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Results of Whole-Rock Organic Geochemical Analyses of the CRP-3 Drillcore, Victoria Land Basin, Antarctica

R.M. KETTLER

Department of Geosciences, University of Nebraska-Lincoln, Lincoln, NE 68588-0340 - USA (rkettler1@unl.edu)

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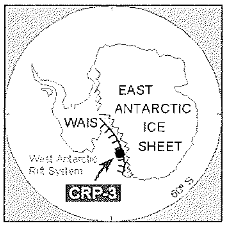
Abstract - Sediments and rocks recovered in CRP-3 coring operations contain minute amounts of organic matter (average 0.3% TOC). TOC contents and C:N ratios are zoned systematically: those rocks encountered at depths greater than 330 meters below sea floor (mbsf) contain less organic matter and have higher TOC:N ratios (after correcting for inorganic N) than do shallower rocks. The only two samples that have TOC values greater than 1% also contain abundant granule to silt-sized particles of coal. The total sulphur contents of these rocks is very low and indicates either that only small amounts of deposited organic matter were labile, or that no source of reactive iron was present during diagenesis.



INTRODUCTION

The Oligocene and Eocene(?) rocks penetrated by the CRP-3 core (Fig. 1) were deposited in environments that included terrestrial fluvial systems, deltaic systems with iceberg influences, and clear glacial-marine settings. (Cape Roberts Science Team, 2000; p. 187-197). These different depositional environments could lead to differences in the amount, type, and provenance of organic matter preserved within the rocks. Analysis of organic matter present in the CRP-3 core was undertaken as part of the initial core characterisation effort. Owing to the small amounts of organic matter in these rocks, this effort was limited to whole-rock measurements of total organic carbon, total nitrogen and total sulfur. The principal objective of this work is to provide information on the organic matter preserved in these sediments and rocks. This information can be used to determine whether more detailed studies might be fruitful and to make some conclusions regarding the source and composition of organic matter preserved in these sediments and rocks.

METHODS

Eighteen major lithostratigraphical units consisting of 37 lithostratigraphical subunits (LSUs) were described by the Cape Roberts Science Team (2000; p. 59-68) (Fig. 2). Seventy one samples (Tab. 1) representative of the major lithologies penetrated by the CRP-3 hole were collected at *c.* 11 m intervals by the CRP curatorial staff at McMurdo Station. Eight of the subunits were not sampled. The unsampled subunits included LSUs 16.1-18.1 (Fig. 2) which are apparently Devonian and outside the scope of the Cape Roberts Project, as well as the subunits defined in the dolerite conglomerate and related lithologies present from 789.77-823.11 mbsf (Fig. 2). These latter lithologies are unlikely to contain significant amounts of organic matter. LSU 10.1 was not sampled and consists of a mudstone similar to that found in LSU 3.1 and LSU 8.1 (Fig. 2). The samples were shipped unfrozen to Lincoln, Nebraska. After arrival in Lincoln the samples were dried at 35°C for 24 hours and ground and homogenised using an Angstrom mill. All glassware and equipment used in sample preparation was washed in Micro solution and

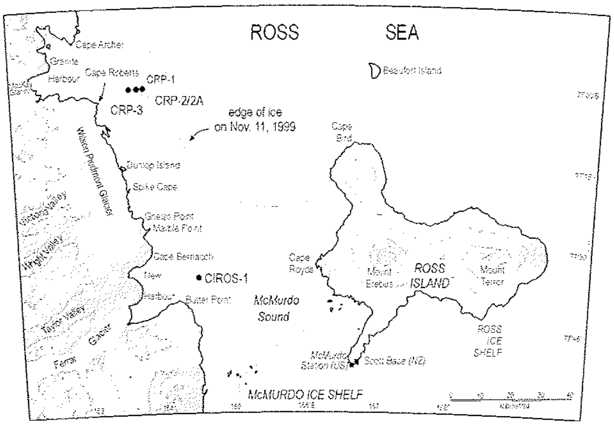


Fig. 1 - Map of the south west corner of the Ross Sea, showing the locations of the CRP-1, CRP-2/2a, and CRP-3 drill sites (Taken from Cape Roberts Science Team, 2000).

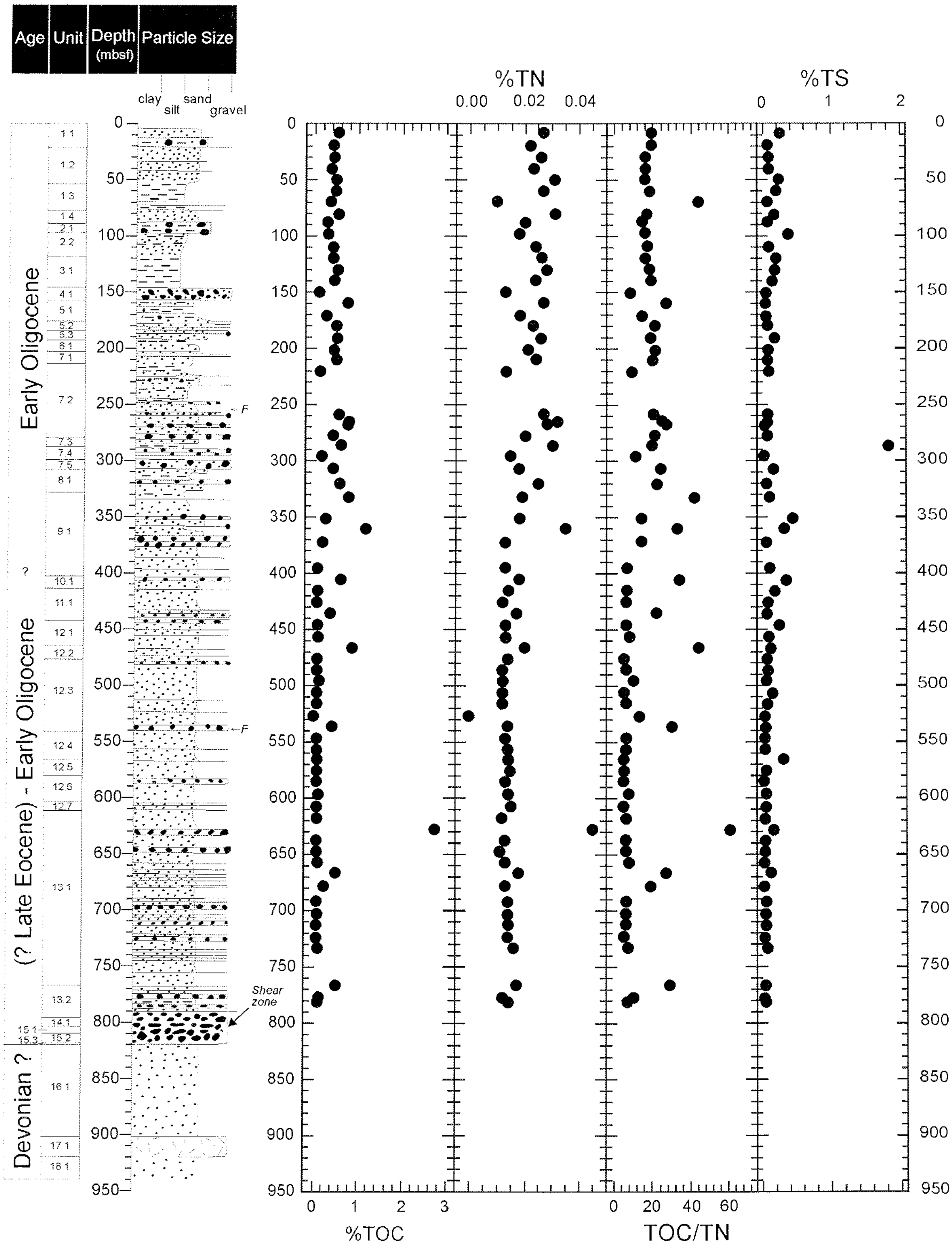


Fig. 2 - Comparison of values of TOC, TN, TS and TOC:TN with the lithology of CRP-3 core (Cape Roberts Science Team, 2000; p. 7).

rinsed in purified water. This cleaning was followed by sequential rinses with 1% hydrochloric acid, methanol, and dichloromethane.

Measurements of total organic carbon (TOC), total carbon (TC), total nitrogen (TN), and total sulphur (TS) were made on whole-rock samples using the Carlo Erba-EA 1108 at the University of Nebraska. Total organic carbon was measured using the low-temperature vapour acidification technique outlined by Hedges & Stern (1984). The results of these analyses are presented in table 1.

RESULTS AND DISCUSSION

The sediments and rocks penetrated by the CRP-3 drill hole contain very little organic matter: the TOC values measured average 0.3% (Tab. 1). Most of these

Tab. 1 - Organic geochemical data for samples obtained from CRP-3.

Depth (mbsf)	*LSU*	*%TN*	*%TC*	*%TOC*	*%TS*	*TOC/TN*	*TOC/TON*
8.13-8.15	1.1	0.027±0.006	0.49±0.01	0.53±0.02	0.24±0.03	20	31
19.17-19.19	1.2	0.022±0.007	0.38±0.01	0.41±0.03	0.06±0.03	19	34
29.96-29.98	1.2	0.026±0.007	0.42±0.01	0.43±0.03	0.08±0.04	17	27
40.24-40.26	1.2	0.023±0.007	0.35±0.01	0.37±0.03	0.07±0.03	16	28
50.00-50.02	1.2	0.031±0.006	0.41±0.01	0.48±0.03	0.22±0.03	15	23
60.07-60.09	1.3	0.027±0.006	0.61±0.01	0.47±0.03	0.18±0.04	17	28
69.71-69.73	1.3	n.q.	0.32±0.01	0.35±0.03	0.05±0.03	??	??
80.57-50.59	1.4	0.031±0.007	0.64±0.02	0.53±0.03	0.16±0.05	17	31
87.63-87.65	2.1	0.020±0.007	0.484±0.009	0.28±0.03	0.05±0.03	14	100
98.14-98.16	2.2	0.018±0.006	0.256±0.007	0.30±0.03	0.37±0.02	17	38
109.87-109.89	2.2	0.024±0.007	0.627±0.009	0.42±0.03	0.08±0.03	18	30
119.70-119.72	2.2	0.026±0.006	0.492±0.008	0.41±0.03	0.19±0.02	16	26
130.18-130.20	3.1	0.028±0.006	0.47±0.01	0.52±0.03	0.16±0.03	19	29
139.68-139.70	3.1	0.024±0.006	0.392±0.008	0.44±0.03	0.13±0.02	18	31
150.11-150.13	4.1	0.013±0.006	0.064±0.008	0.10±0.03	0.04±0.02	8	33
159.78-159.80	5.1	0.027±0.006	1.57±0.01	0.74±0.03	n.q.	27	44
171.17-171.19	5.2	0.018±0.006	0.243±0.009	0.26±0.03	n.q.	14	32
180.05-180.07	5.3	0.023±0.006	0.821±0.008	0.49±0.03	0.05±0.02	21	38
190.91-190.93	6.1	0.026±0.007	0.532±0.008	0.51±0.03	0.16±0.02	20	32
201.41-201.43	6.1	0.021±0.006	0.414±0.006	0.43±0.03	n.q.	20	39
210.45-210.47	7.1	0.024±0.006	0.450±0.009	0.49±0.03	0.06±0.03	20	35
220.66-220.68	7.2	0.013±0.006	0.087±0.005	0.13±0.03	0.08±0.06	10	43
259.10-259.12	7.2	0.027±0.006	0.54±0.01	0.55±0.03	0.06±0.03	20	32
265.21-265.23	7.3	0.032±0.007	1.087±0.009	0.79±0.03	0.05±0.03	25	36
268.02-268.04	7.3	0.028±0.006	1.140±0.005	0.76±0.03	n.q.	27	42
277.74-277.76	7.4	0.020±0.006	0.368±0.008	0.42±0.02	0.06±0.02	21	42
286.77-286.79	7.4	0.030±0.006	0.568±0.008	0.60±0.03	1.83±0.02	20	30
296.07-296.09	7.5	0.015±0.007	0.126±0.005	0.17±0.03	n.q.	11	34
307.17-307.19	8.1	0.018±0.006	0.500±0.008	0.43±0.02	0.15±0.02	24	54
320.54-320.56	8.1	0.025±0.006	0.532±0.006	0.57±0.02	n.q.	23	38
332.52-332.54	9.1	0.019±0.006	0.908±0.006	0.78±0.03	0.09±0.02	41	87
351.43-351.45	9.1	0.018±0.006	0.21±0.01	0.25±0.03	0.42±0.04	14	31
360.29-360.31	9.1	0.035±0.006	1.371±0.007	1.16±0.03	0.30±0.02	33	46
372.60-372.62	9.1	0.013±0.006	1.155±0.006	0.18±0.03	n.q.	14	60
395.45-395.47	9.1	0.013±0.006	0.08±0.01	0.08±0.03	0.09±0.01	6	27
405.75-405.77	9.1	0.018±0.006	0.766±0.008	0.61±0.03	0.33±0.02	34	76
415.58-415.60	11.1	0.014±0.007	0.37±0.01	0.08±0.03	0.16±0.05	6	20
426.16-426.18	11.1	0.012±0.006	0.061±0.007	0.07±0.02	0.06±0.02	6	35
436.20-436.22	11.1	0.017±0.006	0.39±0.01	0.37±0.03	n.q.	22	53
446.20-446.22	12.1	0.013±0.006	0.530±0.005	0.08±0.03	0.23±0.02	6	27
456.97-456.99	12.1	0.013±0.006	0.57±0.01	0.10±0.03	0.08±0.05	8	33
466.71-466.73	12.3	0.020±0.006	0.956±0.007	0.86±0.02	0.11±0.02	43	86
476.69-476.71	12.3	0.014±0.006	0.154±0.006	0.08±0.03	n.q.	6	20
486.32-486.34	12.3	0.012±0.006	0.491±0.007	0.08±0.02	0.07±0.02	7	40
496.07-496.08	12.3	0.012±0.006	0.100±0.005	0.12±0.02	n.q.	10	60
506.75-506.77	12.3	0.012±0.006	0.051±0.007	0.07±0.03	0.13±0.02	6	35
516.46-516.46	12.3	0.012±0.006	0.51±0.01	0.07±0.02	n.q.	6	35
527.06-527.08	12.3	n.q.	0.250±0.007	n.q.	n.q.	??	??
536.69-536.71	12.3	0.014±0.007	2.573±0.007	0.42±0.03	n.q.	30	105
546.97-546.99	12.4	0.013±0.006	0.12±0.01	0.08±0.03	n.q.	6	27
557.11-557.13	12.4	0.014±0.007	0.290±0.006	0.08±0.03	n.q.	6	20
566.01-566.03	12.5	0.014±0.007	0.10±0.01	0.08±0.03	0.29±0.05	6	20
576.06-576.08	12.5	0.015±0.007	0.529±0.007	0.08±0.03	0.04±0.02	5	16

Tab. 1 - Continued.

Depth (mbsf)	*LSU*	*%TN*	*%TC*	*%TOC*	*%TS*	*TOC/TN*	*TOC/TON*
585.45-585.47	12.6	0.013±0.006	0.43±0.01	0.07±0.03	n.q.	5	23
596.67-596.69	12.6	0.014±0.007	0.458±0.007	0.12±0.03	0.03±0.02	9	30
607.76-607.78	12.7	0.015±0.007	0.212±0.005	0.07±0.03	n.q.	5	14
618.49-618.51	13.1	0.012±0.006	0.463±0.006	0.08±0.02	n.q.	7	40
628.19-628.21	13.1	0.045±0.006	2.867±0.006	2.75±0.03	0.15±0.02	61	78
637.62-637.64	13.1	0.013±0.006	0.084±0.007	0.08±0.03	n.q.	6	27
647.84-647.86	13.1	0.011±0.005	0.036±0.008	0.07±0.02	0.03±0.02	6	70
657.10-657.12	13.1	0.013±0.006	0.059±0.007	0.10±0.03	n.q.	8	33
666.70-666.72	13.1	0.018±0.007	0.451±0.009	0.50±0.03	0.11±0.03	28	62
678.36-678.38	13.1	0.013±0.006	0.909±0.005	0.24±0.03	n.q.	18	80
692.36-692.38	13.1	0.014±0.007	0.045±0.008	0.08±0.03	0.04±0.02	6	20
703.42-703.44	13.1	0.014±0.006	0.056±0.007	0.09±0.03	n.q.	6	22
713.08-713.10	13.1	0.014±0.007	0.056±0.008	0.08±0.03	0.04±0.02	6	20
724.10-724.12	13.1	0.014±0.006	0.036±0.006	0.07±0.03	n.q.	5	18
733.48-733.50	13.1	0.016±0.007	0.10±0.01	0.10±0.03	0.05±0.03	6	17
766.75-766.77	13.1	0.017±0.006	0.50±0.01	0.51±0.03	n.q.	30	73
777.89-777.91	13.2	0.012±0.006	0.189±0.005	0.12±0.02	n.q.	10	60
781.68-781.70	13.2	0.014±0.006	0.186±0.008	0.11±0.03	0.03±0.02	8	28

Notes: n.q.-not quantified (concentration exceeded limit of detection but cannot be shown to be greater than zero). Errors listed represent one standard deviation.

samples do not contain significant amounts of carbonate carbon: only 16 of these samples have total carbon (TC) values that exceed the TOC contents by an amount greater than the combined errors (Tab. 1). The TOC content of these rocks changes at two scales. 1) Samples of Early Oligocene rocks encountered at depths more shallow than 330 mbsf contain more organic carbon than do samples obtained from older rocks. The average TOC values for rocks above 330 mbsf is 0.46% whereas the deeper rocks have average TOC values of 0.26%. The TOC values of the samples obtained at depths above 330 mbsf are comparable to those measured in samples obtained from the Oligocene section penetrated by CRP-2/2A (Fig. 3). This zoning is also evident in Fig. 2 and can be recognized by the low and uniform TOC values below 330 mbsf: only 3 of the 30 shallow samples have TOC values that are less than 0.2%, whereas 30 of the 41 deep samples have TOC values that are less than 0.2%. 2) At depths more shallow than 330 mbsf, rocks assigned to highstand systems tracts contain more organic carbon than other rocks. The Cape Roberts Science Team described 23 sequences in the top 483 m of the CRP-3 core and fine-grained rocks were assigned to the highstand systems tract (HST) (Cape Roberts Science Team, 2000; p. 69). Lithostratigraphical Subunits assigned to HSTs included LSUs 1.3, 3.1, 5.1 and 8.1. Each of these has TOC values that are slightly greater than those found in adjacent rocks (Tab. 1; Fig. 2). This relationship is much less well developed in CRP-3 than the similar relationship described for CRP-2/2A (Kettler and Papastavros, 2000). Although it was possible to identify condensed sections in the CRP-2/2A core using the diatom abundance data collected by members of the Cape Roberts Science Team (Kettler and Papastavros, 2000), microfossils are almost completely absent from much of the CRP-3 core. The interpretation that higher TOC values in rocks assigned to a HST correspond to periods of relative clastic sediment starvation remains, however. This relationship is not observed in the deeper portions of the hole (Fig. 2).

The TOC:TN ratios measured in these rocks are high and range from 5 to 61. TOC:TN ratios must be interpreted with caution in rocks that contain very little organic carbon. Typically the caution is warranted because inorganic nitrogen will become an important contributor when TOC values are very low (Stein, 1991). Inorganic nitrogen is apparently a significant contributor to the N budget of many samples from the CRP-3 core. The relatively coarse-grained rocks in the deep samples would be expected to contain little aquatic organic matter, yet 24 of the 41 samples obtained from depths greater than 330 mbsf have TOC/TN values less than 10. The TOC/TN values can be corrected for contributions by inorganic nitrogen by regressing the TN values on the TOC data (Leventhal, pers. comm.). Although the shallow and deep samples plot along two different trends in TN vs TOC space (Fig. 4), both yield TN values of *c.* 0.01% when organic carbon is absent.

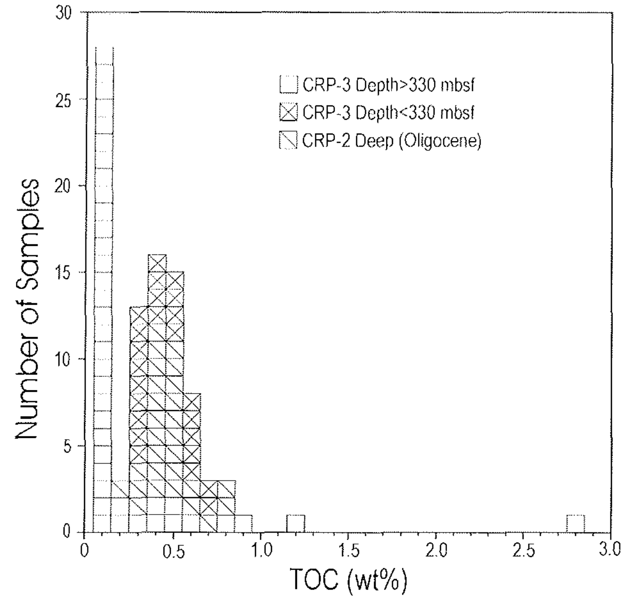


Fig. 3 - Comparison of TOC values in CRP-3 samples obtained from above 330 mbsf, below 330 mbsf and with the Oligocene section in CRP-2/2A.

Ratios of TOC:TON (total organic nitrogen) can then be calculated assuming a constant inorganic N value of 0.01% (Tab. 1). Whereas the average TOC/TN and TOC/TON values for the deep samples are 14 and 42, respectively, they are 18 and 36, respectively, for the shallow samples. Although the high TOC:TN and TOC/TON ratios obtained in this work should be interpreted cautiously, two mutually consistent interpretations are possible. 1) Organic matter produced in the water column experienced extensive remineralization and only the most resistant fraction of the aquatic organic matter was preserved. 2) A significant fraction of the preserved organic matter comprises detrital coal. The second interpretation is confirmed easily by visual inspection of the samples: the sample (CRP-3-628.19-628.21) that has the highest TOC value (2.75%) also contains abundant granule-sized (2-4 mm) clasts of coal.

Interpretation of the S data is complicated by the very low TOC values of these rocks. When plotted in TS vs TOC space (Fig. 5), the CRP-3 samples plot around the "normal marine" trend and include a number of samples with very low TS:TOC ratios. Although very low TS:TOC ratios are considered evidence that sediments were deposited in fresh water (Berner and Raiswell, 1984), that conclusion is not appropriate for these samples for two reasons. 1) TS:TOC ratios discriminate between marine and freshwater sedimentary rocks poorly when the TOC values of are less than 1% (Berner and Raiswell, 1984). 2) The organic matter deposited at the CRP-3 site comprises a mixture of aquatic organic matter and coal. Because coal is resistant to bacterial degradation, the low TS:TOC ratio of CRP-3-628.19-628.21 need not be evidence of a freshwater depositional environment.

There are a few samples that have TS:TOC ratios that exceed 1 and would be considered to be anomalous (Fig. 5). Only one sample (CRP-3-286.77-286.79) has a TS:TOC ratio that is clearly indicative of epigenetic addition of sulphur (Leventhal, 1995) and that sample also contains pyrite veinlets. Although six other samples have TS:TOC ratios that exceed unity (Fig. 5) it is unlikely that these samples have experienced epigenetic addition of sulfur. A number of these samples occur near the tops of stratigraphic sequences in rocks that were assigned to the HST. Others occur at the tops of small groups of samples in which the TS content increases upwards (Fig. 2). Relating these latter high TS:TOC ratios to positions within the sequences is difficult because the Cape Roberts Science Team was not able to define sequences in this portion of the core during the initial core description. Why should TS:TOC ratios be related to stratigraphic position? The tops of stratigraphic sequences were apparently marked by decreased rates of clastic sedimentation and greater relative inputs of biogenous material. Aquatic organic matter would have been far a better substrate than detrital coal for sulfate-reducing bacteria. Although the ratio of aquatic organic matter to coal detritus delivered to the sediment would have been maximized during interglacial episodes (HST), this ratio -as reflected by TOC:TN ratios or TOC values- would not necessarily be preserved. The aquatic organic matter could be almost completely mineralized during early diagenesis whereas the refractory coal detritus would remain.

The sulphur data are also important because of suggestions that modiolid mussels found in sub units 1.1 and 13.1 are indicative of peculiar bottom conditions that might be characterized by significant H_2S production (Cape Roberts Science Team, 2000; p. 169-170). The TS:TOC ratios observed in these

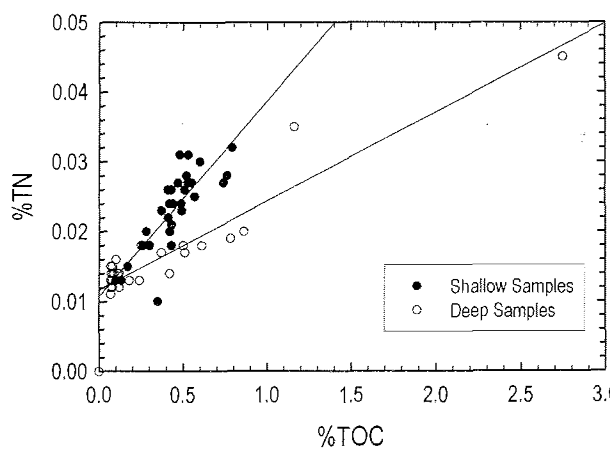


Fig. 4 - Plot of TN versus TOC for CRP-3 samples. Lines are the result of least squares regressions of the shallow (depth<330 mbsf) and deep (depth>330 mbsf) samples.

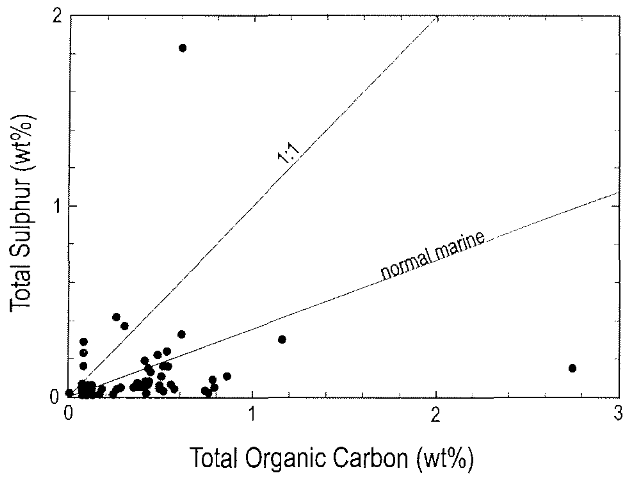


Fig. 5 - Plot of TS versus TOC for CRP-3 samples with "normal marine" trends and unit TS:TOC ratio shown for reference.

subunits (Tab. 1) do not support such an interpretation. The TS:TOC ratio in sample 8.13-8.15 is 0.45; a value that is wholly compatible with normal marine rocks containing less than 1% TOC. Although S is detectable in LSU 13.1, 11 of the 12 samples from this sub-unit have less than 0.1% S and 8 have TOC values less than 0.1%. Even the three samples that have TOC values greater than 0.5% have very low sulphur contents. A conventional interpretation of these data is that very little labile organic matter was deposited with these sediments and, therefore, very little H_2S was produced. It is unlikely, therefore, that the modiolid mussel communities reflect an H_2S-rich environment unless the samples obtained in this study are not representative of the sedimentary section in which the mussels occur or the iron in the sediments was resistant to sulfidation.

These rocks probably contain little solvent-soluble organic matter: the very low TOC values require that little solvent soluble organic matter be present. It is unlikely that Rock-Eval pyrolysis of these or other CRP-3 samples would yield useful data because Rock-Eval pyrolysis data are very difficult to interpret when the samples analyzed have very low TOC and bitumen contents (Peters, 1986). Molecular characterisation of solvent-soluble organic matter would also be unlikely to yield valuable information. Previous extraction of rocks with similarly low TOC values has yielded masses of bitumen that are typically less than 0.001 g (Kettler, 1998; Kettler and Papastavros, 2000). The molecular composition of the small amounts of extractable organic matter in these rocks could have been affected significantly by contamination at the drill site, during core processing, or by microbial alteration during shipping. Any conclusions drawn from molecular analyses would likely be equivocal; thus, isolation and molecular characterisation of the bitumen was not undertaken.

CONCLUSIONS

The sedimentary rocks recovered by the CRP-3 core contain small amounts of organic matter. Although the Oligocene section above 330 mbsf contains amounts of organic matter similar to the Oligocene section in the CRP-2/2A core, most of the samples obtained from below 330 mbsf contain less than 0.2% TOC. Interpretation of TOC:TN ratios is difficult in rocks that have such low TOC values. The TOC:TN ratios do increase with increasing TOC values. This relationship is evidence that inorganic N contributes significantly to TN values in samples that contain little TOC, and that much of the preserved organic matter in these rocks comprises detrital coal. The TS:TOC ratios are consistent with a marine system in which much of the deposited organic carbon was refractory. There is evidence in one sample of epigenetic addition of sulfur (confirmed by the presence of pyrite veinlets). Although six other samples have TS:TOC ratios that exceed unity, it is likely that these elevated TS:TOC ratios result from near complete consumption of aquatic organic matter by sulfate reducing bacteria. The sulphur data do not support the hypothesis that the depositional environments of LSUs 1.1 and 13.1 were H_2S-rich.

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