# Preliminary Results of Bitumen and Kerogen Analyses of the CRP-1 Core

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Abstract - Sediments and rocks recovered in CRP-1 coring operations contain relatively little organic matter (average 0.4% TOC) and very small amounts of solvent-soluble organic matter (average 60 µg bitumen/g rock). The kerogen recovered from these rocks has atomic H:C ratios that range from 0.7 to 1.0 and atomic O:C ratios that range from 0.14-0.22. This range of values could be produced by mixing coal detritus with aquatic organic matter. Coal with the O:C ratios necessary to produce the kerogen present in the CRP-1 samples occurs in outcrops of the Permian Beacon Supergroup proximal to the drillsite.
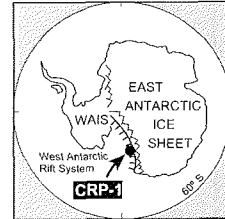
INTRODUCTION

The Quaternary and Miocene sediments and rocks penetrated by the CRP-1 core were deposited in environments which were variably influenced by glacial activity. Environments ranged from proximal glacimarine to shallow marine settings in which small amounts of detritus was ice-rafted to the CRP-1 drillsite (Fig. 1) (Cape Roberts Science Team, 1998a). These different depositional environments may lead to differences in the amount, type, and provenance of organic matter preserved with the sediments. Analysis of kerogen and solvent-soluble organic matter present in the CRP-1 core was undertaken as part of the initial core characterisation effort. This effort included whole-rock measurements of elemental abundances, extraction of solvent-soluble organic matter, and measurement of the chemical composition of kerogen obtained from these sediments and rocks. The principal objective of this work is to provide preliminary information on the organic matter preserved in these sediments and rocks. This information can be used to guide more detailed studies and to make some provisional conclusions regarding the source and composition of organic matter preserved in these sediments and rocks.
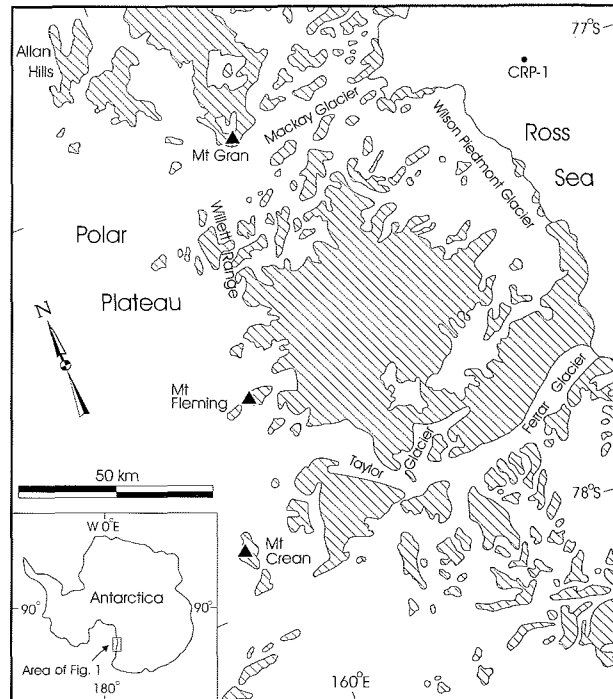

Fig. 1 - Map of a portion of southern Victoria Land showing the locations of exposures (diagonal shading), the CRP-1 drillsite, and a number of localities referred to in text (after Young, 1991).

METHODS

All glassware and equipment used in sample preparation was washed in Micro solution and rinsed in purified water. This cleaning was followed by sequential rinses with 1% hydrochloric acid, methanol, and dichloromethane. Seven major lithostratigraphic units consisting of 18 subunits were described by Cape Roberts Science Team (1998b) (Fig. 2). Twenty five samples representative of the major lithologies penetrated by the CRP-1 hole were collected at c. 5 m intervals. While at McMurdo, the samples were freeze-dried, ground and homogenised with a mortar and pestle and stored in 15 ml glass vials. Measurements of total organic carbon (TOC), total carbon (TC), total nitrogen (TN), and total sulphur (TS) were made using the Carlo Erba-NA1500 at the Crary Science and Engineering Center at McMurdo. These results are presented in table 1 and the experimental procedures used are summarised in Cape Roberts Science Team (1998c).

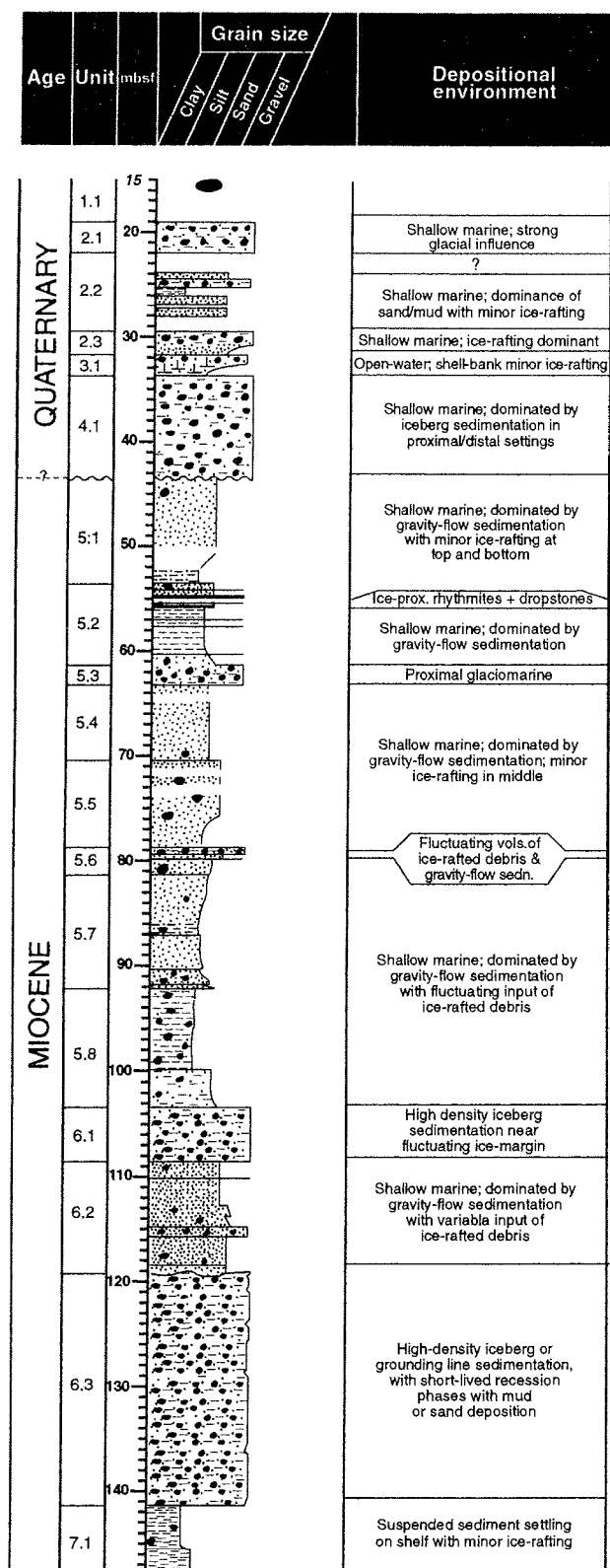Bitumen was extracted from the sedimentary rocks in

Fig. 2 - Stratigraphic column showing lithologies penetrated by the CRP-1 core (from Cape Roberts Science Team, 1998b, Fig. 18).

rinsing them with purified water. The residues were then reacted with concentrated HF. The spent HF was decanted and replaced daily. Complete dissolution of the sedimentary rock samples was difficult owing to the presence of significant amounts of mafic minerals and siderite and the consequent formation of Fe and Mg fluoride precipitates. Neo-formed fluorides were removed using a 1M solution of $AlCl_3$ in 6N HCl. Pyrite was removed with a 1 M acidic chromous chloride solution. Although chromous chloride reduction is not believed to affect carbon-bonded sulphur in the kerogen (Canfield et al., 1986), the risk of "laboratory-induced diagenesis" attends all procedures for de-mineralising rocks The separates were washed with a large amount of purified water and dried at 40°C. Pyrite removal was not complete and thus the ash content of the kerogen separates is high (Tab. 1). The elemental ratios presented in table 1 should not be affected however. Elemental analysis of the kerogen separates was carried out using a Carlo-Erba EA-1108. CHNS analyses were carried out by combustion whereas the O analyses were performed by pyrolysis. These data were converted to atomic elemental ratios and are displayed in table 1.

RESULTS AND DISCUSSION

The sediments and rocks penetrated by the CRP-1 drillhole contain little organic matter: the TOC values measured at the Crary Laboratory average 0.4% (Tab. 1). The C:N ratios measured at the Crary Laboratory are high and range from 10 to 700. C:N ratios must be interpreted with caution in rocks that contain very little organic carbon. Although the presence of inorganic N is typically cited as the reason that caution is warranted (Stein, 1991), the presence of siderite or other refractory carbonate minerals can produce erroneously high C:N ratios. The analytical techniques typically used to quantify the inorganic and organic carbon contents of marine sediments and rocks (*e.g.* Hedges & Stern, 1984; Müller & Gastner, 1971) rely on low-temperature acidification of all carbonate phases. Siderite is much more refractory than calcite or dolomite and complete dissolution at low temperature may require weeks or months (Rosenbaum & Sheppard, 1986). Although the high C:N 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 largely detrital coal or fragments of higher land plants. The extraordinarily high C:N ratios (*e.g.* 200-700) are more consistent with the presence of detrital coal than terrigenous plant debris: terrigenous plant debris typically has C:N ratios ranging from 12 to 37 (Stein, 1991).

These rocks and sediments contain little solvent-soluble organic matter. The dichloromethane-bitumen solutions obtained by the Soxhlet extractions are colourless. The mass of bitumen extracted is low and averages 60 µg bitumen/g rock. The bitumen ratios (mg bitumen/g organic

a Soxhlet apparatus using dichloromethane. The dichloromethane was removed by evaporation and the extract was weighed (Tab. 1).

Kerogen separates were obtained from the extracted samples by reacting them with 6N HCl overnight and

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

| Depth (mbsf) | Whole-rock | | | Kerogen | | | Bitumen | |
	%TOC[a]	C/N[b]	%TS[c]	H/C[d]	O/C[d]	%TOC	Mass[e]	Bitumen Ratio[f]
19.31-19.31	0.2±0.1	30	0.024±0.005	n.d.[g]	n.d.	n.d.	1.30	100
26.35-26.36	0.2±0.1	40	0.024±0.005	n.d.	n.d.	n.d.	1.60	80
33.68-33.69	0.4±0.2	20	0.05±0.01	n.d.	n.d.	n.d.	1.70	40
38.83-38.84	0.2±0.1	20	0.28±0.06	0.77	0.17	49.1±0.4	0.94	30
44.40-44.41	0.2±0.1	20	0.43±0.09	1.00	0.22	42.8±0.4	1.50	30
54.22-54.23	0.7±0.4	60	0.32±0.06	0.70	0.16	56.0±0.4	0.90	10
58.00-58.01	0.6±0.3	50	0.14±0.03	0.90	0.19	53.2±0.4	0.56	10
65.65-65.66	0.2±0.1	40	0.11±0.02	n.d.	n.d.	n.d.	0.31	10
69.94-69.95	0.8±0.4	40	0.50±0.1	0.79	0.15	60.1±0.4	0.73	10
77.00-77.01	0.7±0.3	60	0.14±0.03	0.97	0.17	52.1±0.4	0.31	10
83.20-83.21	0.7±0.3	60	0.14±0.03	0.88	0.17	55.1±0.4	0.80	10
86.50-86.51	0.4±0.2	40	0.14±0.03	0.96	0.19	49.1±0.4	0.37	5
91.17-91.18	0.06±0.03	10	0.24±0.05	n.d.	n.d.	n.d.	1.10	100
94.89-94.90	0.3±0.2	50	0.42±0.08	0.88	0.18	45.2±0.4	0.17	3
97.45-97.46	0.5±0.3	40	0.13±0.02	0.96	0.19	53.5±0.4	1.10	20
101.44-101.45	0.2±0.1	10	0.18±0.03	1.00	0.20	53.6±0.4	1.20	30
106.60-106.61	0.2±0.1	50	0.11±0.02	0.85	0.16	44.2±0.4	0.74	20
112.86-112.87	0.4±0.2	40	0.15±0.03	0.90	0.19	48.6±0.4	0.61	20
118.44-118.45	0.4±0.2	40	0.30±0.06	0.70	0.18	40.4±0.4	1.10	10
123.60-123.61	0.4±0.2	200	0.08±0.02	0.80	0.18	45.2±0.4	0.14	2
126.93-126.94	0.4±0.2	200	0.06±0.01	0.73	0.14	47.9±0.4	1.50	40
130.46-130.47	0.4±0.2	700	0.12±0.02	0.77	0.16	46.0±0.4	0.46	7
137.40-137.41	0.5±0.3	60	0.13±0.03	0.81	0.17	48.1±0.4	0.72	6
142.16-142.17	0.8±0.4	60	0.16±0.03	0.88	0.18	55.3±0.4	1.80	20
146.84-146.85	0.4±0.2	30	0.21±0.04	0.80	0.16	55.0±0.4	1.10	30

Note: [a]Total Organic Carbon (TOC). [b]Mass ratio of organic Carbon:total Nitrogen. [c]Total Sulphur. [d]Elemental atomic ratios. [e]Mass (mg) of bitumen. [f]mg of bitumen extracted/g organic carbon. [g]Ratio not determined (n.d.) because sufficient kerogen could not be isolated for analysis.

carbon) obtained (Tab. 1) are exceedingly low, and average less than 30 mg bitumen/g organic carbon. It is unlikely that Rock-Eval pyrolysis of these or other CRP-1 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). That the Quaternary samples have slightly higher bitumen ratios (Tab. 1) is to be expected: in the classical view of kerogen formation (e.g. Durand, 1980), lipids, alcohols, and organic acids present in sediment may undergo polymerisation over geologic time and contribute to the kerogen fraction. The molecular composition of the small amounts of extractable organic matter in these rocks could have been affected significantly by contamination at the drillsite or during the initial stages of core processing. Any conclusions drawn from molecular analyses would probably be equivocal; thus, molecular characterisation of the bitumen was not undertaken.

Although the H:C and O:C ratios of the kerogen separates plot along and above the evolution curve for Type III organic matter (Fig. 3), higher land plant detritus need not have comprised a significant fraction of the organic matter deposited at Cape Roberts. All organic matter present in sedimentary rocks is a mixture of materials derived from aquatic and terrigenous sources. Among the possible sources of terrigenous organic matter at Cape Roberts are outcrops of coal-bearing rocks in the Permian Beacon Supergroup that are exposed in the Transantarctic Mountains. Coates et al. (1990) have compiled the results of numerous analyses of coal from the Beacon Supergroup in the Transantarctic Mountains. These data have been converted to atomic O:C and H:C ratios and, when plotted

on figure 3, define a trend that is grossly parallel to the evolution curve for Type III organic matter but displaced to lower H/C values. Such displacement to lower H/C values is typical for organic matter that has been weathered (Jones, 1987). Although the C:N data are suggestive that little aquatic organic matter was preserved, the most refractory portion of the aquatic material may have been
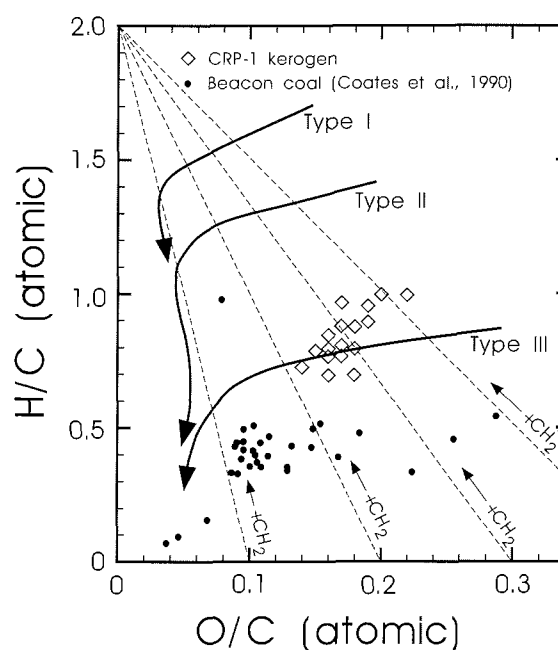

Fig. 3 - Van Krevelen diagram showing the composition of kerogen present in CRP-1 samples and coals from the Transantarctic Mountains.

preserved. The most refractory portion of aquatic organic matter consists largely of resistant, aliphatic biopolymers such as algaenans produced by diatoms and other algae (Tegelaar et al., 1989; de Leeuw & Largeau, 1993). These materials have high H:C ratios and very low O:C ratios. The aquatic organic fractions with higher O:C ratios, such as carbohydrates and amino acids, are typically mineralized during diagenesis (e.g. Martens et al., 1992). The addition of aliphatic aquatic organic matter to coal detritus would displace the elemental composition of the preserved organic matter from the H/C and O/C values of the coal detritus along paths similar to those defined by the "+CH₂" lines in figure 3.

The high O:C ratios measured in this study require that the coal detritus must have had high O:C ratios. Relatively few elemental analyses of Beacon Supergroup coal are available; those data that are plotted on figure 3 represent samples from the Victoria Land Basin and from the northern portion of the Nimrod-Ohio basin (Coates et al., 1990). If the organic matter preserved in the sediments and rocks penetrated by CRP-1 is a mixture of coal detritus and aliphatic aquatic organic matter, then the best potential source areas for the coal detritus would contain coals with O:C ratios that exceed 0.16. Four of the samples from the Victoria Land Basin tabulated by Coates et al. (1990) meet that criterion. Those samples were obtained from the Willett Range and Mt. Gran; localities that are proximal to the CRP-1 site and adjacent to the valley occupied by the Mackay Glacier (Fig. 1). Coal from the Willett Range and Mt. Gran localities also has very high C:N ratios: the four samples plotted on figure 3 that have O:C ratios greater than 0.16 have an average C:N ratio of 166. This value is considerably higher than that observed in many coal samples obtained from the Beacon Supergroup (Coates et al., 1990) and is consistent with the high C:N ratios observed in the CRP-1 whole-rock samples (Tab. 1).

CONCLUSIONS

The rocks and sediments penetrated by the CRP-1 contain little solvent-soluble organic matter or kerogen. The data collected in this initial core characterisation effort supports strongly the conclusion made in the Initial Report (Cape Roberts Science Team, 1998c) that much of the organic matter in these rocks and sediments is a mixture of detrital coal and aquatic organic matter. The elemental composition of the kerogen and the whole-rock C:N ratios are consistent with (but do not require) derivation of the coal detritus from outcrops in the drainage area of the Mackay Glacier.

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