Originally published as:

Niggemann, J., Ferdelman, T. G., Lomstein, B. A., Kallmeyer, J., Schubert, C. J. (2007): How depositional conditions control input, composition, and degradation of organic matter in sediments from the Chilean coastal upwelling region. - *Geochimica et Cosmochimica Acta*, 71, 6, 1513-1527

DOI: [10.1016/j.gca.2006.12.012](https://doi.org/10.1016/j.gca.2006.12.012).

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 order to elucidate how depositional conditions and organic matter (OM) composition influence organic carbon turnover in sediments, we compared two different depositional systems in the Chilean coastal upwelling region: (1) at ~23°S off Antofagasta bordering the Atacama desert, and (2) at ~36°S off Concepción with a more humid hinterland. Eight sediment cores from water depths of 126-1350 m and core lengths up to 30 cm were investigated for excess ^{210}Pb ($^{210}\text{Pb}_{\text{xs}}$) activity, total organic and total inorganic carbon concentrations (TOC and TIC), 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}Pb -analysis were similar in both regions (0.04-0.15 cm yr^{-1} at 23°S, 0.10-0.19 cm yr^{-1} at 36°S), though vertical particle flux, as reflected in $^{210}\text{Pb}_{\text{xs}}$ fluxes, and input of lithogenic terrestrial material, as reflected in dilution of autochthonous TOC and TIC, were higher at 36°S than at 23°S. We propose that sampling of isolated deposition centers, that collect particles originally distributed over a much wider area led to unexpectedly high sediment accumulation rates in the northern area. Bioturbation was intense at 36°S even in sediments within the oxygen minimum zone, whereas there were no indications for sediment mixing at 23°S. $\delta^{13}\text{C}$ -values (-24.5‰ to -20.1‰ vs. VPDB) and C/N-ratios (molar, 8.6-12.8) 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. Reaction rate constants derived from the depth profiles of TOC (k_{TOC}) decreased with increasing water depth (0.0005-0.0023 yr^{-1}), confirming the dominant control of water column degradation on the reactivity of sedimentary OM. SRR were lower at 23°S (areal SRR 0.12-0.60 $\text{mmol m}^{-2} \text{d}^{-1}$) than at 36°S (areal SRR 0.82-1.18 $\text{mmol m}^{-2} \text{d}^{-1}$) 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°S. Reaction rate constants for TOC degradation that were obtained from measured SRR (k_{SRR}) decreased with increasing water depth (0.0004-0.0030 yr⁻¹) and showed a good correspondence to k_{TOC} . Relating composition and degradation of OM to the prevailing depositional conditions provides important insights to improve our understanding of processes affecting deposition and degradation of OM in marine sediments.

Keywords: coastal upwelling; organic carbon; organic carbon reactivity; sulfate reduction; bioturbation; freshness indicator; sedimentation rates

Regional index terms: Chile, Antofagasta (~23°S, ~70°W), Concepción (~36°S, ~73°W)

Geographic bounding coordinates: 22-37°S, 70-74°W

1. INTRODUCTION

In coastal upwelling areas, advection of nutrient rich waters fuels primary production rates 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, and 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). Due to the high sedimentation rates, these sediments provide the opportunity to study early diagenetic processes with high temporal resolution. In general, depositional conditions in coastal upwelling regions might differ significantly over small distances, particularly with respect to water depth and oxygen availability.

Heterotrophic processes in the water column and in sediments reduce the total amount of sedimentary OM and change its molecular composition (Wakeham et al., 1997). Ongoing early diagenesis decreases the availability of OM for further microbial decomposition, thus the reactivity of organic carbon is a function of its degree of alteration. Furthermore, the kinetic of organic carbon degradation appears to be a function of the prevailing degradation pathways. Microbial degradation has been observed to be slower under anoxic than under oxic conditions, though the difference is smaller for fresh, easily hydrolysable, than for more refractory substrates (Henrichs and Farrington, 1987; Lee, 1992; Sun et al., 1993; Harvey et al., 1995; Kristensen et al., 1995; Sun et al., 1997; Lehmann et al., 2002). 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).

Bioturbation might extend the oxygen exposure time as mixing and burrowing activity

transport particles towards the oxic zone and oxygen might penetrate deeper into the sediment (Aller, 1994; Ziebis et al., 1996). In addition, macrofaunal organisms directly feed on the sedimentary OM and also stimulate microbial degradation (Aller, 1982).

In the absence of dissolved oxygen, bacterial dissimilatory sulfate reduction is the quantitatively most important terminal electron acceptor process 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 on 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 the availability of labile marine OM as indicated by total protein and chlorin concentrations was correlated with higher sulfate reduction rates (SRR), 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.

Beside differences in OM composition, depositional conditions should also affect the sedimentary carbon turnover. Here, we test these hypotheses by comparing two sedimentary regimes in the Chilean upwelling region, both underlying important upwelling cells, but representing different depositional environments. We present data characterizing (1) the depositional environment, (2) the bulk organic geochemical composition of the sedimentary OM, and (3) sedimentary organic carbon turnover as measured by sulfate reduction. We expected to find distinct differences between the depositional conditions near 23°S off

Antofagasta and near 36°S off Concepción, that are partly reflected in differences in organic geochemical composition and turnover rates. Finally, we link these differences in OM composition to observed differences in sedimentary organic carbon turnover.

2. SITE DESCRIPTION

Observations of sea surface temperature (Fonseca and Farías, 1987) and coastal zone color scanning recording pigment concentrations (Thomas, 1999) along the Chilean coast identify areas of especially pronounced upwelling near 20°S, 23°S, 30°S, 33°S, 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.

In general, upwelling off northern Chile is concentrated close to the coast and 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). Continental shelf and slope off Concepción extend further offshore than off northern Chile and therefore are more favourable to sediment accumulation (Muñoz et al., 2004). Annual precipitation in the Chilean coastal region increases from north to south, leading to enhanced 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). At that time, the OMZ ($<22 \mu\text{mol O}_2 \text{ l}^{-1}$) in the water column off Antofagasta
5 extended from 30-50 m to 400 m water depth near the coast and from 70 m to 450-500 m water depth further offshore. Near Concepción, the OMZ was narrower than in the northern area, extending from 80-140 m water depth down to the seafloor at the shelf sites and from 70 m to 400 m water depth further offshore (Hebbeln et al., 2001). The narrowing of the water column OMZ from north to south is mainly due to the mixing of the southward flowing
10 oxygen depleted Equatorial Subsurface Water with well-oxygenated Subantarctic Water above and Intermediate Antarctic Water below (Brandhorst, 1971). Off central Chile, 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).

Bottom water oxygen concentrations reported from CTD casts during the cruise
15 ranged from 0.4 to 105 μM at the different sites (Hebbeln et al., 2001; Tab. 1). Lowest concentrations were found at the shallowest sites A1, C1, and C2, reflecting their location within the actual position of the water column OMZ (Fig. 1b/c). Highest oxygen concentrations were measured in the bottom waters of the deeper sites A4, C3, and C4.

3. MATERIAL AND METHODS

3.1 Sampling and sample processing

5 Table 1 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°C immediately after sampling. The sediment
samples were later freeze-dried and homogenized by grinding in an agate mortar. Particulate
10 material more than 0.5 cm in size, 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, 30 cm long Plexiglas core tubes (26 mm
diameter) were used, with silicone plugged holes every 1 cm. (2) For sampling in 5-cm
15 intervals, 7 cm long glass tubes (10 mm diameter) made from a glass barrel were used, with a
piston from a 5 ml plastic syringe on one side and 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 (Tab. 1).

Additional samples were taken for the determination of porosity and wet density as
20 well as for ²¹⁰Pb-counting. The cores were sliced into 1-cm or 2-cm intervals, transferred to
petri-dishes, sealed tightly with electric tape, and stored at 4°C until further analysis.

3.2 Elemental analysis

25 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 CO₂ 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.

5 For the determination of the isotopic composition of TOC, samples were first treated with hydrochloric acid (3 M) to eliminate carbonates, rinsed three times with distilled water, and dried overnight at 60°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 CO₂ was passed to an Isoprime isotope-ratio mass spectrometer (GU Instruments, UK) in a continuous flow of helium. The results are reported
10 in the δ notation relative to Vienna Pee Dee Belemnite (VPDB):

$$\delta^{13}\text{C}(\text{‰}) = \left(\frac{(^{13}\text{C}/^{12}\text{C})_{\text{sample}}}{(^{13}\text{C}/^{12}\text{C})_{\text{standard}}} - 1 \right) * 1000 \quad (1)$$

Average standard deviation for four replicates was $\pm 0.4\text{‰}$.

15 **3.3 Chlorins and Chlorin Index (CI)**

For the determination of chlorins, we followed the procedure described in Schubert et al. (2005). 100-200 mg of freeze-dried sediment was extracted successively three times with 5 ml acetone (HPLC-grade, Roth, Germany) by sonication and centrifugation. The sediment
20 extracts were measured on a Hitachi F-2000 fluorometer ($\lambda_{\text{ex}}=428$ nm, $\lambda_{\text{em}}=671$ nm) immediately after extraction. Phaeophytin *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 Chlorin Index (Schubert et al., 2005):

$$\text{Chlorin Index (CI)} = \frac{\text{FI}_{\text{acidified_extract}}}{\text{FI}_{\text{original_extract}}} \quad (2)$$

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

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 ~5 μl of carrier-free $^{35}\text{SO}_4^{2-}$ (80 kBq μl^{-1} , Amersham) was injected through ports along the side, whereas in the glass-subcores, $^{35}\text{SO}_4^{2-}$ (~5-10 μl) was injected along the longitudinal axis. Incubation times varied between 6 and 42 hours. Bacterial activity was halted by transferring 1 cm slices of the sediment from the acrylic cores and the sediment extruded from the glass barrels, respectively, into 20 ml of 20% zinc acetate (20 g $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$ per 100 ml solution) and freezing (-20°C). Blank controls were determined by fixing sediment in zinc acetate solution and subsequently adding $^{35}\text{SO}_4^{2-}$. Incorporation 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). Sulfate concentrations used in the calculations were assumed to be 28 mM as pore water measurements using anion chromatography (Ferdelman et al., 1997) showed no significant depletion from seawater sulfate concentration in sediment cores from different water depth along the Chilean shelf and slope, including OMZ-sites (Kallmeyer, unpublished data).

3.5 ^{210}Pb -counting

For gamma-counting, dry sediments were homogenized by grinding in a mortar and 5-25 g transferred to polysulfone screw (diameter 45 mm) screw-top jars. Samples were kept for at least 20 days to reach secular equilibrium between the parent isotope ^{226}Ra and its short-lived daughter products ^{222}Rn , ^{214}Pb , and ^{214}Bi . Activities were then 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}Pb (46.4 keV), ^{214}Pb (295.2 and 352 keV), and ^{214}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}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}Pb source (AEA Technology). Supported ^{210}Pb activity from the in situ decay of ^{226}Ra in the samples was determined as the activity of its short-lived daughter products ^{214}Pb and ^{214}Bi . Unsupported, excess ^{210}Pb ($^{210}\text{Pb}_{\text{xs}}$) activity was calculated as the difference of total ^{210}Pb activity and ^{226}Ra activity.

3.6 Calculation of sediment accumulation rates

Sediment accumulation rates (ω) were calculated from the down-core changes of $^{210}\text{Pb}_{\text{xs}}$ activity. To account for differences in sediment porosity and consolidation $^{210}\text{Pb}_{\text{xs}}$ 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 appeared to be unaffected by mixing (Carpenter et al., 1982):

$$r = \frac{\lambda}{S} \quad \text{with} \quad \lambda = \frac{\ln 2}{t_{1/2}} \quad (3.1 \text{ and } 3.2)$$

Herein, λ is the decay coefficient of ^{210}Pb ; half-life ($t_{1/2}$) of ^{210}Pb is 22.3 years. For each depth an age was calculated from cumulative dry weight and r ($\text{g cm}^{-2} \text{ yr}^{-1}$). Then, ω (cm yr^{-1}) were calculated from age and depth of the individual samples.

5 The calculation of sedimentation rates is based on the assumption that $^{210}\text{Pb}_{\text{xs}}$ flux and sedimentation were constant over time. In general, smaller variations in ^{210}Pb flux and sedimentation are concealed by the low sample resolution - the samples investigated in this study (1-2 cm) integrate over 5-50 years of sediment deposition. However, it should be noted, that ω calculated from profiles of $^{210}\text{Pb}_{\text{xs}}$ often overestimate the actual accumulation rates, as

10 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

5 Near Antofagasta the sediments mainly consisted of sandy mud, whereas near
Concepción hemipelagic mud dominated the sediments. The porosity profiles of C1, C3, and
C4 (not shown) reflect a change in sediment texture that was also observed during sampling:
the lower part of the sediments (16-36 cm, 6-18 cm, and 10-20 cm, respectively) appeared
stiffer than the softer upper part. At C3 and C4 the depth of this change corresponds to the
10 lower boundary of the mixed layer. In contrast, at C1 the transition is not related to the
extension of the mixed layer and the difference in sediment texture is more pronounced than
at C3 and C4, indicating that the observed change reflects a change in sedimentation. In a
sediment core from a site close to C1, Thamdrup and Canfield (1996) and Ferdelman et al.
(1997) observed a sharp transition from silt in the upper ~15 cm to clay below this depth.

15 In the Antofagasta area living sediment organisms were only observed at A1, where
several small worms and annelids occurred. No *Thioploca* were reported for the investigated
sites, and the upper 50 cm of gravity cores taken at sites A2, A3, and A4 showed no
indications of bioturbation (Hebbeln et al., 2001). Accordingly, the freeze-dried samples did
not reveal any remains of bioturbating infauna, but we found numerous tests of benthic
20 foraminifera in all sediments from this region, being especially abundant 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).

At 36°S all sites were strongly bioturbated. Living organisms were found in the cores
of C2 and C3, up to 16 cm and 12 cm sediment depth, respectively. At C1 several tubes with
25 vital worms escaped the sediment surface and at C4 a worm burrow was observed but no
living organisms were found. *Thioploca* were present at all four sites, but a significant

Thioploca biomass (5.2 g m^{-2}) was only found at C1, where filaments penetrated down to 18 cm sediment depth (Hebbeln et al., 2001). However, the observed *Thioploca* biomass was lower than the average value of 10 g m^{-2} reported for the Chilean shelf (Schulz et al., 1996).

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), in accordance with the obvious 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 the zone of effective sediment mixing most likely due to bioturbation. This well mixed zone penetrated deeper at C2 and C4 compared to C1 and C3. 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 compared to the region off Concepción (Tab. 2), consistent with the findings of Muñoz et al. (2004). However, using a different approach, Muñoz et al. (2004) calculated sediment accumulation rates that are on average 44% higher than those observed in our study. However, they also report high variability for parallel cores and cores retrieved in close proximity, which is most likely a result of small scale differences in seafloor topography and patchiness of bioturbation activity. In our study samples of A1 contained only very small amounts of $^{210}\text{Pb}_{\text{xs}}$, at most depth measured ^{226}Ra activity (supported ^{210}Pb) was higher than ^{210}Pb activity, indicating a lack of recent input of ^{210}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 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 (Tab. 2). Accordingly, total $^{210}\text{Pb}_{\text{xs}}$ fluxes calculated from these inventories by multiplying by λ were also significantly ($p<0.05$) lower off Antofagasta than off Concepción. These findings are consistent with the results of Muñoz et al. (2004),
5 who report similar $^{210}\text{Pb}_{\text{xs}}$ inventories and fluxes.

4.3 Elemental composition

4.3.1 Total organic carbon and total inorganic carbon

TOC concentrations ranged from 1.6% to 12.4% (sediment dry weight) in the Antofagasta sediments and from 1.5% to 4.2% in the Concepción sediments (Fig. 3). The TOC profile at A1 departed from those at the other investigated sites. The TOC concentration remained relatively constant ($5.4\pm0.3\%$, $n=5$) within the upper 5 cm of the sediment,
10 gradually increased to 12.4% at 9 cm depth, and then decreased to 6.4% at the end of the core. In general, high TOC concentrations coincided with high porosity and low density. At A2 and A3, TOC concentrations fell in the range 5.1%-6.1% and 1.6%-2.0%, respectively, and slightly decreased with sediment depth. At A4 the TOC concentrations exhibited strong scatter in the upper 10 cm and were relatively constant deeper in the sediment ($4.3\pm0.1\%$,
15 $n=6$).

At all sites from the Concepción region, TOC concentrations decreased with increasing sediment depth. This decrease was attenuated in the mixed layers and stronger in the unmixed deeper layers. At C3 and C4, TOC concentrations continuously decreased from the sediment surface to the end of the core, from 2.6% to 2.3% and from 2.1% to 1.5%,
20 respectively. At C2 the TOC concentration ranged around $3.0\pm0.1\%$ ($n=8$) within the mixed layer and decreased below to 2.5% at the end of the core. The strongest decrease was

observed at C1 from $3.9 \pm 0.4\%$ (n=7) in the upper mixed layer to 2.6% at 21 cm depth. A sharp minimum of 3.1% was present at 3.5 cm depth. The pronounced decrease towards the lowermost sample (1.5%) reflected changes in sediment texture observed at this site.

TIC concentrations (data not shown) were significantly higher ($p < 0.05$) off Antofagasta (up to 2.2% dw) than off Concepción ($< 0.4\%$ dw), consistent with the high abundances of calcareous foraminifera tests observed in the Antofagasta sediments. In general, the higher TOC and TIC concentrations in the Antofagasta sediments compared to the Concepción sediments result from a stronger dilution with lithogenic terrestrial material in the southern region.

4.3.2 C/N-ratios

Increasing C/N-ratios with increasing sediment depth reflect the preferential remineralization of nitrogen containing compounds with ongoing degradation of sedimentary OM (e.g. Emery and Uchupi, 1984). Near Antofagasta, C/N-ratios increased gradually at A2, ranging from 10.3 to 11.5 (Fig. 3). At A1, C/N-ratios increased strongly from 8.6 at the sediment surface (the lowest ratio observed in this study) to 12.2 at 7 cm depth. In the deeper part of the sediment C/N-ratios were high (12.4 ± 0.2 , n=9), with a maximum of 12.8 at 15 cm depth (the highest ratio observed in this study). At A3, C/N-ratios fell in the range 9.6-10.2, without a distinct depth pattern. C/N-ratios at A4 were > 10 in the upper 2 cm of the sediment and constantly lower (9.8 ± 0.1 , n=6) in the section 2.5-9 cm. In the deeper part of the sediment, they gradually increased to 11.4 at the end of the core.

In all Concepción sediments, C/N-ratios increased with sediment depth (Fig. 3). The observed increase was less pronounced at C2 (9.8-10.7), C3 (9.8-10.7), and C4 (9.9-10.4) compared to C1, which showed a strong increase from 9.3 at the sediment surface to 11.0 at

21 cm sediment depth. The high C/N-ratio of 12.3 at the end of the core coincided with the change in sediment texture mentioned above.

4.3.3 Organic carbon isotopic composition

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The organic carbon isotopic composition provides information on the organic carbon source. $\delta^{13}\text{C}$ of marine OM is typically in the range -22‰ to -19‰, whereas terrestrial OM from C₃-plants varies from -28‰ to -26‰ (Fry and Sherr, 1984). $\delta^{13}\text{C}$ observed in this study ranged from -20.1‰ to -24.5‰ and showed a clear separation (significance: $p < 0.05$) between the two investigated areas (Fig. 4). Near Antofagasta, the carbon isotopic composition was lightest at A1 ranging from -24.5‰ to -22.6‰. All other $\delta^{13}\text{C}$ in this area were between -23.4‰ and -21.4‰. With the exception of the light isotopic composition at C1 at 2.5 cm depth (-22.7‰), all samples from the Concepción region fell in the narrow range -21.0‰ to -20.1‰, indicating a predominantly marine source of the sedimentary OM.

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4.4 Total chlorins and Chlorin Index

Chlorins comprise chlorophylls and a variety of their degradation products, thereby providing a measure for the input of phytoplankton detritus. 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 of 31 $\mu\text{g gdw}^{-1}$ 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, off Antofagasta, the surface concentration was highest at A2 (24 $\mu\text{g gdw}^{-1}$) and lowest at A3 (6 $\mu\text{g gdw}^{-1}$). At most sites the chlorin concentration decreased with sediment depth, and, at all sites, the decrease was most extreme in the upper 3 cm, where 18-56% of the

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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 (0.58 ± 0.04 , $n=16$) and A1 (0.59 ± 0.04 , $n=16$), indicating that the phytodetritus was freshest at these sites. At A3 the average CI of 0.80 ± 0.04 ($n=10$) was significantly higher than at all other sites ($p < 0.05$), characterizing the pigment material to be the most degraded. At all other sites the average CI fell in the range 0.66 to 0.69, indicating the presence of moderately altered chlorins.

4.5 Sulfate reduction rates

In general, we found a good correspondence of SRR derived from the analysis of 1-cm and 5-cm intervals (Fig. 6). Though the lower resolution did not resolve distinct peaks, in most cases, the average of all 1-cm values in a 5-cm interval fell in the range of the respective 5-cm values. The deep peaks at C2 (20-22 cm) and C4 (18 cm) were only resolved by high resolution sampling and not present in the 5 cm samples and most likely reflect local sediment heterogeneity, e.g. worm burrows with freshly introduced OM. We can exclude that the high SRR were caused by sulfate reduction coupled to the anaerobic oxidation of methane as (1) pore-water sulfate concentrations did not change significantly in the upper 30 cm of the investigated sediments and (2) in a gravity core retrieved at the position of C4, Treude et al. (2005) located the zone of sulfate-methane transition at 320-450 cm sediment depth.

In the Antofagasta region only the SRR profile at A1 showed a distinct depth trend. Here we observed a pronounced surface peak of $11.4 \text{ nmol cm}^{-3} \text{ d}^{-1}$ and an exponential decrease to rates $< 1 \text{ nmol cm}^{-3} \text{ d}^{-1}$ at sediment depth $> 8 \text{ cm}$. At A2, SRR varied around $4 \text{ nmol cm}^{-3} \text{ d}^{-1}$ throughout the upper 15 cm and in the deeper part slightly decreased to values

$<1 \text{ nmol cm}^{-3} \text{ d}^{-1}$. SRR at A3 ranged around $1 \text{ nmol cm}^{-3} \text{ d}^{-1}$ throughout the core; the surface peak observed in the 1 cm sampling was not reflected in the 5 cm sampling. At A4, SRR were $<0.2 \text{ nmol cm}^{-3} \text{ d}^{-1}$ near the sediment surface and higher ($2.1 \pm 0.9 \text{ nmol cm}^{-3} \text{ d}^{-1}$, $n=15$) in the deeper part of the core (5-15 cm).

5 In the Concepción sediments, SRR were high throughout the mixed layer. In the upper 6 cm at C1 rates were $6.8\text{-}15.5 \text{ nmol cm}^{-3} \text{ d}^{-1}$, with even higher SRR derived from 5 cm sampling ($15.4\text{-}20.9 \text{ nmol cm}^{-3} \text{ d}^{-1}$). A sharp down-core decrease to $\text{SRR} < 1 \text{ nmol cm}^{-3} \text{ d}^{-1}$ 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
10 revealed a factor 10-50 higher maximum SRR, reflecting seasonal changes in the availability of fresh organic carbon typically occurring at shelf sites. At C2, SRR were low at the sediment surface ($<0.2 \text{ nmol cm}^{-3} \text{ d}^{-1}$) and a subsurface peak of $7.2 \text{ nmol cm}^{-3} \text{ d}^{-1}$ was found at 2.5 cm depth. Down-core, SRR gradually decreased. At C4, SRR were $<0.2 \text{ nmol cm}^{-3} \text{ d}^{-1}$ at the sediment surface, increased towards a maximum of $8.2 \text{ nmol cm}^{-3} \text{ d}^{-1}$ at 8 cm depth, and
15 decreased further down-core.

 At most sites, subsurface or deep peaks of SRR indicated that other terminal electron acceptor processes accounted for part of the carbon oxidation. In consequence, depth integrated SRR (0-15 cm) underestimate the TOC remineralization rate and rather provide a minimum estimate (Tab. 3). Areal SRR were significantly higher ($p<0.05$) in sediments at
20 36°S than at 23°S . In both regions the depth integrated rates were highest at the shallowest sites and overall decreased with increasing water depth.

5. DISCUSSION

5.1 Differences in depositional conditions off Antofagasta and off Concepción

5.1.1 Upwelling intensity and particle flux

The flux of $^{210}\text{Pb}_{\text{xs}}$ to the sediments provides information on the upwelling intensity in the overlying water column. Two sources account for $^{210}\text{Pb}_{\text{xs}}$ inventories in marine sediments: (1) dry and wet deposition of atmospheric ^{210}Pb onto the ocean surface and (2) production of ^{210}Pb in the water column by the decay of ^{226}Ra . Dissolved ^{210}Pb is effectively scavenged on sinking particles and transported to the sediments. Consequently the flux of ^{210}Pb to the sediment is a function of ^{210}Pb supply in the water column and of particle flux. Upwelling supports both factors: (1) upwelling waters are fed by lateral inflow of open ocean water enriched in dissolved ^{210}Pb , and (2) high nutrient concentrations fuel particle production in the euphotic zone.

Atmospheric deposition of ^{210}Pb accounts for a $^{210}\text{Pb}_{\text{xs}}$ flux of $0.2 \text{ dpm cm}^{-2} \text{ yr}^{-1}$ to the sediments off Concepción (Muñoz and Salamanca, 2003). We assume a similar contribution for the sediments off Antofagasta, although the lack of wet deposition might reduce the atmospheric input in this region. For the coastal ocean off California, Alexander and Venherm (2003) estimated that in-situ decay of ^{226}Ra accounted for a maximum flux of $0.37 \text{ dpm cm}^{-2} \text{ yr}^{-1}$ at 800 m water depth. Assuming a similar ^{226}Ra concentration in the coastal Pacific waters off South America as off California and effective scavenging of the produced ^{210}Pb by sinking particles, in-situ decay of ^{226}Ra supports a $^{210}\text{Pb}_{\text{xs}}$ flux to the sediments of $<0.1 \text{ dpm cm}^{-2} \text{ yr}^{-1}$ at the shallowest site and $\sim 0.6 \text{ dpm cm}^{-2} \text{ yr}^{-1}$ at the deepest site. Thus, atmospheric supply and in-situ decay together account for $<20\%$ of the observed

$^{210}\text{Pb}_{\text{xs}}$ flux to sediments off Concepción, whereas off Antofagasta the fraction is >40%. The remaining flux is supported by the processes coupled to upwelling.

5 $^{210}\text{Pb}_{\text{xs}}$ fluxes are lower off Antofagasta than off Concepción indicating a reduced lateral inflow of dissolved $^{210}\text{Pb}_{\text{xs}}$ and/or a smaller particle flux and therefore less effective scavenging of ^{210}Pb in the Antofagasta area. Upwelling off northern Chile (18°S-24°S) is limited to a narrow region close to the coast (Morales et al., 1996), whereas further South upwelling reaches a wider extension towards the ocean (Thomas, 1999). The locally restricted upwelling near Antofagasta might be less effective in sustaining lateral inflow of ^{210}Pb enriched water into the coastal region. In addition, primary productivity in this region is also
10 limited to the inshore area where nutrient supply is highest (Morales et al., 1996) and thus enhanced particle fluxes are more likely to occur close to the coast.

Near Concepción $^{210}\text{Pb}_{\text{xs}}$ fluxes increase with increasing water depth, i.e. distance to coast, and no relation to sediment accumulation rates exists. Approaching the coast, the upwelling water becomes more depleted in dissolved ^{210}Pb as high particle fluxes extending
15 far offshore effectively scavenge the imported ^{210}Pb . Obviously, the supply of radioisotopes controls ^{210}Pb fluxes to the sediments near 36°S. Accordingly, sediments from shallower water depth in the adjacent Bay of Concepción receive a reduced ^{210}Pb flux of 0.9 dpm cm⁻² yr⁻¹ at the bay mouth and of 0.2 dpm cm⁻² yr⁻¹ within the bay, respectively (Muñoz and Salamanca, 2003).

20 Off Antofagasta $^{210}\text{Pb}_{\text{xs}}$ fluxes show no relation to water depth, i.e. distance to coast, but are positively correlated with sediment accumulation rates ($r^2=1.00$, $n=3$). Apparently, the loading of sedimentary particles with $^{210}\text{Pb}_{\text{xs}}$ is similar for all investigated sites indicating that the water column particle flux is the controlling factor on $^{210}\text{Pb}_{\text{xs}}$ fluxes in this region. We conclude that off Antofagasta ^{210}Pb is not limited in the water column and is equally
25 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}Pb supply.

5.1.2 Sediment mixing (bioturbation)

5

The prevailing bottom water oxygen concentrations fail to explain the obvious absence of bioturbating macrofauna in the Antofagasta region, as oxygen concentrations determined off Antofagasta (7-53 μM) do not fall below the range observed off Concepción (0.4-105 μM). Furthermore, as we observed living organisms at the time of sampling, we can
10 exclude that mixing in the OMZ-sediments near Concepción occurs only occasionally during periods of oxygenation in the non-upwelling season or during El Niño events.

We assume that limited food supply impedes effective bioturbation off Antofagasta. Although TOC concentrations were higher in the sediments off Antofagasta than off Concepción (Fig. 3), the OM accumulating near Antofagasta was most likely more reworked
15 and of low nutritional value. Consequently, sediment mixing is primarily controlled by input fluxes of fresh OM which in turn depend on rates of primary productivity and extent of water column degradation.

5.1.3 Sediment accumulation

20

We expected the sediment accumulation rates off Antofagasta to be significantly lower than off Concepción, since terrestrial input off northern Chile is generally low and earlier studies showed that sediment accumulation rates in the Chilean coastal region increase from North to South (Lamy et al., 1998; Hebbeln et al., 2000). Sediment accumulation rates for the
25 late Holocene obtained from ^{14}C -dating of deep-sea cores (2500 m and 800 m water depth,

respectively) showed the expected latitudinal trend, $\sim 15 \text{ cm kyr}^{-1}$ at 24°S (Mohtadi et al., 2004) and $\sim 128 \text{ cm kyr}^{-1}$ at 36°S (D. Hebbeln, personal communication).

Compared to the latter studies the sediment accumulation rates observed in our study are high, reflecting that input from upwelling induced productivity is higher closer to the coast than further offshore at deep sea sites. Furthermore, in the Antofagasta region, the sampling strategy might explain the unexpectedly high sediment accumulation rates. Strong bottom currents and the steep slope off Antofagasta limit sediment accumulation to locally restricted depositional centers. Those areas that were specifically chosen for coring collect sedimentary material that was originally distributed over a much wider area (Muñoz et al., 2004). Therefore, the obtained sediment accumulation rates 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.

In summary, the depositional conditions near Antofagasta are characterized by small vertical particle fluxes and little dilution with terrestrial material. However, sediment accumulation rates in this region are large, but only in locally restricted depositional centers, representing a relatively small area of the continental margin at 23°N . Furthermore, the rapidly accumulating sediments in these basins must principally consist of reworked, radiochemically (^{210}Pb) dead material, as the overall fluxes of $^{210}\text{Pb}_{\text{xs}}$ are low, and evenly distributed over all water depths. A predominance of reworked material is consistent with the lack of bioturbation in the northern region. In the Concepción region, direct pelagic sedimentation of particles from the water column accounts for a larger fraction of the accumulating sediments. Consequently, though the total amount of OM in these sediments is lower than off Antofagasta, they contain a larger fraction of fresh OM. As we will see, the differences in the depositional environment are strongly reflected in the organic carbon composition of the sediments.

5.2 Sedimentary organic matter

5.2.1 OM sources

5 The C/N-ratios indicate that the OM in the investigated sediments is predominantly of marine origin. Freshly produced plankton OM, typically rich in protein, shows C/N-ratios of 5-7, whereas 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). Due to the preferential degradation of N-containing compounds, early diagenesis of marine OM results
10 in C/N-ratios of up to 12 (Emery and Uchupi, 1984). As shown by the profiles in Fig. 3, the C/N-ratios in the investigated sediments are primarily controlled by ongoing degradation and therefore not applicable to identify a possibly small contribution of terrestrial OM.

 The organic carbon isotopic compositions 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
15 Antofagasta sediments is unlikely to result from an enhanced contribution of terrestrial OM, as (1) terrestrial input in this region is generally low, (2) the C/N-ratios are 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, accepted).

 The observed difference in $\delta^{13}\text{C}$ between the two investigated areas might reflect
20 differences in the extent of diagenetic alteration. Early diagenetic alteration can result in a slightly lighter carbon isotopic composition of the residual OM (Lehmann et al., 2002), most likely due to the preferential degradation of carbohydrates and proteins that are generally enriched in ^{13}C compared to total plant tissue. However, such an early diagenetic change in isotopic composition should be expressed in all investigated sediments and besides make up
25 <1‰ of the initial composition (Freudenthal et al., 2001). A contribution of isotopically light OM produced by chemoautotrophic bacteria might also explain a ^{13}C depletion of the

sedimentary TOC (Cowie et al., 1999). However, a significant contribution is more likely to occur in the Concepción sediments with higher organic carbon degradation rates and abundant *Thioploca*.

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. Most of the factors affecting the carbon isotopic composition of phytoplankton, e.g. water temperature, dissolved CO_2 concentration, growth rate, and species composition (see review: Popp et al., 1997), are directly or indirectly influenced by the nature of the prevailing surface water. In both investigated areas, Equatorial Subsurface Water of the Gunther Undercurrent is the main source of upwelled waters (Brandhorst, 1971; Morales et al., 1996), but strength and seasonality of upwelling vary. Thereby, southern, cold waters might occur off central Chile, as indicated by the diatom assemblages in surface sediments near Concepción (Romero and Hebbeln, 2003).

5.2.2 Factors controlling sedimentary OM composition

Chlorin concentrations provide information on the amount of phytoplankton detritus reaching the sediment and thereby are 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, where lateral input of reworked material predominates. Pigments belong to the labile fraction of sedimentary organic compounds and are selectively degraded during the earliest stages of OM transformation in the water column and in sediments (Wakeham et al., 1997; Lee et al., 2000). Accordingly, TOC-normalized chlorin concentrations are significantly lower ($p < 0.05$) in the Antofagasta sediments

(<0.5 mg gTOC⁻¹) compared to the Concepción sediments (0.7-1.2 mg gTOC⁻¹), reflecting the advanced degradation state of the OM accumulating in the Antofagasta region.

A similar distribution as for chlorins was observed for fatty acids (Niggemann and Schubert, accepted), whereas concentrations of total hydrolysable amino acids were more strongly related to water depth (Lomstein et al., *subm.*). The C/N-ratios, characterizing the entire OM pool of the sediments, at the sediment surface increased with water depth of the sampling site and were generally higher in the Antofagasta region (except at A1; Fig. 7b), pointing to a strong influence of water column degradation on bulk OM composition and confirming the overall more reworked state of the Antofagasta sediments.

We can only speculate about possible effects of oxygen availability on the sedimentary OM composition, since oxygen concentrations are closely related to water depth (Tab. 1) and furthermore display seasonal variations, particularly off central Chile. The highest surface chlorin concentration found at C1 can be explained by the shallow water depth (126 m) as well as by the low bottom water oxygen concentration (0.4 μM). There is strong evidence that oxygen limitation generally favors the preservation of OM (Hartnett et al., 1998; Hartnett and Devol, 2003), and Sun et al. (1993) reported lower degradation rates for chlorophyll *a* in the absence than in the presence of oxygen. On the other hand, labile organic compounds have been shown to degrade at equal rates under oxic and anoxic conditions (e.g. Hulthe et al., 1998; Lehmann et al., 2002). Based on a study of chlorin distributions in Arabian Sea sediments, Shankle et al. (2002) excluded a direct effect of oxygen concentration on the degradation of chlorins and suggested that “the presence of oxygen at even very low concentrations (6 μM) was sufficient to stimulate oxic degradation” of sedimentary chlorins. Although we cannot exclude an effect of oxygen limitation on composition and degradation of the OM in the investigated sediments, we assume that this effect was of minor importance and concealed by other factors, particularly differences in water depth and extent of redistribution processes.

5.2.3. OM quality (freshness)

Whereas chlorin concentrations are a measure for the amount of phytodetritus in the sediments, the Chlorin Index provides information on the quality of this OM pool (Schubert et al., 2005). According to the CI, sedimentary chlorins were freshest at C1 and A1, consistent with the shallow water depth and the low bottom water oxygen concentration at these sites, as both factors are considered to favor the deposition of labile compounds. The most refractory chlorins were found at A3, in accordance with the low sediment accumulation rate at this site (Tab. 2) and an advanced degradation state of the comparably old sediment.

In the Concepción region, the quality of the sedimentary chlorins is related to the water depth of the sampling site (Fig. 7c). The CI increase with increasing water depth, indicating that water column alteration dominantly controls the quality of the sedimentary OM - the low surface CI at C3 might reflect a recent input of fresh phytoplankton material. Bioturbation affected the distribution of fresh chlorins in the sediments, in that the CI was on average slightly lower in the mixed layer than in the non-bioturbated deeper part (Fig. 5). In the Antofagasta region, the CI at the three deeper sites showed no relation to water depth. The prevalence of moderately altered chlorins at A2 and A4 - sites where reworked material accumulates - suggest that part of the chlorins escaped degradation in the water column and in the sediment and that the quality of this remaining pool remained unchanged.

The depth profiles of chlorins and CI support a protection scenario for labile chlorins: While the chlorin concentration strongly decreased within the uppermost sediment layer (0-3 cm), at most sites the CI changed only slightly throughout the core (Fig. 5). Shankle et al. (2002) also report relatively little down-core changes in the relative concentrations of the different pigment groups. Most likely the labile chlorins were preserved within their original organic matrices or through adsorption to minerals as proposed by Keil et al. (1994).

Differences in the OM composition between the two investigated areas become apparent when comparing the distribution of CI and C/N-ratios. Off Concepción, both parameters are positively correlated ($r^2=0.85$, $n=4$; depth-averaged values), indicating that quality changes in the sedimentary chlorins are related to quality changes in the bulk sedimentary OM. In contrast, in the Antofagasta region there is no relation between CI and C/N-ratios. As the C/N-ratio describes the degradation state of all compound classes present in the sediment, the prevalence of highly refractory N-depleted OM might conceal a smaller pool of fresh material. Although the CI was obviously not representative for the entire TOC pool in the Antofagasta sediments, it provides valuable information on the small fraction of labile chlorins, making up <0.1% of the total OM in the investigated samples. In general, information on the freshness of the phytodetritus is important since earlier studies indicated that the rate of organic carbon degradation can be a function of quality rather than of quantity of sedimentary OM (Hedges et al., 1988; Lee, 1994).

5.3 Organic matter degradation in the sediments

5.3.1 Reaction rate coefficients of TOC degradation (k_{TOC})

Reaction rate coefficients of TOC degradation (k_{TOC}) were estimated from the down-core decrease of TOC concentrations. 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 by (Berner, 1980):

$$\frac{\partial C}{\partial t} = -kC, \quad (4)$$

where C is the TOC concentration at time t . For the boundary condition $C=C_0$ at time $t=t_0$ the solution to equation 4 is:

$$C = C_0 e^{-kt}, \quad (5)$$

with C_0 being the TOC concentration at the time corresponding to the deposition of the uppermost sediment layer considered (t_0). Rearranging equation 5 yields:

$$k = -\frac{\ln(C/C_0)}{t} \quad (6)$$

The natural logarithm of the TOC concentration was plotted versus sediment age as determined from $^{210}\text{Pb}_{\text{xs}}$, and k_{TOC} was obtained from the slope of a linear regression (Fig. 8).

k_{TOC} decrease with increasing water depth of the sampling site (Fig. 7d), again indicating that the quality of the sedimentary organic carbon - here measured as reactivity - is a function of water depth and that water column alteration strongly affects sedimentary processes. In general, the k_{TOC} determined off Chile cover a similar range as those values reported for the Northern Gulf of California (Camacho-Ibar et al., 2003). However, for a sediment at 2100 m water depth in the Black Sea, Sun and Wakeham (1994) calculated a k_{TOC} of 0.015 yr^{-1} , which is on average an order of magnitude higher than the k_{TOC} observed off Chile. The apparently lower reaction rate coefficients off Chile might in part be the result of disturbed depth profiles due to the mixing of bioturbating organisms. Particularly the k_{TOC} estimated for the bioturbated sediments near Concepción most likely underestimate the true values, as sediment mixing attenuates changes in the depth profiles of TOC, thereby obscuring the real extent of degradation.

In conclusion, what do the k_{TOC} -values tell us? The k_{TOC} -values quantify the average long-term reactivity of OM: the higher the k_{TOC} , the bigger the fraction of the OM pool that is degraded per time interval. This fraction is lower off Antofagasta than off Concepción, consistent with the predominance of reworked, less-reactive OM in the Antofagasta region.

5

5.3.2 Reaction rate coefficient k_{SRR}

The reactivity of sedimentary organic carbon has also been estimated from SRR (Westrich and Berner, 1984; Schubert et al., 2000). The first step in anaerobic
10 remineralization is the hydrolytic breakdown of macromolecular OM by fermenting bacteria. This step is thought to be the slow, rate limiting step in OM remineralization, whereas the second step, the final oxidation of low-molecular fermentation products and H_2 is fast and operates near equilibrium (e.g. Hoehler et al., 1998). In sediments where sulfate reduction is the dominant terminal electron acceptor process, SRR provide a direct measure for the
15 reactivity of the sedimentary organic carbon. Given that pore-water sulfate is not limited, the rate of carbon remineralization 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 equation 4 (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_{SRR} can be calculated as

$$k_{SRR} = \frac{2 * SRR}{C_{TOC}} . \quad (8)$$

We assumed sulfate reduction to be the dominant process at sediment depths where
25 SRR were maximum. For the SRR peaks we calculated the lowest k_{SRR} of 0.0013 yr^{-1} at the

deepest site A4 and the highest k_{SRR} of 0.0070 yr^{-1} at the shallowest site C1 (Tab. 3). Note that the observed difference can partly be explained by a general decrease of organic carbon reactivity with sediment depths as OM deeper in the sediment is already in an advanced state of degradation. Further, k_{SRR} calculated from peak rates deeper in the sediments is not
5 representative for the reactivity of initially deposited OM. However, the generally lower k_{SRR} in the Antofagasta region are in accordance with a reduced OM reactivity in the Antofagasta compared to the Concepción sediments, and the influence of water depth alteration is reflected in decreasing k_{SRR} with increasing water depth (Tab. 3). For sediments from the Bay of Concepción, Schubert et al. (2000) calculated k_{SRR} in the range $0.0008\text{-}0.0300 \text{ yr}^{-1}$ for
10 sulfate reduction peak rates following the same approach applied in our study. The higher values observed in the bay sediments are consistent with the shallower water depth.

Depth-averaged values, including k_{SRR} at all sediment depths, ranged from 0.0004 yr^{-1} at A3 to 0.0033 yr^{-1} at C1, and were generally lower in the Antofagasta than in the Concepción sediments (Tab. 3). We compared the bulk organic carbon reactivity as assessed
15 by k_{SRR} with the CI describing the freshness of sedimentary pigments (Fig. 9). The lowest k_{SRR} coincided with the highest CI (A3) and the highest k_{SRR} with low CI (C1), but we could not derive a functional relation of chlorin freshness (CI) and OM reactivity (k_{SRR}). It has been shown that sedimentary micro-organisms might thrive on a small highly reactive fraction that is not reflected in bulk OM parameters (Arnosti and Holmer, 2003). Therefore, a small
20 portion of reactive OM might fuel high SRR though most of the chlorins are already old and degraded (high CI). On the other hand, reactive fresh pigments might be protected from degradation by sediment bacteria (Keil et al., 1994), but manifest themselves in a low CI.

5.3.3 Linking k_{SRR} and k_{TOC}

The reaction rate coefficients k_{TOC} calculated from the depth profiles of TOC concentrations show a good correspondence to the reaction rate coefficients k_{SRR} that describe TOC remineralization coupled to sulfate reduction (Fig. 10). Although the two coefficients are calculated based on different approaches, the obtained values fall in the same range: 0.0004-0.0033 yr⁻¹ for k_{SRR} and 0.0005-0.0023 yr⁻¹ for k_{TOC} , respectively, and were highest at C1 and lowest at A3.

The overall good relation for 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} is considered to reflect the actual reactivity of the sedimentary organic carbon at the time of sampling. 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} . Other factors also influence the parameters used to calculate k_{TOC} and k_{SRR} . Bioturbation might attenuate the TOC decrease depicted in the depth profile and lead to an underestimation of the organic carbon reactivity obtained as k_{TOC} - a possible reason why k_{TOC} in the bioturbated Concepción sediments is lower than k_{SRR} . On the other hand, k_{SRR} might also underestimate the actual organic carbon reactivity, when other pathways of organic carbon oxidation account for part of the total TOC degradation - which is a likely explanation why k_{SRR} near Antofagasta is lower than k_{TOC} .

However, though it may in part be based on the combined effect of several compensating parameters, in general, a coupling of the two coefficients is consistent with the predominance of bacterial sulfate reduction for organic carbon remineralization in anoxic marine sediments (Jørgensen, 1982; Canfield, 1989).

6. CONCLUSIONS

We showed 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 in the northern region are mostly old and reworked. Bioturbation is intense off Concepción but lacking off Antofagasta, further, input of terrestrially derived clastic material is higher in the humid central region than off northern Chile. 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 older and less reactive off Antofagasta than off Concepción. The differences in sedimentary OM composition are consistent with a generally more reworked state of the Antofagasta sediments, but might also reflect the greater water depth of most sites sampled in the northern region. 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. Decreasing degradation rate constants k_{TOC} with increasing water depth suggest that water column degradation is a major control on the long-term reactivity of sedimentary OM. Finally, 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.

- 5 Chile) might display significant differences in OM content, composition, and turnover that are independent from water column productivity and vertical particle flux.

Acknowledgements. We thank the officers, crew, and shipboard scientific party of RV Sonne cruise SO-156 for their help and cooperation, particularly Dierk Hebbeln (University of Bremen) for logistical support. We are grateful to Gabriele Klockgether and Kirsten Imhoff (MPI Bremen) for help in the home laboratory. Furthermore, we thank Peter Berg (University of Virginia) for interpretation of ^{210}Pb data and Tomas Cedhagen (University of Aarhus) for identification of foraminifera. The comments and suggestions of three anonymous reviewers on an earlier version led to substantial improvements of this manuscript. This work was part of the project PUCK (Interrelationships between productivity and environmental conditions along the Chilean continental slope, grant 03G0156A) supported by the BMBF (Federal Ministry of Education and Research, Germany). Further support was given from the Max Planck Society, Germany, and the Danish Natural Science Research Council (grant 21-01-0475). Part of this manuscript was written during a stay of Jutta Niggemann at the University of Aarhus made possible by a scholarship of SOAS (School of Aquatic Sciences, Denmark).

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Table 1

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

sampling site ^a		latitude	longitude	water depth (m)	bottom water temperature ^b (°C)	bottom water O ₂ ^b (μmol 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. ^c	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

^aoriginal site names were renamed for this study: A (Antofagasta), C (Concepción), increasing numbers indicate increasing water depth (see also

Fig. 1)

^bdata from CTD-profiling (Hebbeln et al., 2001)

^cn.d. = not determined

Table 2

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

site	mixed zone (cm)	ω (cm yr ⁻¹)	$^{210}\text{Pb}_{\text{xs}}$ inventory (dpm cm ⁻²)	$^{210}\text{Pb}_{\text{xs}}$ flux (dpm cm ⁻² yr ⁻¹)
A2	none	0.15±0.02 (0.19-0.13)	50	1.5
A3	none	0.04±0.01 (0.06-0.04)	19	0.6
A4	none	0.11±0.02 (0.13-0.07)	40	1.2
		0.26±0.01 (0.28-0.25) ^a		
C1	8	0.10±0.01 (0.12-0.07)	71	2.2
C2	10	0.19±0.02 (0.23-0.17)	124	3.9
C3	5	0.15±0.03 (0.19-0.11)	111	3.5
C4	10	0.17±0.01 (0.19-0.16)	170	5.3

^ahigher rates were observed in the deeper part of the sediment (8-20 cm)

Table 3

Depth integrated areal sulfate reduction rate (0-15 cm), reaction rate constant k_{SRR} at depth of SRR peak (given in parentheses) and average k_{SRR} (all depths).

site	areal SRR ^a (mmol m ⁻² d ⁻¹)	k_{SRR} at peak depth (yr ⁻¹)	average k_{SRR} ^a (yr ⁻¹)
A1	0.60 ± 0.19	0.0035 (0.5 cm)	0.0009 ± 0.0013
A2	0.53 ± 0.14	0.0017 (4.5 cm)	0.0008 ± 0.0005
A3	0.12 ± 0.03	0.0022 (0.5 cm)	0.0004 ± 0.0003
A4	0.24 ± 0.07	0.0013 (13 cm)	0.0008 ± 0.0004
C1	1.18 ± 0.28	0.0070 (1.5 cm)	0.0033 ± 0.0042
C2	0.78 ± 0.36	0.0040 (2.5 cm)	0.0022 ± 0.0025 ^b
C4	0.82 ± 0.19	0.0047 (8 cm)	0.0030 ± 0.0016 ^b

^aall parallels included (1-cm and 5-cm samples)

^bdeep peaks (1-cm sampling) not included

Figure captions

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

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

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 lower boundary of mixed layer.

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

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

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

Fig. 7. Water depth dependence of sedimentary organic matter characteristics. (a) total chlorin concentrations, (b) C/N-ratios, (c) Chlorin Indices, and (d) reaction rate coefficients of TOC degradation (k_{TOC}). Data points represent surface sediments (0-1 cm), except k_{TOC} that describe down-core degradation. Depth-averaged Chlorin Indices are given in grey symbols (c).

Fig. 8. Calculation of reaction rate coefficients of TOC degradation (k_{TOC}). The natural logarithms ($\ln$) of the TOC concentrations (%dw) are plotted versus sediment age derived from ^{210}Pb dating. The slope of the linear regression gives k_{TOC} . Open circles mark data points that are not included in regression.

Fig. 9. Reaction rate coefficients k_{SRR} , derived from sulfate reduction rates and TOC concentrations, versus Chlorin Indices. Plotted are depth-averaged values (all depths).

Fig. 10. Comparison of the reaction rate coefficients derived from depth profiles of TOC (k_{TOC}) and measured sulfate reduction rates (k_{SRR}). The 1:1-line is plotted.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9

Fig. 10