope record needed for time series analysis. Consequently, we spliced the $\delta^{18}O$ record of *Globigerina bulloides* into the benthic record be-

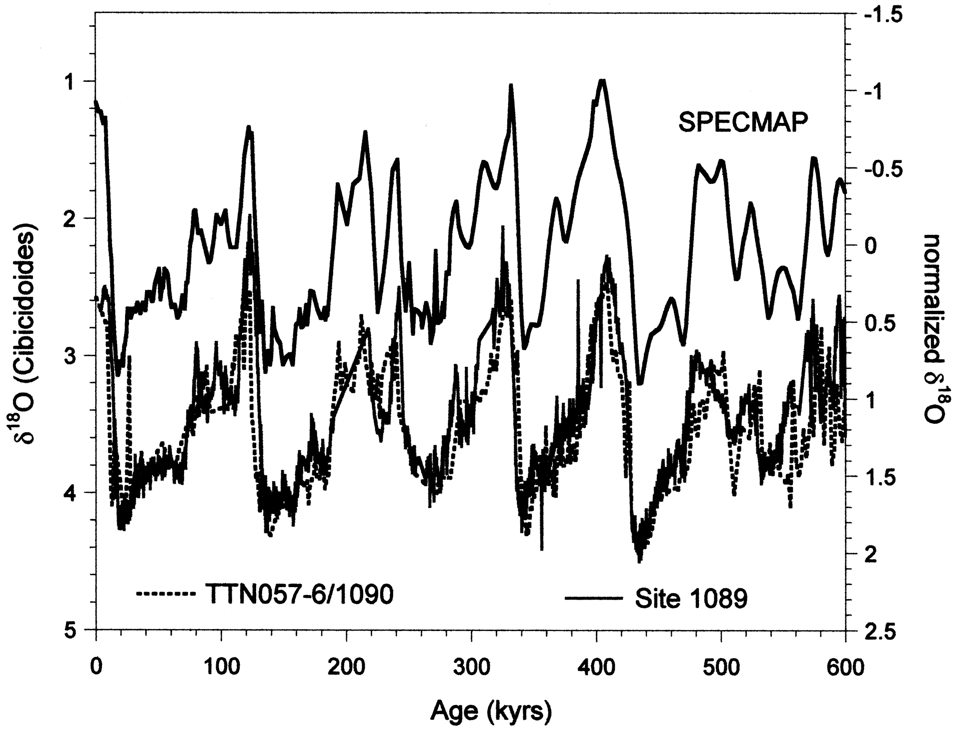

Fig. 2. Ages for cores TTN057-6/1090 and TTN057-21/1089 were derived by correlating benthic $\delta^{18}O$ signals to the SPECMAP stack [30,31].

tween ~185 and 220 kyr by adding 0.6‰ to the $\delta^{18}O$ values of *G. bulloides*.

5. Carbonate dissolution patterns

5.1. Site 1089 (4620 m)

The carbonate content for the last 600 kyr at Site 1089 varies from 0 to 70% (Fig. 3a). In general, carbonate concentrations are higher during full glacial periods (higher $\delta^{18}O$) and lower during interglacial stages, which is characteristic of a 'Pacific-type' carbonate stratigraphy. However, the carbonate maxima and minima in Site 1089 are offset from the $\delta^{18}O$ maxima and minima. Cross-correlation analysis indicates that the best correlation ($r = 0.69$) of the two signals is obtained if the carbonate record is shifted older by ~7.6 kyr relative to the $\delta^{18}O$ signal (Fig. 3b,c). Cross-spec-

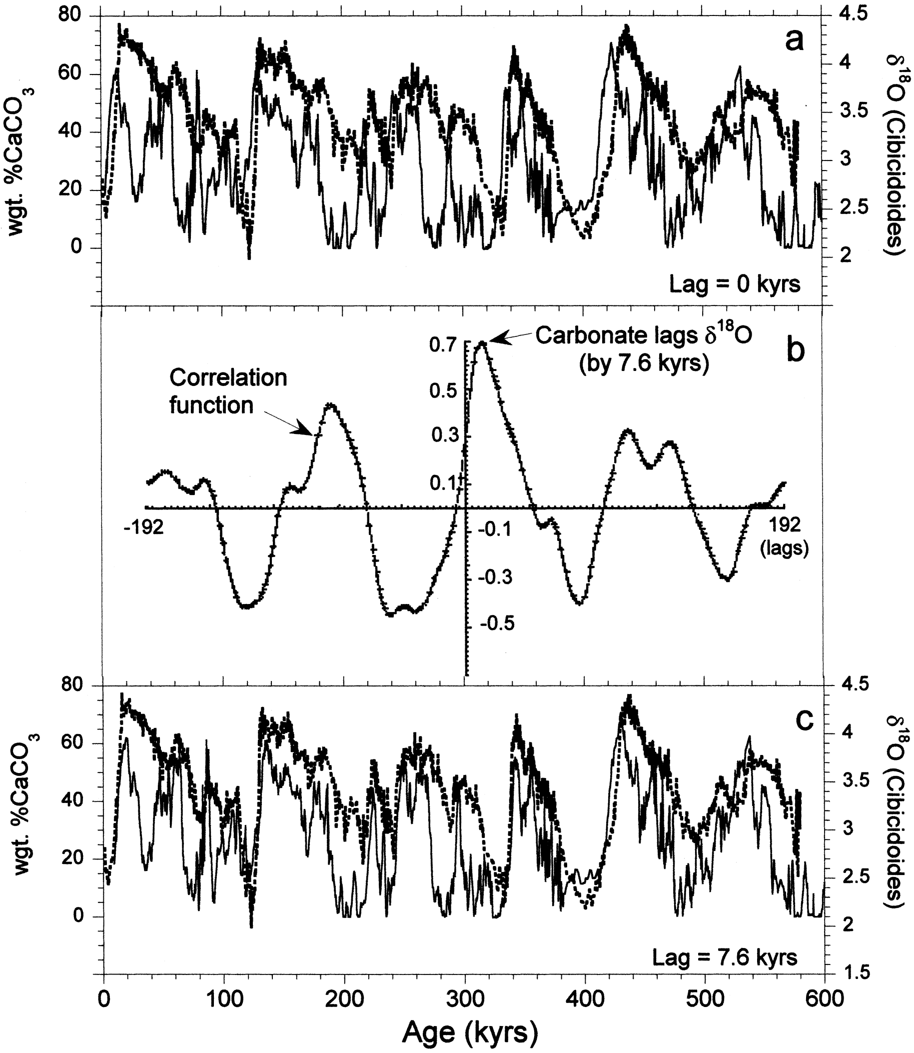

Fig. 3. (a) Wt% $CaCO_3$ (solid line) and benthic $\delta^{18}O$ (dashed line) signals from Site 1089 with no offset between records. (b) Cross-correlation function of $\%CaCO_3$ and benthic $\delta^{18}O$. (c) Same signal as (a) except that 7.6 kyr was added to the ages of the wt% $CaCO_3$ record to bring it in-phase with benthic $\delta^{18}O$. Note that Site 1089 (4621 m) displays 'Indo–Pacific-type' carbonate stratigraphy with higher $\%CaCO_3$ during glacial periods.

tral analysis of the carbonate and benthic δ^{18}O record reveals that the two signals are highly coherent at Milankovitch periods of 100, 41, and 23 kyr (Table 2), and the carbonate signal lags the benthic δ^{18}O signal at all periods. This phasing is consistent with Pleistocene records in the Pacific where dissolution maxima lag ice volume minima by 6–20 kyr [32].

Keir and Berger [33] and Peterson and Prell [18] found that carbonate dissolution maxima and minimum in Indo–Pacific cores coincided with the maximum rate of change in the δ^{18}O record. In Site 1089, the highest carbonate values are centered on glacial terminations, whereas low values tend to occur on the transitions from interglacial to glacial stages (Fig. 3a). A comparison of the Site 1089 carbonate record and the first derivative of the interpolated benthic δ^{18}O signal reveals a general similarity of the two curves (Fig. 4). Cross-correlation and cross-spectral analysis between %$CaCO_3$ and dδ^{18}O/dt demonstrates that the two are nearly in-phase for all Milankovitch periods (Table 2).

The Site 1089 carbonate record mirrors changes in percent foraminiferal fragmentation (Fig. 5), suggesting that carbonate content is controlled mainly by dissolution. Cross-spectral analysis, however, indicates that %carbonate lags fragmentation (neg.) at all Milkankovitch periods (Table 2). We believe this phase relationship is an artifact of the non-linear relationship between %fragmentation and dissolution as discussed by Le and Shackleton [32]. At early stages of dissolution, the proportion of fragments increases because whole foraminifera begin to break into fragments and few fine fragments are entirely dissolved. As dissolution intensifies, however, more of the fine fragments dissolve completely and the %fragmentation begins to decrease with increasing dissolution. Carbonate lags fragmentation (neg.) because percent fragmentation begins to decline before the %$CaCO_3$ signal decreases. In Site 1089, changes in carbonate and fragmentation are simultaneous on terminations when dissolution is first increasing. They are out of phase, however, on the interglacial to glacial transitions when dissolution reaches its maximum as carbonate approaches zero, yet fragmentation decreases due to the complete dissolution of fine fragments.

Consequently, we adopt the phasing of %$CaCO_3$ relative to benthic δ^{18}O to determine the relationship between dissolution and ice volume. This choice is supported by a comparison of the structure and phasing of the Site 1089 carbonate record with various dissolution proxies from the Indo–Pacific Ocean (Fig. 5) [18,32,34]. The resolution of the Indo–Pacific dissolution records is poor, however, in comparison to the Site 1089 carbonate signal. At Site 1089, the accumulation of terrigenous material is high and, more importantly, constant enough that the timing and amplitude of dissolution and preservation pulses are recorded with high fidelity. The Site 1089 carbonate signal is free from many of the complications that plague other records. For example, the central equatorial Pacific has been an important area for carbonate dissolution studies because the accumulation rate of non-carbonate sedimentary

Table 2
Results of cross-spectral analysis

Site	Variables	100 kyr		41 kyr		23 kyr	
		ϕ	k	ϕ	k	ϕ	k
1089	%$CaCO_3$ δ^{18}O	0.95	-51 ± 6	0.75	-86 ± 15	0.81	-127 ± 12
	%$CaCO_3$ and dδ^{18}O/dt	0.86	-36 ± 11	0.93	-10 ± 7	0.83	41 ± 12
	δ^{18}O and $-$frag.	0.97	6 ± 4	0.86	22 ± 11	0.40	-11 ± 29
	%$CaCO_3$ and $-$frag.	0.97	-46 ± 5	0.55	-70 ± 22	0.34	-149 ± 32
1090	%$CaCO_3$ and $-\delta^{18}$O	0.85	9 ± 11	0.65	2 ± 18	0.72	11 ± 16
	$-$frag. and δ^{18}O	0.49	41 ± 25	0.58	51 ± 21	0.52	-20 ± 24
	%$CaCO_3$ and $-$frag,	0.68	-23 ± 17	0.72	-27 ± 16	0.72	32 ± 16
1090–1089	%$CaCO_3$ and %$CaCO_3$	0.80	-113 ± 13	0.70	-69 ± 16	0.59	-37 ± 21
	$-$frag. and $CaCO_3$	0.47	105 ± 26	0.85	143 ± 11	0.72	105 ± 16

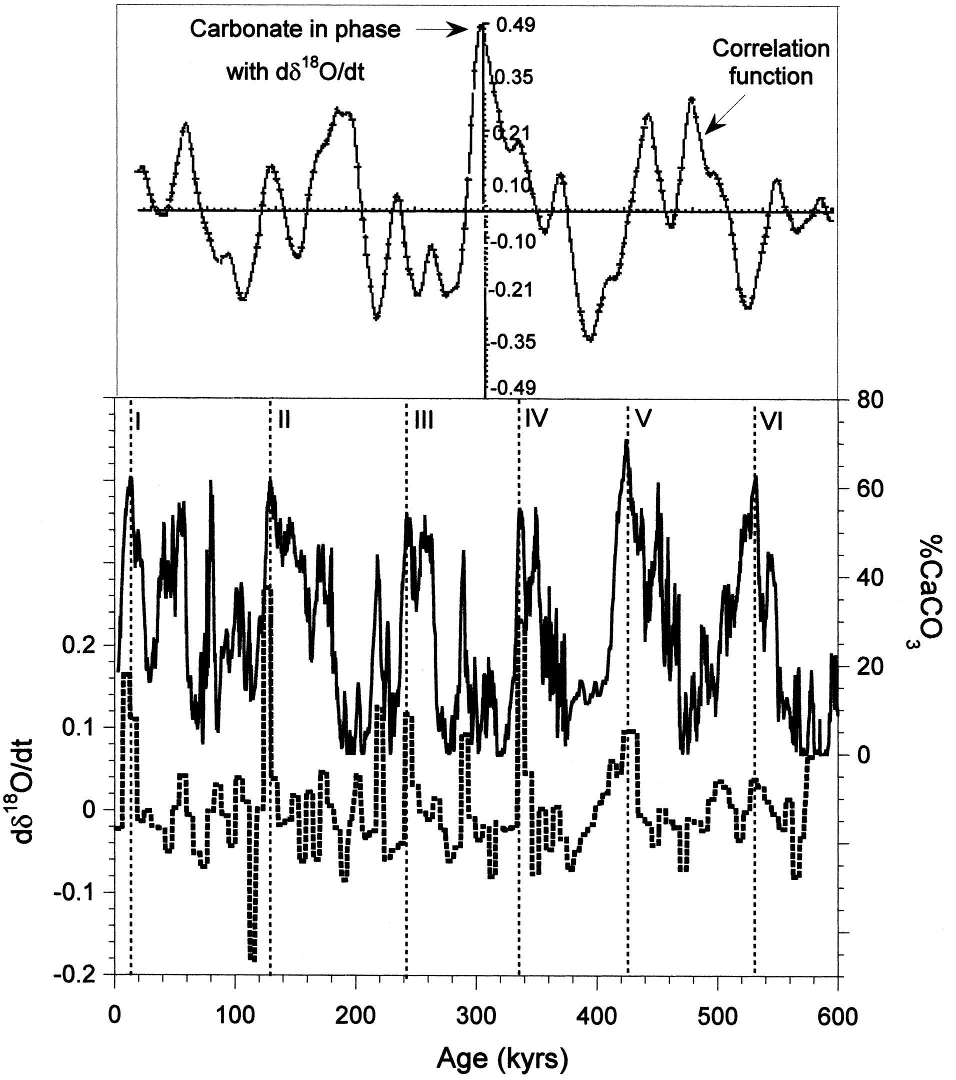

Fig. 4. (Top) Cross-correlation function for wt% $CaCO_3$ and the first derivative of the benthic $\delta^{18}O$ signal. (Bottom) Peak carbonate values are centered on glacial terminations whereas the start of glacial periods is marked by intense carbonate dissolution.

components is low and relatively invariant [13,18]. However, the low sedimentation rates often lead to blurring of the signal by bioturbation and truncation of the record by intense chemical erosion during interglacial periods. In addition, the wt% $CaCO_3$ in these sediments is relatively insensitive to even large amounts of dissolution because the rain rate and accumulation of non-$CaCO_3$ material are low [10]. Carbonate dissolution studies in low sedimentation rate cores from the Indian Ocean suffer from some of the same problems.

5.2. Site TTN057-6/1090 (~3750 m)

The carbonate content from Site TTN057-6/1090 (~3750 m water depth) varies from 40 to 90% and exhibits the opposite relationship between carbonate and benthic $\delta^{18}O$ than Site 1089 at 4621 m (Fig. 6). Carbonate concentrations

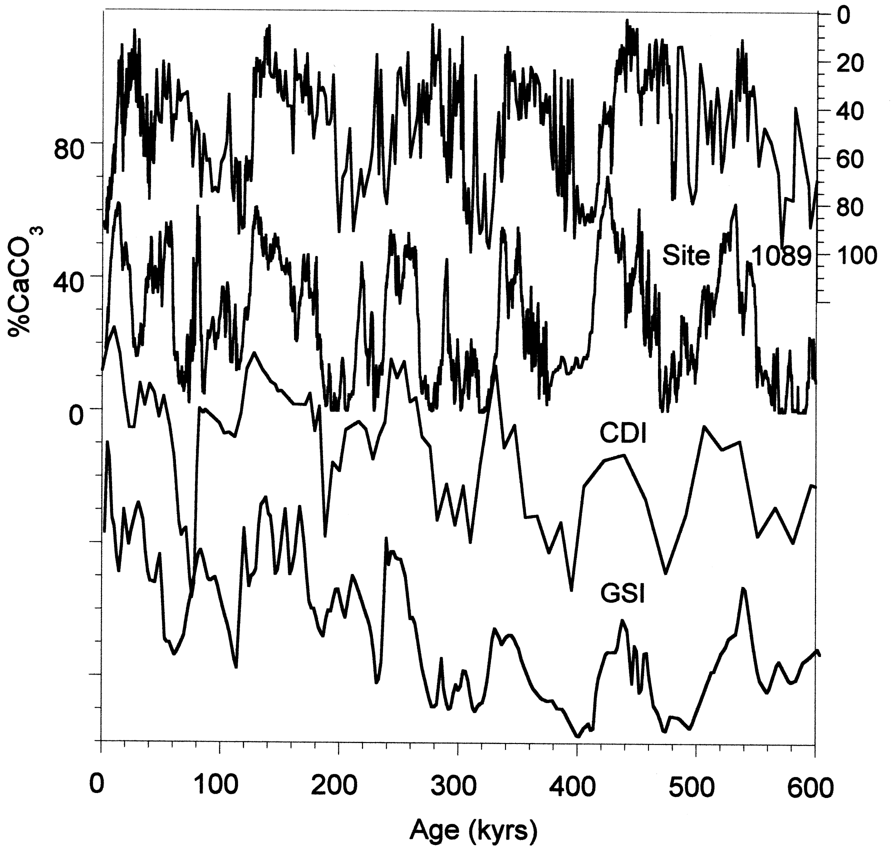

Fig. 5. Comparison of foraminiferal fragmentation and percent carbonate in Site 1089 with dissolution indices from the Indian Ocean. CDI = composite dissolution index [18]; GSI = grain size index [34].

are high during interglacial periods (lower benthic $\delta^{18}O$) and low during glacial stages, which is typical of cores from the Atlantic [35]. Peak carbonate (low dissolution) is in-phase with minimum $\delta^{18}O$ (minimum ice volume) at all Milankovitch frequencies (Table 2). Percent fragmentation is similar to the percent carbonate signal, indicating greater fragmentation (more dissolution) during glacial periods and less fragmentation (better preservation) during interglacials (Fig. 6).

Comparison of the carbonate record from Sites 1090/TTN057-6 (3702 m) with cores in the northern Cape Basin in water depths < 4200 m (RC13-228 = 3204 m, RC13-229 = 4191 m) reveals they are similar and display the 'Atlantic-type' carbonate stratigraphy (Fig. 7). The carbonate signal at Site 1090/TTN057-6 (3702 m) is out of phase with carbonate at Site 1089 (4620 m) such that the carbonate minima at Site 1090 lead the carbonate maxima at Site 1089 by ~12 kyr (Table 2). The shallow carbonate records in the Cape Basin are often, but not always, out of phase with the carbonate signal at Site 1089 (4621 m). For example, all cores regardless of water depth display low carbonate at the start of most glacial periods (e.g. carbonate minima at 25, 64, 187, and 275 kyr).

6. Discussion

6.1. *Causes of carbonate dissolution patterns in the Cape Basin*

Why do sites shallower than 4200 m in the Cape Basin exhibit an 'Atlantic-type' carbonate

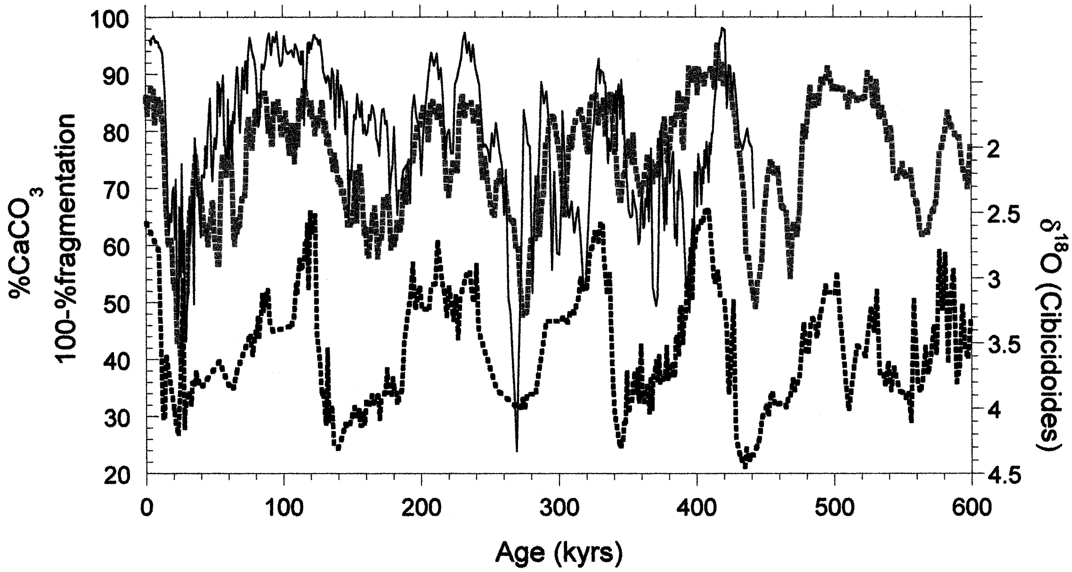

Fig. 6. Wt% $CaCO_3$ (gray dashed line), foraminiferal fragmentation (solid black line), and benthic $\delta^{18}O$ (black dashed line) signals from Site 1090 and piston core TTN057-6.

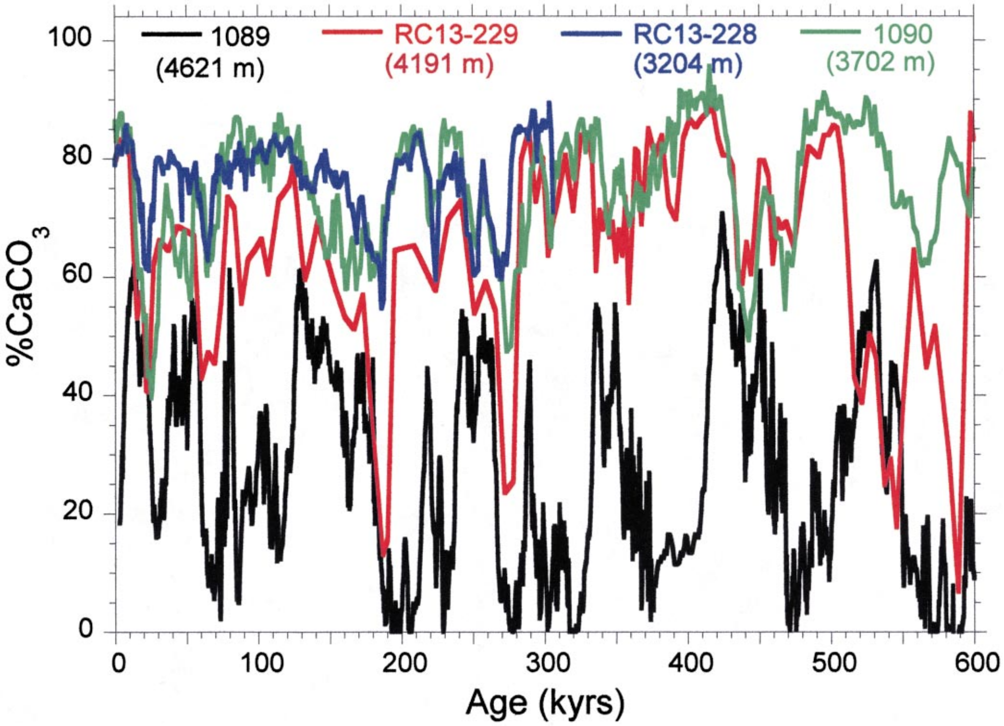

Fig. 7. Wt% $CaCO_3$ from records in the Cape Basin including piston core RC13-228 (blue; ~3200 m) [21]; Site 1090 (green; ~3700); piston core RC13-229 (red; ~4200 m) [21]; and Site 1089 (black, ~4600 m).

stratigraphy, whereas those deeper than ~4600 m exhibit a 'Pacific-type' pattern? The 'Pacific-type' pattern at Site 1089 is not unexpected because the physical and chemical properties of water overlying the site are nearly identical to waters entering the South Atlantic from the Pacific at the sill depth of the Drake Passage [24]. Because of its high sedimentation rates, we suggest that the Site 1089 carbonate signal represents a high-resolution record of the temporal evolution of the carbonate saturation state of deep Indo–Pacific waters.

The asymmetry between Atlantic and Pacific dissolution patterns has been attributed previously to basin to basin fractionation resulting from changes in the production of NADW [35,36]. Likewise, the difference in carbonate patterns of cores above and below ~4300 m in the Cape Basin is attributed to glacial to interglacial variations in NADW production. NADW is slightly supersaturated with respect to calcium carbonate, whereas CDW is undersaturated (Fig. 1) [10]. As the mixing ratio of NADW and CDW changed on glacial and interglacial time scales, so did carbonate saturation and dissolution.

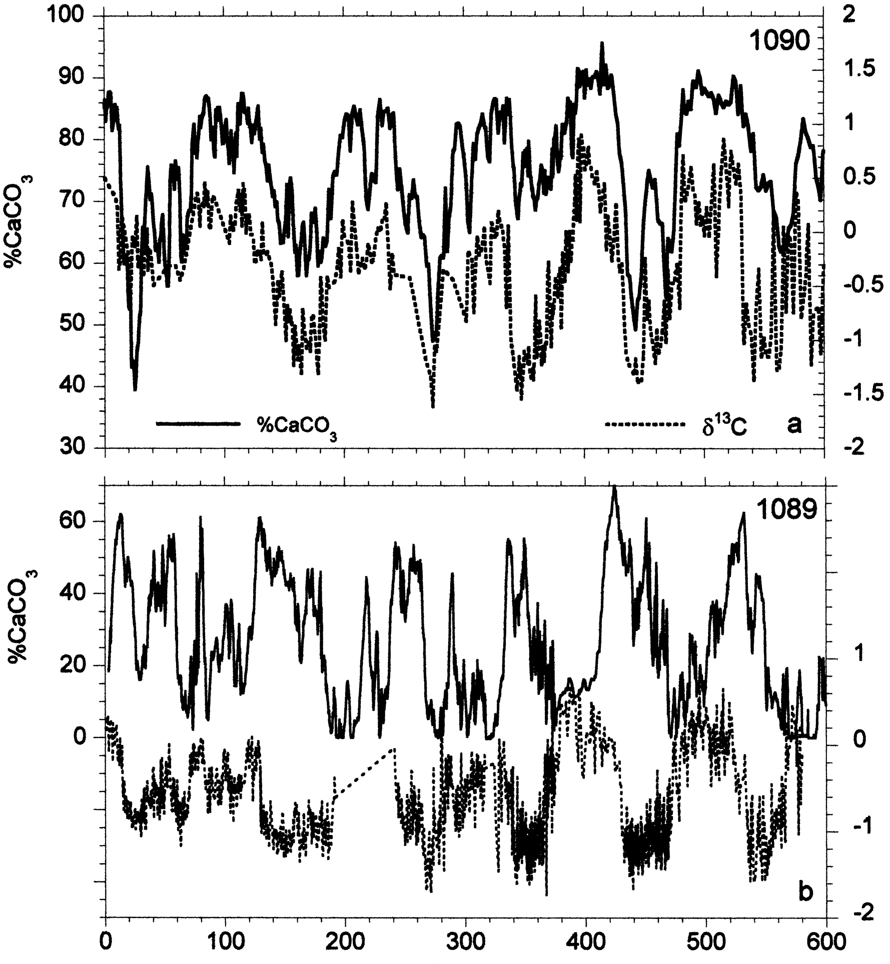

Fig. 8. (a) Signals of wt% $CaCO_3$ and benthic $\delta^{13}C$ are positively correlated at Site 1090 suggesting that $\%CaCO_3$ varies with changes in NADW production. (b) Wt% $CaCO_3$ at Site 1089 is negatively correlated with benthic $\delta^{13}C$ implying that changes in NADW production are not affecting carbonate dissolution at this site.

Differences in the gradient and phasing of carbonate variations between Site 1089 (4620 m) and shallower cores are greater during interglacial periods when the flux of NADW was strong (Fig. 7). Using benthic δ^{13}C as a proxy for variations in the proportion of NADW, the positive correlation between %CaCO$_3$ and benthic δ^{13}C in Site TTN057-6/1090 supports an influence of NADW on carbonate saturation at 3700 m (Fig. 8a). At Site 1089, however, the negative relationship between %CaCO$_3$ and benthic δ^{13}C is opposite to that predicted if changes in NADW were affecting the carbonate saturation state of deep water at 4621 m (Fig. 8b).

6.2. *Implications for mechanisms of [CO_3^{2-}] change in the deep sea*

If we accept that the carbonate signal of Site 1089 represents a qualitative, high-resolution record of changes in deep-sea carbonate ion concentration, then comparison of the timing and pattern of Site 1089 carbonate variations with those predicted by models of carbonate dissolution may help to constrain the mechanism of deep-sea [CO_3^{2-}] variations and their implications for atmospheric pCO$_2$ change. The observations that: (1) wt% carbonate lags changes in benthic δ^{18}O, and (2) carbonate variations are in-phase with the rate of change (first derivative) of benthic δ^{18}O imply fundamentally different responses of the marine carbonate system that involve steady-state and transient effects, respectively.

6.2.1. *Steady-state mass balance of oceanic alkalinity*

The lag of %CaCO$_3$ relative to benthic δ^{18}O is compelling even in the fine structure of the signals when the signal is adjusted by 7.8 kyr (Fig. 4). If we assume benthic δ^{18}O partly reflects changes in continental ice volume, then sea level variation is an important mechanism for controlling deep-sea [CO_3^{2-}]. Glacial to interglacial variations in sea level change the locus of carbonate deposition between continental shelves and ocean basins and the lysocline adjusts to maintain alkalinity balance between riverine input and marine burial [2]. During marine transgressions, the transfer of carbonate from the deep-sea to shelf environment results in a rise of the lysocline and carbonate dissolution in the deep sea. The observed lag between carbonate and δ^{18}O in Site 1089 averages 7.6 kyr (Fig. 5), which is considerably longer than the 2500 yr predicted by Berger [2]. The magnitude of the carbonate lag is dependent upon: (1) the starting position of sea level during the lowstand; (2) the rate of sea level rise and shelf area flooded; (3) the rate of coral reef growth; and (4) the mixing time of the oceans. The lag is longer on Termination V than any of the other deglaciations (Fig. 3a). This may reflect the fact that sea level during MIS12 stood 20 m lower than the last glaciation [37] and, therefore, it took longer for sea level rise to flood the continental shelves and thereby increase the living space for corals. During the last deglaciation, the rapid rise in sea level between 16 and 8 kyr exceeded the ability for most coralgal reefs to keep pace in terms of vertical growth [38]. As a result, maximum rates of reef accumulation lagged the onset of deglaciation by at least 8 kyr.

Changes in the locus of carbonate deposition between the shelves and deep sea not only predict variations in deep-sea [CO_3^{2-}], but also predict changes in atmospheric pCO$_2$ [2,39] and the Sr/Ca of seawater [40]. Carbonate deposition on the shelf in coral reefs consists mainly of aragonite, which has a much higher Sr/Ca ratio than calcite that is dominantly deposited in the ocean basins. During sea level highstands, we would expect lower Sr/Ca ratios of seawater and increased dissolution in the deep sea. During times of regression, weathering of Sr from aragonitic shelf sediments raises the Sr/Ca of seawater by 1–3% [40]. If shelf-basin fractionation were responsible for the observed pattern of carbonate dissolution in Site 1089, then we expect a correlation between Site 1089 %CaCO$_3$ and Sr/Ca of seawater. Using records of foraminiferal Sr/Ca from six cores located in different ocean basins, Martin et al. [1] produced a stacked record that they interpret as reflecting, in part, whole-ocean changes in the Sr/Ca ratio of seawater. A comparison of the stacked record of foraminiferal Sr/Ca and the

Site 1089 carbonate signal for the last 250 kyr reveals a remarkable similarity (Fig. 9). This relationship is not predicted by other models of deep-sea [CO_3^{2-}] change that do not involve shelf-basin fractionation of carbonate and Sr. Furthermore, changes in Sr/Ca are in-phase with Site 1089 carbonate variations and both signals lag benthic $\delta^{18}O$, thereby supporting a sea level control.

Although the relationship between Sr/Ca and 1089 carbonate is compelling, the observed 4–5% change in glacial to interglacial Sr/Ca is too large to be explained by changes in shelf carbonate deposition or erosion alone [1,40]. Martin et al. [1] argued that their stacked Sr/Ca record is not controlled by dissolution because cores from ocean basins with differing glacial to interglacial histories of carbonate dissolution show the same pattern of Sr/Ca variation. Although factors other than changing seawater Sr/Ca may be amplifying the late Pleistocene foraminiferal Sr/Ca signal [41], the strong correlation and similar phase relationship between the stacked Sr/Ca signal and Site 1089 carbonate record point to a common process that controls both signals, i.e. sea level and/or dissolution.

6.2.2. *Transient-state redistribution of alkalinity and DIC*

Although steady-state processes alone can explain the observed lag between carbonate and ice volume, transient responses of the carbonate system may also have played a role. Carbonate variations at Site 1089 are in-phase with the rate of change (first derivative) of benthic $\delta^{18}O$ (Figs. 5 and 6), indicating intense dissolution during the transition from interglacial to glacial periods and enhanced preservation on glacial terminations. This pattern may have been caused by a transient redistribution of alkalinity and DIC in the ocean at the transitions into and out of glacial periods. Many of the proposed mechanisms of pCO_2 variation create significant transient changes in the deep ocean's carbonate content at the transitions into and out of glacial stages [42]. The carbonate system adjusts to these changes (i.e. carbonate compensation) [3] until steady-state conditions are restored. The time required for carbonate compensation is on the order of several thousand years [3]. Most deep-sea cores do not record such short-term events because bioturbation and chemical erosion obscure the carbonate signal owing to

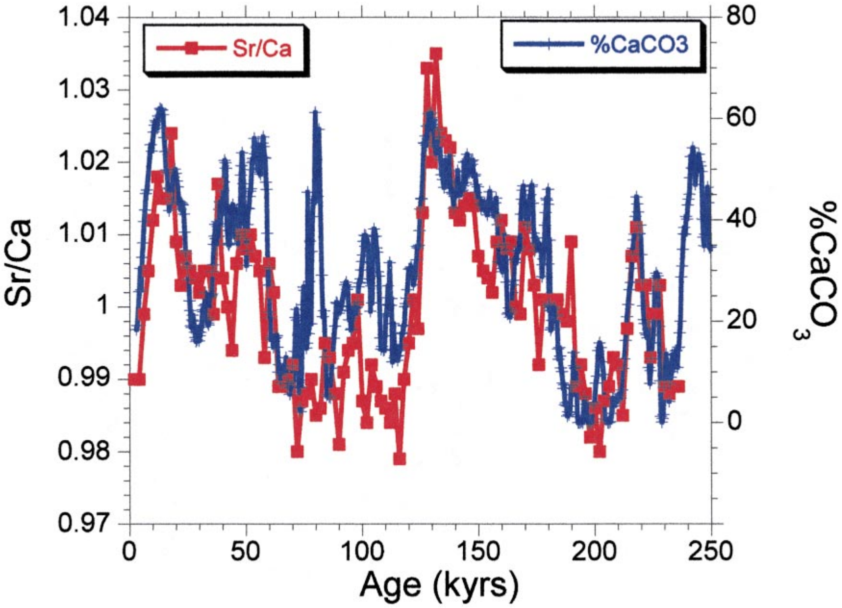

Fig. 9. Wt% $CaCO_3$ in Site 1089 (blue) versus the stacked record of foraminiferal Sr/Ca [1]. These records are highly correlated as would be expected if both were controlled by sea level driven changes in the locus of carbonate deposition (i.e. shelf versus ocean basins).

low sedimentation rates. At Site 1089, however, the high-resolution carbonate signal clearly records preservation events centered on terminations followed by increased dissolution (carbonate compensation) during the subsequent interglacial. Similarly, severe carbonate dissolution events mark the start of glacial stages. Although the Site 1089 carbonate record does not indicate which mechanism was responsible for the primary change in $p\mathrm{CO}_2$ at glacial–interglacial transitions, it provides a detailed record of the timing and response of the carbonate system that acts to reinforce the initial $p\mathrm{CO}_2$ change.

6.3. *Implications for atmospheric pCO₂*

Regardless of what specific mechanism is controlling carbonate compensation in the deep sea, changes in deep-sea $[\mathrm{CO}_3^{2-}]$ must play a role in atmospheric $p\mathrm{CO}_2$ variation; the questions are 'when' and 'by how much'. The Site 1089 carbonate record can address the 'when' but only loose minimum constraints on the magnitude of the effect exist from %carbonate records alone. For example, the core-top carbonate content of cores below 4600 is essentially nil – abundant carbonate does not appear in recent sediments of the southern Cape Basin unless the core is above the 4200 m horizon. By contrast, during the time of peak deglacial carbonate burial, carbonate obviously survived dissolution at depths greater than 4970 m (in core TTN057-21). These carbonate dynamics suggest that the lysocline shifted vertically by at least 700 m. This change is certainly large enough to have a significant impact on atmospheric CO_2 (a few tens of μatm), though it is

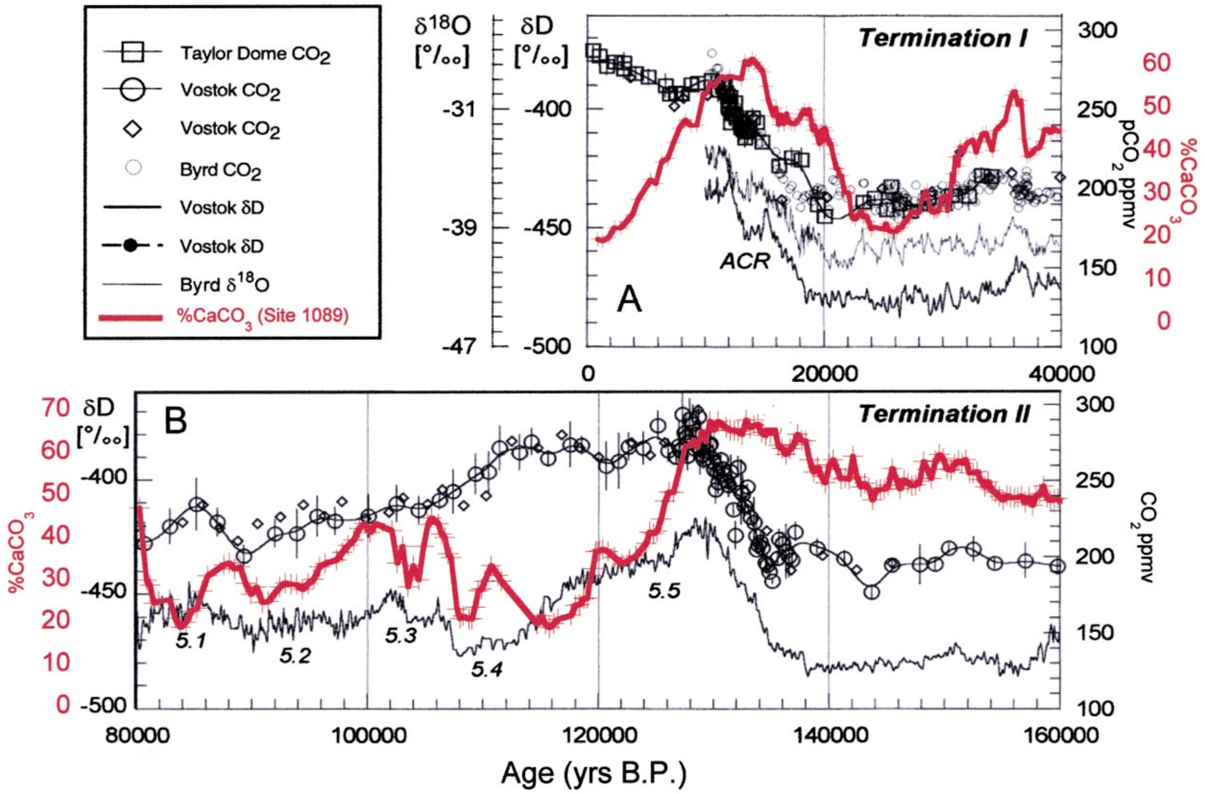

Fig. 10. (A) Comparison of $\%\mathrm{CaCO}_3$ in Site 1089 (red) with $p\mathrm{CO}_2$ and δD changes in the Vostok ice core [43] over Termination I and the Holocene. (B) Comparison of $\%\mathrm{CaCO}_3$ in Site 1089 with $p\mathrm{CO}_2$, δD, and $\delta^{18}\mathrm{O}$ changes in Antarctic ice core [43] over Termination II and MIS5. Modified after Fischer et al. [43].

not large enough to account for the entire glacial–interglacial signal. Firm quantification of the carbonate ion changes in the deep ocean must await measurement of dissolution indices [4,5] along a true depth transect. However, compilation of cores along topographic features in the southern Cape Basin might constitute an ideal opportunity for this pursuit.

Questions of magnitude aside, the timing of carbonate changes in the Site 1089 record strongly suggests a role of deep-sea $[CO_3^{2-}]$ in explaining some of the fine structure observed in atmospheric pCO_2 records. For example, detailed records of pCO_2 change in Vostok indicate a lag between decreasing temperature and CO_2 response during the last interglacial period [43]. Not until 6000 yr after the cooling at the stage 5.5/5.4 boundary does a substantial decline in CO_2 occur. The high values of atmospheric pCO_2 that continue into stage 5.4 may be attributed to a lagged response of carbonate compensation because dissolution, which began in the Eemian, also continued well into stage 5.4 (Fig. 10B). This explanation is completely consistent with the sedimentary changes we observe. Similar considerations apply to Termination I and the Holocene [25]. Carbonate peaks during termination as a consequence of oceanic redistribution of alkalinity and DIC and is followed by a decline in carbonate due to compensation (Fig. 10A). Consequently, the atmospheric pCO_2 continues to rise throughout the Holocene except for a temporary decline in the early Holocene that was probably related to forest growth [25].

7. Summary and conclusions

We propose the carbonate record from ODP Site 1089 in the deep Cape Basin (>4600 m) provides a view of the temporal evolution of the carbonate system with a fidelity that is unmatched by other records. The signal is free from many of the complications that limit other records from the Indo–Pacific Oceans (low sedimentation rates, blurring by chemical erosion, bioturbation, etc.). The phase relationship of the Site 1089 carbonate signal is similar to the Indo–Pacific in that lag changes in benthic $\delta^{18}O$ by an average of 7.6 kyr, and is in-phase with the rate of change (first derivative) of benthic $\delta^{18}O$. These relationships represent two fundamentally different responses of the marine carbonate system that involve steady-state and transient effects.

The lag between carbonate and benthic $\delta^{18}O$ may reflect a delayed response in the carbonate system to changes in continental ice volume and sea level. This interpretation supports a sea level control of carbonate compensation in the deep sea and is consistent with the 'Coral Reef Hypothesis' whereby sea level changes control the locus of carbonate deposition between the shelf and deep-sea environments during glacial to interglacial cycles [2,39]. Further support comes from the observation that the Site 1089 carbonate signal is remarkably similar to inferred changes in the Sr/Ca of seawater for the past 250 kyr [1]. This relationship is predicted by sea level control of shelf-basin fractionation of carbonate and Sr. However, the observed 5% changes in Sr/Ca are large given the long residence times of Sr and Ca in the ocean, and other processes may be affecting the Sr/Ca of foraminifera [41].

The in-phase relationship between carbonate and the rate of change (first derivative) of benthic $\delta^{18}O$ may reflect a transient redistribution of alkalinity and TDIC in the oceans followed by carbonate compensation [3,25]. The timing of carbonate changes in Site 1089 qualitatively suggests a significant role for carbonate compensation in amplifying pCO_2 variations caused by other mechanisms and in controlling at least some of the second-order features of the atmospheric CO_2 curve from ice cores. This fact coupled with available evidence suggesting that the magnitude is not trivial makes it all the more important to resolve the mechanisms of deep-sea carbonate compensation. We have made an initial step here by developing a continuous, high-resolution carbonate signal that appears to accurately record changes in the saturation state of deep water. With additional measurement of dissolution indices along a true depth transect in the southern Cape Basin, it may be possible to quantitatively determine deep-sea carbonate ion changes and evaluate its impact on atmospheric CO_2 variability over glacial cycles.

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