



Organic matter composition and sulfate reduction rates in sediments off Chile

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Abstract

Various organic geochemical parameters and rates of sulfate reduction (SRR) were determined in four sediment cores off the coast of central Chile. To examine the effect of organic matter composition on the sulfate reduction rates, we estimated the marine and terrestrial contributions to the organic matter fraction using C/N ratios, carbon isotopic composition, protein and chlorin concentrations. Whereas three cores, one from the Bay of Concepción, one at the entrance of the Bay and one on the shelf appear to be similarly dominated by marine organic matter input, the organic fraction of another core from the shelf is strongly influenced by terrestrial organic matter. This is demonstrated by higher C/N ratios, lighter $^{13}\text{C}_{\text{org}}$ values, lower protein and lower chlorin concentrations. Additionally, the distribution of sulfate reduction activity with depth at this station differed considerably from the other stations. The marine influenced stations exhibited distinct near-surface peaks of sulfate reduction rates with quasi-exponentially decreasing rates at depth. Sulfate reduction rates at the station influenced by terrestrial organic material exhibited an attenuated near-surface peak and relatively constant rates with depth. Using sulfate reduction rates as a measure of organic carbon reactivity, we were unable to identify differences with respect to degradation kinetics between the terrestrially dominated and marine dominated shelf sediments. It was therefore proposed that the marine organic matter being degraded through the sulfate reduction process is diluted by non-reactive components, including terrestrially derived organic matter leading to the observed sulfate reduction rate distribution. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Since 1994, the continental shelf near Concepción, Chile (36°34'S, 73°03'W) has been the site of an intense study of the population ecology of *Thioploca*, a large sulfur bacterium that forms thick, yellowish mats on the sediment surface, and of the carbon, nitrogen and sulfur biogeochemistry of the sediments. In particular, four stations have been frequently visited (see Fig. 1) — Station 4 in the Bay of Concepcion (34 m water depth), Station 7 on the shelf near the Bay entrance (37 m water depth), and Stations 14 and 18 further out on the shelf

(at 57 and 87 m water depth, respectively). During the course of these investigations, it has become apparent that Station 14 is somewhat exceptional, in spite of its geographical closeness to the two flanking stations, 7 and 18. For instance, H. Schulz (pers. comm., 1999) has noted that the population distribution of the various *Thioploca* species differs strikingly from both Stations 7 and 18, with a preponderance of smaller sheath diameters. However, no clear reason could be thus found to explain the differences.

The distribution of bacterial sulfate reduction rates at Station 14 are also noteworthy. B. Strotmann (pers. comm., 1999) observed average depth-integrated (0–15 cm) SR rates of 22.4 ± 2.6 , 9.4 ± 0.8 , and 8.5 ± 0.9 mmol $\text{S m}^{-2} \text{d}^{-1}$ for the shelf stations 7, 14, and 18, respectively, obtained from monthly samplings over 14 months of 1996–97. Although the depth-integrated rates

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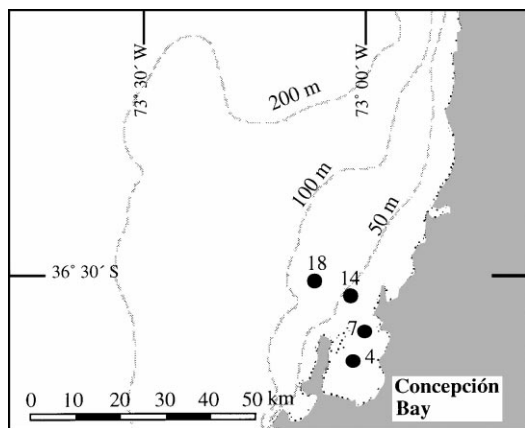


Fig. 1. Sampling sites in the Bay of Concepción and the Chilean continental shelf.

are similar between Stations 14 and 18, the distribution of sulfate reduction exhibits differing patterns. At Station 18, like Station 7, sulfate reduction rates typically show a surface or very-near surface peak, and they decrease quasi-exponentially with depth to some background rate at depth. Conversely, at Station 14, peak sulfate reduction rates are usually not as high as at Stations 7 and 18, the sulfate reduction rates do not exhibit nearly as striking a decrease with depth, and exhibit (relative to the surface peak) high background rates at depth.

These observations have led us to hypothesize that the “quality” of the organic matter deposited at the various sites are responsible for the differences in the pattern of sulfate reduction. Therefore, in this study, we compared sulfate reduction rate measurements with the organic carbon composition of sediment cores, obtained during a sampling trip in March 1998. As before, sulfate reduction rates were measured as a function of station and sediment depth. Furthermore, we investigated the organic carbon composition in respect to their terrestrial and marine source. Bulk characterization of the organic matter using C/N values and the carbon isotopic composition were performed, and total proteins and chlorins, the degradation products of chlorophyll were measured.

2. Site description

The continental shelf region off central Chile (Concepción) is characterized by intense upwelling during summer (December to April) that leads to one of the highest primary productivity rates of the world oceans ($9.6 \text{ gC m}^{-2} \text{ day}^{-1}$; Fossing et al., 1995). Even during non-upwelling times primary productivity rates are still high compared to other ocean areas. Due to this high rate of primary production, the water column is oxygen

depleted between 30 and 300 m. High rates of primary productivity in the water column lead to correspondingly high rates of organic carbon remineralization in the sediments of the Chilean continental shelf. Measurements during March 1995 showed that the rate of carbon remineralization, as measured by CO_2 production in sediment incubations, nearly matched the integrated rate of primary productivity within the overlying water column, and that bacterially driven sulfate reduction accounted for nearly 100% of this remineralization process (Thamdrup and Canfield, 1996).

The continental shelf off Chile is also distinguished by the massive occurrence of the giant sulphur bacterium *Thioploca* spp. in sediments accumulating below oxygen depleted bottom waters (Gallardo, 1977; Fossing et al., 1995; Schulz et al., 1996). *Thioploca* grows chemoautotrophically, ostensibly fixing CO_2 and oxidizing hydrogen sulfide with nitrate that has been concentrated from the overlying water and stored in its large central vacuole. *Thioploca* species occur as mobile filaments, living bundled together in polysaccharide sheaths. Biomasses of *Thioploca*, inclusive of both sheaths and filaments, range between 10 and 1000 g m^{-2} (Gallardo, 1977; Schulz et al., 1996), and thus can contribute significantly to the total organic content of the sediment.

The Bay of Concepción is a shallow embayment (max. depth 45 m) with one major and one minor opening to the continental shelf, which extends 40 km offshore. Two major flow systems influence the shelf and continental slope off the central Chilean coast. The northward flowing sub-Antarctic surface water down to 100 m and underneath, between 100 and 400 m, the southward flowing Peru–Chile undercurrent, which is characterized by high salinity, low temperature, high nutrient, and low O_2 concentrations (Shaffer et al., 1995). Enhanced upwelling of this water mass results in lower dissolved oxygen concentrations on the shelf in the investigated area at $36^\circ 34' \text{S}$ (Ahumada et al., 1983). Between a strong upwelling period in summer and a relaxed or non-upwelling period during winter two short transitional periods occur in fall and spring (Ahumada et al., 1983). Bottom waters in the Bay of Concepción during these month-long upwelling events in summer are characterized by low O_2 concentrations ($< 40 \mu\text{M}$), high salinity, high nitrate concentrations ($> 20 \mu\text{M}$) and occasional build-ups of sulfide accompanied by discoloration of the water column (Ahumada et al., 1983). During El Niño years, the upwelling of nutrient rich waters may weaken and cease due to atmospheric changes over the South Pacific. These El Niño events lead to lower primary productivity in the surface waters, and the oxygen depletion in the water column is not as pronounced as in normal years. Furthermore, lower concentrations of *Thioploca* spp. are found in the sediments (Schulz et al., in preparation) during these events.

3. Experimental

Duplicate multicorer cores from the shelf off Chile were collected in March 1998 in a period which was strongly influenced by an El Niño event. Sediment cores were taken at Station 4 (36°38'S, 73°37'W) in the Bay of Concepción, at Station 7 (36°37'S, 73°01'W) at the entrance of the bay and at Station 14 (36°32'S, 73°03'W) and Station 18 (36°31'S, 73°08'W) on the shelf (Fig. 1).

Total (TC) and organic carbon (OC) were determined by combustion/gas chromatography (Carlo Erba NA-1500 CNS analyzer) with a precision of $\pm 1.2\%$ on the bulk and carbonate-free subsamples, respectively.

For the determination of $\delta^{13}\text{C}$ values, decarbonated samples were combusted in an online Heraeus element analyser and the evolved CO_2 was passed to a Finnigan Delta isotope-ratio mass spectrometer in a continuous flow of helium. Results are reported in the δ notation, $\delta^{13}\text{C} = \{(^{13}\text{C}/^{12}\text{C})_{\text{sample}} / (^{13}\text{C}/^{12}\text{C})_{\text{standard}} - 1\}$ per mil, relative to VPDB and the measurement precision is better than $\pm 0.2\text{‰}$.

For the determination of lipids, freeze-dried and gently ground sub-samples (~ 2 g) were extracted by successive sonication and centrifugation in methanol, methanol:methylene chloride (1:1) and methylene chloride, respectively. The extracts were saponified (6% KOH), further extracted with hexane, and derivatized with BSTFA (Sigma) prior to injection onto a HP1 chromatographic column (50 m length, 0.32 mm I.D., 0.17 μm film thickness).

For the determination of chlorins, which include a whole suite of degradation products of chlorophyll, freeze dried sub-samples (~ 0.6 g) were extracted by threefold sonication and centrifugation in acetone. The samples were cooled with ice under low light conditions during extraction to prevent decomposition of the chlorins. Sediment extracts were measured fluorimetrically (Hitachi F-2000 fluorometer) immediately after extraction. Chlorophyll a (Sigma) which was acidified with a few drops of hydrochloric acid was used as a standard. The precision of the method was $\pm 10\%$.

Total proteins were extracted by hydrolysis of the ground sediment using 0.5 N sodium hydroxide (Bradford, 1976). The protein concentration of the hydrolysate was determined photometrically by the Coomassie Blue reaction using a Shimadzu UV-160A spectrophotometer.

Lignin-derived phenols were determined by gas chromatography–flame ionisation detection of the trimethylsilyl derivatives following CuO oxidation of bulk samples under alkaline conditions (Hedges and Ertel, 1982).

In contrast to the measurement of most other respiratory processes in marine sediments, a robust and relatively simple method for the determination of bacterial dissimilatory sulfate reduction exists in the form

of the whole-core $^{35}\text{SO}_4^{2-}$ incubation method (Jørgensen, 1978). This method also has the advantage that sediments can be rapidly labeled with tracer amounts of $^{35}\text{SO}_4^{2-}$, thus minimizing sample manipulation. Duplicate sub-cores of 26 mm were injected with radio-labeled sulfate (typically 200 kBq of carrier-free $^{35}\text{SO}_4^{2-}$) at 1 cm intervals and incubated for 6 h in the dark at temperatures reflecting in situ conditions. Bacterial sulfate reduction was terminated by slicing the cores at 1 cm intervals, placing the slices into 10 ml of 20% (weight/volume) zinc acetate solution, and freezing. Reduced ^{35}S attributed to the reduction of sulfate was determined using the one-step acidic Cr-II distillation method (Fossing and Jørgensen, 1989). Carrier ZnS and FeS_2 were added to the distillation procedure to insure $\geq 90\%$ recovery of the radiolabeled sulfide, which was trapped as Zn^{35}S in Zn acetate traps. Scintillation counting of $^{35}\text{SO}_4^{2-}$ and Zn^{35}S from the acid-Cr-II distillation was performed on a Canberra-Packard 2400 TR liquid scintillation counter using Packard Ultima Gold XR as the scintillation fluid. Sulfate was measured using nonsuppressed ion chromatography with a Waters 510 HPLC pump, Waters WISP 712 autosampler, Waters IC-Pak anion exchange column (50 \times 4.6 mm), and a Waters 430 conductivity detector (Ferdelman et al., 1997). Rates of sulfate reduction are calculated using the equation:

$$\text{SRR} = {}^{35}\text{S}_{\text{red}} / ({}^{35}\text{SO}_4^{2-} + {}^{35}\text{S}_{\text{red}}) \cdot [\text{SO}_4^{2-}] \cdot 1/t \cdot 1.06 \quad (1)$$

where SRR is the sulfate reduction rate ($\text{nmol SO}_4^{2-} \text{ cm}^{-3} \text{ d}^{-1}$), ${}^{35}\text{S}_{\text{red}}$ is the reduced sulfur radioactivity, ${}^{35}\text{SO}_4^{2-}$ is the radioactivity of sulfate at the end of the incubation, $[\text{SO}_4^{2-}]$ is the concentration of sulfate per volume sediment ($\text{nmol SO}_4^{2-} \text{ cm}^{-3}$), t is length of incubation in days, and 1.06 is an isotopic fractionation factor (Jørgensen and Fenchel, 1974). Precision of the method is about $\pm 7\%$.

4. Results

4.1. Water column conditions and sediment texture

During our sampling, measured oxygen concentrations of the bottom water varied between 18 to 40 μM . These values are significantly higher than values measured during a cruise in 1994 where O_2 concentrations were below 2 μM (R. Glud and J. Gundersen, pers. comm.) and are attributed to the weakening of the upwelling due to the El Niño conditions. Sediments of all stations consist of clayey silty to silty clayey mud with no general trend between the stations. Biomass of *Thioploca* spp. was low with 3 and 1 g m^{-2} for Stations 7 and 14, and with 5 g m^{-2} higher for Station 18; the downward extension was 6–10 cm at Station 7, 8–11 cm

at Station 14, and 8–9 cm at Station 18 (H. Schulz, pers. comm.). For Station 4 no detailed information about *Thioploca* spp. exists.

4.2. Organic carbon concentrations

At Station 4, organic carbon concentrations varied from 3.7% at the top to 1.9% at 31 cm (Fig. 2). After a sharp decrease in the uppermost 5 cm to 2%, values increased again to 3% at 15 cm and declined rapidly to the core end. At Station 7, OC values declined linearly from 3.3 to 1.7% from the core top to 24 cm (Fig. 2). At Station 14, OC values were relatively stable downcore and varied between 1.9 and 2.8% with a minimum at 7 cm (Fig. 2). At Station 18, organic carbon concentrations at the top 6 cm varied around 4% (Fig. 2). Values declined rapidly at 7 cm and varied downwards within the entire core with values around 2.5%. The drastic decrease in organic carbon concentration at Station 18 between 6 and 7 cm is related to the rapid decline of the occurrence of *Thioploca* spp. dominating the uppermost sediment (H. Schulz, pers. comm.).

In general, organic carbon values of all cores decreased most likely due to degradation of the organic material from the top to the bottom of the cores by 46% (Station 4), 27% (Station 7), 16% (Station 14), and 30% (Station 18), although the decrease at this station is due to the abrupt change in *Thioploca* biomass at 6 to 7 cm not observed at the other stations). From this simple comparison of bottom to top organic carbon values in the core the degradation of the organic material at Station 14 appears lower than at the other stations.

4.3. C/N values and carbon isotopic composition

As an initial characterization of the organic material, C/N values have been measured. In general, low C/N values of 5–7 are characteristic for marine organic matter (Redfield et al., 1963), values higher than 20 indicate a terrestrial source for the organic matter (Scheffer and Schachtschabel, 1984). During degradation of marine organic matter, protein rich material is lost and C/N values, therefore, increase up to 10 (Emery and Uchupy, 1984). On the other hand, it has been shown earlier that adsorption of ammonium on clay minerals (mainly illites) can significantly lower the C/N values (Müller, 1977), especially in illite rich sediments (Schubert, unpubl. results). We have treated samples of Station 18 with KOBR to eliminate the organic nitrogen of the sample (Silva and Bremner, 1966) and remeasured the remaining fraction with a CNS analyzer. It turned out that the fraction of bound ammonium is smaller than 6%, i.e. more than 94% of the nitrogen of the sample is organic nitrogen and the calculated OC/N_{total} values can be interpreted as OC/N_{org} values, with only a slight uncertainty.

Carbon isotope ratios measured on the organic carbon fraction of sediments are widely used to distinguish between marine and terrestrial organic material input. Relatively heavy carbon isotope values of -19 to -21% are characteristic for marine organic matter, whereas terrestrial organic material shows values of -25% (Sackett, 1964). Variations in the carbon isotope ratio of plankton and therefore sediments as has been observed on an glacial/interglacial time-scale or spatially due to changes in the concentration of CO_2 in surface waters (Rau et al., 1982; Jasper and Hayes, 1990; Rau et al., 1992) are assumed to be negligible in this study due to the short time frame [a sedimentation rate of 1 to 2.2 mm/year was estimated by M. Salamanca and P. Munõz (pers. comm.), which leads to a maximum age of 300 years for the cores] and the restricted locality of the cores.

In interpreting these data it has to be taken into account that using C/N values alone does not allow a convincing distinction between the cores. However, the C/N values taken together with supporting $\delta^{13}C$ values can justifiably be used to discriminate terrestrial versus marine dominance of the organic matter in the Chilean shelf sediments. A plot showing C/N ratios versus carbon isotope values (Fig. 3) demonstrates the difference in organic carbon composition between the stations.

At Station 4, C/N values vary from 4 to 10 ($\bar{x}=7$) indicating a mainly marine source for the organic material (Fig. 2). This is supported by the carbon isotopic composition which varies from -20.6 to -22.0% VPDB ($\bar{x}=-21.5\%$ VPDB; Fig. 2). C/N values of Station 7 are higher and have a narrower range from 7 to 10 ($\bar{x}=9$; Fig. 2) indicating a moderate increase in terrestrial organic matter. This is also demonstrated in the $\delta^{13}C$ values which are slightly lighter and range from -21.5 to -22.3% VPDB ($\bar{x}=-22.1\%$ VPDB). Station 14 shows the highest C/N values ranging from 7 to 11 ($\bar{x}=10$) indicating higher amounts of terrestrial organic material being mixed in, which is supported by light $\delta^{13}C_{org}$ values of -23.0 to -24.0% VPDB ($\bar{x}=-23.6\%$ VPDB, Fig. 2). At Station 18, C/N values average at 9 (8–10) demonstrating again decreasing amounts of terrestrial organic matter (Fig. 2). This is also supported by slightly heavier carbon isotope values averaging at -22.2% VPDB (-20.9 to -22.8% VPDB).

Additionally, at Station 18 a significant change from heavier to lighter carbon isotopes at 6 cm can be observed; a similar pattern as in the OC profile. We attribute the signal within the upper 6 cm to *Thioploca* biomass, which occurs from the sediment surface down to 6 to 7 cm and is correlated with the high organic carbon content in the same layers. McCaffrey et al. (1989) measured an isotopic composition for *Thioploca* spp. of -21.8% VPDB, values that match those that we measured within the first 6 cm of sediment at Station 18.

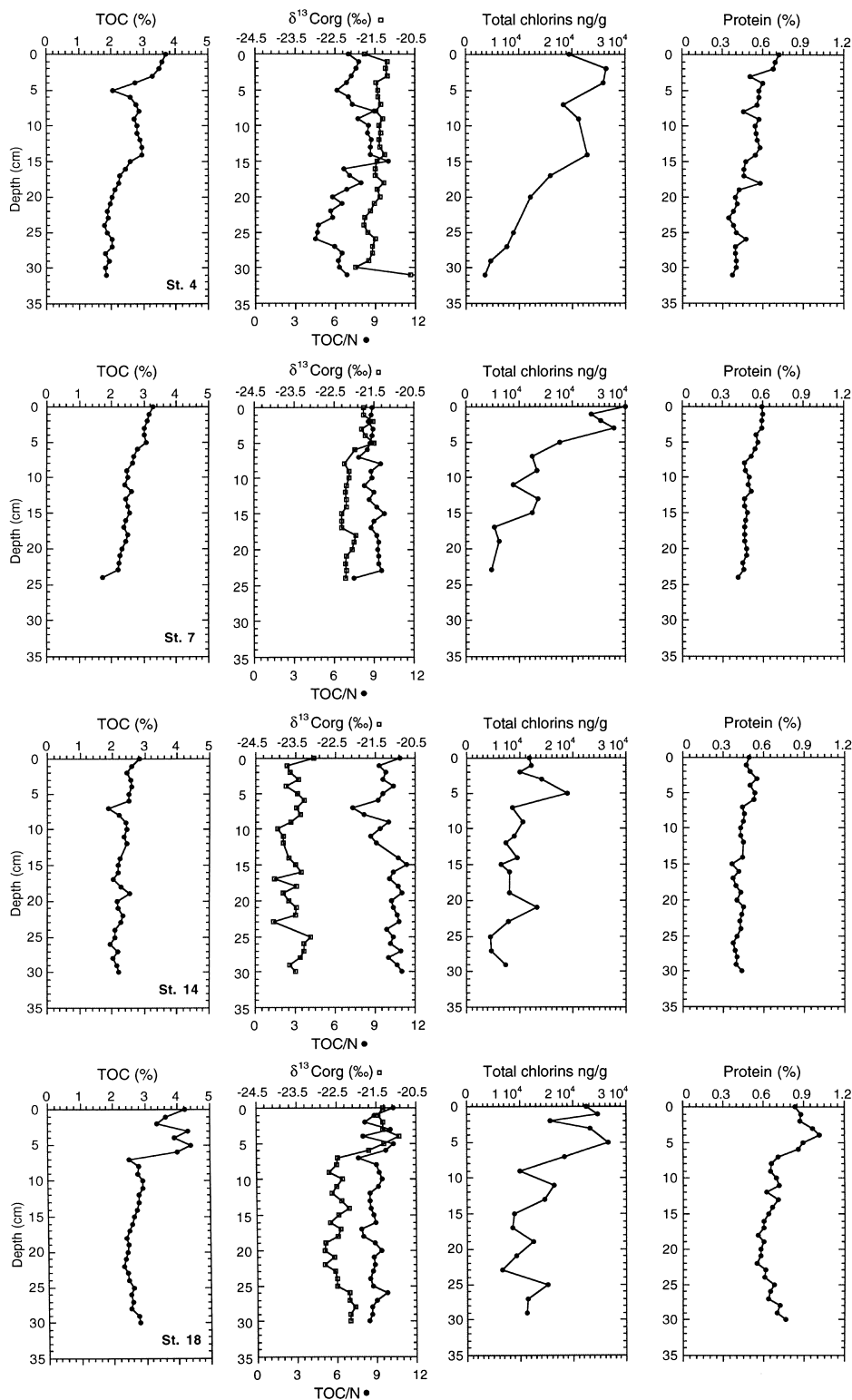


Fig. 2. Organic carbon concentrations (wt%), carbon isotopic composition (‰ vs. VPDB), C/N (wt) values, chlorin concentrations (ng/g dry wt), and total protein concentrations (wt%) of sediments from Stations 4, 7, 14, and 18.

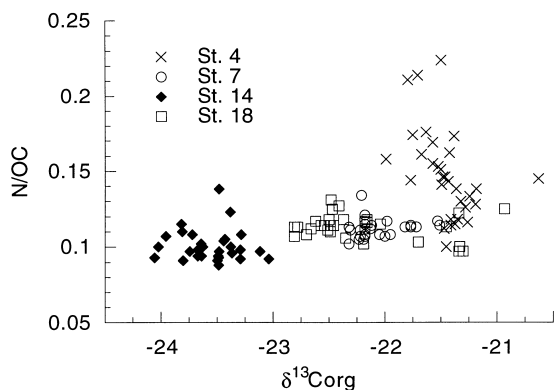


Fig. 3. Plot showing the nitrogen/organic carbon ratio (N/OC, wt.) versus the carbon isotopic composition (‰ vs. VPDB).

4.4. Total chlorins concentrations

Chlorins, the degradation products of chlorophyll have recently been used as productivity indicators in paleoceanographical reconstructions (Harris et al., 1996; Schubert et al., 1998). In this study dealing with the uppermost centimeters of the sediments, chlorins should be useful for indicating input and degradation of phytoplankton detritus in the surface sediments.

At Station 4, concentrations first increased from a value of 19.5 $\mu\text{g/g}$ sediment at the core top to 26.4 $\mu\text{g/g}$ at 2 cm and then decreased slowly to concentrations of 3.6 $\mu\text{g/g}$ (Fig. 2). At Station 7, highest chlorin concentrations were measured at 29.9 $\mu\text{g/g}$. Going down-core, values decreased with some fluctuations to 4.7 $\mu\text{g/g}$ at the lowermost sample (Fig. 2). At Station 14, chlorin values were lower and varied from 18.9 to 4.6 $\mu\text{g/g}$ (Fig. 2). Additionally, there was no clear trend of high values at the top and low values for the lowermost samples like in the other cores, instead relatively low concentrations fluctuated over the entire core. Therefore, lower concentrations of chlorins at this site also support the interpretation that Station 14 sediments consist of a greater fraction of terrestrial organic material as indicated by C/N values and carbon isotopic composition.

Concentrations at Station 18 were higher and fluctuated between 6.7 and 26.5 $\mu\text{g/g}$ (Fig. 2). A trend from higher concentrations at the top and lower concentrations at the bottom of the core could be observed but was not as clear as in the cores from Stations 4 and 7 which might also be related to the higher occurrence of the *Thioploca* spp. mat at Station 18.

To estimate the extent of chlorin degradation during early diagenesis we have, like with the organic carbon concentrations, calculated the chlorin content from the core top to the bottom of the cores. At Stations 4 and 7 more than 70% of the chlorins present at the core top are degraded by 31 and 23 cm, respectively. These values show the higher lability of chlorins compared to

the total organic material deposited at these locations. Due to the high variability of chlorins concentrations at Stations 14 and 18 we have not calculated any values.

4.5. Protein concentrations

To estimate labile components of living and detrital organic material total proteins were measured. Station 4 showed a value of 0.72% in the uppermost centimeter which linearly decreased to 0.37% in the lowermost part ($\bar{x}=0.49\%$; Fig. 2). The percentage of proteins were correlated to the organic carbon content ($r^2=0.74$). At Station 7, the decrease from the uppermost (0.59%) to the lowermost sample (0.42%) was weaker ($\bar{x}=0.50\%$; Fig. 2) and followed nicely the OC content ($r^2=0.86$).

Station 14 exhibited the lowest concentrations in proteins with highest values from 3 to 6 cm (~ 0.54) and relatively stable values (0.42%), i.e. no further decrease, down to the core bottom ($\bar{x}=0.44\%$; Fig. 2). At this station the weakest correlation between protein and organic carbon concentrations were calculated ($r^2=0.51$). If the organic matter would be build up by high amounts of protein we would expect a higher correlation between the parameters as observed at the other stations. The fact that only a low correlation occurs might indicate that protein material is not a main contributor to the sedimentary organic material at this station. Lower on average protein concentrations at Station 14 support the earlier interpretation that a higher terrestrial contribution is detected at this site, since protein content of land plants is much lower than of marine organisms (Parsons et al., 1984; Scheffer and Schachtschabel, 1984).

At Station 18, the highest protein values between 0.55 and 1.0% were measured ($\bar{x}=0.70\%$; Fig. 2). Similar to the organic carbon and chlorin profiles, higher values were determined at the top of the core with decreasing values from 5 cm down to the core bottom. This is also consistent with the *Thioploca* spp. occurrence in the uppermost sediments since these bacteria are rich in protein content (9–10 dry wt% protein, McCaffrey, 1990).

4.6. Lignin phenols

At Stations 4 and 7 the mean of Λ values (total weight of all eight vanillyl, syringyl, and cinnamyl phenols) are 0.44 and 0.60 mg/100 mg OC, respectively. Stations 14 and 18 show mean Λ values of 1.0 and 0.49 mg/100 mg OC, respectively.

4.7. Sulfate reduction rates

Sulfate reduction rates (SRR), as shown in Fig. 4, exhibited a general trend of decreasing from peak values within the Bay of Concepción (Station 4) to lower rates

on the continental shelf (Station 18), consistent with earlier studies of SRR (Thamdrup and Canfield, 1996; Ferdelman et al., 1997). Due to the El Niño conditions, at the time of sampling, 20–40 μM O_2 were present in the overlying waters. Thus, with the exception of Station 4, the peaks in SRR were not directly at the sediment–water interface but at 2 to 5 cm. At Station 4, SRR peaked at the surface at 185–250 $\text{nmol cm}^{-3} \text{ day}^{-1}$ and decreased quasi-exponentially with depth to rates of 40–82 $\text{nmol cm}^{-3} \text{ day}^{-1}$ at depths of 19 cm. Station 7 exhibited a sub-surface SRR peak of 86–100 $\text{nmol cm}^{-3} \text{ day}^{-1}$ at 2 cm and decreased to rates of 31–38 $\text{nmol cm}^{-3} \text{ day}^{-1}$ at 19 cm. Station 14 differed considerably

from Station 7 inshore and Station 18 on the shelf. SRR peaked at 4 to 5 cm depth at Station 14, but did not exhibit such a striking quasi-exponential drop-off as at the other stations. Although peak rates of sulfate reduction were low (47–69 $\text{nmol cm}^{-3} \text{ d}^{-1}$), SRR remained at a relatively higher rate at depth (23–48 $\text{nmol cm}^{-3} \text{ d}^{-1}$) to a depth of 19 cm.

The duplicate cores from Station 18 exhibited SRR shapes similar to that for Station 7, with a peak in the upper 2 to 5 cm and then a quasi-exponential decrease with depth. However, a 5-fold difference in SRR between the two cores were observed. In the first Station 18 duplicate, a peak of 62 $\text{nmol cm}^{-3} \text{ day}^{-1}$ at 2 to 3 cm

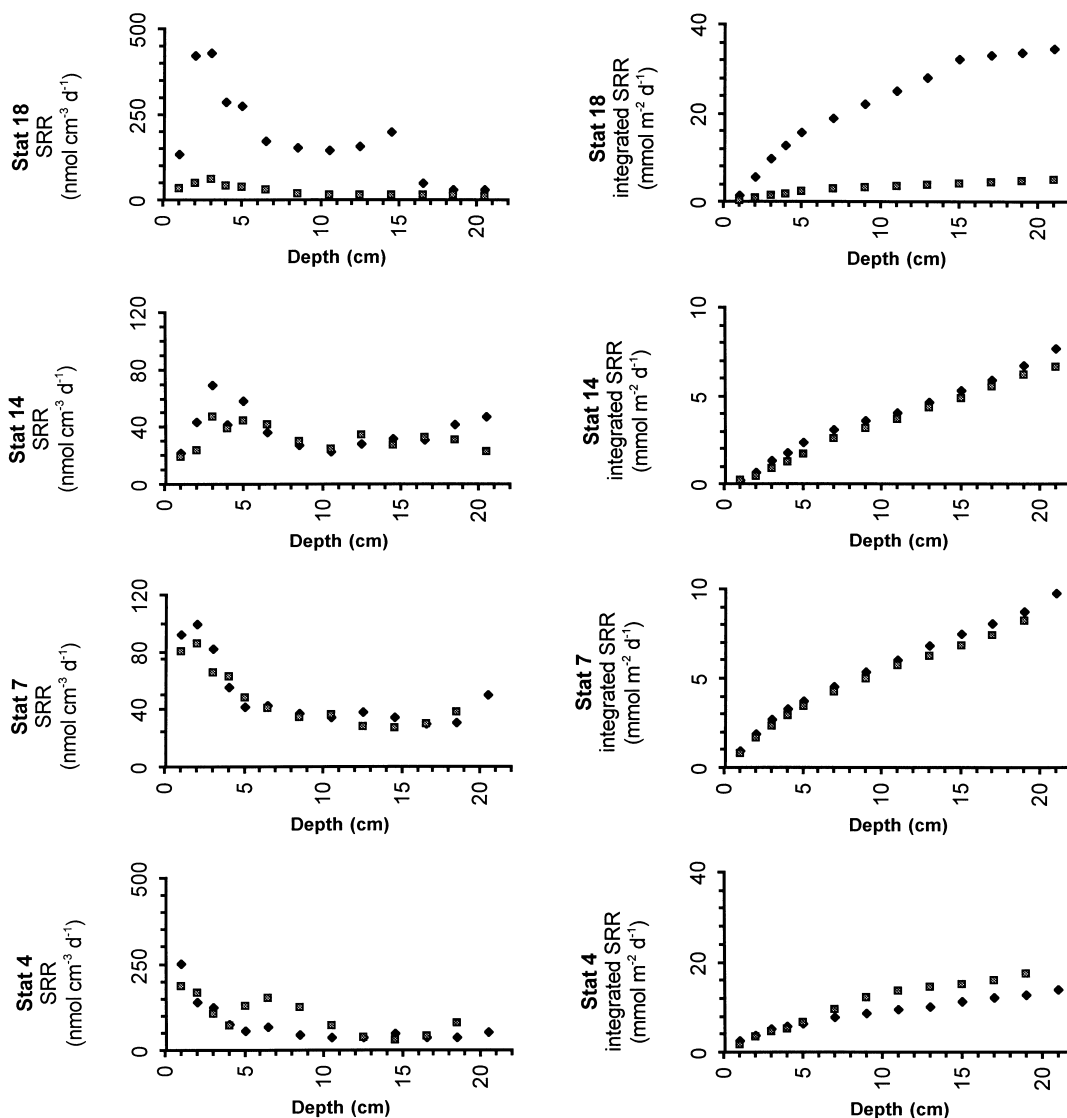


Fig. 4. Sulfate reduction rates ($\text{nmol cm}^{-3} \text{ day}^{-1}$) and depth integrated sulfate reduction rates ($\text{mmol m}^{-2} \text{ day}^{-1}$) measured at Stations 4, 7, 14, and 18. Note the different scales in both graphs of Stations 4 and 18, and 7 and 14. Symbols (squares and diamonds) represent measurements on two different cores of each station.

and then rapidly decreasing to rates of 12 to 14 nmol cm⁻³ day⁻¹ at depth. In the second core, SRR exhibited peak rates of 430 nmol cm⁻³ day⁻¹ at the 3–4 cm depth interval, and although rates quasi-exponentially decreased with depth, SRR in this core remained above 100 nmol cm⁻³ day⁻¹ until 17 cm depth. Below this depth SRR declined to background rates of <35 nmol cm⁻³ day⁻¹. At the time of sampling, obvious visual differences between the two duplicate Station 18 cores were observed. The core with the higher SRR appeared black and highly reducing. We may have sampled a sediment containing decaying *Thioploca* biomass, as the ambient O₂ concentrations in the water column were relatively high, which eventually leads to massive *Thioploca* mortality (H. Schulz, pers. comm.).

Differences between the shape of the profiles of SRR can be seen in profiles of SRR on a cumulative, areal basis (Fig. 4). In all of the cumulative SRR profiles, a break occurs at approximately 5–7 cm. However, at Station 14, this break is only very slight as compared to the other shelf stations, 7 and 18. As shown from the normalized profiles in Fig. 5, intra-station variability in the shape of the profiles is minimal, even in spite of the large differences in the actual rates at Station 18, but inter-station variations are clear. Station 14 exhibits a normalized distribution that falls close to the line describing a constant SRR distribution with depth.

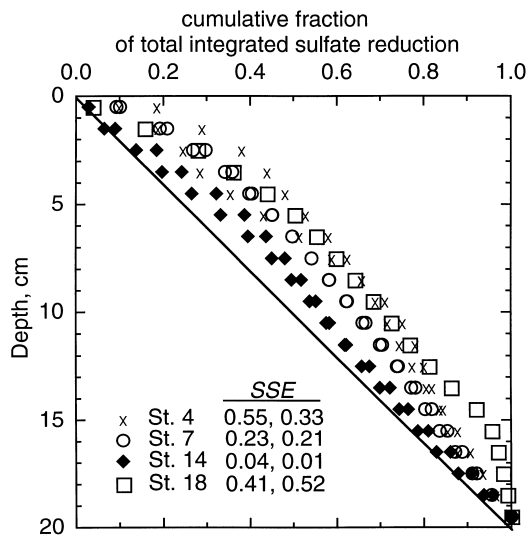


Fig. 5. Rates of the cumulative fraction of depth integrated sulfate reduction normalized to the sum-total integrated sulfate reduction for the investigated cores (from Station 18 only one core is shown). The solid line is a theoretical line for a fully constant sulfate reduction rate over depth. The more the data points differ from this line the greater is the variability in sulfate reduction. Also shown in the box are the values (SSE) describing the sum of the squares of the deviation (residuals) from the theoretical fit, where 0.0 describes a perfect fit to the theoretical line.

5. Discussion

Most interesting is the obvious difference between Station 14 and the other three sites, both with respect to the pattern of sulfate reduction as a function of depth and the biomarker indices for terrestrial versus marine organic matter input. Based upon the C/N ratios, $\delta^{13}\text{C}_{\text{org}}$ and the concentrations of chlorins, and proteins, Stations 4, 7, and 18 appear to be dominated by marine input, whereas Station 14 exhibits a clear terrestrial signal. In Fig. 3 the ratio of nitrogen to organic matter (N/OC) for each station is plotted against the carbon isotopic composition. Station 14 with a low N/OC ratio (terrestrial organic material has a lower nitrogen content than marine organic matter; Parsons et al., 1984; Scheffer and Schachtschabel, 1984) and relatively light $\delta^{13}\text{C}_{\text{org}}$ values plots in the lower left-hand side corner of the diagram illustrating clearly the difference in organic carbon composition compared to the other stations. The low and only slightly changing protein content at Station 14 is also consistent with the higher C/N values and a greater terrestrial origin for the organic material at this site.

Lignin phenols are one of the most reliable indicators for terrestrial organic matter input (Hedges and Parker, 1976). Whereas the mean for Λ (total weight of all eight vanillyl, syringyl, and cinnamyl phenols) of Stations 4, 7, and 18 lies at 0.44, 0.60, and 0.49 mg/100 mg OC, the mean yield for Station 14 is significantly higher (1.0 mg/100 mg OC) supporting again the higher terrestrial influence at this station. Although Station 14 is in the middle of the transect from enclosed bay to open shelf, it is therefore clear that the bulk of the organic carbon deposited there is significantly different in origin than that of the other stations.

The differing inputs of terrestrial versus marine organic matter are also manifested in the SRR profiles. Where marine inputs dominate, whether they be in the bay (Stations 4 and 7) or on the open shelf (Station 18), volumetric rates of sulfate reduction exhibit relatively high rates near the surface with rapidly, nearly exponentially decreasing rates with depth. As discussed above and shown in Figs. 4 and 5, the cumulative distribution of sulfate reduction rates at Station 14 is significantly different than at the other stations. However, although the volumetric rates at Station 14 are exceptional, in contrast, the depth integrated rates nevertheless show a gentle decrease going from the bay to the shelf and are independent of core top organic carbon contents. Thus, although the peak volumetric rates appear to be lower at the terrestrially influenced Station 14, the overall depth integrated rates are actually in line with those for the other stations.

What causes the observed difference between the distribution of SRR at the site influenced by terrestrial input (Station 14) and the other marine influenced

stations? One possibility is that the kinetics of degradation of terrestrial organic material is thought to be slower than that for protein-rich marine material, i.e., terrestrial organic material is degraded through sulfate reduction, albeit, more slowly. In the following discussion we explore this possibility and begin with the consideration of how sulfate reduction is linked with organic matter remineralization.

The anaerobic remineralization of organic carbon in marine sediments depends on bacterial consortia capable of both enzymatic hydrolysis of macromolecular organic matter by fermenting bacteria and oxidation to CO₂ of fermentation products, such as H₂ and short-chain organic compounds, and by bacteria utilizing various terminal electron acceptors, such as NO₃⁻, Mn(IV), Fe(III), SO₄²⁻, and CO₂. Current biogeochemical theory holds that the first step, the hydrolytic breakdown of macromolecular organic matter is the slower, rate limiting step in organic matter breakdown, and that the second step, the oxidation of low-molecular weight organic compounds and H₂, is not only fast, but operates near equilibrium (Postma and Jakobsen, 1996; Hoehler et al., 1998; Jakobsen and Postma, 1999).

Given that an abundant excess of sulfate is present in most marine sediments, rates of bacterial sulfate reduction, which reflect the overall reaction:



depend on the concentration and reactivity of the organic carbon being remineralized. The rate of organic matter remineralization, under conditions of excess oxidant (i.e., sulfate) can be simply written as:

$$dG/dt = -k[G] \quad (2)$$

(Berner, 1980; Westrich and Berner, 1984), where $[G]$ is the total organic matter concentration, dG/dt is the rate of organic carbon remineralization, which is equal to 2 times SRR based on the stoichiometry in Eq. (1), and k is the reaction rate coefficient for the bulk mixture of organic matter in the sediment.

Dissimilatory sulfate reduction has been demonstrated to be the overwhelmingly dominant terminal electron acceptor process in the remineralization of organic carbon in the Chilean shelf sediments (Thamdrup and Canfield, 1996). For every depth we can calculate a value for k from Eq. (2), simply by dividing the OC concentration (corrected for sediment density) by 2 times the sulfate reduction rate. As sulfate reduction should be the dominant process, values of k will be diagnostic for the “reactivity” of the organic matter in the Chilean shelf sediments.

Fig. 6 shows calculated values of k for all the stations. Two points are especially noteworthy. First, Station 4 sediments and the high rate core from Station 18, exhi-

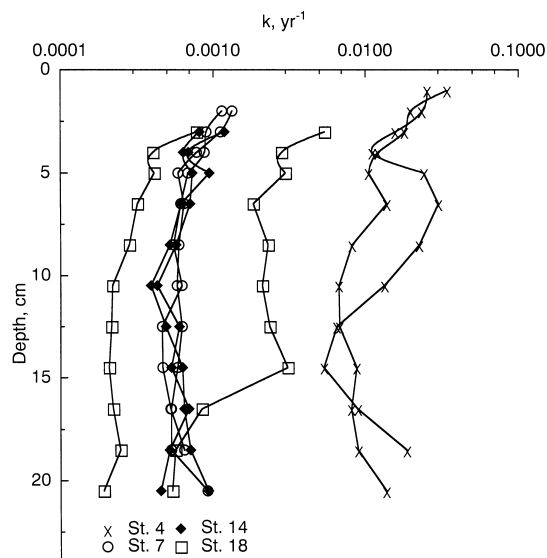


Fig. 6. Reaction rate coefficient, k , for all four investigated stations (replicates at each station) on a log scale. Data are plotted, where sulfate reaction rates are assumed to dominate the total organic carbon degradation processes, which we assume to start at the peak in sulfate reduction and continue with depth.

bit an order of magnitude greater turnover constants than the other stations. Decaying *Thioploca* biomass is probably driving the high rates of SRR at the Station 18. Only at depth do the values of k at Station 18, approach those of Stations 7 and 14.

Remarkably, in spite of the differences in both the SRR distribution, and in bulk organic matter provenance, the kinetics of organic matter degradation in sediments of Stations 7 and 14 are equivalent throughout most of the cores. The low SRR core from Station 18 exhibits even lower values at depth for the coefficient k . Thus, the overall rates, and more importantly, the *kinetics* of organic carbon degradation do not seem to be strictly related to the source of the organic matter as measured by our chosen parameters in these cores. This would suggest that the fraction being degraded is to a certain extent independent of the bulk of organic carbon that is being buried in the Chilean shelf sediments. Where the source and type of organic matter does appear to play a role is in the *distribution* of the sulfate reduction rate activity with depth.

It is possible that organic matter being degraded is simply diluted by non-reactive components at Station 14, including terrestrially derived organic matter. The less pronounced decrease of OC concentrations with depth at Station 14 would support the latter scenario. However, ²¹⁰Pb fluxes and derived sedimentation rates at Station 14 do not appear anomalously low or high when compared to other shelf sites (M. Salamanca and

P. Muñoz, pers. comm.), so this question remains unresolved. Nevertheless, this study demonstrates that a combination of bulk organic carbon parameters and biomarkers with a direct measure of organic carbon reactivity, promises to provide us with important insights into the relationship between the type of organic matter input and its subsequent rate of degradation under natural conditions.

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