

## 20. INTERSTITIAL WATER CHEMISTRY OF DEEPLY BURIED SEDIMENTS FROM THE SOUTHWEST AFRICAN MARGIN: A PRELIMINARY SYNTHESIS OF RESULTS FROM LEG 175<sup>1</sup>

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### ABSTRACT

The distribution of dissolved species in interstitial waters of sediments sampled by Ocean Drilling Program (ODP) Leg 175 along the southwest African margin indicates that organic matter remineralization and carbonate dissolution/precipitation reactions dominate diagenetic processes in this region. Degradation of organic matter in the shallowest sediments generates extremely high alkalinities as well as large concentrations of dissolved ammonium and phosphate. For example, Site 1084 (Cape Basin), with an average of 8 wt% organic carbon and maximum values approaching 20 wt%, records the second highest alkalinity and dissolved ammonium concentrations observed in the history of Deep Sea Drilling Project/ODP drilling. These high alkalinities drive the shallow precipitation of authigenic carbonate phases, resulting in depletions of dissolved  $\text{Ca}^{2+}$  that overwhelms the  $\text{Ca}^{2+}$  release by dissolution of biogenic calcite (that is indicated by increases with depth in dissolved strontium). Dolomite precipitation causes significant negative excursions of dissolved magnesium from background downcore trends. These excursions are coincident with minima in dissolved  $\text{Ca}^{2+}$ . Diatom dissolution causes dissolved silica concentrations to be higher than in seawater, and downcore trends in dissolved silica usually correspond to variations in sedimentary diatom abundance. At many sites, a shallow increase in dissolved chloride appears to record a diffusional signal of glacial seawater.

### INTRODUCTION

Deep drilling throughout the Benguela upwelling system during Ocean Drilling Program (ODP) Leg 175 provided a terrific opportunity for chemists, sedimentologists, and paleoceanographers to study processes related to the deposition, decomposition, and preservation of organic matter; precipitation and dissolution of carbonate phases such as calcite and dolomite; and diagenetic processes involving clay mineral authigenesis. By careful selection of drill sites located in various basins along the southwest African margin (Fig. 1), we were able to sample a variety of depositional regimes characterized by contrasts in terrigenous supply, organic matter content, export production, and sedimentation rate. Variations in these components directly influence the distribution of many important chemical species dissolved in the interstitial waters of the sedimentary sequence at a given site. Because interstitial waters record diagenetic chemical reactions that are often unobservable in the bulk sediment, it is critical to identify the sources and sinks of these dissolved species.

We have several goals with this paper: (1) to provide a preliminary synthesis of results from the analytical program undertaken on the *JOIDES Resolution* during Leg 175, (2) to identify first-order similarities and differences between the depositional and chemical regimes along the southwest African margin, and (3) to highlight where ongoing and future shore-based geochemical studies are most likely to yield productive insights into the sedimentological and paleoceanographic processes operating in the Benguela Current system throughout the Neogene. In the spirit of a preliminary synthesis, we hope to raise more questions here than we answer.

### SITE CHARACTERISTICS, SAMPLING PLAN, AND ANALYTICAL METHODS

A total of 335 interstitial water samples were gathered from 13 sites during Leg 175 (Table 1). The sampling protocol was developed to ensure essentially complete coverage of the stratigraphy at each site, and, with a few exceptions, we were able to obtain our deepest sample very near the total depth of penetration at each site (Table 1). Because of end-of-leg time constraints, the database from Site 1087 was not completed; consequently, a discussion of the chemistry at this site is not included here.

As described in the "Explanatory Notes" chapter and the individual site chapters (all this volume), the sampling frequency occurred in two main modes: (1) standard sampling of one sample per core for the uppermost 100 meters below sea floor (mbsf) and then every third core to the total depth of the hole and (2) at three sites (Table 1), ultra-high-resolution sampling at a frequency of one sample per section of core for the uppermost 60 mbsf, below which the standard sampling protocol was followed. These acquisition strategies ensured that we are able to address the early-, mid-, and late-stage diagenetic processes occurring at the various depths at a given site.

At each site, we generated a data set that included pH, alkalinity,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$  (by charge balance),  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{H}_4\text{SiO}_4$ ,  $\text{PO}_4^{3-}$ ,  $\text{NH}_4^+$ , and  $\text{Sr}^{2+}$ . Because of the extremely high core recovery during Leg 175 and the multitude of extra sites drilled, we were not able to utilize the shipboard atomic absorption facility for analyses other than for dissolved  $\text{Sr}^{2+}$ . Analytical methods are described in the "Explanatory Notes" chapter (this volume) as well as by Gieskes et al. (1991). Postcruise analyses will specifically target trace metal (iron, manganese, barium, and others) and isotopic ( $\delta^{18}\text{O}$ ,  $\delta^{13}\text{C}$ ,  $^{87}\text{Sr}/^{86}\text{Sr}$ ) distributions to further expand this data set.

### RESULTS AND DISCUSSION

We summarize here the principal results of the shipboard interstitial water program. At many of the sites, either specific sampling strategies were implemented or unique chemical behavior(s) were

<sup>1</sup>Wefer, G., Berger, W.H., Richter, C., et al., 1998. *Proc. ODP, Init. Repts.*, 175: College Station, TX (Ocean Drilling Program).

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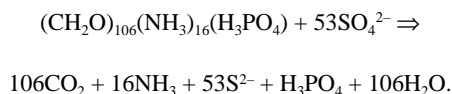
<sup>4</sup>Shipboard Scientific Party is given in the list preceding the Table of Contents.

discovered (e.g., at Sites 1077 and 1079; see Table 1), and additional details of the chemical distributions within the interstitial waters may be found in the individual site chapters (this volume). Of particular interest are the extremely high alkalinities and large concentrations of  $\text{NH}_4^+$  observed at Site 1084 in the Northern Cape Basin. This unique site is discussed separately below.

### Organic Matter, Biogenic Inputs, and Remineralization

Throughout the Benguela upwelling system, the rates of supply and decomposition of biogenically produced organic matter exert a profound influence on the concentration-depth gradients of many dissolved chemical species, including alkalinity,  $\text{SO}_4^{2-}$ ,  $\text{NH}_4^+$ ,  $\text{PO}_4^{3-}$ , and  $\text{H}_4\text{SiO}_4$ . With the high concentrations of organic carbon in these sediments (Meyers et al., Chap. 21, this volume), the production of alkalinity in the uppermost ~50 mbsf reflects the progressive degradation of organic matter in the youngest sediments. Inter- and intrabasin contrasts in the alkalinity profiles (Fig. 2) most likely reflect subtle variations in organic matter reactivity and in sedimentation rate. The observed increases in alkalinity are tied to the total production of  $\text{CO}_2$  by reduction/consumption of  $\text{SO}_4^{2-}$  and other electron acceptors. The asymptotic distribution of alkalinity at depth confirms that the dominant chemical process affecting its distribution is the destruction of organic matter in the shallowest sediments. At some sites, however, carbonate reprecipitation reactions also affect the alkalinity profile, albeit to a lesser degree, as discussed in the individual site chapters (this volume).

The suboxic degradation of organic matter (Froelich et al., 1979) also consumes dissolved  $\text{SO}_4^{2-}$  via the reaction (assuming a Redfield stoichiometry)



Information may be gained by examining the relationship between sedimentation rate and the rate of  $\text{SO}_4^{2-}$  consumption (Fig. 3). In theory, all other parameters being equal (notably, the concentration and type of organic matter), complete  $\text{SO}_4^{2-}$  consumption at drilling sites with slower sedimentation rates should occur at greater depths than at sites where faster sedimentation occurs (Berner, 1980). At sites with slower sedimentation, the downward diffusion from the overlying seawater reservoir will replenish that  $\text{SO}_4^{2-}$  consumed during early degradation of organic matter, which, in turn, delays the successive onset and completion of  $\text{SO}_4^{2-}$  destruction. Thus, the sedimentation rate and apparent rate of  $\text{SO}_4^{2-}$  consumption are often positively correlated. In regimes where such a relationship is not ob-

served, other factors, such as the nature of the organic matter, must be more important than the sedimentation rate control.

Within the Congo Basin, the depth to the complete consumption of  $\text{SO}_4^{2-}$  is relatively uniform (Fig. 2; Table 1), and a positive relationship is observed between the sedimentation rate and the  $\text{SO}_4^{2-}$

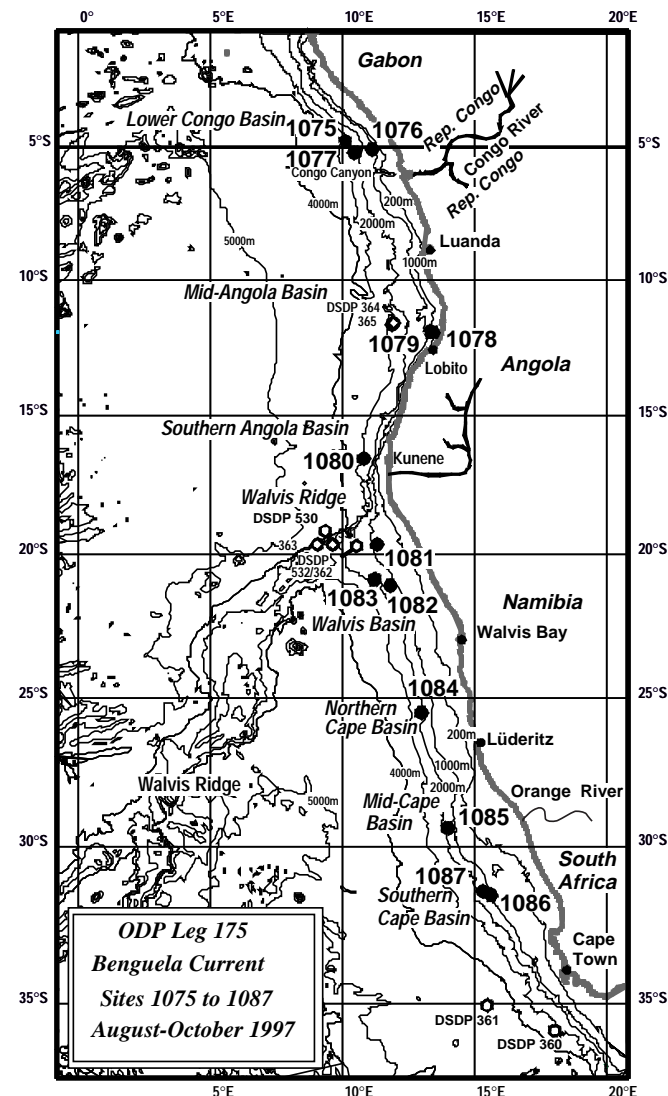


Figure 1. Location map of sites drilled during ODP Leg 175.

Table 1. Summary of interstitial water sampling and chemistry, ODP Leg 175.

Site	Location (basin)	Depth of deepest IW (mbsf)	Total depth sampled (mbsf)	Total depth sampled by IWs (%)	Depth to $\text{SO}_4^{2-}$ depletion (mbsf)	Maximum alkalinity (mM)	Maximum $\text{NH}_4^+$ (mM)	Comments
1075	Lower Congo	191	201	95	31.40	41.5	6.1	High-resolution to 60 mbsf
1076	Lower Congo	202	204	99	28.20	36.2	9.2	
1077	Lower Congo	204	205	100	28.50	36.0	6.2	Hydrate test 100–130 mbsf
1078	Mid-Angola	150	166	90	21.40	86.5	15.8	
1079	Mid-Angola	120	121	99	47.60	59.0	12.8	Brine at depth?
1080	Southern Angola	50	52	96	6.20	47.7	13.0	High-resolution, entire hole
1081	Walvis Ridge	441	453	97	62.30	28.8	11.6	Deep penetration site
1082	Walvis	586	601	98	21.35	75.6	27.3	High-resolution 60 mbsf, deep penetration
1083	Walvis	187	201	93	34.60	37.0	8.7	
1084	Northern Cape	600	605	99	5.90	171.7	50.4	Second highest alkalinity, $\text{NH}_4^+$ DSDP/ODP
1085	Mid-Cape	599	604	99	46.10	27.5	5.8	Deep penetration site
1086	Southern Cape	201	206	98	182.10	17.4	2.8	
1087	Southern Cape	477	492	97	79.10	31.2	4.9	Deep penetration site

Notes: Sulfate depletion is defined as the shallowest occurrence of  $\text{SO}_4^{2-} < 1$  mM. IW = interstitial water.

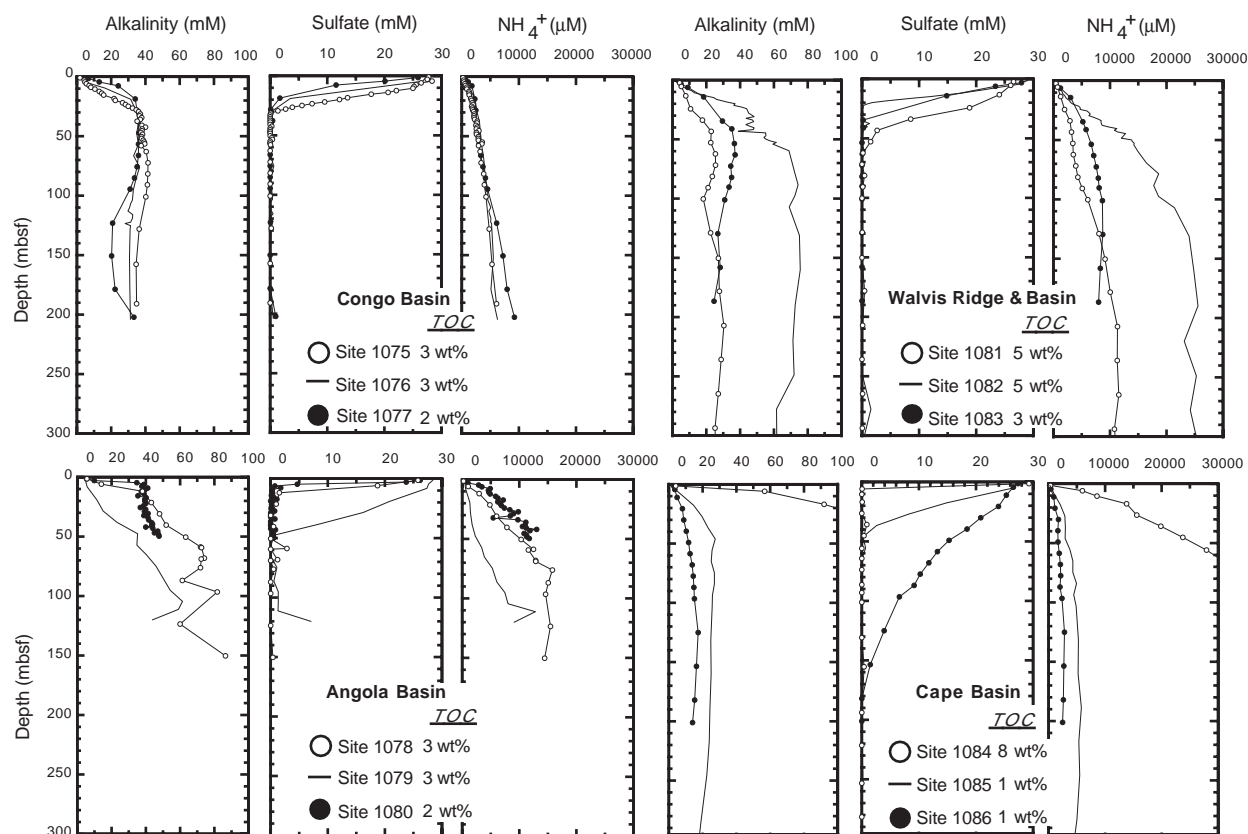


Figure 2. Downcore profiles of alkalinity,  $\text{SO}_4^{2-}$ , and  $\text{NH}_4^+$  in interstitial waters of sites drilled during Leg 175 (except Site 1087; see text). All panels for a given dissolved constituent are plotted to a common scale on the abscissa and to the identical depth scale. For complete profiles to total depth at a given site, please refer to the individual site chapters (this volume). Note off-scale values of alkalinity and dissolved  $\text{NH}_4^+$  at Site 1084; please refer to Figure 6 for discussion of this site. The concentration values of total organic carbon (TOC) in the sediments (in weight percent) are taken from the “Organic Geochemistry” sections of the individual site chapters (this volume).

consumption rate, although gradients at the three sites are quite similar (Fig. 3; Sites 1075, 1076, and 1077). As outlined above, this implies that the variation in organic matter among these sites is minimal. Such an argument can also be made, albeit less convincingly, for the relative distributions at the Walvis Ridge/Basin sites (Fig. 3; Sites 1081, 1082, and 1083). In contrast, at Site 1079 within the Angola Basin, the consumption of  $\text{SO}_4^{2-}$  is not achieved until 50 mbsf, which is significantly deeper than at Sites 1078 and 1080, also located in the Angola Basin (Fig. 2; Table 1). It is clear that sedimentation rate is not the dominant controlling parameter of organic degradation in the Angola Basin because Site 1079 records the deepest penetration of dissolved  $\text{SO}_4^{2-}$  (Fig. 2), yet has the highest sedimentation rate of the three Angola sites (Fig. 3). Finally, the depositional regimes within the Cape Basin display the largest variability of organic matter diagenesis of the entire leg. Because of the extremely high organic matter loadings at Site 1084 (Fig. 2),  $\text{SO}_4^{2-}$  is completely consumed within the uppermost 5 mbsf (as described below), whereas at Site 1086, the very high carbonate concentration, the low organic matter concentration, and the low sedimentation rate (Fig. 3) combine to allow the penetration of  $\text{SO}_4^{2-}$  to the relatively great depth of ~200 mbsf. Overall, when one considers the entire database of the southwest African margin sites drilled during Leg 175—with the exception of Sites 1080 and 1084 (Fig. 3, inset)—there is a broad positive relationship between sedimentation rate and  $\text{SO}_4^{2-}$  reduction, indicating that the general relationship between these two parameters holds true and that the local variations caused by contrasts in export production modify, but do not obscure, this overall pattern.

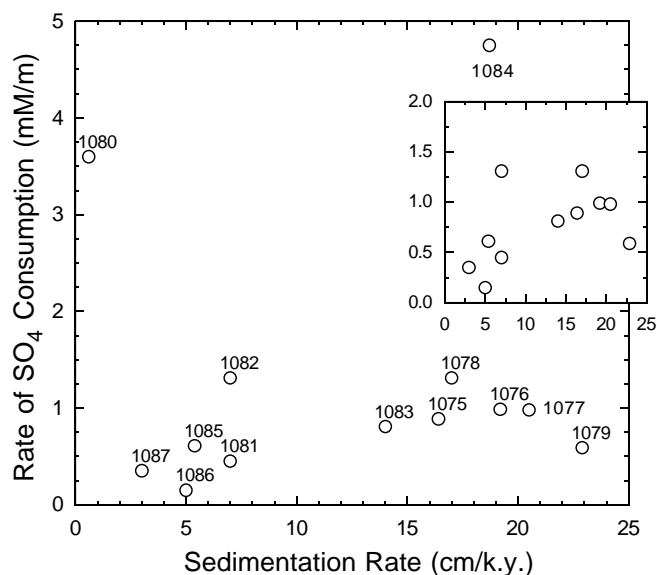


Figure 3. Sedimentation rate (cm/k.y.) plotted vs. the rate of dissolved  $\text{SO}_4^{2-}$  consumption (mM/m) at all Leg 175 sites, including Site 1087. Inset shows an expanded view of the same plot without Sites 1080 and 1084, which plot away from the general pattern in the main panel.

Variations in organic matter diagenesis suggested by the distributions in alkalinity and dissolved  $\text{SO}_4^{2-}$  are also confirmed by the downhole variations in dissolved  $\text{NH}_4^+$  (Fig. 2). Like  $\text{CO}_2$ ,  $\text{NH}_4^+$  is a product of organic matter degradation, but it is produced more continuously than alkalinity throughout a sediment column. Ammonium also is involved in clay exchange reactions and can either be released through exchange with  $\text{K}^+$  or be taken up during authigenic clay formation (e.g., Stevenson and Cheng, 1972). The sites within the Congo Basin record essentially identical downhole dissolved  $\text{NH}_4^+$  patterns, which are more subdued than at the Angola and Walvis sites (Fig. 2). The largest increases in dissolved  $\text{NH}_4^+$  are found at Site 1082 (Walvis Basin) and Site 1084 (Cape Basin), which are two of the sites with the highest concentrations of organic matter. Those sites with the deepest  $\text{SO}_4^{2-}$  penetration (e.g., Sites 1079, 1081, and 1086) also record the smallest increases in dissolved  $\text{NH}_4^+$ . In general, as with the  $\text{SO}_4^{2-}$  and alkalinity profiles, these inter- and intrabasinal variations in dissolved  $\text{NH}_4^+$  speak to the relative similarity among the three sites drilled within the Congo Basin, the heterogeneity within the other basins, and the overall strong influence of sedimentary organic carbon on the interstitial water chemistry.

Dissolved  $\text{PO}_4^{3-}$  and  $\text{H}_4\text{SiO}_4$  distributions within interstitial waters also reflect organic and biogenic inputs, remineralization, and dissolution. At each site, dissolved  $\text{PO}_4^{3-}$  increases to maximum values usually within the uppermost ~50 mbsf (Fig. 4), reflecting degradation of organic matter. Below this maximum, dissolved  $\text{PO}_4^{3-}$  decreases to minimal values at depth, suggesting authigenic uptake into apatite phases. Postcruise studies focusing on the specific rates of  $\text{PO}_4^{3-}$  generation, when interpreted in the context of the site-by-site variations in alkalinity and  $\text{NH}_4^+$  distributions, will provide additional quantitative constraints regarding the remineralization of organic matter.

Dissolved  $\text{H}_4\text{SiO}_4$  in the interstitial waters along the southwest African margin is always greater than that in average seawater (Fig.

4), indicating an additive contribution of  $\text{H}_4\text{SiO}_4$  from the dissolution of diatoms (see Giraudeau et al, Chap. 19, this volume). As with many other dissolved constituents, the distributions of dissolved  $\text{H}_4\text{SiO}_4$  between the Congo Basin sites are comparable, providing further confirmation of the broad geochemical similarity among these sites. Other sites record varying degrees of shallow enrichments, diatom dissolution, and deeper flattenings (or decreases) of the chemical gradient (see individual site chapters, this volume). At these greater depths, decreases in dissolved  $\text{H}_4\text{SiO}_4$  most likely are responding to authigenic clay formation. Also, stratigraphically local variations in the sedimentary diatom abundance exert a strong control on the concentration of dissolved  $\text{H}_4\text{SiO}_4$  (see Giraudeau et al, Chap. 19, this volume).

### Carbonate Dissolution and Reprecipitation

The discovery of widespread and pervasive dolomite layers throughout the southwest African margin was one of the principal findings of Leg 175 (Wefer et al. Chap. 16, this volume). The distributions of dissolved  $\text{Sr}^{2+}$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$  provide important constraints on the diagenetic dissolution of biogenic carbonates as well as the secondary precipitation of authigenic dolomites (Fig. 5).

Increases with depth of dissolved  $\text{Sr}^{2+}$  indicate the dissolution of biogenic calcite, which releases  $\text{Sr}^{2+}$  to the interstitial waters. Throughout the Benguela Current system, there appear to be two modes of such diagenetic release. First, as typified by Site 1077 in the Congo Basin (Fig. 5, inset), many sites display a rapid increase in dissolved  $\text{Sr}^{2+}$  through the uppermost 50 mbsf, followed by gradual increases to total depth. Even at locations with only minimal absolute increases in dissolved  $\text{Sr}^{2+}$  over the entire recovered section (such as within the Congo and Angola Basins and at Site 1084 in the Cape Basin), there often is a shallow rapid increase downhole. Second, as typified by Site 1086 in the Cape Basin, several sites display an essentially linear increase with

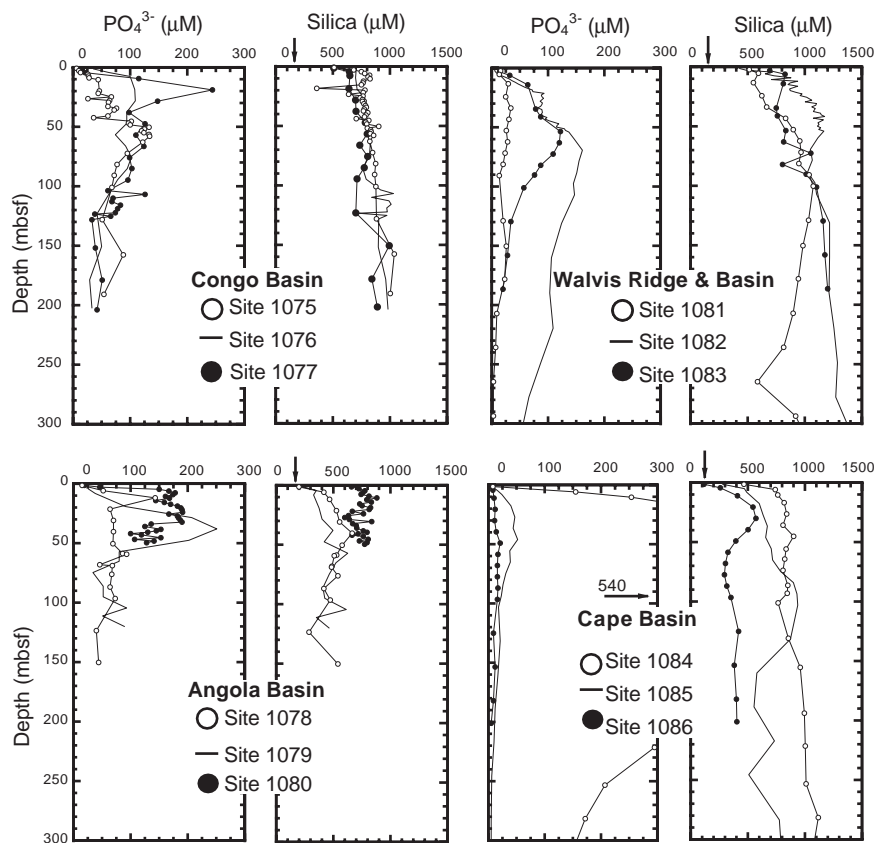


Figure 4. Downcore profiles of dissolved  $\text{PO}_4^{3-}$  and  $\text{H}_4\text{SiO}_4$  in interstitial waters of sites drilled during Leg 175 (except Site 1087; see text). All panels for a given dissolved constituent are plotted to a common scale on the abscissa and to the identical depth scale. For complete profiles to total depth at a given site, please refer to the individual site chapters (this volume). Note off-scale value of dissolved  $\text{PO}_4^{3-}$  at Site 1084; please refer to Figure 6 for a discussion of this site. Arrows = representative modern seawater value (Millero and Sohn, 1992).

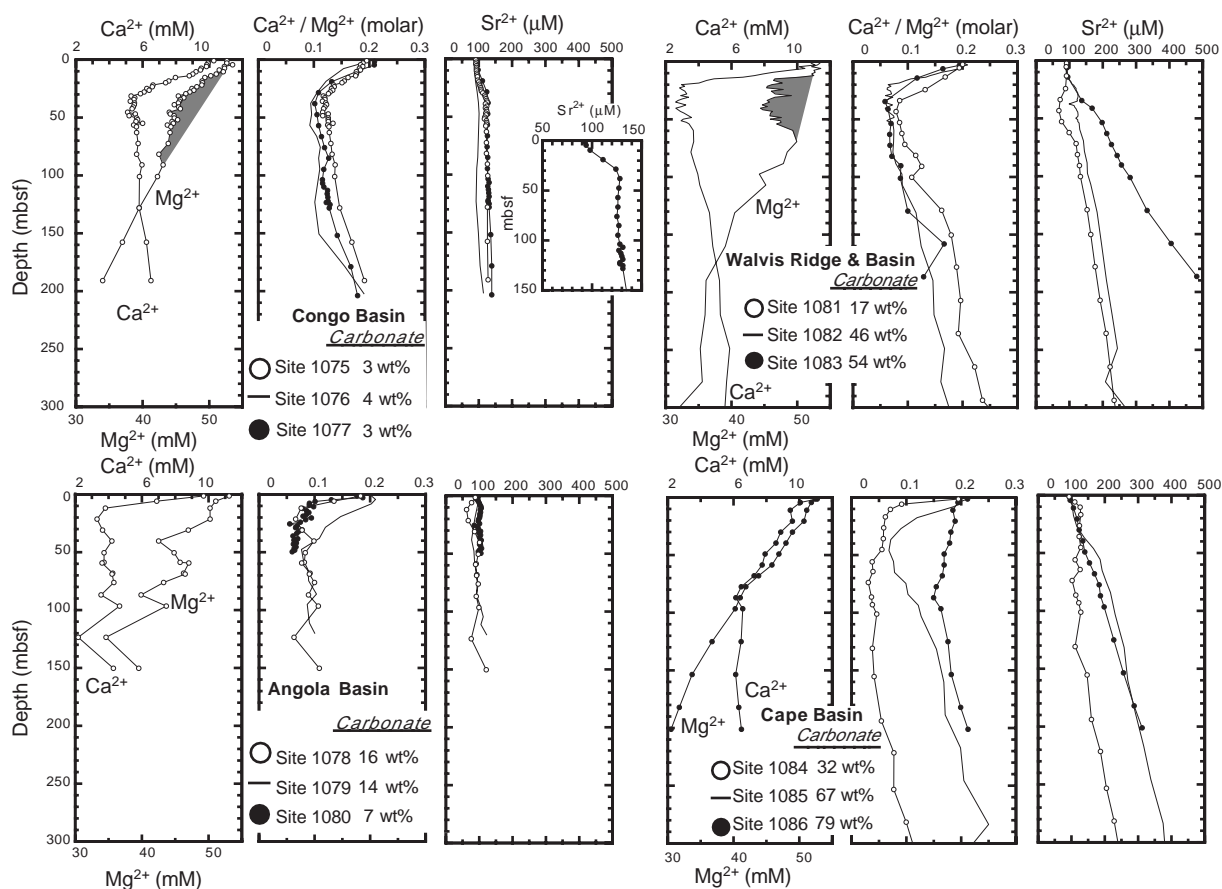
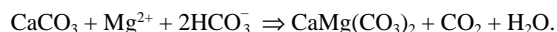


Figure 5. Downcore profiles of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , the  $\text{Ca}^{2+}/\text{Mg}^{2+}$  molar ratio, and dissolved  $\text{Sr}^{2+}$  in interstitial waters of sites drilled during Leg 175 (except Site 1087; see text). For graphical clarity, profiles of dissolved  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  are provided for representative sites only. All panels for a given dissolved constituent are plotted to a common scale on the abscissa and to the identical depth scale. For complete profiles to total depth at a given site, please refer to the individual site chapters (this volume). Shaded regions of dissolved  $\text{Mg}^{2+}$  profiles indicate regions of current dolomite precipitation (see text). Inset shows an expanded view of dissolved  $\text{Sr}^{2+}$  at Site 1077 (Congo Basin). The concentration values of  $\text{CaCO}_3$  in the sediments (in weight percent) are taken from the "Organic Geochemistry" sections of the individual site chapters (this volume).

depth of dissolved  $\text{Sr}^{2+}$ , without the rapid, shallow increase, indicating the continual dissolution of biogenic calcite with depth.

In the absence of significant exchange with either igneous basement rocks or volcanic ash dispersed through the sediment column, distributions of dissolved  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  predominantly reflect carbonate recrystallization processes. These  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  changes are best interpreted in the context of the  $\text{Sr}^{2+}$  variations discussed above, which indicate dissolution of biogenic calcite throughout the sediment column. Despite this dissolution, which will serve as a source of dissolved  $\text{Ca}^{2+}$ , at essentially all sites the concentration of  $\text{Ca}^{2+}$  decreases through the uppermost ~50 mbsf. This decrease reflects the precipitation of diagenetic carbonate, driven by the marked increase in alkalinity through the same portion of the section at each site (Fig. 2).

Sinks for dissolved  $\text{Mg}^{2+}$  in this environment include dolomite precipitation and uptake by clay minerals. In all likelihood, both sinks are operating through the recovered sequences, and the challenge is to resolve the relative contribution of each. Following the logic of Baker and Burns (1985), it appears most likely that dolomite precipitation is occurring according to



As Baker and Burns (1985) note, this stoichiometry is intended to be representative, not unique, of dolomite formation by an intermedi-

ate process involving both  $\text{CaCO}_3$  (calcite or aragonite) dissolution and the supply of dissolved species from solution.

We are able to identify more specifically the depth ranges over which dolomitization is occurring by detailed investigation of the dissolved  $\text{Mg}^{2+}$  profiles (Fig. 5; also see volume site chapters). Many sites record a significant negative excursion in the dissolved  $\text{Mg}^{2+}$  profile superimposed on a broad linear decrease from seawater values at the surface to minimum values at total depth. At a given site, the location of this negative excursion (Fig. 5, shaded region of  $\text{Mg}^{2+}$  profile at Sites 1075 and 1082) coincides with the minimum in dissolved  $\text{Ca}^{2+}$ , as well as with the alkalinity maximum. Assuming that the linear  $\text{Mg}^{2+}$  decrease represents a background level of uptake by clay minerals, the negative excursion appears to delineate the depth range through which dolomite precipitation is occurring. These depth intervals also are indicated by a minimum in the depth profile of the  $\text{Ca}^{2+}/\text{Mg}^{2+}$  (molar) ratio (Fig. 5). If correct, this interpretation confirms the relationships among organic matter degradation (acting as a bicarbonate source),  $\text{CaCO}_3$  dissolution (recorded in the  $\text{Sr}^{2+}$  profile), and secondary dolomite precipitation (delineated by the negative  $\text{Mg}^{2+}$  excursion and the  $\text{Ca}^{2+}$  minimum).

#### Site 1084 (Northern Cape Basin)

Site 1084 possesses several qualities that justify its separate consideration (Fig. 6). Because of the extremely high levels of sedimen-

tary organic matter at this site, the alkalinity and dissolved  $\text{NH}_4^+$  concentrations are the second highest ever observed in the history of Deep Sea Drilling Project (DSDP)/ODP drilling, being exceeded only by those observed at ODP Site 688 along the Peruvian margin (Kastner et al., 1990). Sulfate is completely consumed within the uppermost 5 mbsf (Fig. 2), and dissolved  $\text{PO}_4^{3-}$  reaches a maximum value (540  $\mu\text{M}$ ) that is far greater than that found at any other Benguela site (Figs. 3, 6).

The carbonate system at Site 1084 is also affected by these organically mediated constituents. Authigenic carbonate precipitation apparently begins both more intensively (causing a lower  $\text{Ca}^{2+}$  minimum) and earlier (at a more shallow depth) than at any other Leg 175 site, as indicated by the extreme drawdown of dissolved  $\text{Ca}^{2+}$  within the uppermost 5 mbsf (compare Figs. 6 and 5). Also, whereas the dissolved  $\text{Mg}^{2+}$  at all other sites records linear decreases on which are superimposed negative excursions, the depth profile of dissolved  $\text{Mg}^{2+}$  at Site 1084 increases to maximum values at 80 mbsf (Fig. 6). Because of the strong similarity between the alkalinity and  $\text{Mg}^{2+}$  profiles, we suggest that this increase may reflect complexation of  $\text{Mg}^{2+}$  with the ultra-high levels of bicarbonate (J. Gieskes, pers. comm., 1997). Also, at Site 1084 dissolved  $\text{Cl}^-$  records a decrease with depth, unlike at any other site (Fig. 7).

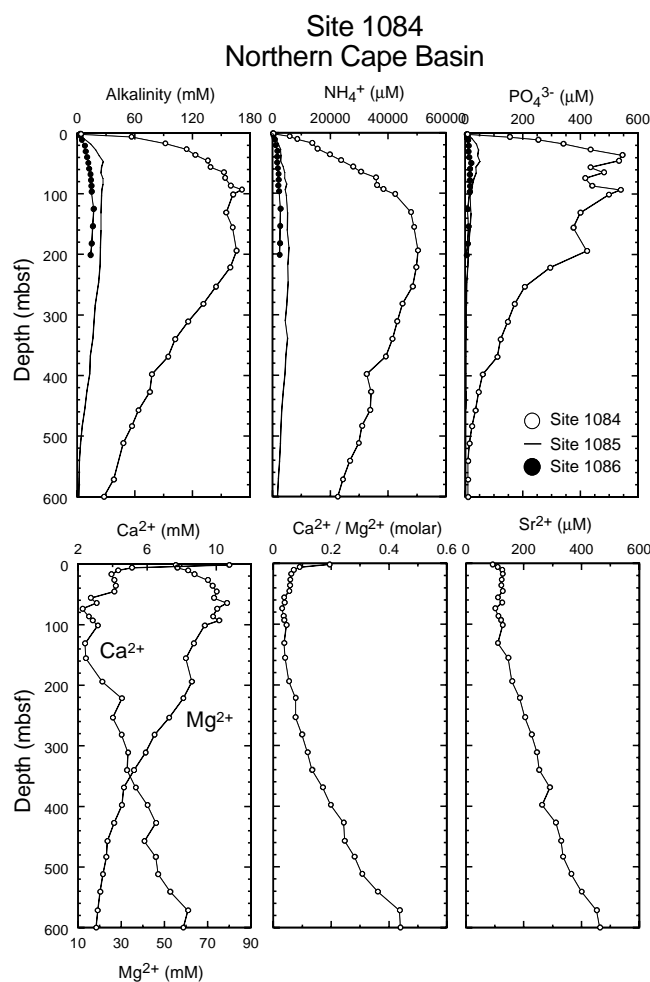


Figure 6. Complete chemical profiles at Site 1084 (Northern Cape Basin) to total depth. These are the second highest values of alkalinity and dissolved  $\text{NH}_4^+$  ever observed in DSDP/ODP drilling history (see text). Other Cape Basin sites are plotted for comparison.

The behavior of dissolved  $\text{H}_4\text{SiO}_4$  (Fig. 3) and dissolved  $\text{Sr}^{2+}$  (Figs. 5, 6) sheds further light on the chemical processes acting at Site 1084. Whereas the dissolved  $\text{H}_4\text{SiO}_4$  profile plateaus relatively shallowly at Site 1084, the maximum value is not significantly greater than that at the other Cape Basin sites, nor is it significantly greater than that observed elsewhere along the southwest African margin (Fig. 3). Also, the dissolved  $\text{Sr}^{2+}$  profile is actually lower here than at any other Cape Basin site and is approximately equal to that observed elsewhere (Figs. 5, 6). These two observations, in concert with the relatively modest  $\text{CaCO}_3$  concentrations in the sediment (Fig. 3), suggest that the elevated sedimentary organic matter concentrations at Site 1084 reflect the primary accumulation of organic matter, rather than organic matter uniquely associated with diatomaceous or carbonate plankton.

### Dissolved Chloride: Tracking Glacial/Interglacial Seawater Changes?

At most sites drilled during Leg 175, dissolved  $\text{Cl}^-$  records a pronounced subsurface maximum found in the upper ~50 mbsf (Fig. 7). Although the sharpness of this maximum and its exact depth varies somewhat from site to site, its presence through a variety of deposi-

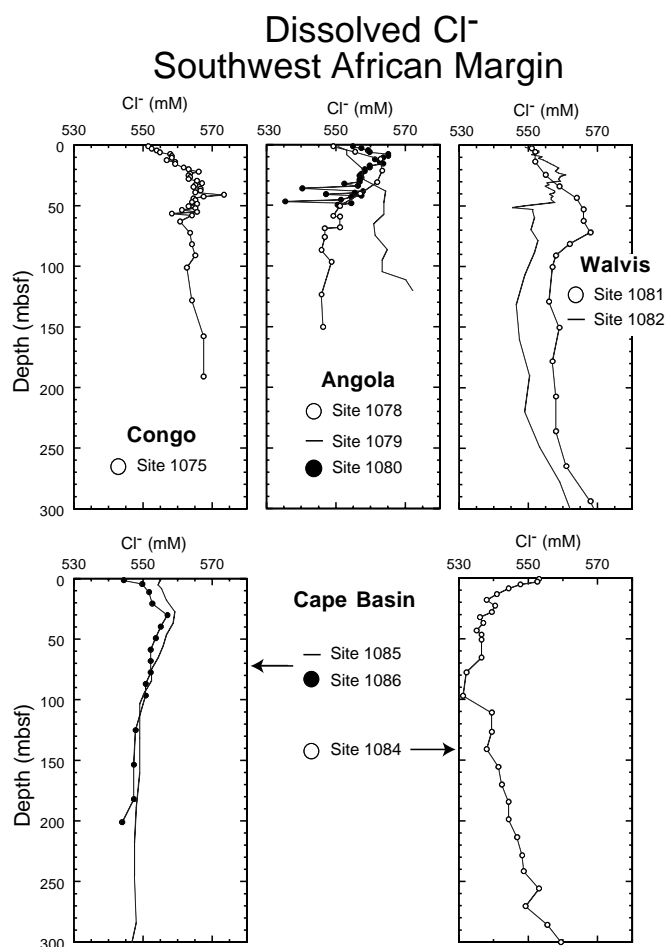


Figure 7. Downcore profiles of dissolved  $\text{Cl}^-$  for those sites that record pronounced maxima in this component.

tional and diagenetic regimes suggests that the occurrence is regionally significant and relevant. Because  $\text{Cl}^-$  generally behaves conservatively in the absence of significant clay dewatering reactions or brine influences, we interpret these increases as records of a diffusively damped signal of the chlorinity of seawater during glacial periods. Because glacial periods last longer than interglacials, the putative  $\text{Cl}^-$  signal may reflect a stacked, multiglacial signal. Postcruise studies of  $\delta^{18}\text{O}$  variability at the high-resolution sites (Table 1) will shed further insights into the preservation of glacial chemical signatures.

### SUMMARY

The interstitial water chemistry at ODP sites drilled along the southwest African margin is dominated by chemical processes involved in the degradation of organic matter and the dissolution and reprecipitation of carbonate phases. These processes are best considered as being related, with the alkalinity being generated by organic remineralization fueling carbonate diagenesis. In concert with a general north-to-south gradient of increasing sedimentary  $\text{CaCO}_3$  concentrations, therefore, variations in organic supply and preservation also intimately affect carbonate precipitation. In turn, carbonate diagenesis regulates distributions of dissolved  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Sr}^{2+}$ , in addition to forming rigid dolomite layers and horizons in the sediment column. Analogously,  $\text{PO}_4^{3-}$  released from organic matter during remineralization in the uppermost sediments serves as a source for the deeper precipitation of authigenic apatite phases. Downhole distributions of dissolved  $\text{H}_4\text{SiO}_4$  appear to be influenced by diatom dissolution (source) and authigenic clay formation (sink). Finally, superimposed on these relatively long-term processes are perhaps diffusional signals of glacial-aged seawater variations in dissolved  $\text{Cl}^-$ . These preliminary observations and hypotheses will be amplified upon and tested by postcruise research of a variety of dissolved constituents, including a suite of additional trace metal and isotopic measurements.

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