



# Chlorin Index: A new parameter for organic matter freshness in sediments

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[1] Total chlorins, comprising degradation products of chlorophyll, have been used recently to reconstruct paleoproductivity from marine sediment cores. Here, we report on a new index, the Chlorin Index (CI), that proves to be a helpful tool for rapidly estimating organic matter freshness in marine sediments. The CI is a ratio between the fluorescence intensity of a sediment extracted with acetone and treated with hydrochloric acid and the original sediment extract. It represents the ratio of chlorophyll and its degradation products deposited in the sediments that could still be chemically transformed and those that are inert to chemical attack. The ratio is lower in sediments that include freshly deposited phytoplankton material and higher in older, more degraded sediments. We measured this new parameter on surface sediments, and sediments from several short and a long sediment core from different oceanic settings. CI values range from 0.2 for chlorophyll *a* to 0.36–0.56 for fresh material deposited on the shelf off Namibia to values around 0.67 in sediments off Chile and Peru to values up to 0.97 for sediments in a deep core from the northeastern slope of the Arabian Sea. We have compared the CI to rates of bacterial sulfate reduction, as a direct measure of organic matter reactivity and to other degradation indices based on amino acid composition. We conclude that the CI is a reliable and simple tool for the characterization of organic material freshness in sediments in respect to its degradation state.

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## 1. Introduction

[2] Most sediment biogeochemical processes are driven by the degradation and transformation of organic matter. Since the late 1980s it has been hypothesized that not only the quantity, but also the quality drives sediment biogeochemical cycles

[Hedges *et al.*, 1988; Cowie and Hedges, 1992a; Lee, 1994]. Quality and freshness, or degradability, are coupled, because the quality of organic material changes with progressive degradation, i.e., ageing, and these changes in quality are linked to an increasing resistance of the organic carbon pool toward microbially mediated degradation or min-

**Table 1.** Location and Water Depth of the Sediment Stations off Namibia, Chile, and Peru

Station	Latitude	Longitude	Water Depth, m
Namibia 1	22°52'S	14°29'E	25
Namibia 2	22°49'S	14°27'E	40
Namibia 20	23°26'S	14°14'E	104
Namibia 7	23°10'S	13°32'E	200
Namibia 8	23°11'S	13°24'E	300
Namibia 9	23°13'S	13°11'E	400
Namibia 12	25°31'S	13°02'E	2000
Chile 4	36°38'S	73°37'W	34
Chile 7	36°37'S	73°01'W	37
Chile 14	36°32'S	73°03'W	57
Chile 18	36°31'S	73°08'W	87
Peru 29	10°03'S	78°17'W	102
Peru 88	11°02'S	77°52'W	127
Peru 45	09°42'S	78°41'W	153
Peru 71	10°23'S	78°34'W	238
Peru 17	11°02'S	78°05'W	252
Peru 14	11°08'S	78°21'W	654
Peru 35	09°51'S	79°20'W	598
Peru 81	10°40'S	78°51'W	1278
Peru 33	09°45'S	79°44'W	1369

eralization. This knowledge has been adopted almost universally by the early diagenetic modeling community (multiG and continuum models) and serves there as a basic paradigm [Berner, 1980; Westrich and Berner, 1984; Boudreau, 1997, and references therein].

[3] A number of studies have been successful in deriving parameters describing the freshness of organic material [Cowie and Hedges, 1992a, 1992b, 1994; Wakeham et al., 1997; Dauwe and Middelburg, 1998; Dauwe et al., 1999]. However, most of these studies require rather advanced techniques including high performance/pressure liquid chromatography (HPLC) and/or gas chromatography (GC) and a requisite amount of expertise to obtain reliable results. The analytical work is quite labor intensive limiting the number of samples that can be processed. Moreover, these methods tend to exclude high-resolution down-core studies and hamper the ability to obtain data for extended research areas in a reasonable time. To overcome these limitations, we have developed a very simple method that might be used by every scientist who has some basic chemistry knowledge and a laboratory that is equipped with a fluorescence spectrophotometer.

[4] Chlorophylls, the major pigments required by all phytoplankton for photosynthesis, and their transformation products have been used not only as a measure of present-day algal productivity but also in reconstructing paleoproductivity from sed-

iment cores [Brassell et al., 1986; Summerhayes et al., 1995; Harris et al., 1996; Schubert et al., 1998]. Whereas chlorins comprise the immediate diagenetic products of chlorophylls, geoporphyrins result from long-term diagenesis [cf. Callot et al., 1990]. In our study we concentrate on chlorins as the more recent diagenetic products and exclude geoporphyrins, which do not appear in considerable amounts in sediments younger than the upper Pliocene [Keely et al., 1994].

[5] We introduce a new proxy, the Chlorin Index (CI), as an indicator for organic matter freshness. We compare the measured CI values with other amino acid based degradation indices, such as the Dauwe Index [Dauwe et al., 1999] and the percent of  $\beta$ -alanine of total hydrolysable amino acids [Cowie and Hedges, 1992b], in order to evaluate the CI as a proxy for the remineralization advancement of organic matter. Furthermore, the CI's of various sediments from coastal upwelling regions, where bacterial sulfate reduction is a dominant organic carbon degradation pathway, are compared to directly measured rates of sulfate reduction. Sulfate reduction rates depend on the concentration and reactivity of organic matter deposited under anaerobic conditions and therefore provide a sensitive means of directly assessing overall organic matter reactivity.

## 2. Site Descriptions

[6] Data from three different regimes have been included in this study. Sediments from short sediment cores from upwelling regions off Chile, Namibia, and Peru representing relatively fresh, organic rich marine sediments, and sediments from a long core taken in the Arabian Sea representing old, more refractory material. We have chosen sediments from the upwelling area off Namibia, Peru, and Chile, because they all show relatively similar organic carbon composition in respect to that they all comprise mainly marine organic material with a minimal terrestrial contribution.

### 2.1. Namibia

[7] Seven multicorer cores from the shelf off Namibia were collected in May 1999 (R/V *Poseidon*) from water depths between 25 and 2000 m spanning a wide range of sediments from the shelf to the deeper slope (Table 1). Sulfate reduction rates from these stations are reported by Brüchert et al. [2003]. The cores are located in the Benguela upwelling zone where upwelling intensity

and the associated phytoplankton productivity is high year-round. This high productivity leads to oxygen free waters on the shelf and oxygen depleted bottom waters further down the slope. Off Namibia no bottom water oxygen could be measured at shallow water Stations 1, 2, 20 and 7 [Brüchert *et al.*, 2003]. Instead, free hydrogen sulfide up to 40  $\mu\text{M}$  has been detected at the shallower stations.

## 2.2. Chile

[8] Four multicorer sediment cores were retrieved from the coast off Chile (Concepción) in about 34 to 87 m water depth during a cruise with R/V *Kay Kay* in 1998 (Table 1). Enhanced upwelling of the nutrient rich southward flowing Peru-Chile undercurrent water mass [Shaffer *et al.*, 1995] results in lower dissolved oxygen concentrations on the shelf in the investigated area at 36°34'S [Ahumada *et al.*, 1983]. Bottom waters in the Bay of Concepción during these month-long upwelling events in summer are characterized by low oxygen concentrations (<40  $\mu\text{M}$ ), high salinity, high nitrate concentrations (>20  $\mu\text{M}$ ) and occasional build-up of sulfide accompanied by discoloration of the water column [Ahumada *et al.*, 1983]. Details concerning the geochemistry and sulfate reduction rates of these sediments are given by Schubert *et al.* [2000].

## 2.3. Peru

[9] During R/V *Sonne* cruise 147 in 2000, surface sediments from 9 stations were sampled on the shelf and slope off Peru. The investigated area is characterized by year-round strong upwelling (except during El Niño events), oxygen-depleted to oxygen-free bottom waters and organic rich sediments [Neira *et al.*, 2001]. We analyzed sediments from different water depth (100–1370 m, Table 1). At the time of sampling the oxygen minimum zone in the water column ranged from 30 m to 600 m water depth; therefore 7 out of 9 sediment cores presented here underlay bottom waters with oxygen concentrations <15  $\mu\text{M}$ . Sulfate reduction rates are reported by Böning *et al.* [2004].

## 2.4. Arabian Sea

[10] For comparison, we also included a core from the Arabian Sea (SO 111KL, 23°05'N, 66°29'E) that has been recovered from the oxygen minimum zone during the Pakomin expedition (*Sonne* 90, Federal Institute for Geosciences and Mineral Resources, BGR, Hannover, Germany) in 1993 from 775 m water depth [von Rad *et al.*, 1995]. The core position is strongly influenced by mon-

soonal winds leading to high surface water phytoplankton productivity and, as a result, high organic carbon settling rates through the water column. Samples presented in this study are approximately up to 31,000 years old as revealed by <sup>14</sup>C dating and represent the oldest end-members of the CI.

## 3. Methods

[11] For the determination of chlorins, sediment samples that were stored at  $-20^{\circ}\text{C}$  were freeze dried, homogenized by grinding, and subsampled (10 to 20 mg). Subsamples were extracted by sonication (10 min.) three times in glass vials (kept at  $450^{\circ}\text{C}$  for 12 hours before use) with 5 mL acetone (HPLC grade). A ratio of 10 to 20 mg of sediment and 15 mL acetone (3 times 5 mL) gave good fluorescence intensities while avoiding concentrations that are too high for fluorescence measurements (concentration quenching). However, the ratio of solvent volume to sample might differ if other samples are used. During extraction and centrifugation, samples were cooled with ice and kept under low light conditions to prevent decomposition of chlorins. After each extraction, vials were centrifuged and the supernatant transferred to a new vial. The supernatant should be particle free since particles could potentially disturb the fluorescence measurements by absorbing and or scattering light. Sediment extracts were brought to equal volume and measured fluorometrically (Hitachi F-2000 fluorometer) immediately after extraction. Excitation wavelength was 428 nm and emission wavelength was 671 nm. Chlorophyll *a* (Sigma) was transformed to phaeophytin *a* by acidification with a few drops (approximately 100  $\mu\text{l}$ ) of 25% hydrochloric acid and used as a standard. The precision for the chlorin concentration method tested on ten samples with similar weight was better than 5%.

[12] Fluorescence intensity is typically directly proportional (linear) to concentration. There are, however, factors that affect this linear relationship called *quenching* [Guilbault, 1990]. Collisional quenching involves collisions with other molecules that result in the loss of excitation energy as heat instead of as emitted light. This process is always present to some extent in solution samples and leads to lower readings. Likewise, resonance energy transfer is an excited state interaction between two participating molecules over distances of 100 angstroms or more. In signal terms the result is either fluorescence at longer wavelength or no fluorescence at all depending on whether the

acceptor is itself fluorescent or nonfluorescent. Another, important effect is called “inner filter effect” which is a measurement artifact as opposed to a quenching process. It occurs when concentration is too high and light cannot pass through the sample to cause excitation; thus very high concentrations can have very low fluorescence. At intermediate concentrations, the surface portion of a sample nearest the light absorbs so much light that little is available for the rest of the sample; thus the readings will not be linear, though they will be within the range of a calibration curve. To avoid inner filter effects (and other artifacts), it is generally advisable for the sample absorbance measured at the excitation wavelength to not exceed 0.1. In all fluorescence measurements the person carrying out the measurements should be aware of these points, i.e., not to work with too high concentrated solutions and to perform tests on linearity and absorbance whenever starting with fluorescence measurements. Additionally, it is very important to treat standards, blanks, and samples in exactly the same manner, i.e., using the same solvent and measuring at the same temperature to produce reliable results. For the sediments in our study we have tested these points and the relation between sample weight and solvent volume stated above gave reliable and reproducible results.

[13] To calculate the Chlorin Index (CI), we acidified the original sample extract after the fluorescent measurement with a few drops of 25% hydrochloric acid (approximately 100  $\mu$ l) and remeasured the acidified extract. Due to the acidification, chemically labile pigments present in the sample are transformed and change their optical properties leading to a lower fluorescent yield. An extract of fresh phytoplankton will therefore change its fluorescent properties due to acidification much more dramatically than an extract of old sediments where pigments are already transformed during degradation and/or even diagenesis.

[14] The Chlorin Index is defined as the relation between the fluorescent intensities of acidified to nonacidified extract:

$$\text{Chlorin Index (CI)} = \frac{\text{Fl. intensity}_{\text{acidified extract}}}{\text{Fl. intensity}_{\text{original extract}}}$$

The range of the CI is from 0.2 for fresh chlorophyll *a* to 1 for samples with very refractory, i.e., chemically inert material. To further evaluate the changes occurring during the acidification step, we measured an original and an acidified extract of sample MC 88 (10–12 cm) from Peru with a CI of

0.6 on a HPLC system connected to a diode array detector. We screened for chlorophyll-like compounds with absorption maxima at 431 nm and 662 nm and for phaeophytin-like compounds at 410 nm and 665 nm, respectively. After acidification of the original extract, all chlorophyll-like peaks (beside two small remaining peaks) had been transformed to phaeophytin-like peaks. This explains why after acidification the fluorescent yield of the extract is much smaller and therefore sets the basis for the CI.

[15] The aforementioned excitation and emission wavelengths for the fluorescent measurements were used since first chlorin measurements by us have been historically performed on a Turner fluorometer 10-AU equipped with filters with these wavelengths. In contrast, *Harris and Maxwell* [1995] have used an excitation wavelength of 407 nm and an emission wavelength of 662 nm for measuring chlorins. At these wavelengths they found the highest signal response for phaeophytin *a*, pyropheophorbide *a*, and pyropheophytin *a*; all compounds are degradation products of chlorophyll. We have done measurements with both excitation and emission wavelengths and found that the emission at the wavelengths used by *Harris and Maxwell* [1995] is about 67% higher than what we get with the wavelengths used by us. In addition, we observed that the CI calculated from the wavelengths used by us is about 5% higher than the one calculated from the *Harris and Maxwell* [1995] wavelengths (in the sample from Peru that we have used for the statistics and the wavelengths investigation shown here it increased from 0.77 to 0.82). This is related to the different optical properties of the investigated degradation products at different wavelengths. In principle, either of the two excitation and emission wavelengths could be used. However, for internal consistency within data sets, one wavelength couple should be chosen and always reported.

[16] Carbon isotopic composition of the samples were determined on decarbonated subsamples via a Carlo Erba NA-1500 CNS analyzer linked to an isotope mass spectrometer (Delta Plus, Finnigan, Bremen or Isoprime, Micromass, Manchester) and expressed against the VPDB standard. Precision of the measurements were about  $\pm 0.3\%$ .

## 4. Results

[17] Since the main aim of this paper is the introduction of the CI as a new indicator for



**Table 2.** Geochemical Parameters for the Cores From Peru, Namibia, and Chile<sup>a</sup>

Station	SRR, mmol m <sup>-2</sup> d <sup>-1</sup>	OC, %	Chlorins, μg/g	CI	THAA, μg/gOC
Peru 45 <sup>b</sup>	3.0	14.1	254	0.74	17935
Peru 35 <sup>b</sup>	0.2	6.4	51	0.77	7981
Peru 33 <sup>b</sup>	0.4	5.7	22	0.83	13018
Peru 29	5.9	4.9	332	0.63	23464
Peru 71 <sup>b</sup>	0.5	14.3	138	0.75	18464
Peru 81 <sup>b</sup>	0.4	3.3	13	0.78	11467
Peru 88	10.9	7.8	408	0.71	20129
Peru 17	1.5	12.2	228	0.75	18748
Peru 14 <sup>b</sup>	0.2	6.1	31	0.81	10509
Namibia 1 <sup>c</sup>	62.7	5.4	7.2	0.39	34407
Namibia 2 <sup>c</sup>	20.3	5.1	19	0.53	27022
Namibia 20 <sup>c</sup>	52.2	4.7	8	0.36	32149
Namibia 7 <sup>c</sup>	3.1	10.5	12	0.84	
Namibia 8 <sup>c</sup>	1.5	12.1	8.7	0.90	5165
Namibia 9 <sup>c</sup>	0.4	2.3	5.5	0.92	23348
Namibia 12 <sup>c</sup>	0.7	9.5	6.2	0.85	
Chile 4 <sup>d</sup>	10.6	2.9	22	0.67	22655
Chile 7 <sup>d</sup>	6.6	2.8	19	0.70	20214
Chile 14 <sup>d</sup>	4.7	2.4	11	0.78	18042
Chile 18 <sup>d</sup>	3.5	3.3	18	0.68	19758

<sup>a</sup> Shown are the areal SRR (mmol m<sup>-2</sup> d<sup>-1</sup>) [Böning *et al.*, 2004; Brüchert *et al.*, 2003; Schubert *et al.*, 2000], organic carbon content (OC, %) [Schubert *et al.*, 2000], chlorin concentration (μg/g sediment), the Chlorin Index, and the amount of total hydrolysable amino acids (μg/g TOC).

<sup>b</sup> Böning *et al.* [2004].

<sup>c</sup> Brüchert *et al.* [2003].

<sup>d</sup> Schubert *et al.* [2000].

freshness of organic material in sediment cores, we did not include all the data that exist on the sediments [Schubert *et al.*, 2000; J. Niggemann *et al.*, unpublished results; C. J. Schubert *et al.*, unpublished results], but instead concentrate on the essential data to introduce the CI.

#### 4.1. Namibia

[18] Organic carbon concentrations of the sediments on the profile from 40 to 2000 m water depth vary from 1 to 14% with relatively small changes within the same core. There is no trend from shallower to deeper water depth in respect to organic carbon concentrations that might have been anticipated from a profile perpendicular to the coast, due to the extensive lateral transport on the shelf [Brüchert *et al.*, 2003]. Carbon isotopic composition is very stable for all the cores and varies only slightly from -18.9 to -19.7‰, indicating that the material has a marine origin. This is not surprising since the next river as a possible contributor of terrestrial organic matter is about 800 km away from the investigated area; additionally, the hinterland comprises the Namibian desert, and therefore no significant terrestrial material could be introduced by wind transport. Total chlorin concentrations for the cores vary from 5.5 to 19 μg/g dry weight sediment (mean values for

0–15 cm, the depth in which sulfate reduction is the main organic matter degrading process in these cores, Table 2). Areal sulfate reduction rates integrated over the uppermost 15 cm [Brüchert *et al.*, 2003] vary between 0.7 (Station 12) and 62.7 mmol m<sup>-2</sup> d<sup>-1</sup> (Station 1), the highest value of this study. The calculated Chlorin Indices range between 0.36 and 0.92.

#### 4.2. Chile

[19] Compared to the cores off Namibia covering shelf and slope sediments, sediment cores from Chile have been recovered in relatively shallow water depth (34–87 m). Organic carbon concentrations show very little variations between each other (1.7 to 4.2%). Concerning the composition of the organic carbon, it has been shown earlier [Schubert *et al.*, 2000] that cores from Station 4, 7, and 18 comprise basically marine derived autochthonous organic material (δ<sup>13</sup>C values around -21.0‰), whereas the core at Station 14 is more influenced by allochthonous terrestrial organic carbon (δ<sup>13</sup>C values around -23.5‰). Station 14 is therefore the only station in our data set from the upwelling zone that consists of a significant contribution of terrestrial organic material. Total chlorin concentrations in the cores containing more marine organic material decline from values around

**Table 3.** Various Parameters of Core 111KL From the Arabian Sea<sup>a</sup>

Core Depth, cm	Age, <sup>b</sup> kyr	OC, %	Structure <sup>c</sup>	Chlorin conc. μg/g	CI
40	7.6	3.67	1	8.2	0.83
61	8.59	2.56	1	2.6	0.78
100	10.38	0.55	2	1.7	0.89
122	11.4	0.54	2	1.0	0.89
150	12.68	0.71	2	1.4	0.88
200	14.98	1.58	1	5.5	0.90
220	15.7	n.d.	1	8.5	0.92
250	16.78	0.84	2	1.8	0.96
290	17.55	0.83	2	2.0	0.97
310	17.88	1.01	2	1.9	0.95
370	19.03	1.83	1	4.8	0.95
410	19.87	1.55	1	3.7	0.92
450	20.7	1.65	1	4.6	0.90
530	22.56	1.54	2	3.4	0.93
540	22.83	1.77	2	4.5	0.92
560	23.38	2.28	1	4.1	0.92
590	24.21	2.84	1	4.6	0.94
640	25.82	1.93	1	5.1	0.93
690	27.66	1.26	2	1.5	0.95
710	28.4	1.07	2	1.5	0.95
730	29.16	1.73	2	2.5	0.95
760	30.31	1.88	1	3.1	0.91
780	31.08	2.59	1	3.5	0.90

<sup>a</sup> Shown are sediment depth (cm), age of sediment as revealed by AMS <sup>14</sup>C dating, organic carbon content, the structure, where 1 means laminated and 2 means bioturbated, the chlorin concentrations as phaeophytin equivalent in μg/g sediment, and the CI.

<sup>b</sup> Schulz *et al.* [1998].

<sup>c</sup> von Rad *et al.* [1995].

30 μg/g (dry weight sediment) at the core top to values of 4 μg/g at the bottom of the cores. In contrast, chlorin concentrations are not as high at the top and relatively stable with 10 μg/g at Station 14. Averaged values for 0–15 cm sediment depth vary from 11 to 22 μg/g. Calculating the CI, we find that values are very similar and vary only slightly from 0.67 (Station 4) to 0.78 (Station 14). Nevertheless, the station effected by higher terrestrial and therefore by more robust organic material (Station 14) shows the highest CI value as would be expected from a degradation state indicator (Table 2). Areal sulfate reduction rates (integrated SRR down to 15 cm [Schubert *et al.*, 2000]) for the four cores vary between 3.5 (Station 18 on the shelf) and 10.6 mmol m<sup>-2</sup> d<sup>-1</sup> (Station 4 in the Bay).

#### 4.3. Peru

[20] The organic material in the investigated sediments is mainly of marine origin. The C/N-ratios range from 6.6 (shallow shelf stations) to 9.5 (deep sea stations) and δ<sup>13</sup>C values range from –19.7 to

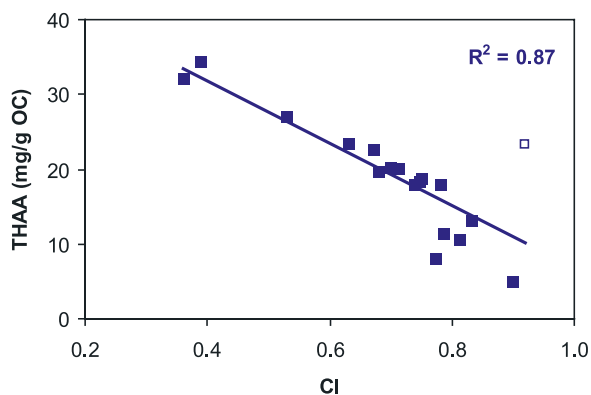
–20.7‰. Preliminary results of lipid analysis support these data and show little indication for terrestrial contribution (J. Niggemann, unpublished results). Organic carbon concentrations range from 3.3 to 14.3% with the highest values occurring in sediments from the center of the oxygen minimum zone. Total chlorin contents for the surface sediments (0–1 cm) are much higher than for sediments from Namibia and Chile ranging from 13 to 408 μg/g dry weight (note that only surface sediments were investigated from Peru). The Chlorin Index varies from 0.63 to 0.83 and indicates a diagenetic stage similar to the organic material in the sediments from Chile. The sulfate reduction rates are also comparable with the exception of the deep-sea sediments underlying oxygenated bottom waters where, obviously, sulfate reduction is not the dominant degradation process. Including these sediments, however, the total range of depth integrated sulfate reduction is 0.2 to 10.9 mmol m<sup>-2</sup> d<sup>-1</sup> (Table 2).

#### 4.4. Arabian Sea

[21] We have included results on older sediments in this report to validate this method also for more degraded organic material. A long core (SO111KL) from the Arabian Sea has been measured down to 780 cm, corresponding to an age of 31,000 years [Schulz *et al.*, 1998] (Table 3). Core 111KL is neatly separated into laminated and bioturbated sections and exhibits organic carbon values from 0.54 to 2.84% and carbon isotopic values around –20.5‰, indicating very little terrestrial organic material influence [Schubert *et al.*, 1997]. The alternating laminated and bioturbated core sections are suggested to be related to variations in the bottom water oxygen content during deposition [Schulz *et al.*, 1998]. Measured chlorin concentrations vary from 1 to 8 μg/g, values comparable to the lowest values measured off Chile and Namibia. The calculated CI values are between 0.78 and 0.97 and therefore represent the high end of the CI values presented in this work.

### 5. Discussion

[22] To establish the CI as a new tool for describing the diagenetic status of organic material, we compared it to other parameters that are already used as indicators for organic matter degradation state. We included a comparison with the degradation or Dauwe Index (DI) that is based on a Principal Component Analysis (PCA) of amino acid distributions in, at first, North Sea sediments [Dauwe



**Figure 1.** Correlation between the total hydrolysable amino acids normalized to TOC and the CI for sediments off Chile, Peru, and Namibia (closed squares). The data point from Station 9 off Namibia (open square) has been omitted from the regression for reasons explained in the text.

and Middelburg, 1998] and, later on, on a whole suite of organic materials ranging from phytoplankton and bacteria to a deep sea turbidite [Dauwe *et al.*, 1999]. Additionally, we also investigated the relation of the CI to THAA (total hydrolysable amino acids) and to  $\beta$ -alanine as a nonprotein amino acid [Lee and Cronin, 1984].

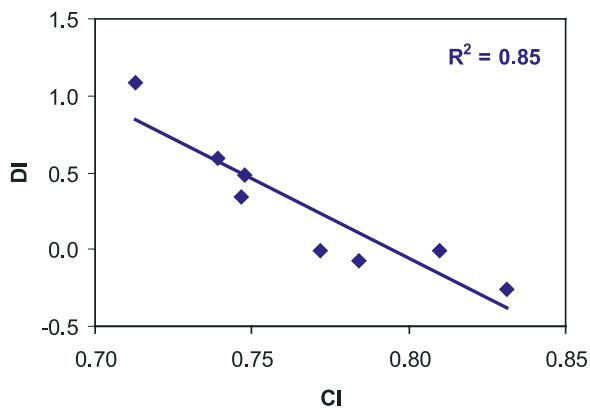
### 5.1. Total Hydrolysable Amino Acids and the Chlorin Index

[23] First, the CI is compared to the amount of hydrolysable amino acids, because amino acids are known to represent a relatively labile fraction of the organic carbon formed and deposited in the marine realm [Lee and Crown, 1982]. It has been shown earlier that the sum of amino acids and/or single amino acids are prone to preferential degradation during their settling through the water column and in sediments [Lee and Cronin, 1984; Lee *et al.*, 2000; Cowie and Hedges, 1993]. The fraction of the total organic carbon made up by THAA thus decreases with increasing degradation state. In Figure 1 the amount of total hydrolysable amino acids normalized to organic carbon and integrated over 15 cm sediment depth from sediments off Chile, Namibia, and Peru has been plotted against the CI. If we neglect Station 9 from Namibia (for the reason explained below), both parameters show a very high correlation ( $r^2 = 0.87$ ) between each other and strongly support the CI as an index for organic matter freshness. (We have excluded the samples from Station 9 off Namibia, because this station is at a location where high bottom water currents occur and redistribution of

the sediments can not be excluded. Whereas all parameters (low TOC, low SRR, low chlorin concentration, low protein content) are consistent with one another and indicate that highly degraded material is deposited at this site, the THAA content (normalized to TOC) is high.) Higher THAA concentrations (normalized to TOC) in a sample should indicate a lessened state of degradation. Although comprising differing classes of compounds, the correlation of low CI values with high THAA concentrations suggests that the CI, or the relative amount of nonacid hydrolysable chlorins, responds to the overall degradation of organic matter in a manner likewise to THAAs and thus is also indicative of organic matter freshness.

### 5.2. Degradation Index, $\beta$ -Alanine, and the Chlorin Index

[24] The DI (Dauwe or degradation index) has been developed on sediments from the North Sea coast [Dauwe and Middelburg, 1998]. The idea behind this index was to provide a tool to describe the state of degradation of sedimentary organic material based on compounds (amino acids) that are relatively widely distributed in the environment. The calculated DI for a whole range of environmental samples varies between 1.48 for fresh phytoplankton to  $-2.17$  for an oxidized turbidite [Dauwe *et al.*, 1999]. We have measured amino acid concentrations and calculated the DI for the surface sediments off Peru using the factor coefficients given by Dauwe *et al.* [1999]. DI values for the surface sediments vary from 0.60 to  $-0.26$  for a sample (45) from 153 m on the shelf composed of relatively fresh material and a sample (33) from 1369 m composed of degraded material, respectively. These values lie in the mid range of the possible DI values shown above and could have been expected for the range of sediments investigated in this study. We compared the DI values based on the Dauwe and Middelburg calculation with the CI (Figure 2). The correlation shows a very high correlation coefficient for the samples chosen of  $r^2 = 0.85$  (we have omitted station 29 since the very low CI falls out of the range of the other samples; this might be related to the *Thioploca* bacteria mat overgrowing the station). This finding strongly supports the CI as a degradation index. Although it is based on a completely different organic compound class, i.e., pigments instead of protein material, it shows the same behavior as the DI and CI values increase with higher degradation state of the organic material. It is also interesting that even though both groups of compounds (amino acids and pigments) only comprise a



**Figure 2.** Correlation between the CI and the Dauwe or degradation index (DI) based on the amino acid distribution. The very high correlation supports the CI as a degradation index.

part of the organic material deposited, both parameters appear to describe the overall state of degradation though there is a whole suite of other organic compounds included in the deposited OM.

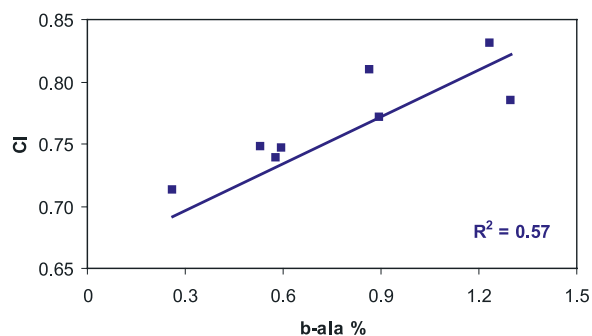
[25] *Lee and Cronin* [1984] and *Cowie and Hedges* [1992a, 1992b, 1993] have used another parameter linked to amino acids to describe the degradation state of OM in coastal sediments. It is based on the two nonprotein amino acids  $\beta$ -alanine and  $\gamma$ -aminobutyric acid. These amino acids are degradation products of protein amino acids and therefore accumulate in the sediments with progressive degradation. *Cowie and Hedges* [1992b] relate the sum of the two amino acids to the total amount of hydrolysable amino acids and obtained a fraction of the sum from 0% for fresh organisms to 36% for an oxidized pelagic turbidite. As in our samples almost no  $\gamma$ -aminobutyric acid was present, we have used only the percentage of  $\beta$ -alanine of the total hydrolysable amino acids from the surface sediments off Peru and compared it to the CI. In our data set the percentage of  $\beta$ -alanine varies from 0.3 to 1.3% for a shallow (88) to a deep site (81). The correlation between the CI and the percentage of  $\beta$ -alanine (Figure 3) is weaker ( $r^2 = 0.57$ ) than it is between the Chlorin Index and the degradation index by *Dauwe et al.* [1999]; however, the correlation is still high for natural samples especially when considering the fact that both indices are based on chemically very different compounds.

### 5.3. Comparison of Sulfate Reduction Rates and CI

[26] The rate of mineralization of complex biopolymers to  $\text{CO}_2$  within a given sediment horizon

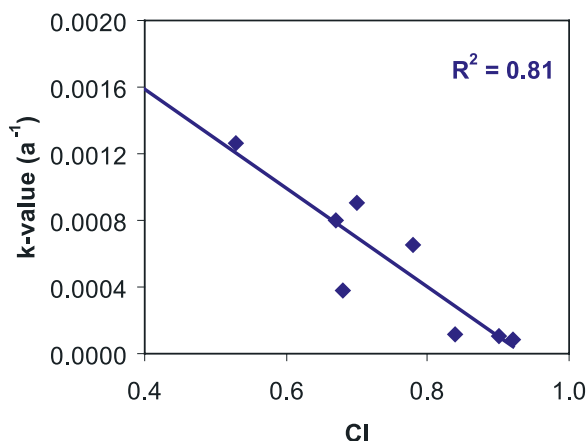
depends both on the rate of organic carbon supply to the horizon as well as the overall reactivity of the organic matter. Here we define reactivity as the overall propensity of an entire pool of sedimentary organic matter toward mineralization to  $\text{CO}_2$ . “Reactivity”, so defined, reflects the combined action of organic carbon composition, packaging, and the mode of microbial degradation. Molecular composition is not the only variable determining the reactivity of the organic matter pool. For instance, aerobic respiration pathways have been generally shown to be more efficient and complete in degrading organic biopolymers than anaerobic pathways [*Hartnett and Devol*, 2003]. Furthermore, the manner of particle association of organic matter may strongly influence the availability of organic compounds toward microbial attack [*Keil et al.*, 1994].

[27] For many of the sites investigated here, there exist direct measurements of bacterial sulfate reduction under near in situ conditions that provide direct information on the rates of organic carbon mineralization under anaerobic conditions. The anaerobic mineralization 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  $\text{CO}_2$  of fermentation products, such as short-chain organic compounds, and by bacteria utilizing various terminal electron acceptors, such as  $\text{NO}_3^-$ ,  $\text{Mn(IV)}$ ,  $\text{Fe(III)}$ , and  $\text{SO}_4^{2-}$ . 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  $\text{H}_2$ , is not only fast, but operates near equilibrium [*Postma and Jakobsen*, 1996; *Hoehler et al.*, 1998; *Jakobsen and Postma*,



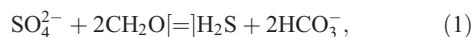
**Figure 3.** Correlation showing the relation between the nonprotein amino acid  $\beta$ -alanine and the CI in surface sediments off Peru.





**Figure 4.** Correlation showing the relation between the  $k$  value ( $\text{a}^{-1}$ ) and the CI in sediments off Namibia and Chile. This relation links the Chlorin Index to the reactivity of the buried sedimentary organic carbon.

1999]. Given that an abundant excess of sulfate is present in most marine sediments, rates of bacterial sulfate reduction, which are reflected in the overall reaction



depend on the concentration and reactivity of the organic carbon being mineralized. Therefore the rate of organic matter mineralization, under conditions of excess oxidant (i.e., sulfate), can be construed as a pseudo-first-order reaction [Berner, 1980; Westrich and Berner, 1984]:

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

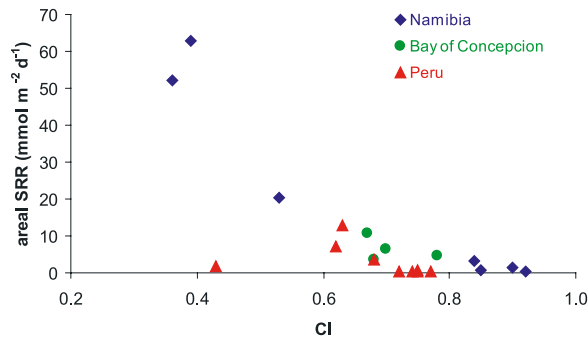
where  $[G]$  is the total organic matter concentration,  $dG/dt$  is the rate of organic carbon remineralization, which is equal to 2 times SRR based on the stoichiometry in equation (1), and  $k$  is the reaction rate coefficient constant for the bulk mixture of organic matter at a given depth (age) in the sediment. The coefficient  $k$  for any given sample point (i.e., sample in space and time) represents some point along a continuum of a mixture of individual kinetic constants of individual and discrete classes of compounds (see, for instance, discussion by Boudreau [1997]). Therefore, assuming a steady state delivery of organic carbon to some sediment horizon, the rate of organic carbon mineralization, when normalized to the organic carbon concentration, provides information on the reactivity of the organic carbon pool.

[28] Theoretically, we could derive  $k$  for various aerobic and anaerobic processes, if any given process could be shown to be the dominant terminal electron acceptor process. We have chosen to use available volumetric sulfate reduction rates obtained from whole-core incubations, because (1) an extensive data set for a wide range of sites was available and (2) dissimilatory sulfate reduction has been demonstrated to be the overwhelmingly dominant terminal electron acceptor process in the mineralization of organic carbon in the Chilean and Namibian shelf sediments [Thamdrup and Canfield, 1996; Brüchert et al., 2003]. For every depth we can calculate a value for  $k$  from equation (2), simply by dividing 2 times the sulfate reduction rate (i.e.,  $dG/dt$  or  $\text{mole SO}_4^{2-} \text{cm}^{-3} \text{a}^{-1}$ ) by the TOC concentration ( $\text{mole TOC cm}^{-3}$ ). As sulfate reduction should be the dominating process, values of  $k$  should be diagnostic for the “reactivity” of the organic matter in the Chilean and Namibian shelf sediments under anaerobic conditions.

[29] Comparison of the  $k$  and CI values allows us to compare a direct measurement of organic matter reactivity under in situ, anaerobic conditions with a parameter for organic matter freshness. We compared  $k$  and CI values both averaged over the upper part of the sediment cores from Namibia and Chile where sulfate reduction is prominent. Average values of  $k$  vary from  $0.00008 \text{ a}^{-1}$  to  $0.0012 \text{ a}^{-1}$ . A correlation between the  $k$  values and the CI gave an  $r^2$  of 0.81, which is very high for the mélange of sediments we have chosen (Figure 4). This high correlation suggests that the CI roughly describes the state of organic matter degradation, i.e., the more degraded the organic matter in the sediments, the lower the reactivity of the sediments.

[30] We have also plotted the areal sulfate reduction rates from stations from the shelf and upper slope off Namibia, Peru, and Chile versus the Chlorin Index (Figure 5). In this case rate of organic carbon decomposition, mainly as areal sulfate reduction, reflects both the supply and the reactivity of the organic matter arriving at the seafloor. We observe a good correlation between the CI and carbon decomposition rates both independently for each oceanographic region as well as for an overall trend of decreasing areal sulfate reduction rates with increasing CI values (extent of degradation).

[31] Earlier studies off Chile showed a strong correlation between the chlorin concentrations and the sulfate reduction rate as a measure of



**Figure 5.** Areal sulfate reduction rates as a measure of reactivity of sedimentary organic material plotted versus the CI (for explanation, see text).

organic carbon reactivity [Schubert *et al.*, 2000]. Accordingly, a correlation between the sulfate reduction rate and the Chlorin Index has been performed to explore whether a relation exists between these two parameters in sediments off Chile. The areal sulfate reduction rate and CI data from Chile co-vary ( $r^2 = 0.89$ ). Furthermore, it appears that Station 14, although strongly influenced by terrestrial organic matter, does not deviate from the trend. Thus it seems that sediments not entirely consisting of marine derived organic material can also be assessed with this new tool.

[32] In Namibia, whereas the concentration of organic carbon in the sediments shows almost no correlation ( $r^2 = 0.19$ ) to the areal sulfate reduction rates, a strong correlation between the CI ( $r^2 = 0.90$ ) and areal sulfate reduction rate is observed. This suggests that areal sulfate reduction rates in the shelf and upper slope sediments are not driven by the amount of organic material being deposited at a particular site (obviously here it could include diagenetically degraded “old” organic carbon from lateral transport), but are strongly related to the freshness or diagenetic stage of the organic material (CI), i.e., its reactivity or its availability to the microorganisms, here mainly the sulfate reducing bacteria. Hence the lowest value of 0.36 at Station 20 indicates that the organic material deposited could be very easily destroyed by our chemical treatment; hence it is relatively fresh and very little altered due to diagenesis. On the other hand, the organic material at Station 9 with the highest value of 0.92 demonstrates that the organic material deposited here has already been heavily altered and is only slightly affected by our applied chemical treatment.

[33] The Peru data also fit very well in the correlation of areal sulfate reduction rates and

CI (Figure 5). We find smaller CI for sediments with high areal SRR and higher CI for sediments with low SRR. To further evaluate the relation between the CI and the water depth, we cross plotted these parameters. A correlation of  $r^2 = 0.63$  between water depth and CI off Peru and even higher off Namibia for stations down to 400 m ( $r^2 = 0.78$ ) is found. It is well known that chlorophyll and other organic material that have been produced in the surface waters are heavily degraded during their settling through the water column [Yentsch, 1965; Wakeham *et al.*, 1997]. The correlation between the water depth and degradation stage of the organic matter as expressed by the CI therefore is consistent with this model and indicates that the “freshness” of organic material is principally determined by the extent of degradation during transit in the water column.

#### 5.4. Application to Older Sediments: Arabian Sea

[34] We also examine a deeper Arabian Sea core. Here, the sediments are much older than at the other sites at which sediments have ages of only hundreds to maybe a few thousand years based on  $^{210}\text{Pb}$  data [Muñoz *et al.*, 2004; T. Ferdelman, unpublished data]. Although a clear linear down-core trend with lower CI values at the core top and higher CI values at the core bottom is not observed, lowest CI values of 0.78 to 0.83 are observed in the upper 70 cm and suggest the organic material related to pigments to be fresher than further down-core where CI values up to 0.97 prevail. Chlorin concentrations are correlated to laminated (high concentrations) and bioturbated (low concentrations) core sections ( $r^2$  of 0.47) and to the organic carbon content ( $r^2$  of 0.61), i.e., 50 and 60% of the variation in chlorin concentration can be explained by the different sediment structure and organic carbon content, respectively.

[35] In contrast, variations in the CI are neither correlated to laminated and bioturbated sections ( $r^2$  of 0.13) nor to the organic carbon content ( $r^2$  of 0.18). Most importantly, the degradation state as represented by CI, is not influenced by the organic carbon content. This implies that although varying amounts of chlorins are deposited in the sediments due to productivity and or preservation changes over time, the freshness or degradation stage of organic matter (expressed by the CI) below a certain sediment depth (here >70 cm) is very similar and stays at high values.

[36] It could be shown earlier in the North Atlantic [Harris *et al.*, 1996] and at a site near to our core

(core SO94KL [Schubert *et al.*, 1998]) that chlorin concentrations work very well as a productivity indicator over longer time spans, i.e., variations in productivity are very well reflected in the concentrations of chlorins in the sediment. Together with the CI it should now be possible not only to reconstruct productivity changes but also rapidly reveal changes in the degree of degradation of the material preserved. First results in a study where the CI has been applied to sediments from Lake Zug, Switzerland, look promising [Meckler *et al.*, 2004]. However, further research should be carried out to further evaluate the utility of this parameter especially in other regions and regimes of the world oceans.

## 6. Conclusions

[37] We introduce the Chlorin Index as a new parameter for evaluating the degradation stage of deposited organic material. Using the CI, sediments can be assessed for whether they are already highly degraded and therefore pigments could not or only slightly be degraded further by the applied chemical treatment with hydrochloric acid, or if they are in a degradation stage still containing high amounts of labile pigments that chemically could be easily degraded. High correlation with an already well established degradation index, the Dauwe degradation index, strongly supports the applicability of the CI. Additionally, CI values vary in a consistent manner with rates of anaerobic organic carbon decomposition, as estimated from rates of bacterial sulfate reduction, and therefore with the overall reactivity of the total sedimentary organic matter.

[38] For comprehensive examination of sediments it is recommended to use the Chlorin Index in conjunction with a series of proxies; however, for a rapid method to assess the degradation state of suspended or sedimentary material, the Chlorin Index should prove to be an inexpensive and easy-to-apply method. This technique gives paleo-oceanographers and biogeochemists an easy-to-apply tool for assessing the freshness of organic matter that might be useful when estimating paleo-productivities from sedimentary organic carbon data or estimating bacterial carbon turnover.

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