



# How depositional conditions control input, composition, and degradation of organic matter in sediments from the Chilean coastal upwelling region

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## Abstract

In a comprehensive study, we compared depositional conditions, organic matter (OM) composition, and organic carbon turnover in sediments from two different depositional systems along the Chilean continental margin: at  $\sim 23^\circ$  S off Antofagasta and at  $\sim 36^\circ$  S off Concepción. Both sites lie within the Chilean coastal upwelling system and have an extended oxygen minimum zone in the water column. However, the northern site ( $23^\circ$  S) borders the Atacama Desert, while the southern site ( $36^\circ$  S) has a humid hinterland. Eight surface sediment cores (up to 30 cm long) from water depths of 126–1350 m were investigated for excess  $^{210}\text{Pb}$  ( $^{210}\text{Pb}_{\text{xs}}$ ) activity, total organic and total inorganic carbon concentrations (TOC and TIC, respectively), C/N-ratios, organic carbon isotopic compositions ( $\delta^{13}\text{C}$ ), chlorin concentrations, Chlorin Indices (CI), and sulfate reduction rates (SRR). Sediment accumulation rates obtained from  $^{210}\text{Pb}$ -analysis were similar in both regions ( $0.04\text{--}0.15\text{ cm yr}^{-1}$  at  $23^\circ$  S,  $0.10\text{--}0.19\text{ cm yr}^{-1}$  at  $36^\circ$  S), although total  $^{210}\text{Pb}_{\text{xs}}$  fluxes indicated that the vertical particle flux was higher at  $36^\circ$  S than at  $23^\circ$  S. We propose that sediment focusing in isolated deposition centers led to high sediment accumulation rates at  $23^\circ$  S. Furthermore, there were no indications for sediment mixing at  $23^\circ$  S, while bioturbation was intense at  $36^\circ$  S.  $\delta^{13}\text{C}$ -values ( $-24.5\text{‰}$  to  $-20.1\text{‰}$  vs. VPDB) and C/N-ratios (molar,  $8.6\text{--}12.8$ ) were characteristic of a predominantly marine origin of the sedimentary OM in both investigated areas. The extent of OM alteration in the water column was partly reflected in the surface sediments as chlorin concentrations decreased and C/N-ratios and CI increased with increasing water depth of the sampling site. SRR were lower at  $23^\circ$  S (areal SRR  $0.12\text{--}0.60\text{ mmol m}^{-2}\text{ d}^{-1}$ ) than at  $36^\circ$  S (areal SRR  $0.82\text{--}1.18\text{ mmol m}^{-2}\text{ d}^{-1}$ ), which was partly due to the greater water depth of most of the sediments investigated in the northern region and consistent with a lower quality of the sedimentary OM at  $23^\circ$  S. Reaction rate constants for TOC degradation that were obtained from measured SRR ( $k_{\text{SRR}}$ ;  $0.0004\text{--}0.0022\text{ yr}^{-1}$ ) showed a good correspondence to  $k_{\text{TOC}}$  that were derived from the depth profiles of TOC ( $0.0003\text{--}0.0014\text{ yr}^{-1}$ ). Both,  $k_{\text{SRR}}$  and  $k_{\text{TOC}}$ , reflect differences in OM composition. At  $36^\circ$  S they were related to the degradation state of bulk OM (represented by C/N-ratios), whereas near  $23^\circ$  S they were related to the freshness of a small fraction of labile OM (represented by CI). Our study shows that although rates of organic carbon accumulation were similar in both investigated sites, the extent and kinetics of organic carbon degradation were closely linked to differing depositional conditions.

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## 1. INTRODUCTION

Understanding the processes that control accumulation and turnover of organic carbon in sediments from high-productivity regions is of significance for reconstructions of the global carbon cycle. Therefore, coastal upwelling sediments are important subjects in biogeochemical and paleo-environmental research. In coastal upwelling areas, advection of nutrient-rich waters fuels primary production rates that are up to three orders of magnitude higher than the mean open ocean production (Ryther, 1963). The permanent supply of freshly produced organic matter (OM), overall high sedimentation rates, oxygen depletion in the water column and at the sediment-water interface, as well as the shallow water depth of shelf and slope sediments favor the accumulation of organic-rich sediments (e.g. Thiede and Suess, 1983; Stein, 1991; Summerhayes et al., 1995). Although sediments underlying coastal upwelling regimes share many characteristics and overall accumulation rates of organic carbon may appear similar, the total flux, composition, and degradation of OM in these sediments change with space and time. Depositional conditions might differ significantly over small distances, particularly with respect to surface productivity, water depth, and oxygen availability.

Oxygen-deficient conditions have been shown to enhance organic carbon preservation, as an existing oxygen minimum zone (OMZ) in the water column allows a greater fraction of the export flux to reach the sediments and low bottom water oxygen concentrations decrease the efficiency of carbon oxidation in the sediment (Hartnett et al., 1998; Hartnett and Devol, 2003). In the absence of dissolved oxygen, bacterial dissimilatory sulfate reduction is responsible for most of the carbon oxidation in most marine upwelling sediments (Jørgensen, 1982; Canfield, 1989; Ferdelman et al., 1999; Hartnett and Devol, 2003). In sediments off central Chile (36° S), organic carbon mineralization rates determined by Thamdrup and Canfield (1996) indicated that sulfate reduction accounted for 100% of carbon oxidation in shelf sediments underlying oxygen-depleted bottom waters, and for at least 55% of carbon oxidation in slope sediments.

In a study of sediments from the Bay of Concepción and the adjacent shelf area off Chile, Schubert et al. (2000) linked the distribution of sulfate reduction activity and overall rates of sulfate reduction to the composition of sedimentary OM. They showed that higher sulfate reduction rates (SRR) were positively correlated with the availability of labile marine OM as indicated by total protein and chlorin concentrations, whereas a dilution with less-reactive terrestrially derived OM significantly altered the depth profiles of SRR. Schubert et al. (2000) hypothesized that variations in the regional distribution of marine OM (or variations in the amount of diluting terrestrial OM) determine the distribution of organic carbon degradation rates as measured by sulfate reduction. This suggested that the depositional conditions, in addition to upwelling intensity and water column oxygen concentration, also control sedimentary OM composition and turnover.

To test this hypothesis, we compare two sedimentary regimes in the Chilean upwelling region, both underlying important upwelling cells, but representing different depositional environments: (1) at ~23° S off Antofagasta with an arid hinterland and low clastic sediment inputs and (2) at ~36° S off Concepción with a humid hinterland and high sediment loading (Hebbeln et al., 2000). Data from this comprehensive study are used to characterize the depositional environment, the bulk organic geochemical composition of the sedimentary OM, and sedimentary organic carbon turnover as measured by sulfate reduction. This work comprises part of a larger project concerning interrelationships between productivity and environmental conditions along the Chilean continental slope (Hebbeln et al., 2001). An important goal of the project is to gain a better understanding of how present-day environmental conditions affect sedimentary processes in the Chilean upwelling region. Knowledge of recent upwelling processes and their effects on the sediments provides a key for the reconstruction of paleo-environmental conditions in this important high-productivity region. Here, we show how differences in depositional conditions along the Chilean continental margin are reflected in differences in composition and turnover rates of sedimentary OM.

## 2. SITE DESCRIPTION

Observations along the Chilean coast of sea surface temperature (Fonseca and Farías, 1987) and coastal zone color scanning recording pigment concentrations (Thomas, 1999) identify areas of especially pronounced upwelling near 20°, 23°, 30°, 33°, and 37° S. For this study, we concentrated on sediments underlying the upwelling cells off Antofagasta (~23° S) in the north and off Concepción (~36° S) in the central region (Fig. 1). The two areas of investigation are located more than 1500 km away from each other and represent different depositional environments (Table 1).

In general, upwelling off northern Chile is concentrated close to the coast and is attenuated during winter times (Morales et al., 1996; Blanco et al., 2001). However, in the upwelling cell off Antofagasta, primary production rates are high throughout the year, reaching up to  $9.3 \text{ g C m}^{-2} \text{ d}^{-1}$  (Daneri et al., 2000; Iriarte et al., 2000). The sediments in this region receive only small amounts of terrestrial material due to extremely low precipitation and prevailing alongshore winds that limit river discharge and eolian input from the adjacent Atacama Desert (Lamy et al., 1998). Sediment accumulation on the narrow shelf and steep slope is affected by redistribution processes including lateral and down-slope transport of sediment particles (Muñoz et al., 2004).

Off central Chile, upwelling occurs seasonally during austral summer months (Brandhorst, 1971; Ahumada et al., 1983) giving rise to high primary production rates of up to  $19.9 \text{ g C m}^{-2} \text{ d}^{-1}$  (Peterson et al., 1988; Daneri et al., 2000). The continental shelf and slope off Concepción extend further offshore than off northern Chile and therefore are more favorable to sediment accumulation (Muñoz et al., 2004). Annual precipitation in the Chilean coastal region increases from north to south, leading to enhanced

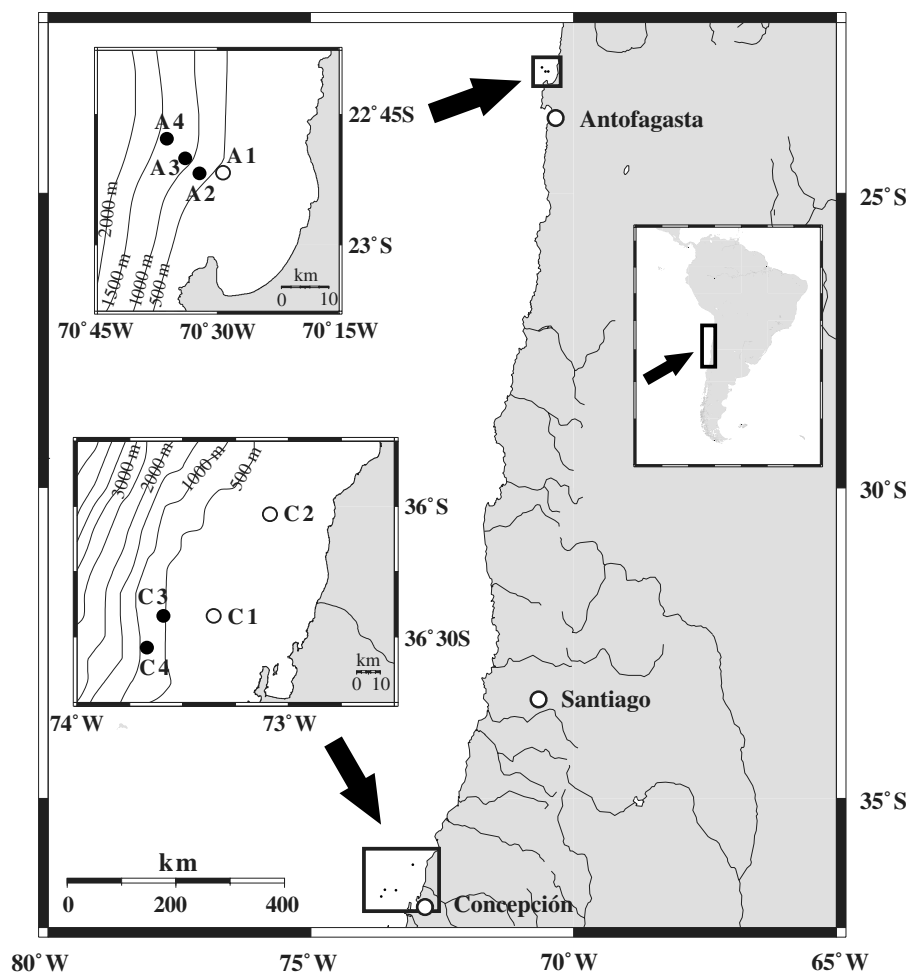


Fig. 1. Investigation area and location of sampling sites off Antofagasta and off Concepción. Open circles mark OMZ sites.

Table 1  
Characteristics of the two investigated regions off Antofagasta and off Concepción

|  | Antofagasta region  | Concepción region  |
|--|---|--|
| Upwelling                              | Year-round  | Seasonal during summer   |
| Primary production <sup>a</sup>        | Up to $9.3 \text{ g C m}^{-2} \text{ d}^{-1}$   | Up to $19.9 \text{ g C m}^{-2} \text{ d}^{-1}$                                   |
| Oxygen minimum zone                    | Stationary  | Seasonal variations  |
| Extension during sampling (April 2001) | Near coast: 30–50 to 400 m<br>Offshore: 70 to 450–500 m                               | Near coast: 80–140 m to seafloor<br>Offshore: 70 to 400 m                        |
| Terrestrial input                      | Small, eolian   | High, riverine   |
| Seafloor topography                    | Narrow shelf, steep slope   | Wider shelf and slope  |
| Sedimentation                          | Focusing in depocenters<br>Sediment reworking by currents                             | Pelagic sedimentation<br>No redistribution                                       |
| Sediment texture                       | Sandy mud   | Hemipelagic mud  |
| Benthic organisms                      | No bioturbating organisms<br>No <i>Thioploca</i><br>High foraminifera test abundances | Living infauna (worms)<br><i>Thioploca</i><br>Lower foraminifera test abundances |
| Bioturbation                           | No bioturbation   | Intense bioturbation   |

<sup>a</sup> From Daneri et al. (2000).

river runoff and higher input of terrestrial material to the sediments (Hebbeln et al., 2000). Several rivers, mainly the Itata, Bio-Bio, and Andalién River, drain the coastal region near Concepción, supplying terrestrial detritus to the adjacent sediments (Lamy et al., 1998; Schubert et al., 2000).

Sampling was carried out during *RV Sonne* cruise SO-156 in April 2001 (Hebbeln et al., 2001). Bottom water oxygen concentrations reported from CTD casts during the cruise were lowest at the shallowest sites A1, C1, and C2 (Hebbeln et al., 2001; Table 2), reflecting their location

relative to the water column OMZ ( $<22 \mu\text{mol O}_2 \text{ l}^{-1}$ ; Fig. 1). It is important to note, that off central Chile, the position and extension of the OMZ are seasonal, i.e. bottom waters overlying the shelf sediments near Concepción are oxygenated during non-upwelling periods (austral winter).

### 3. MATERIAL AND METHODS

#### 3.1. Sampling and sample processing

Table 2 summarizes the characteristics of the sampling sites. At each site three multi-corer cores were sampled. For geochemical analyses the sediment cores were sliced in 1-cm intervals in the uppermost 6 cm and in 2-cm intervals below 6 cm. The samples were transferred to clean glass vials and frozen at  $-25^\circ\text{C}$  immediately after sampling. The sediment samples were later freeze-dried and homogenized by grinding in an agate mortar. Particulate material  $>0.5 \text{ cm}$ , e.g. fish bones, shells, worm-tubes, and remains of worms, was excluded from the sediments.

For SRR incubations sub-cores were taken from individual multi-corer cores in two different ways: (1) for sampling in 1-cm resolution, we used 30 cm long Plexiglas core tubes (26 mm diameter), with silicone plugged holes every 1 cm. (2) For sampling in 5-cm intervals, 7 cm long glass tubes (10 mm diameter) were inserted longitudinally into the sediment cores. These tubes had a piston from a 5-ml plastic syringe on one side and were sealed with a butyl rubber stopper on the other side. All samples were immediately transferred into a dark incubator and stored close to in situ temperatures (Table 2).

Additional samples were taken for the determination of water content, wet density, and  $^{210}\text{Pb}$  activity. The cores were sliced in 1- or 2-cm intervals, transferred to Petri-dishes, sealed tightly with electric tape, and stored at  $4^\circ\text{C}$  until further analysis.

#### 3.2. Elemental analysis

Total carbon (TC) and total nitrogen (TN) concentrations were determined on freeze-dried samples by combustion/gas chromatography (Carlo Erba NA-1500 CNS

analyzer) with a precision of  $\pm 0.7\%$  for N and  $\pm 0.6\%$  for C, respectively. Total inorganic carbon (TIC) was measured on a CM 5012  $\text{CO}_2$  Coulometer (UIC) after acidification with phosphoric acid (3 M). The precision for TIC was  $\pm 0.4\%$ . Total organic carbon (TOC) was calculated as the difference of TC and TIC. The C/N-ratio was calculated as the molar ratio of TOC and TN. For the determination of the isotopic composition of TOC, samples were treated with hydrochloric acid (3 M) to eliminate carbonates, rinsed three times with distilled water, and dried overnight at  $60^\circ\text{C}$  (Schubert and Nielsen, 2000). Based on the TOC concentration, 0.2–1.1 mg of the decarbonated samples were combusted in a Thermo Quest elemental analyzer NC2500. The evolved  $\text{CO}_2$  was passed to an Isoprime isotope-ratio mass spectrometer (GU Instruments, UK) in a continuous flow of helium. The results are reported in the standard  $\delta$  notation relative to Vienna Pee Dee Belemnite (VPDB). Average standard deviation for four replicates was  $\pm 0.4\text{‰}$ .

#### 3.3. Chlorins and Chlorin Index (CI)

For the determination of chlorins, we followed the procedure described in Schubert et al. (2005). Freeze-dried sediment (100–200 mg) was extracted successively three times with 5 ml acetone (HPLC-grade, Roth, Germany). The sediment extracts were measured on a Hitachi F-2000 fluorometer ( $\lambda_{\text{ex}} = 428 \text{ nm}$ ,  $\lambda_{\text{em}} = 671 \text{ nm}$ ) immediately after extraction. Pheophytin *a*, derived from acidification of chlorophyll *a* (Fluka), was used as a standard. The precision of the method was  $\pm 10\%$ . In addition, the pigment extracts were acidified and measured again. The ratio of the fluorescence intensities (FI) of the acid-treated pigment extract and the untreated one has been shown to provide a measure for the degradability of the pigments and is defined as the Chlorin Index (Schubert et al., 2005):

$$\text{Chlorin Index (CI)} = \frac{\text{FI}_{\text{acidified\_extract}}}{\text{FI}_{\text{original\_extract}}} \quad (1)$$

For intact chlorophyll *a* (pure standard) the CI is 0.2, whereas highly degraded pigments, inert to acid treatment, approach a CI of 1 (Schubert et al., 2005).

Table 2

Sampling sites with position, water depth, bottom water temperature and oxygen concentration, and location relative to position of water column OMZ

| Sampling site <sup>a</sup> |           | Latitude   | Longitude  | Water depth (m) | Bottom water temperature <sup>b</sup> ( $^\circ\text{C}$ ) | Bottom water $\text{O}_2^b$ ( $\mu\text{mol l}^{-1}$ ) | Location relative to position of OMZ |
|----------------------------|-----------|------------|------------|-----------------|--|--|--------------------------------------|
| A1                         | GeoB 7104 | 22°52.00 S | 70°29.42 W | 307             | 11.6   | 7  | Within                               |
| A2                         | GeoB 7103 | 22°51.99 S | 70°32.54 W | 891             | 4.6  | 45   | Below                                |
| A3                         | GeoB 7108 | 22°50.50 S | 70°34.79 W | 1007            | 3.9  | n.d. <sup>c</sup>                                      | Below                                |
| A4                         | GeoB 7106 | 22°48.00 S | 70°36.70 W | 1350            | 3.2  | 53   | Below                                |
| C1                         | GeoB 7161 | 36°25.51 S | 73°23.32 W | 126             | 11.1   | 0.4  | Within                               |
| C2                         | GeoB 7160 | 36°02.33 S | 73°04.39 W | 367             | 8.8  | 7  | Within                               |
| C3                         | GeoB 7163 | 36°25.55 S | 73°35.71 W | 536             | 6.2  | 103  | Below                                |
| C4                         | GeoB 7162 | 36°32.52 S | 73°40.02 W | 798             | 4.5  | 105  | Below                                |

<sup>a</sup> Original site names were renamed for this study: A (Antofagasta), C (Concepción), increasing numbers indicate increasing water depth (see also Fig. 1).

<sup>b</sup> Data from CTD-profiling (Hebbeln et al., 2001).

<sup>c</sup> n.d., not determined.

### 3.4. Sulfate reduction rates (SRR)

SRR were determined using the whole-core  $^{35}\text{SO}_4^{2-}$  injection method. Details and caveats to this method are given in Jørgensen (1978) and Ferdelman et al. (1999). For the Plexiglas sub-cores  $\sim 5\ \mu\text{l}$  of carrier-free  $^{35}\text{SO}_4^{2-}$  ( $80\ \text{kBq}\ \mu\text{l}^{-1}$ , Amersham) was injected through ports along the side, whereas in the glass-subcores,  $^{35}\text{SO}_4^{2-}$  ( $\sim 5\text{--}10\ \mu\text{l}$ ) was injected along the longitudinal axis. Incubation times varied between 6 and 42 h. Bacterial activity was halted by transferring 1-cm slices of the sediment from the acrylic cores and the sediment extruded from the glass barrels (5 cm), respectively, into 20 ml of 20% w/v ZnAc. Samples were stored frozen at  $-20\ ^\circ\text{C}$  until analysis. Blanks were sediment fixed in ZnAc solution to which was added  $^{35}\text{SO}_4^{2-}$ .  $^{35}\text{S}$  incorporated into total reducible inorganic sulfur (TRIS) was determined using the cold Chromium-II method (Kallmeyer et al., 2004). A Packard 2500 TR liquid scintillation counter (scintillation fluid Lumasafe Plus; Lumac LSC, Inc) was used to quantify the  $^{35}\text{SO}_4^{2-}$  and  $^{35}\text{S}_{\text{TRIS}}$  activities. SRR were calculated according to Kallmeyer et al. (2004), assuming that the  $\text{SO}_4^{2-}$  concentration was 28 mM for all samples. At the sites analyzed for pore-water  $\text{SO}_4^{2-}$  (including OMZ sites) there was no down-core depletion from seawater  $\text{SO}_4^{2-}$  concentration (data not shown).

### 3.5. Determination of excess $^{210}\text{Pb}$ activity

For gamma-counting, dry sediments were homogenized by grinding in a mortar and 5–25 g transferred to polysulf-

one screw-top jars (diameter 45 mm). Samples were kept for at least 20 days to reach secular equilibrium between the parent isotope  $^{226}\text{Ra}$  and its short-lived daughter products  $^{222}\text{Rn}$ ,  $^{214}\text{Pb}$ , and  $^{214}\text{Bi}$ . Activities were determined by non-destructive gamma spectrometry using an ultra-low-level germanium gamma detector (Canberra, EURISYS coaxial type N). Depending on the expected activity individual samples were counted for 1–4 days. Activities of the isotopes  $^{210}\text{Pb}$  (46.4 keV),  $^{214}\text{Pb}$  (295.2 and 352 keV), and  $^{214}\text{Bi}$  (609.3 keV) were corrected for detector efficiency and intensity obtained from calibration with a uranium-thorium ore reference standard (DL-1a, Canadian Certified Reference Materials Project).  $^{210}\text{Pb}$  self-absorption in the sample was checked individually for every sample by the method of Cutshall et al. (1983), using a 10-kBq  $^{210}\text{Pb}$  source (AEA Technology). Supported  $^{210}\text{Pb}$  activity from the in situ decay of  $^{226}\text{Ra}$  in the samples was determined as the activity of its short-lived daughter products  $^{214}\text{Pb}$  and  $^{214}\text{Bi}$ . Unsupported, excess  $^{210}\text{Pb}$  ( $^{210}\text{Pb}_{\text{xs}}$ ) activity was calculated as the difference of total  $^{210}\text{Pb}$  activity and  $^{226}\text{Ra}$  activity.

### 3.6. Calculation of sediment accumulation rates

Sediment accumulation rates ( $\omega$ ) were calculated from the down-core changes of  $^{210}\text{Pb}_{\text{xs}}$  activity. To account for differences in sediment porosity and consolidation  $^{210}\text{Pb}_{\text{xs}}$  activity was plotted versus cumulative sediment dry weight (Fig. 2). Sedimentation rates ( $r$ ) were derived from the slope ( $S$ ) of linear regression in those parts of the sediments that

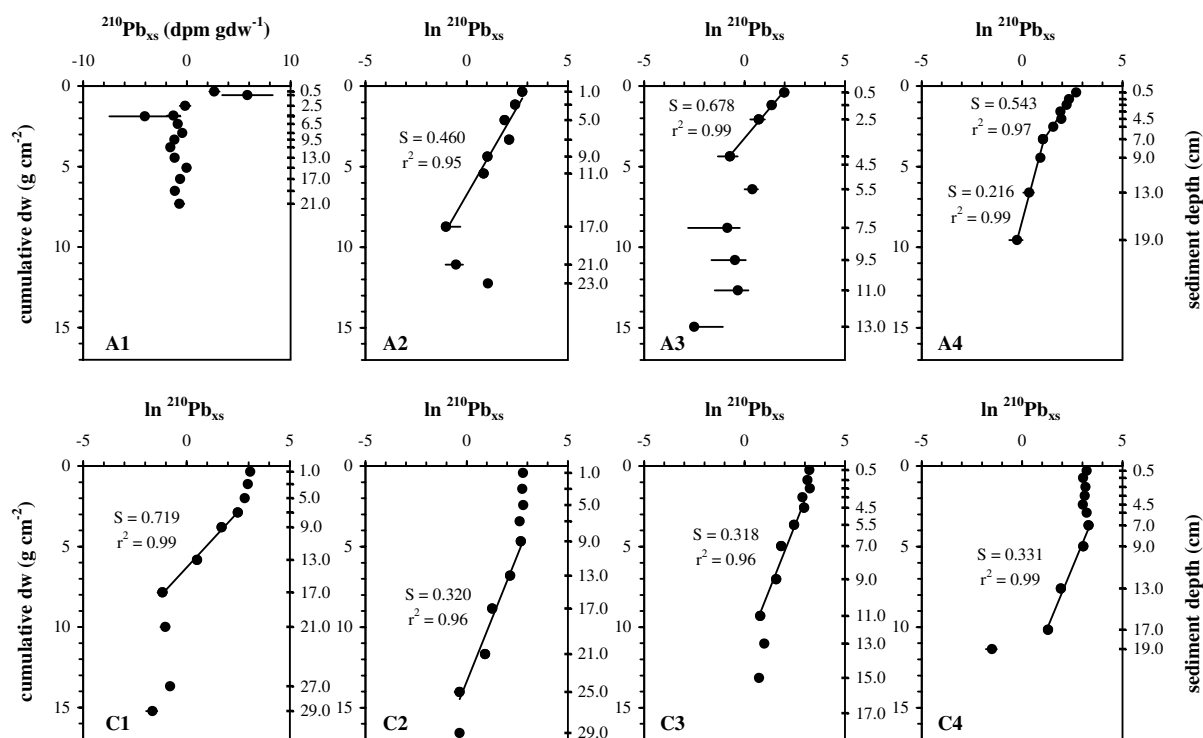


Fig. 2. Profiles of  $^{210}\text{Pb}_{\text{xs}}$  activity ( $\text{dpm}\ \text{gdw}^{-1}$ ) plotted as  $\ln$  activity (except A1) versus cumulative sediment dry weight (left axis); corresponding sediment depths are given on the right axis. Error bars give  $\ln$  of standard deviation ( $1\sigma$ ) for  $^{210}\text{Pb}_{\text{xs}}$  activity. Regression lines are plotted for the data points that indicate exponential decay.



appeared to be unaffected by mixing (Carpenter et al., 1982):

$$r = \frac{\lambda}{S} \quad \text{with} \quad \lambda = \frac{\ln 2}{t_{1/2}} \quad (2.1 \text{ and } 2.2)$$

$\lambda$  is the decay coefficient of  $^{210}\text{Pb}$  and  $t_{1/2}$  is the half-life of  $^{210}\text{Pb}$  (22.3 years). The age of the sediment at each depth was calculated from cumulative dry weight and  $r$  ( $\text{g cm}^{-2} \text{yr}^{-1}$ ).  $\omega$  ( $\text{cm yr}^{-1}$ ) was calculated from age and depth of the individual samples.

The calculation of sedimentation rates is based on the assumption that the  $^{210}\text{Pb}_{\text{xs}}$  flux and sedimentation were constant over time. Smaller variations in the  $^{210}\text{Pb}_{\text{xs}}$  flux and sedimentation are concealed by low sample resolution—the samples investigated in this study (1–2 cm) integrated 5–50 years of sediment deposition. However, it should be noted, that  $\omega$  calculated from profiles of  $^{210}\text{Pb}_{\text{xs}}$  activity often overestimate the actual accumulation rates, as gradually decreasing mixing efficiency with sediment depth might result in a depth profile indicating exponential decay, which is falsely interpreted as undisturbed sediment accumulation (e.g. Nittrouer et al., 1984).

## 4. RESULTS

### 4.1. General sediment characteristics

Near Antofagasta ( $23^\circ \text{S}$ ), the sediments consisted mainly of sandy mud. Benthic macrofauna was only observed at A1, namely small polychaetes and annelids. Conspicuous, large sulfur bacteria *Thioploca* spp. were not observed in the Antofagasta sediments. Numerous benthic foraminifera tests were observed in all sediments from this region, with especially high abundances at A1. Dominant species were of the family *Nonionidae* (T. Cedhagen, personal communication), which are particularly adapted to oxygen-limited conditions (Bernhard et al., 1997).

Near Concepción ( $36^\circ \text{S}$ ), hemipelagic mud dominated the sediments. Benthic macrofauna and *Thioploca* spp. were present at all sites. The highest *Thioploca* biomass ( $5.2 \text{ g m}^{-2}$ ) was found at C1, where single filaments penetrated down to 18 cm sediment depth (Hebbeln et al., 2001).

### 4.2. Sediment mixing and accumulation rates

From the depth profiles of  $^{210}\text{Pb}_{\text{xs}}$  there were no indications of sediment mixing in the Antofagasta region (Fig. 2), which was in accordance with the lack of bioturbating organisms in the sediments from this area. In contrast, the cores from the Concepción area revealed nearly constant  $^{210}\text{Pb}_{\text{xs}}$  activity in the upper part of the sediments (Fig. 2), depicting a zone of effective sediment mixing most likely due to bioturbation. In general, the  $^{210}\text{Pb}_{\text{xs}}$  distributions observed in our study are in good accordance with those reported by Muñoz et al. (2004) for sediments from the same region, including sites A1, A4, C1, C2, and C4.

Near Antofagasta, sediment accumulation rates were slightly lower than off Concepción (Table 3), consistent with the findings of Muñoz et al. (2004). In our study, samples at A1 contained only very little  $^{210}\text{Pb}_{\text{xs}}$ ; at most depths, measured  $^{226}\text{Ra}$  activity (supported  $^{210}\text{Pb}$ ) was higher than  $^{210}\text{Pb}$  activity (hence the apparent negative  $^{210}\text{Pb}_{\text{xs}}$  activities at this site), indicating a lack of recent input of  $^{210}\text{Pb}$  through pelagic sedimentation at this site. In contrast, Muñoz et al. (2004) observed an exponential decrease of  $^{210}\text{Pb}_{\text{xs}}$  and derived a sediment accumulation rate of  $0.04 \text{ cm yr}^{-1}$  for A1.

Total  $^{210}\text{Pb}_{\text{xs}}$  inventories were generally lower (significance:  $p < 0.05$ ) in sediments off Antofagasta than off Concepción (Table 3). Accordingly, total  $^{210}\text{Pb}_{\text{xs}}$  fluxes, calculated by multiplying these inventories by the mean lifetime coefficient  $\lambda$ , were also significantly ( $p < 0.05$ ) lower off Antofagasta than off Concepción.

### 4.3. Elemental composition (TOC, TIC, C/N-ratios, $\delta^{13}\text{C}$ )

TOC concentrations were highest ( $>5\%$  dw; dw, sediment dry weight) at the near-coastal sites A1 and A2 off Antofagasta (Fig. 3). At all other sites, TOC concentrations were in the range of 1.5–4.5% dw. Except for A1 and A4, TOC concentrations decreased with increasing sediment depth. For the Concepción sediments, this decrease was attenuated in the mixed layers and stronger in the unmixed deeper layers.

TIC concentrations (data not shown) were significantly higher ( $p < 0.05$ ) in the sediments off Antofagasta (up to 2.2% dw) than off Concepción ( $<0.4\%$  dw), consistent with

Table 3

Depth interval of the mixed zone, sediment accumulation rates  $\omega$  derived from depth profiles of  $^{210}\text{Pb}_{\text{xs}}$ , inventories of total  $^{210}\text{Pb}_{\text{xs}}$ , and the flux of total  $^{210}\text{Pb}_{\text{xs}}$  to the sediments. For each site the range of calculated  $\omega$  values is given in parentheses

| Site | Mixed zone (cm) | $\omega$ ( $\text{cm yr}^{-1}$ )  | $^{210}\text{Pb}_{\text{xs}}$ inventory ( $\text{dpm cm}^{-2}$ ) | $^{210}\text{Pb}_{\text{xs}}$ flux ( $\text{dpm cm}^{-2} \text{yr}^{-1}$ ) |
|------|-----------------|---|--|--|
| A2   | None            | $0.15 \pm 0.02$ (0.19–0.13)   | 50   | 1.5  |
| A3   | None            | $0.04 \pm 0.01$ (0.06–0.04)   | 19   | 0.6  |
| A4   | None            | $0.11 \pm 0.02$ (0.13–0.07)<br>$0.26 \pm 0.01$ (0.28–0.25) <sup>a</sup> | 40   | 1.2  |
| C1   | 8               | $0.10 \pm 0.01$ (0.12–0.07)   | 71   | 2.2  |
| C2   | 10              | $0.19 \pm 0.02$ (0.23–0.17)   | 124  | 3.9  |
| C3   | 5               | $0.15 \pm 0.03$ (0.19–0.11)   | 111  | 3.5  |
| C4   | 10              | $0.17 \pm 0.01$ (0.19–0.16)   | 170  | 5.3  |

<sup>a</sup> Higher rates were observed in the deeper part of the sediment (8–20 cm).

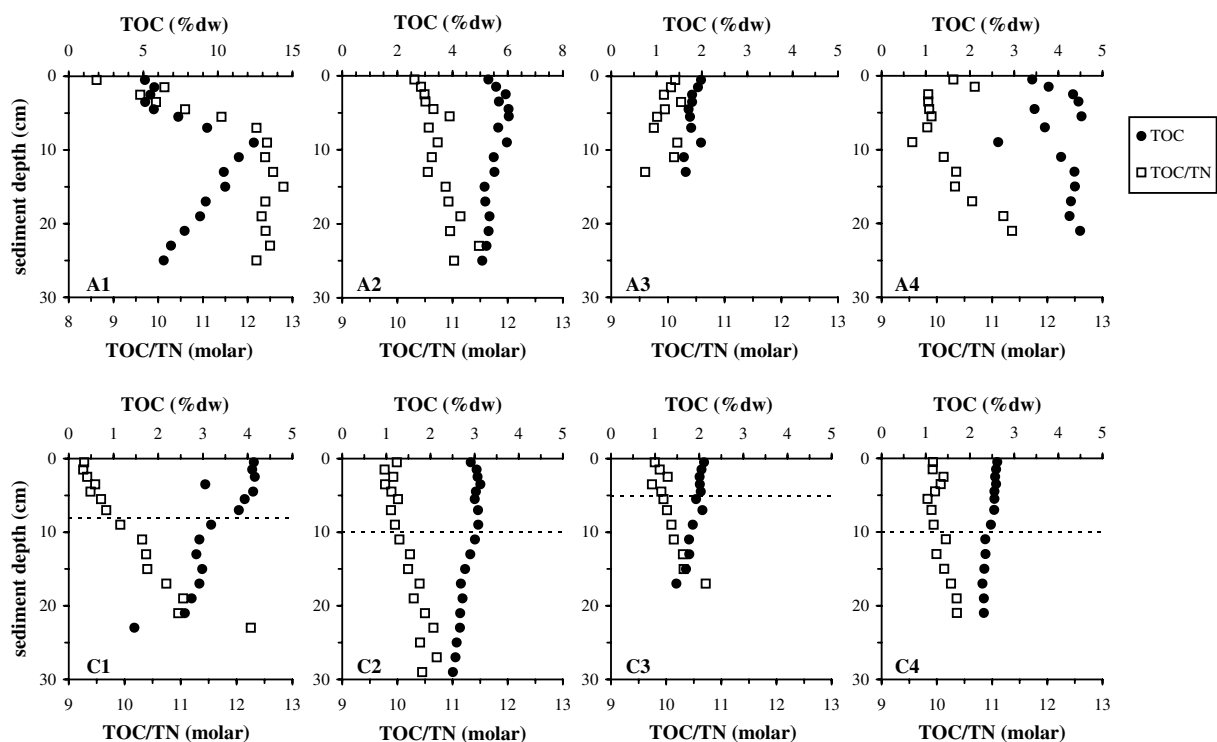


Fig. 3. Depth profiles of TOC concentrations and C/N-ratios calculated from molar concentrations of TOC and TN. Note the different scales for A1 (TOC and C/N) and A2 (TOC). Dotted lines mark the lower boundary of the mixed layer.

the high abundances of calcareous foraminifera tests observed in the Antofagasta sediments.

C/N-ratios (Fig. 3) were lowest at the sediment surface of A1 (8.6) and highest in the deeper part of A1 (>12). At the other sites, C/N-ratios were in the range 9.3–11.5 (except for one sample at 23 cm at C1) and lowest values were found near the sediment surface of the shallowest site C1. In all Concepción sediments and at A2, C/N-ratios increased with increasing sediment depth. There was also a strong increase in the upper 7 cm at A1 and in the deeper part at A4.

The organic carbon isotopic composition ranged from  $-20.1\text{‰}$  to  $-24.5\text{‰}$  and showed a clear separation (signif-

icance:  $p < 0.05$ ) between the two investigated areas (Fig. 4). Near Antofagasta, the carbon isotopic composition was lightest at A1, ranging from  $-24.5\text{‰}$  to  $-22.6\text{‰}$ . All other  $\delta^{13}\text{C}$  in this area were between  $-23.4\text{‰}$  and  $-21.4\text{‰}$ . With the exception of the light isotopic composition at C1 at 2.5 cm depth ( $-22.7\text{‰}$ ), all samples from the Concepción region fell in the narrow range  $-21.0\text{‰}$  to  $-20.1\text{‰}$ .

#### 4.4. Total chlorins and Chlorin Index

Total chlorin concentrations ranged from 4 to  $24 \mu\text{g gdw}^{-1}$  in the Antofagasta region and from 7 to  $31 \mu\text{g gdw}^{-1}$  in the Concepción region. With the exception of C1, where the maximum concentration was found at 17 cm depth, highest concentrations always occurred in the uppermost cm (Fig. 5). Off Concepción, surface concentrations decreased with increasing water depth, whereas off Antofagasta, there was no clear trend with water depth. At most sites the chlorin concentration decreased with sediment depth, and, at all sites, the decrease was most pronounced in the upper 3 cm, where 18–56% of the initial chlorin concentration was lost. The chlorin concentrations at A1 and C1 did not show a distinct depth trend.

The CI at the sediment surface was lowest at C1 (0.56) and highest at A3 (0.77). Within the sediments, the CI did not follow distinct depth trends. The depth-averaged CI was lowest at the shallowest sites C1 and A1, indicating that the phytodetritus was freshest at these sites. According to the CI, the pigment material was most degraded at A3.

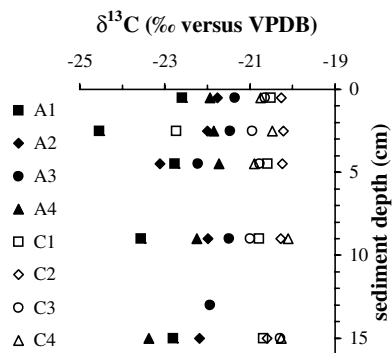


Fig. 4. Depth distribution of the organic carbon isotopic composition ( $\delta^{13}\text{C}$ ) at the different sites.

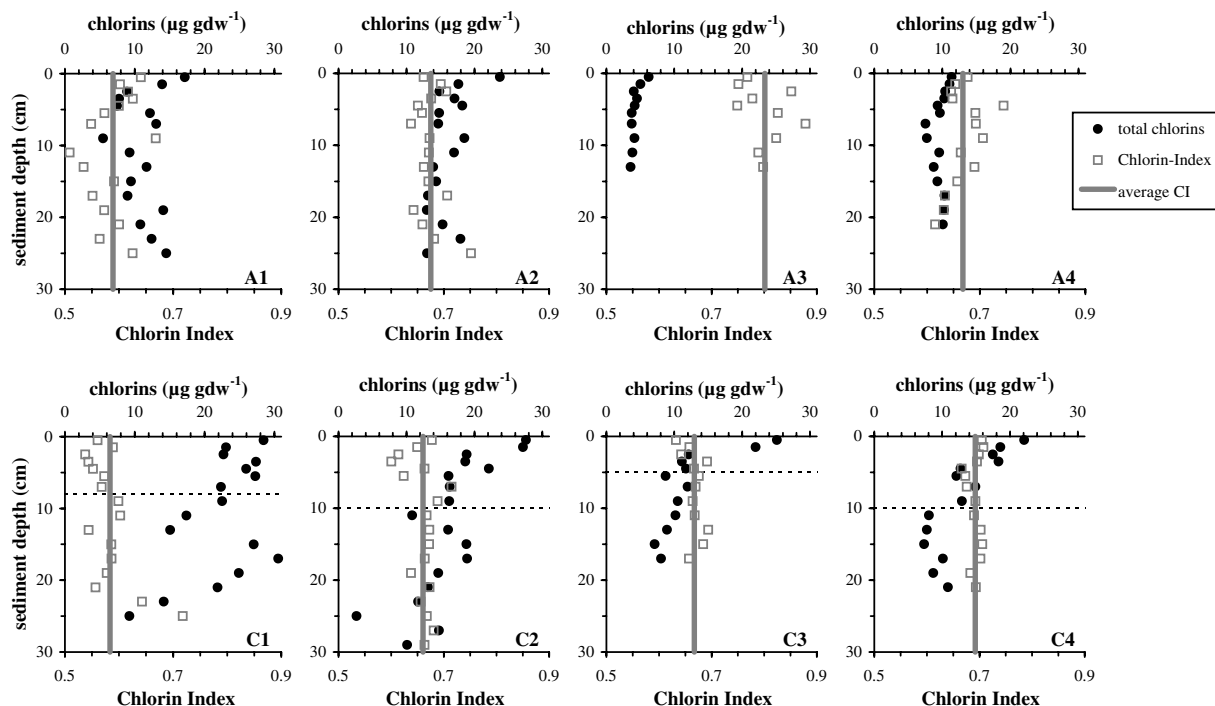


Fig. 5. Depth profiles of total chlorin concentration and Chlorin Index. Average Chlorin Indices (all depths) are given by the grey lines. Dotted lines mark the lower boundary of the mixed layer.

Here, the average CI was significantly higher than at all other sites ( $p < 0.05$ ). At the remaining sites, the average CI indicated the presence of moderately altered chlorins.

#### 4.5. Sulfate reduction rates

There was a good agreement between SRR derived from the analysis of 1- and 5-cm sediment intervals (Fig. 6). The

deep peaks at C2 (20–22 cm) and C4 (18 cm) were only resolved by the high-resolution sampling. They most likely reflected local sediment heterogeneity, e.g. worm burrows with freshly introduced OM.

At most sites depth profiles of SRR suggested that terminal electron acceptor processes other than sulfate reduction accounted for part of the sediment carbon oxidation: surface maxima in SRR were only observed at A1 and

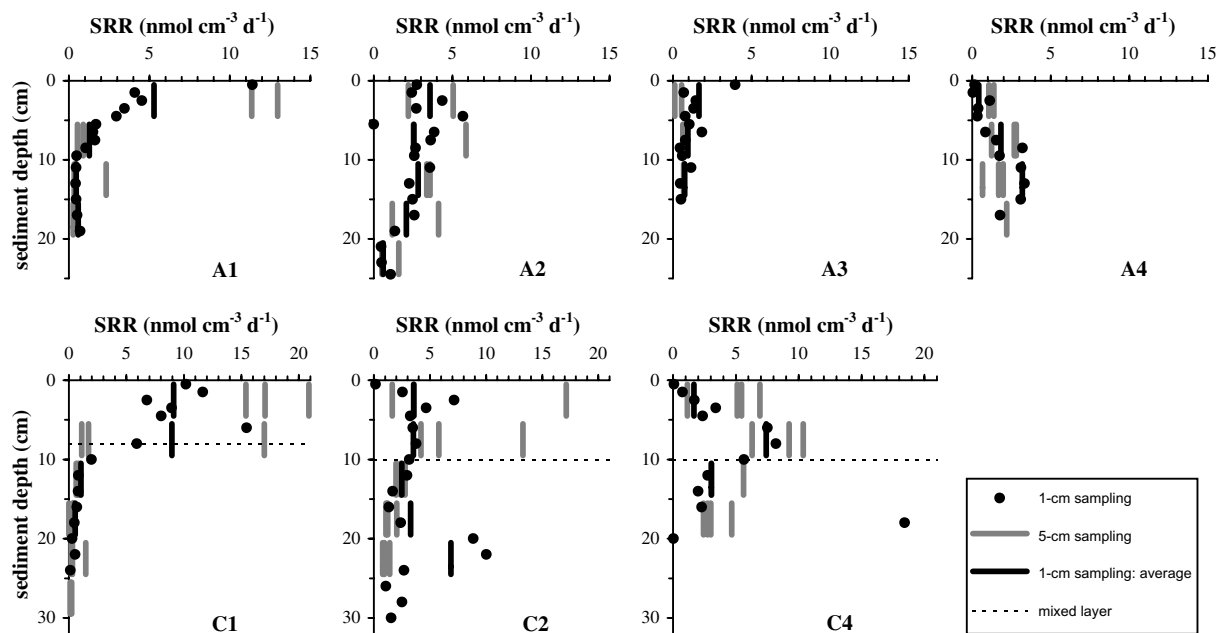


Fig. 6. Depth profiles of sulfate reduction rates (SRR) measured in 1- and 5-cm sampling intervals. Scales are different for the two transects. Dotted lines mark the lower boundary of the mixed layer.



A3, and all other sites showed either subsurface maxima (A2, C1, C2) or deep maxima (A4, C3). In the Concepción sediments, SRR were high throughout the mixed layer and decreased below. At C1 a sharp down-core decrease was observed at >10 cm depth, similar to the depth profiles reported by Thamdrup and Canfield (1996) and Ferdelman et al. (1997) at a site close to C1. However, the latter studies revealed a factor 10–50 higher maximum SRR, reflecting seasonal changes in the availability of fresh organic carbon typically occurring at shelf sites such as these.

Depth integrated SRR (0–15 cm) were significantly higher ( $p < 0.05$ ) in sediments near Concepción ( $0.78\text{--}1.18\text{ mmol m}^{-2}\text{ d}^{-1}$ ) than near Antofagasta ( $0.12\text{--}0.60\text{ mmol m}^{-2}\text{ d}^{-1}$ ). In both regions areal SRR were highest at the shallowest sites.

## 5. DISCUSSION

### 5.1. Differences in depositional conditions off Antofagasta and off Concepción

#### 5.1.1. Vertical particle flux

Dissolved  $^{210}\text{Pb}$  is effectively scavenged on sinking particles and transported to the sediments (Turekian, 1977). Consequently, the flux of  $^{210}\text{Pb}$  to the sediment is a function of both the  $^{210}\text{Pb}$  supply in the water column and the vertical particle flux. Near Concepción,  $^{210}\text{Pb}$  supply controlled  $^{210}\text{Pb}$  fluxes to the sediments.  $^{210}\text{Pb}_{\text{xs}}$  fluxes increased with increasing water depth, i.e. distance to coast, and there was no relation to sediment accumulation rates (Table 3). The upwelling water becomes progressively depleted in dissolved  $^{210}\text{Pb}$  while approaching the coast, as high particle fluxes extending far offshore effectively scavenge the imported  $^{210}\text{Pb}$ . Accordingly, sediments from shallower water depth in the adjacent Bay of Concepción receive a reduced  $^{210}\text{Pb}$  flux of  $0.9\text{ dpm cm}^{-2}\text{ yr}^{-1}$  at the bay mouth and of  $0.2\text{ dpm cm}^{-2}\text{ yr}^{-1}$  within the bay, respectively (Muñoz and Salamanca, 2003).

Off Antofagasta,  $^{210}\text{Pb}_{\text{xs}}$  fluxes showed no relation to water depth, i.e. distance to coast, but were positively correlated with sediment accumulation rates. Apparently, the loading of sedimentary particles with  $^{210}\text{Pb}_{\text{xs}}$  was similar for all investigated sites indicating that the water column particle flux was the controlling factor of  $^{210}\text{Pb}_{\text{xs}}$  fluxes in this region. We conclude that off Antofagasta  $^{210}\text{Pb}$  is not limited in the water column and is equally scavenged on all particles settling down the water column. This means that the overall vertical particle flux in the Antofagasta region is not very large, especially when compared to the region off Concepción, where pelagic sedimentation exceeds  $^{210}\text{Pb}$  supply.

#### 5.1.2. Sediment accumulation

Despite differences in vertical particle flux, sediment accumulation rates were similar in both regions (Table 3). However, we expected the sediment accumulation rates off Antofagasta to be significantly lower than off Concepción for two reasons: (1) terrestrial input off northern Chile is generally low and (2) earlier studies have shown that sediment accumulation rates in the Chilean coastal region

increase from north to south (Lamy et al., 1998; Hebbeln et al., 2000).

In the Concepción region, sediment accumulation rates were similar to those obtained from  $^{14}\text{C}$ -dating of carbonate (planktonic foraminifera) in Late Holocene sediments (D. Hebbeln, personal communication). The unexpectedly high sediment accumulation rates observed in the Antofagasta region can be explained by the sampling strategy. Strong bottom currents and the steep slope off Antofagasta limit sediment accumulation to locally restricted depositional centers. Thus, areas that were specifically chosen for coring collect sedimentary material that was originally distributed over a much wider area (Muñoz et al., 2004). As a result, the sediment accumulation rates obtained here might not be representative for the overall area off northern Chile but represent isolated depositional centers. This scenario of sediment accumulation is consistent with the overall small vertical particle flux observed in the Antofagasta region.

For the purpose of this study, the most relevant difference in the depositional conditions is that pelagic sedimentation prevails in the Concepción area—which therefore represents a more typical continental margin—whereas off Antofagasta, sedimented particles are relocated on the seafloor before they focus in depocenters. As we will show, the different pre-depositional history of sediment particles molds the composition of sedimentary OM and thereby affects carbon turnover in the sediments.

### 5.2. Sedimentary organic matter

#### 5.2.1. OM sources—marine vs. terrestrial

Terrestrial OM is generally regarded as being less reactive towards microbial degradation than marine OM (e.g. Hedges et al., 1988). Therefore, the OM source is an important control on the rates and extent of OM degradation. In the present study, C/N-ratios and organic carbon isotopic compositions indicate a predominantly marine origin of the sedimentary OM—which is a typical feature of sediments in coastal upwelling regions. All observed C/N-ratios were in the range characteristic of marine OM. Freshly produced plankton OM, typically rich in protein, has C/N-ratios of 5–7; preferential degradation of N-containing compounds during early diagenesis results in values up to 12 (Emery and Uchupuy, 1984). In contrast, terrestrial OM dominated by nitrogen-free bio-macromolecules such as cellulose and lignin has significantly higher C/N-ratios of 20–500 (Hedges et al., 1986). Increasing C/N-ratios with increasing sediment depth (Fig. 3) indicate that in the investigated sediments, C/N-ratios were primarily controlled by ongoing degradation and there was no evidence for significant input of terrestrial OM.

The carbon isotopic composition of marine OM is typically in the range of  $-22\text{‰}$  to  $-19\text{‰}$ , whereas terrestrial OM from  $\text{C}_3$ -plants varies from  $-28\text{‰}$  to  $-26\text{‰}$  (Fry and Sherr, 1984). However, light  $\delta^{13}\text{C}$  of up to  $-28\text{‰}$  has also been reported for marine OM (Fogel and Cifuentes, 1993).  $\delta^{13}\text{C}$  observed in the Concepción sediments can clearly be assigned to marine sources (Fig. 4). The shift to generally more negative  $\delta^{13}\text{C}$  in the Antofagasta sediments

is unlikely to result from an enhanced contribution of terrestrial OM, as (1) terrestrial input in this region is generally low and (2) the C/N-ratios were similar to those observed off Concepción and in the typical range for marine OM. Analysis of sedimentary fatty acids also revealed a predominantly marine origin of the OM deposited near Antofagasta (Niggemann and Schubert, 2006). We therefore suggest that the differences in the  $\delta^{13}\text{C}$  of the sedimentary OM reflect differences in the initial isotopic composition of the marine OM.

#### 5.2.2. Linking OM composition and depositional conditions

Since in both regions, sedimentary OM is primarily derived from production in the water column, differences in OM composition are mainly the result of transformation and alteration processes that take place in the water column, during redistribution near the seafloor, and in the sediments.

Chlorin concentrations provide information on the amount of phytoplankton detritus reaching the sediment and therefore are regarded as a function of surface productivity and extent of water column degradation (Harris et al., 1996; Shankle et al., 2002). Near Concepción, decreasing surface chlorin concentrations with increasing water depth reflect the progressive degradation of settling plankton material (Fig. 7a). In contrast, chlorin concentrations are not applicable to assess water column degradation off Antofagasta. It appears that lateral input of reworked material conceals pelagic sedimentation of fresh phytodetritus. In other words, the chlorin signal introduced by a small vertical particle flux is diluted by lateral input of pigment-poor material that had been exposed to sediment reworking. Pigments belong to the most labile fraction of sedimentary organic compounds and are selectively degraded during the earliest stages of OM transformation (Wakeham et al., 1997; Lee et al., 2000). Obviously, pre-depositional reworking effectively reduces the pool of sedimentary pigments. As a result, chlorins made up a smaller fraction of the bulk OM pool in the Antofagasta sediments ( $<0.5 \text{ mg gTOC}^{-1}$ ) than in the Concepción sediments ( $0.7\text{--}1.2 \text{ mg gTOC}^{-1}$ ).

Other labile compounds like fatty acids (Niggemann and Schubert, 2006) and amino acids (Lomstein et al., 2006) do not show such a clear separation of the two regions. TOC-

normalized concentrations of both compound classes are slightly higher at the sediment surface off Concepción than off Antofagasta, but the overall distribution indicates that water column degradation is a major control of these parameters. These findings show that bulk fatty acids and bulk amino acids are less affected by sediment reworking than bulk chlorins, which is in accordance with a generally higher reactivity/lability of phytoplankton pigments (Wakeham et al., 1997; Lee et al., 2000). Surface C/N-ratios, characterizing the degradation state of the entire OM pool, increased with water depth of the sampling site (Fig. 7b). The leveling off at C/N-ratios  $>10$  is consistent with an existing upper limit for the C/N-ratio that can be reached by bacterial transformation of OM (Fenchel et al., 1998).

We conclude that in both regions, sedimentary OM composition is strongly related to the extent of water column degradation. Pre-depositional sediment reworking in the Antofagasta region is reflected in the deposition of chlorin-depleted OM compared to more chlorin-rich OM depositing in the Concepción region.

Based on our data, we can only speculate about possible effects of oxygen availability on the sedimentary OM composition. Oxygen concentrations are closely related to water depth (Table 2) and furthermore display seasonal variations, particularly off central Chile. Moreover, a number of studies have shown that labile organic compounds are degraded at equal rates under oxic and anoxic conditions (e.g. Hulthe et al., 1998; Lehmann et al., 2002). Hence, we assume that oxygen availability was of minor importance for OM composition and concealed by other factors, particularly differences in water depth and extent of redistribution processes.

#### 5.2.3. OM freshness

With regard to carbon turnover in sediments, information on the freshness of sedimentary OM is of crucial importance. Earlier studies indicated that the rate of organic carbon degradation is a function of quality rather than of quantity of sedimentary OM (Hedges et al., 1988; Lomstein et al., 1989; Lee, 1994). Ongoing degradation decreases the availability of OM for further microbial decomposition, thus the reactivity of OM is a function of its degree of alteration.

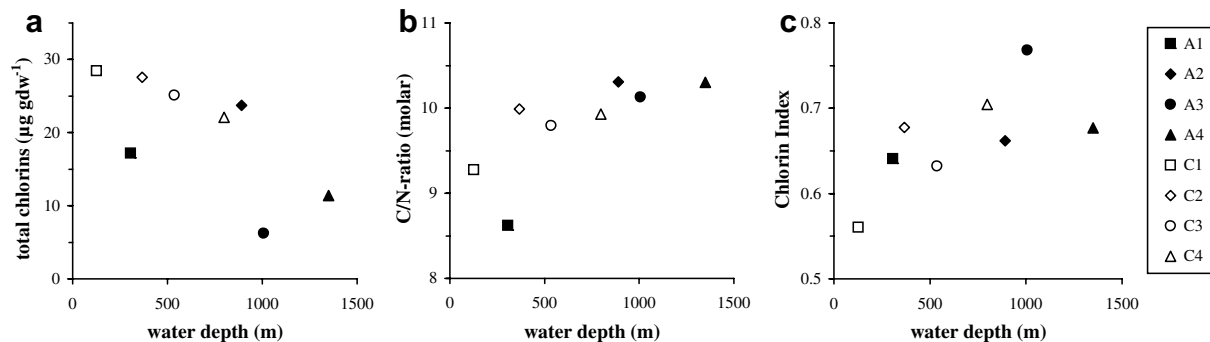


Fig. 7. Water depth dependence of organic matter characteristics: (a) total chlorin concentrations, (b) C/N-ratios, (c) Chlorin Indices. Data points represent surface sediments (0–1 cm).

Increasing CI with increasing water depth (Fig. 7c) indicates that the freshness of the sedimentary chlorins is controlled by alteration in the water column rather than by pre-depositional sediment reworking. Although chlorins make up a much smaller fraction of the OM accumulating off Antofagasta than off Concepción, the quality of the pigment material was similar in both regions. Obviously, the comparably small chlorin fraction in the Antofagasta sediments represents phytodetritus that recently entered the sediments via pelagic sedimentation.

Interestingly, it appears that chlorin degradation in the sediments does not affect the freshness of the pigment pool. While the chlorin concentrations strongly decreased within the uppermost sediment layer (0–3 cm), at most sites, the CI changed only slightly throughout the cores (Fig. 5). Most likely, the labile chlorins were preserved within their original organic matrices (Sun et al., 1993) or through adsorption to minerals (Keil et al., 1994). We assume that those chlorin compounds that lose their protection are readily degraded and that the degradation products do not persist in the sediments. The proposed scenario is in accordance with findings of Shankle et al. (2002) who report relatively little down-core changes in the relative concentrations of the different pigment groups, including intact chlorophylls and their degradation products.

Differences in the OM composition between the two investigated areas become apparent when comparing the distribution of CI and C/N-ratios. Off Concepción, where pelagic sedimentation prevails, both freshness indicators were positively correlated ( $r^2 = 0.85$ ,  $n = 4$ ; depth-averaged values) and primarily controlled by alteration in the water column. Quality changes in the sedimentary chlorins, measured as CI, were related to quality changes in the bulk sedimentary OM, measured as C/N-ratio. In contrast, in the Antofagasta region, there was no relation between CI and C/N-ratios. The C/N-ratios reflect the predominance of reworked N-depleted OM in the sediments off Antofagasta, whereas the CI reveals the presence of a small fraction of labile chlorins derived from recent pelagic sedimentation.

### 5.3. Organic matter degradation in the sediments

#### 5.3.1. Reaction rate coefficients of TOC degradation ( $k_{\text{TOC}}$ )

Sediment profiles reflect OM degradation that goes on in the sediments, e.g. with increasing sediment depth, C/N-ratios increase (Fig. 3) and chlorin concentrations decrease (Fig. 5). From the down-core decrease of TOC concentrations, we estimated reaction rate coefficients of TOC degradation ( $k_{\text{TOC}}$ ). Assuming steady state, i.e. constant sediment deposition rate and constant OM input over time, decreasing concentrations reflect degradation in the sediment. The assumption of steady state does not hold for the sediments at A1 and A4, where down-core variations of the TOC concentration suggest changes in OM input over time (Fig. 3). However, gradually decreasing concentrations at the other sites indicate that OM degradation in the sediments was the most important factor controlling the vertical distribution of TOC at these sites.

OM degradation was considered as a first-order process, i.e. the degradation rate is directly proportional to the OM

concentration, and can be represented according to Berner (1980):

$$\frac{\partial C}{\partial t} = -kC, \quad (3)$$

where  $C$  is the TOC concentration at time  $t$ . We are aware that sedimentary OM consists of different pools with different reactivities and that OM degradation is more adequately described by a “multi-G”-model (Berner, 1980; Westrich and Berner, 1984). However, using the “1-G”-model enables us to compare bulk OM reactivity in the sediments. For the boundary condition  $C = C_0$  at time  $t = t_0$  the solution to Eq. 3 is:

$$C = C_0 e^{-kt}, \quad (4)$$

with  $C_0$  being the TOC concentration at the time corresponding to the deposition of the uppermost sediment layer considered ( $t_0$ ). Rearranging Eq. 4 yields:

$$k = -\frac{\ln(C/C_0)}{t} \quad (5)$$

The natural logarithm of the TOC concentration was plotted versus sediment age as determined from  $^{210}\text{Pb}_{\text{xs}}$ , and  $k_{\text{TOC}}$  was obtained from the slope of a linear regression (Fig. 8). Since bioturbation affected the vertical distribution of OM in the Concepción sediments,  $k_{\text{TOC}}$  was only estimated for the non-bioturbated lower sediment sections.

What do the values of  $k_{\text{TOC}}$  tell us? These rate constants quantify the average long-term reactivity of bulk sedimentary OM, since higher values of  $k_{\text{TOC}}$  imply that a larger fraction of the OM pool is degraded per time interval. We expected this fraction to be lower in the Antofagasta than in the Concepción sediments, since most of the material accumulating off Antofagasta is reworked and less reactive than that depositing off Concepción. Indeed, although values of  $k_{\text{TOC}}$  off Concepción characterize OM deeper in the sediments (OM that had been exposed to sedimentary degradation in the bioturbated layer),  $k_{\text{TOC}}$  at most Concepción sites is still higher than at the deeper Antofagasta sites A2 and A3 (Fig. 8), where  $k_{\text{TOC}}$  was estimated using data from the upper sediment layers.

#### 5.3.2. Reaction rate coefficients $k_{\text{SRR}}$

In sediments where sulfate reduction is the dominant terminal electron acceptor process, SRR provide a direct measure for the reactivity of the sedimentary organic carbon (Westrich and Berner, 1984; Schubert et al., 2000). Given that pore-water sulfate is not limited, the rate of carbon oxidation through bacterial sulfate reduction is a function of the availability of reactive organic compounds and can be construed to follow pseudo-first order kinetics as described in Eq. 3 (Berner, 1980; Westrich and Berner, 1984). According to the stoichiometry of bacterial sulfate reduction



the rate of organic carbon remineralization ( $\delta C/\delta t$ ) equals two times the SRR. Therefore, a reaction rate coefficient  $k_{\text{SRR}}$  can be calculated as

$$k_{\text{SRR}} = \frac{2 \times \text{SRR}}{C_{\text{TOC}}}. \quad (7)$$

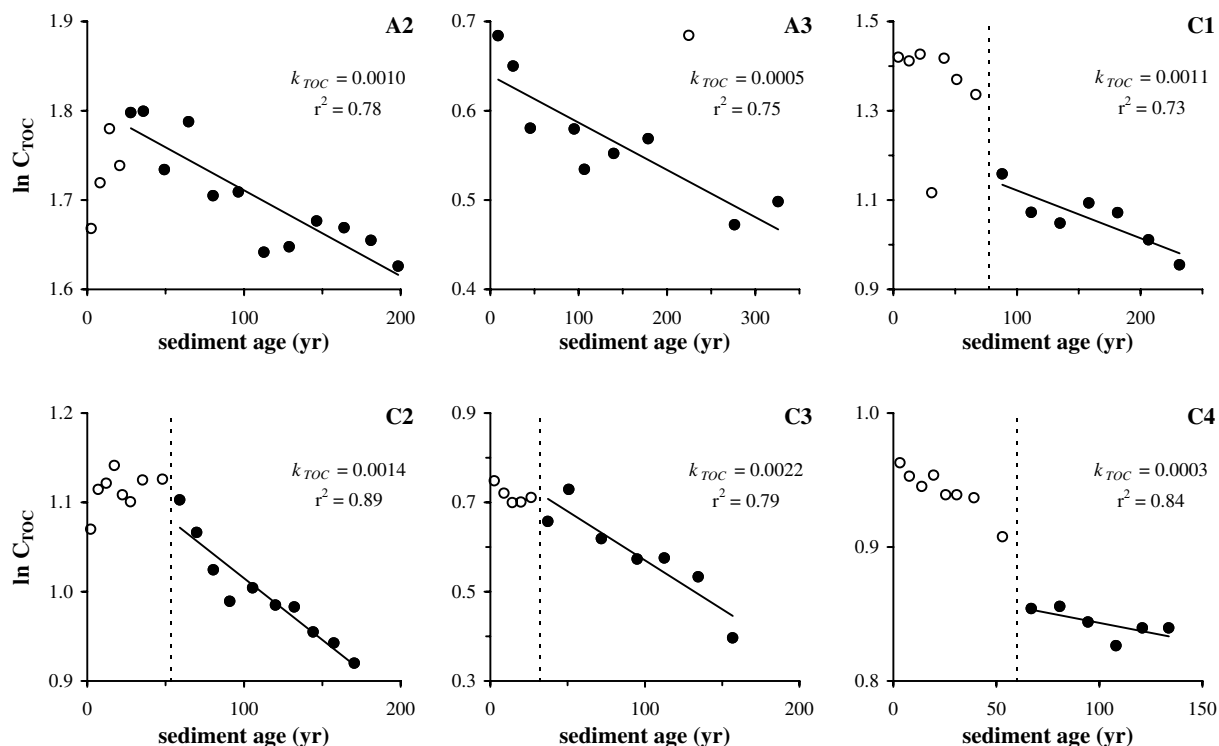


Fig. 8. Calculation of the reaction rate coefficients for TOC degradation ( $k_{TOC}$ ). In each plot, the natural logarithm ( $\ln$ ) of the TOC concentration (% dw) is plotted versus sediment age derived from  $^{210}\text{Pb}$  dating. The slope of the linear regression gives  $k_{TOC}$ . Dotted lines mark the lower boundary of the mixed layer, and open circles mark data points that are not included in the regression.

$C_{TOC}$  is the TOC concentration in the respective sediment layer and includes reactive and non-reactive compounds.

$k_{TOC}$  and  $k_{SRR}$  as a measure for bulk OM reactivity were compared with freshness indicators describing OM quality (Fig. 9). Due to the limited data set, the observed trends have to be interpreted with caution. However, these trends are consistent with differences in depositional conditions and OM composition of the two regions. In the Concepción sediments,  $k_{TOC}$  and  $k_{SRR}$  decreased with increasing C/N-ratios, indicating that in the Concepción sediments the reactivity of bulk OM is linked to the degree of alteration of bulk OM. In contrast, in the Antofagasta region,  $k_{TOC}$  and  $k_{SRR}$  increased with increasing C/N-ratios, but decreased with increasing CI (Fig. 9). This suggests that bulk OM reactivity in the Antofagasta sediments is based on the freshness of the small labile fraction introduced by pelagic sedimentation of fresh phytodetritus. It has been shown by Arnosti and Holmer (2003) that microorganisms are able to thrive on a small highly reactive fraction of sedimentary OM which is not reflected in bulk chemical parameters.

### 5.3.3. Linking $k_{SRR}$ and $k_{TOC}$

The reaction rate coefficients  $k_{TOC}$  calculated from the depth profiles of TOC concentrations showed a good correspondence to the reaction rate coefficients  $k_{SRR}$  that describe TOC remineralization coupled to sulfate reduction (Fig. 10). Although the two coefficients were calculated based on different approaches, the obtained values covered

a similar range:  $0.0004\text{--}0.0022\text{ yr}^{-1}$  for  $k_{SRR}$  and  $0.0003\text{--}0.0014\text{ yr}^{-1}$  for  $k_{TOC}$ , respectively.

The overall good agreement between the different approaches is remarkable. While  $k_{TOC}$  describes the result of several years of sedimentary organic carbon degradation that is imprinted in the depth profiles of TOC,  $k_{SRR}$  more likely reflects the actual reactivity of the sedimentary organic carbon at the time of sampling (Jørgensen, 1978; Schubert et al., 2000). At least at the shelf sites, where SRR display high temporal variability,  $k_{SRR}$  calculated from a single sampling should not be representative for the long-term reactivity of bulk sedimentary organic carbon as assessed by  $k_{TOC}$ . However, at the two shelf sites C1 and C2, we only considered the sediment sections below the bioturbated layer, and therefore, seasonal differences in OM supply and bottom water temperature should have a minor effect on SRR. At most sites,  $k_{SRR}$  is slightly lower than  $k_{TOC}$  (Fig. 10).  $k_{SRR}$  might underestimate organic carbon reactivity, when other pathways of organic carbon oxidation account for part of the OM degradation. The very high  $k_{SRR}$  observed at C4 was most likely a result of spatially heterogeneous OM distribution. Although the deep SRR peak (Fig. 6) was not included in the calculation of  $k_{SRR}$ , the SRR profile shows that fresh OM might recently have entered this sediment layer. As outlined above, such a small fraction of labile OM is able to fuel high remineralization rates (Arnosti and Holmer, 2003).

It is possible that the good agreement of  $k_{TOC}$  and  $k_{SRR}$  is attributable to the combined effect of compensating

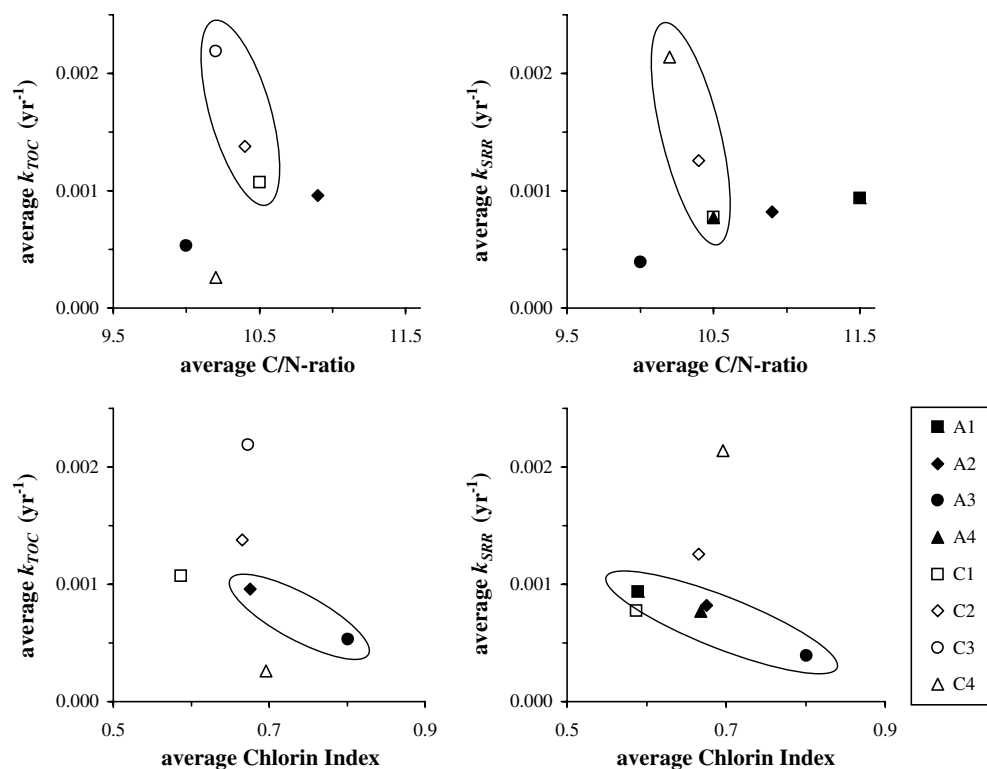


Fig. 9. Comparison of reaction rate coefficients  $k_{\text{TOC}}$  and  $k_{\text{SRR}}$  with OM quality indicators. Average values of  $k_{\text{SRR}}$ , C/N-ratio, and Chlorin Index include data from the sediment depths that were used to derive  $k_{\text{TOC}}$ , i.e. for the Concepción sites only the non-bioturbated sections. Circled data sets highlight trends that are characteristic for the two regions.

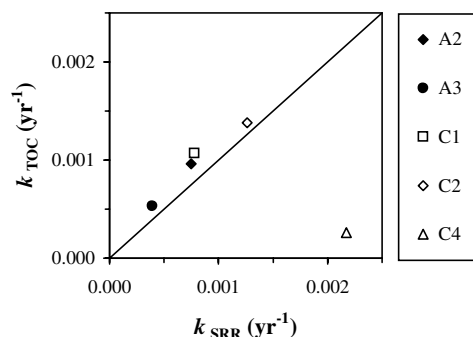


Fig. 10. Comparison of the reaction rate coefficients derived from depth profiles of TOC ( $k_{\text{TOC}}$ ) and measured sulfate reduction rates ( $k_{\text{SRR}}$ ). These values were estimated for non-bioturbated sediment sections. The 1:1-line is also plotted.

parameters; however, a good agreement of the two coefficients is consistent with bacterial sulfate reduction being responsible for most of the carbon oxidation in anoxic marine sediments (Jørgensen, 1982; Canfield, 1989).

## 6. CONCLUSIONS

We have shown that depositional conditions affect sedimentary carbon turnover by controlling OM input and composition. Although both investigated regions represent characteristic upwelling systems, the depositional

conditions differ substantially. Near Antofagasta the vertical particle flux is much lower than near Concepción, and particles accumulating in isolated deposition centers near Antofagasta are mostly old and reworked. Bioturbation is intense off Concepción but lacking off Antofagasta; furthermore, input of terrestrially derived clastic material is higher in the humid central region off Concepción than off northern Chile near Antofagasta. However, these differences are not visible from sediment accumulation rates, which are similar in both investigated regions.

Although sedimentary OM in both regions is predominantly of marine origin—which is a typical feature of sediments in coastal upwelling regions—this material is more reworked and less reactive off Antofagasta than off Concepción. Most parameters describing OM freshness reflect the influence of water column alteration on sedimentary OM composition: with increasing water depth, chlorin concentrations decrease, and C/N-ratios and CI increase. Possible effects of oxygen availability on OM preservation might be concealed as bottom water oxygen concentrations are closely related to water depth. The differences in OM freshness are reflected in SRR that decrease with increasing water depth and are generally lower off Antofagasta than off Concepción.

This study showed that the depositional environment is a dominant control on OM content, composition, and turnover, and leaves its imprint in the sedimentary record. This has major implications for paleo-environmental reconstructions that are based on bulk sediment descriptions. In



particular, sediments deposited in the same general upwelling regime (e.g. off Chile) might display significant differences in OM content, composition, and turnover that are independent from water column productivity and vertical particle flux.

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