Characteristics of organic matter in lagoonal sediments from the Great Barrier Reef

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We have applied organic carbon and total nitrogen analyses, Rock-Eval pyrolysis, and gas chromatography-mass spectrometric lipid analysis with in situ methylation with tetramethylammonium hydroxide (TMAH-pyrolysis-GC/MS) to characterize the organic matter in recent lagoonal sediments from the Great Barrier Reef (GBR). On a pyrogram, GBR sediments showed the unique feature that S1 and S3 values were anomalously high. The high S1 value presumably reflects a higher proportion of hydrolyzed lipids, and the high S3 value is due to the degradation of carbonate minerals in a low temperature range. Associated with a CaCO3 increase towards the offshore area, the organic carbon/total nitrogen ratio (C/N ratio) decreased, S1 and S2 values increased, and total fatty acid and phytol concentrations increased. These changes have negative correlations with the branched/total fatty acid ratio, implying that the changes reflect the degree of eubacterial activity. The higher preservations of lipids and lignin phenols in CaCO3-rich sediments are attributable to their higher preservation effect resulting from an impermeable carbonate matrix. The anteiso/iso-fatty acid ratio has a significant negative correlation with the total fatty acid concentration and a positive correlation with the branched/total fatty acid ratio, indicating that the ratios are closely related to the degree of eubacterial degradation of organic matter.

INTRODUCTION

A coral reef is a mound or ridge of in-place coral colonies and accumulated skeletal fragments, carbonate sands, and limestone resulting from the organic secretion of calcium carbonate that lithifies colonies and sands (Bates and Jackson, 1980). Coral reefs occur today throughout the tropics and subtropics, wherever the temperature is suitable, generally above about 18°C, a winter minimum (Bates and Jackson, 1980). A typical marginal coral reef has a spectrum of zonal areas from the land to the offshore area: lagoon, reef flat, and fore reef. Since the coral reef provides a unique biological and geological setting, numerous studies of the coral reefs have been conducted in both research fields. However, little is known about the organic geochemistry of coral reefs, except for the results of several preliminary studies (Sassen, 1977; Meyers et al., 1978; Saliot et al., 1994; Shaw and Johns, 1985, 1986; Currie and Johns, 1989; Johns et al., 1994; Yamamoto et al., 1997; Yamamoto, 2000).

Subsurface beds of ancient coral reefs sometimes reserve crude oils (North, 1985), and the lagoonal sediments were suspected to be petroleum source rock. In the 1980s, various researchers examined the potentiality of shallow marine carbonates such as coral reef sediments as a petroleum source rock (e.g., Taguchi and Mori, 1985).
The discussion resulted in the conclusion that shallow marine carbonates are generally low in potential as a petroleum source rock due to their low organic carbon contents, below 0.5% (Bordenave, 1993). Geological evidence indicated that organic-rich sediments could be deposited even in an open shelf until the early Paleozoic period, but they could be deposited only in a hydrologically isolated basin afterwards (Klemme and Ulmishek, 1991). This historical change is attributed to the evolution of benthic animals and bacteria (Klemme and Ulmishek, 1991) and/or the increase of dissolved oxygen in the ocean (Berner and Canfield, 1989). In the modern depositional environment of shallow marine carbonates, the produced organic matter is oxidized into carbon dioxide either in water before incorporation in sediments or during early diagenesis, due to the water’s high-energy oxic condition (Bordenave, 1993).

The measurement of organic carbon in a carbonate sediment requires the removal of carbonate carbon by acidification. Results in the measurement of organic carbon contents for recent coral reef sediments depend on the choice of the acid preparation method such as vapor versus washout methods. The organic carbon content obtained by the vapor method is twice as high as that by the washout method for lagoonal sediments (Yamamuro and Kayanne, 1995) and is three to seven times higher than that by the washout method for reefal limestones (Yamamoto et al., 1997) in the case of both sediment and reef from the Palau Islands. This indicates that more than half of organic carbon was lost during washing. The lost organic matter was most likely to have been associated with carbonate minerals (Yamamuro and Kayanne, 1995; Yamamoto et al., 1997; Yamamoto, 2000) removed in the washing process of the washout method.

In this study, we applied organic carbon and total nitrogen analyses, Rock-Eval pyrolysis, and gas chromatography-mass spectrometric lipid analysis with in situ methylation with tetramethylammonium hydroxide (TMAH-pyrolysis-GC/MS) to characterize the organic matter in recent lagoonal sediments from the Great Barrier Reef (GBR), the largest coral reef in the world. This study aimed at examining the factors controlling the quality and quantity of organic matter in coral reef sediments and the role of bacterial activity on the degradation of organic matter by comparing bulk organic matter with lipid compositions in the sediments.

TMAH-pyrolysis-GC/MS has been used recently for the analysis of geomacromolecules such as lignins (e.g., Clifford et al., 1995). In this method, the organic matter is pyrolyzed in the presence of TMAH, and the pyrolysates are transformed to a methyl ester, a methoxy phenol, a methoxy alcohol, etc. The derivatized pyrolysates are analyzed with on-line GC/MS.

The Great Barrier Reef

The Great Barrier Reef (GBR) is the largest coral reef matrix in the world. It extends approximately 2600 km along the eastern coast of Australia, from just north of Fraser Island in the south (25°S) to the coast of Papua New Guinea in the north (9.2°S) (Wolanski, 1994). The studied area covers the inner barrier area that extends from about 14.5°S to about 17°S on the continental shelf off North Queensland. In this area, the waters are very shallow, with a maximum depth seldom exceeding 30 m (Wolanski, 1994). A number of reefs and shoals are scattered very densely all across the shelf width. Elongated reefs are found at the shelf break, separated by narrow reef passages. The CaCO3 content of bottom sediments tends to increase with distance from the land (Maxwell, 1968).

The studied area is situated in a wet tropics climatic zone with moderate to high rainfall (1500–5000 mm/yr) throughout the year and abundant rainforest vegetation on land (Gentilli, 1971). Seven river systems supply the sediment to the inner barrier area investigated. Because of the rivers’ relatively steady water flow throughout the year, the mass of the sediment discharge is much smaller than the mass of the adjacent dry area (Neil and Yu, 1995). Anthropogenic pollution is small in this area (Haynes and Johnson, 2000).
A study of lipids for recent inner GBR sediments indicated that the sources of lipids are higher plants, algae, bacteria, fungi, and meiofauna in descending order of importance (Shaw and Johns, 1985). A systematic decrease of higher plant contribution and an increase of phospholipids were observed with distance from the land along the Cairns-Arlington Reef transect, possibly reflecting decreasing water turbidity effects with the deepening water column (Johns et al., 1994).

SAMPLES AND METHODS

Twenty-two bottom sediments (0–3 cm deep) were collected by gravity coring during the cruise of R/V Lady Basten, Australian Institute of Marine Science, from 25 February to 1 March 1995 in the inner barrier area that extends from about 14.5°S to about 17°S on the continental shelf off North Queensland (Fig. 1). The samples were frozen, freeze-dried, and milled to a particle size under 75 µm.

The sediment samples were analyzed for total organic carbon (TOC), total carbon (TC), and total nitrogen (TN) using a Yanaco MT-5 elemental analyzer. To remove carbonate carbon, the samples were acidified following the vapor method of Yamamuro and Kayanne (1995). Inorganic carbon (IC) and calcium carbonate (CaCO₃) contents were calculated according to the following equations:

\[
IC = TC - TOC, \text{ and}
\]

\[
CaCO_3 = IC \times 8.333.
\]

Five selected samples (Nos. 3–7) were acidified by a washout method (Yamamuro and Kayanne, 1995), and the organic carbon content of the acid residue was measured for comparison with the content measured by the vapor method. The treatment was conducted at a room temperature to prevent the hydrolysis of organic matter.

Rock-Eval analysis was carried out using a DELSI Rock-Eval II. One hundred milligrams of powdered sediment sample was heated under helium gas at 300°C for 3 min, and then the temperature was increased by 25°C/min up to 550°C and held isothermally for 1 min. The generated organic compounds and CO₂ were measured with a flame ionization detector and a thermal conductivity detector, respectively. According to Espitalié et al. (1977), the amounts of organic matter vaporized at 300°C and that generated in a temperature range from 300°C to 550°C were defined as S₁ and S₂, respectively. The amount of CO₂ generated up to a temperature of 350°C was defined as S₃. The temperature when the S₂ is at maximum was defined as \(T_{\text{max}}\).

Pyrolysis gas chromatography-mass spectrometry with in situ methylation with tetramethylammonium hydroxide (TMAH-pyrolysis-GC/MS) was carried out using a Japan Analytical Industry JHP-3 Curie point pyrolyzer that was directly inserted into the injection port of a Hewlett Packard 5973 gas chromatograph-mass selective detector. The column used was a Chrompack CP-Sil5CB (length, 30 m; i.d., 0.25 mm; thickness, 0.25 µm). The sediment sample (ca. 20 mg) was placed on a Ni-Co pyrofoil with 20 µl of 25% TMAH (tetramethylammonium hydroxide) in methanol. The methanol was removed under vacuum, and the sample was wrapped in the pyrofoil. The sample was heated at 590°C for 20 sec in the pyrolyzer, and the generated compounds were transferred to the GC splitless injection system at 300°C with a helium carrier gas. The oven temperature was programmed from 70°C to 310°C at 4°C/min after the initial hold time of 1 min, and then it was held isothermally at 310°C for 30 minutes. The mass spectrometer was run in the full scan ion-monitoring mode (m/z 50-650). Electron impact spectra were obtained at 70 eV. Identification of compounds was achieved by comparison of their mass spectra and retention times with those of standards and those in the literature. The standard deviations in 3 duplicate analyses averaged 13% of the concentration for total fatty acids and 2% of the ratio for C₁₆/total fatty acid. Concentrations of fatty acids and phytol were obtained according to the following equation:
Fig. 1. Map showing the location of sampling points and the distributions of high CaCO$_3$ samples (a), high organic carbon samples (b), high $S_1 + S_2$ samples (c), and the type of organic matter tentatively assessed in Fig. 5(d) in the GBR.
where \( \text{Conc}_A \) is the concentration of compound A, \( \text{Area}_A \) is the peak area of compound A on the ion chromatogram of \( m/z \) 74 for fatty acids or \( m/z \) 85 for phytol, \( \text{RF}_A \) is the response factor of compound A, and \( W_{SD} \) is the sample weight. The response factor of saturated fatty acids (\( \text{RF}_{FA} \)) was determined by the analysis of the authentic standard (\( n \)-hexadecanoic acid) according the following formula:

\[
\text{RF}_{FA} = \frac{\text{Amount}_{AS}}{\text{Area}_{AS}}
\]

where \( \text{Amount}_{AS} \) is the amount of an authentic standard (\( n \)-hexadecanoic acid) that was injected through a pyrolysis system, and \( \text{Area}_{AS} \) is the measured peak area on a \( m/z \) 74 ion chromatogram.

The response factors of unsaturated fatty acids (\( \text{RF}_{UFA} \)) and phytol (\( \text{RF}_{PH} \)) were obtained using the following equations:

\[
\text{RF}_{UFA} = \frac{\text{RF}_{AS} \times (\text{Int}_{UFA(\text{total})}/\text{Int}_{UFA(m/z\ 74)})}{(\text{Int}_{AS(\text{total})}/\text{Int}_{AS(m/z\ 74)})}
\]

\[
\text{RF}_{PH} = \frac{\text{RF}_{AS} \times (\text{Int}_{PH(\text{total})}/\text{Int}_{PH(m/z\ 85)})}{(\text{Int}_{AS(\text{total})}/\text{Int}_{AS(m/z\ 74)})}
\]

where \( \text{Int}_{AS(\text{total})} \) and \( \text{Int}_{AS(m/z\ 74)} \) are the measured intensities of total ions and the \( m/z \) 74 fragment ion, respectively, of the authentic standard, \( \text{Int}_{UFA(\text{total})} \) and \( \text{Int}_{UFA(m/z\ 74)} \) are the measured intensities of total ions and the \( m/z \) 74 fragment ion, respectively, of \( n \)-octadecenoic acid, and \( \text{Int}_{PH(\text{total})} \) and \( \text{Int}_{PH(m/z\ 85)} \) are the measured intensities of total ions and the \( m/z \) 85 fragment ion, respectively, of phytol.

**RESULTS**

**\( \text{CaCO}_3 \), total organic carbon (TOC) and total nitrogen (TN) contents**

The \( \text{CaCO}_3 \) content ranged from 15% to 95% (Table 1). While all the samples from the southern area have a \( \text{CaCO}_3 \) content below 75%, all but one sample from the northern area have a \( \text{CaCO}_3 \) content above 75% (Fig. 1a). The \( \text{CaCO}_3 \) content increased with the distance from land (Fig. 2).

The TOC obtained by the vapor method varied between 0.30% and 1.02% (Table 1). The samples with a TOC above 0.5% occurred at the discharged areas of both the Daintree River and Barron River and at the northern outer shelf areas (Fig. 1b). A comparison of the values obtained by the vapor method with those by the washout method for five selected samples indicated that the former are 1.2–2.1 times higher than the latter (Fig. 3). This indicates that 4–52% of organic carbon was lost by discarding the acidic supernatant.

The lost organic matter was likely associated with the carbonate minerals (Yamamuro and Kayanne, 1995; Yamamoto et al., 1997; Yamamoto, 2000). The differences of values between these two methods are much smaller than those for lagoonal...
Table 1. Lithotype, the contents of total carbon (TC), total organic carbon (TOC), inorganic carbon (IC), calcium carbonate (CaCO$_3$), and total nitrogen (TN), Rock-Eval parameters, and the tentative type of organic matter in GBR sediments

<table>
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<th>S. No.</th>
<th>Lithotype</th>
<th>Bulk or residue</th>
<th>Distance (km)</th>
<th>WD (m)</th>
<th>Residue (%)</th>
<th>TC (%)</th>
<th>TOC (%)</th>
<th>IC (%)</th>
<th>CaCO$_3$ (%)</th>
<th>TN (%)</th>
<th>C/N</th>
<th>$T_{max}$ (°C)</th>
<th>S$_1$ (mg/g)</th>
<th>S$_2$ (mg/g)</th>
<th>S$_3$ (mg/g)</th>
<th>P.I. (mg/g)</th>
<th>H.I. (mg/g)</th>
<th>O.I. (mg/g)</th>
<th>S$_1$ + S$_2$ (mg/g)</th>
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</table>

Notes: Halimeda* = calcareous sand and gravel rich in Halimeda fragments, foram** = calcareous sand with benthic foraminifera, B = bulk sediment, R = acid residue, Distance = distance from continental shoreline, WD = water depth, residue = percentage of HCl residue in bulk sediment, TC = total carbon, TOC = total organic carbon, IC = inorganic carbon, C/N = TOC/TN. The values for HCl residue are calculated as whole sediment basis. The type of organic matter (OM type) was tentatively assessed in Fig. 5.
Organic matter in Great Barrier Reef sediments (Yamamuro and Kayanne, 1995) or patch-reefal limestones (Yamamoto et al., 1997) from the Palau Islands. This is due to the higher acid-residue contents of GBR samples than those of Palau samples.

The TOC/TN ratio (C/N ratio) varied from 4.8 to 11.6 (Table 1), and those for most samples ranged within the values typical of marine organisms (C/N = 4–8; Bordowsky, 1965; Stein, 1991). Two samples (Nos. 13 and 14) had high values (Table 1), presumably reflecting a higher plant contribution. The C/N ratio decreased with the distance from the land (Fig. 2).

**Rock-Eval pyrolysis**

GBR sediments showed a unique pyrogram in that S_1 and S_3 values were anomalously high (Table 1). The S_1 value represents the amount of low-molecular-weight organic matter vaporized at 300°C (Espitalié et al., 1977). For recent sediments, the early cracking of some weak chemical bonds occurs at temperature as low as 300°C and a pseudo S_1 peak may be formed (Bordenave, 1993). A GBR sample (No. 3) has biolipids (Yamamoto, 2000). The biolipids mostly comprised the fatty acids of carbon number range below C_{20} (Yamamoto, 2000). The fatty acids have

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Fig. 3. Comparison of bulk sediment (Bulk) with acid residue (HCl) on the total organic carbon content (TOC), C/N ratio, S_1 and S_2 values, T_{max} value, production index (P.I.), and hydrogen index (H.I.) in samples 3–7.
boiling points below 204°C (Gunstone et al., 1994). Although the proportion of free and bound fatty acids is not clear in this study, some parts of lipids can be detected as S₁. The high S₁ value presumably reflects a higher proportion of hydrolyzed lipids in coral reef sediments than the proportions of bound lipids such as phospholipids and glycolipids or geopolymers such as humin and kerogen that are common in normal marine sediments.

A hydrogen index-oxygen index (H.I.-O.I.) plot indicated that bulk sediments are distributed in an extremely high O.I. region, while the acid residues are distributed between typical types II and III organic matters (Fig. 4). Because Rock-Eval pyrolysis has been proposed as a useful tool for distinguishing the type of organic matter in consolidated rocks, the method has less often been applied for recent carbonate sediments (e.g., Rafalska-Bloch and Cunningham, 1986; Kenig et al., 1990). Nevertheless, the H.I. and S₂ value can be used for roughly characterizing the type of organic matter in recent carbonate sediments, while O.I. and S₃ value are useless due to their anomalously high values (Rafalska-Bloch and Cunningham, 1986; Kenig et al., 1990). Anomalously high O.I. values of carbonate rocks result from the degradation of some carbonate minerals such as siderite in a low temperature range (Katz, 1983). Low S₂ and H.I. values of organic-lean samples (TOC < 0.5%) are sometimes attributed to the adsorption of pyrolysates on clay and calcite minerals (Espitalié et al., 1980). The adsorption on minerals also leads to an increase in the Tmax value (Peters, 1986). Comparison of bulk sediments with the acid residues indicated that the acid residues have higher S₁ and S₂ values, production index (S₁/(S₁ + S₂)), and H.I. (Fig. 3). The differences between these methods are attributable to the adsorption of pyrolysate on calcite matrix.

Fig. 4. H.I.-O.I. plots of bulk and acid residue samples from the GBR.

An S₂-TOC plot is recommended to avoid the matrix effects when identifying organic matter type (Langford and Blanc-Valeron, 1990). In Fig. 5, five samples are plotted on the region of type II, while the other samples are plotted on the region of type III (Fig. 5). Because the organic matter in recent sediments cannot be directly correlated to that in consolidated rocks, we use the words “types II and III” tentatively. Type II samples are distributed mostly in the northern outer shelf area, while type III samples are distributed in the northern inner shelf area and the southern area (Fig. 1d). The distribution of type II samples almost coincides with the distributions of high CaCO₃ and S₁ + S₂ samples (Figs. 1a and 1c).

Fig. 5. TOC-S₂ plots of bulk samples from the GBR. The boundary of organic matter type was defined in Langford and Blanc-Valeron (1990).
**Lipids and lignin phenols**

Major TMAH pyrolysates were methyl esterified fatty acids (Fig. 6) and methoxy phytol. Methoxy lignin phenols and methoxy polyols (sugars) were detected in trace amounts.

The concentration of fatty acids varied between 4 and 170 µg/g (Table 2). The fatty acids were comprised of \( n \)-fatty acids (<C\(_{26}\)), iso-fatty acids (C\(_{13}\)–C\(_{17}\)), and anteiso-fatty acids (C\(_{13}\), C\(_{15}\) and C\(_{17}\)). The \( n \)-fatty acid homologues showed a monomodal distribution with a maximum at C\(_{16}\) and a strong even carbon number preference (Fig. 6). Mono-unsaturated fatty acids detected were minor in this study. An analysis by a solvent extraction method indicated that significant amounts of polyunsaturated fatty acids exist in a GBR sample (No. 3) (Yamamoto, 2000). In contrast, the poly-unsaturated fatty acids were not detected in the same sample by TMAH-pyrolysis-GC/MS in this study. This is presumably due to the degradation of poly-unsaturated fatty acids during the pyrolysis. Nevertheless, the carbon number profiles of saturated fatty acids are almost identical to those obtained by a solvent extraction method. Total fatty acid concentration increased with distance from the land (Fig. 7a), whilst the ratio of branched (iso and anteiso) to total fatty acid concentration (branched/total fatty acid ratio) decreased (Fig. 7b).

Phytol is a hydrolyzed product of photosynthetic chlorophyll of plants (Maxwell et al., 1972), and its presence indicates an algal contribution. The phytol is common in lagoonal sediments (Shaw and Johns, 1985). High phytol concentration was found in the northern outer shelf area (Table 1; Fig. 7c).

Trace amounts of lignin phenols (vanillic acid and syringaldehyde) were detected in six samples. Because of low resolution due to their extremely low concentrations, the peaks of vanillic acid and

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**Fig. 6.** Gas chromatograms of m/z 74 fragment ion of an outer-shelf sample (No. 3) and an inner-shelf sample (No. 13) from the GBR.
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**Table 2. Concentrations of fatty acids and phytol and the occurrence of lignin phenols in GBR sediments**

| Notes: n = normal, i = iso, a = anteiso, Total = total fatty acids, Sat = saturated fatty acids, Unsat = unsaturated fatty acids, Br = branched (iso + anteiso)-fatty acids, Va = vanillic acid, Sh = syringaldehyde, u.d.l. = under detection limit. |
Fig. 7. Map showing the distributions of samples with high fatty acid concentration (a), high branched/total fatty acid ratio (b), high phytol concentration (c), and detectable lignin phenols (d) in the GBR.
syringaldehyde cannot be separated completely on the gas chromatograms. The lignin phenols were detected in samples both from the discharged area of the Daintree River (Nos. 13 and 14) and the northern outer shelf areas (Nos. 3, 4, 7, and 8) (Fig. 7d).

**DISCUSSION**

*The characteristics of organic matter in the GBR*

CaCO₃ content increased with distance from the land (Fig. 2). This tendency is true in the whole GBR, and it most likely reflects the terrigenous inflow from the continent (Maxwell, 1968). C/N ratio decreased with distance from the land (Fig. 2) and showed a significant negative correlation with CaCO₃ content \( r = 0.77, p < 0.01 \) (Fig. 8b). S₁ and S₂ values increased with increasing CaCO₃ content (Fig. 8c), indicating the increase of marine lipids in the outer shelf areas.

Both total fatty acid and phytol concentrations increased with increasing CaCO₃ content \( r = 0.58, p < 0.01 \) and \( r = 0.44, p < 0.05 \) (Figs. 9a and 9b). Phytol derives from the phytol group of chlorophyll, and it is highly unstable in the water column and the sediment surface (Volkman and Maxwell, 1986). Thus the high concentration of phytol indicates the high activity of benthic photosynthetic algae and/or the high preservation of lipids in sediment. The phytol concentration has significant correlations with total fatty acid concentration \( r = 0.87, p < 0.01 \) (Fig. 10d) and \( S₁ + S₂ \) value \( r = 0.78, p < 0.01 \), suggesting that the lipid concentration is proportional to the contribution of intact or fresh organic matter produced by algae. Branched (iso and anteiso) fatty acids derive from the acyl component of eubacterial membrane (Kaneda, 1991). The abundance ratio of branched to total fatty acids (branched/total fatty acid ratio) decreased with increasing CaCO₃ content \( r = 0.56, p < 0.01 \) (Fig. 9c) and showed a significant negative correlation with total fatty

![Fig. 8. Plots of total organic carbon content (a), C/N ratio (b), \( S₁ \) and \( S₂ \) values (c), \( S₃ \) value (d), production index (e), and \( T_{max} \) value (f) against CaCO₃ content in GBR sediments. A regression line was indicated only in the case that the correlation is significant \( r > 0.42, p < 0.05 \).](image-url)
acid concentration ($r = 0.86, p < 0.01$; Fig. 10a), which implies that eubacteria are involved in the degradation of lipids. This evidence indicates that intact or fresh organic matter is preserved in outer shelf CaCO$_3$-rich sediments due to relatively low eubacterial activity, which is concordant with the previous observation that phospholipids increased with the distance from the land along the Cairns-Arlington Reef transect (Johns et al., 1994).

Rock-Eval production index (P.I.) has a negative correlation with CaCO$_3$ content ($r = 0.77, p < 0.01$; Fig. 8e). The P.I. represents the proportion of lower-molecular-weight organic matter vaporized at 300°C and is used as a maturity index (Espitalié et al., 1977). In this case, however, the P.I. presumably reflects either the ratio of free to bound lipids or the vaporized fraction without adsorption on calcite. Although the former is concordant with the increase of phospholipids towards the offshore area (Johns et al., 1994), the latter is also the case. $T_{\text{max}}$ increased with increasing CaCO$_3$ content ($r = 0.65, p < 0.01$; Fig. 8f). This is also attributable either to the ratio of free to bound lipids or to the vaporized fraction without adsorption on calcite.

**Factors controlling the degradation of organic matter**

In this study, the occurrence of lignin phenols was independent of the distance from land (Fig. 7d). This suggests that the occurrence of lignin is controlled by the preservation of organic matter rather than the supply of terrigenous matter. The water is clearer and the water turbidity is lower in the outer shelf area (Wolanski, 1994). The lower water turbidity benefits to preventing the oxidative degradation of organic matter by the decrease of free oxygen to the interstitial water of sediment, but also to increasing the photo-oxidation of organic matter on the sediment surface. If the former effect is dominant, the occurrence of lignin may relate to the area’s lower water turbidity. Johns et al.

**Fig. 9.** Plots of total fatty acid concentration (a), phytol concentration (b), branched/total fatty acid ratio (c), $a$-$C_{15}/i$-$C_{15}$ fatty acid ratio (d), and $a$-$C_{17}/i$-$C_{17}$ fatty acid ratio (e) against CaCO$_3$ content, and the plot of $a$-$C_{15}/i$-$C_{15}$ fatty acid ratio against $a$-$C_{17}/i$-$C_{17}$ fatty acid ratio (f) in GBR sediments. A regression line was indicated only in the case that the correlation is significant ($r > 0.42, p < 0.05$).
al. (1994) attributed the increase of intact lipids with the distance from land in the GBR to the decrease of water turbidity with the deepening water column. This, however, more likely reflect the higher production of intact lipids by benthic organisms rather than the lower degradation degree of organic matter in the outer shelf area. The effect of water turbidity is still questionable.

An alternative factor is the difference in the nature of organic matter in the carbonate and noncarbonate matrices of sediments. Yamamoto et al. (1997) suggested the possible role of impermeable carbonate matrix in preventing the degradation of organic matter, based on the observation that lipids from patch-reefal limestones were solely of coral origin. A study of a GBR sample (No. 3) demonstrated that the lipids liberated by the dissolution of carbonates with acidification (carbonate-associated lipids) enriched microalgal lipids such as poly-unsaturated fatty acids, while the lipids from the acid residue (noncarbonate-associated lipids) enriched higher plant- and diatom-derived lipids (Yamamoto, 2000). The branched/total fatty acid ratio of carbonate-associated lipids (0.014) is lower than that of noncarbonate-associated lipids (0.035) in this sample (Yamamoto, 2000). This indicates that the contribution of eubacteria to carbonate-associated lipids is lower than that to noncarbonate-associated lipids, implying the possible role of impermeable carbonate matrix in preventing organic matter degradation. The high preservation rate of lipids in CaCO₃-rich sediments is attributable to this preservation effect of impermeable carbonate matrix.

**Branched fatty acid profile and eubacterial activity**

The occurrence of branched (iso and anteiso) fatty acids in eubacteria is not nearly as common as that of n-fatty acids but is still very significant as the acyl constituent of phospholipids of
eubacterial membrane (Kaneda, 1991). The fatty acid profile of a bacterium with a branched lipid type is affected by its growth condition such as growth phase, temperature, pH, oxygen supply, carbon sources, and an extensive supply of single primer sources (Kaneda, 1991). The phase transition temperatures of the phospholipids with iso-acyl chains are 18–28°C lower than those with n-acyl chains, and those with anteiso-acyl chains are about 20°C lower than those with iso-acyl chains (Kaneda, 1991). Therefore, the composition of membrane n-, iso-, and anteiso-fatty acids is altered by varying growth temperature to maintain the proper membrane fluidity at a given temperature (Kaneda, 1991). Although the geochemical significance of the ratios of anteiso- to iso-fatty acids is not clear, the physiological property leads us to speculate the use of the ratio as a paleotemperature indicator like an alkenone paleothermometry.

In this study, the ratios of anteiso- to iso-isomers of C₁₅ fatty acids (a-15/i-15 ratio) and C₁₇ fatty acids (a-17/i-17 ratio) increased southwards (Fig. 11). The latitudinal variation of the studied area is about 2°, and the variation of annual mean temperature ranges within 1°C (NOAA, 1998). The temperature variation is much smaller than the difference of the phase transition temperature between phospholipids with iso-acyl and those with anteiso-acyl chains, and therefore it is hard to test the effect of growth temperature to a-15/i-15 and a-17/i-17 ratios using this sample set.

On the other hand, the a-15/i-15 and a-17/i-17 ratios have significant negative correlations with total fatty acid concentrations ($r = 0.82, p < 0.01$ and $r = 0.72, p < 0.01$; Figs. 10b and 10c) and positive correlations with branched/total fatty acid ratio ($r = 0.73, p < 0.01$ and $r = 0.52, p < 0.05$; Figs. 10e and 10f). This indicates that a-15/i-15 and a-17/i-17 ratios are closely related to the degree of eubacterial degradation. The ratios are affected by nonthermal physiological and environmental factors such as growth phase, pH, oxygen supply, carbon sources, and an extensive supply of single primer sources (Kaneda, 1991). Thus the a-15/i-15 and a-17/i-17 ratios most likely reflect some growth condition that is related to the degree of eubacterial activity. The increases of a-15/i-15 and a-17/i-17 ratios southwards possibly reflect higher eubacterial degradation in samples from the southern area. This suggests that a-15/i-15 and a-17/i-17 ratios can be potentially used as the indicator of eubacterial activity.

**CONCLUSIONS**

Rock-Eval $S_1$ and $S_3$ values are anomalously high in GBR sediments. The high $S_1$ value presumably reflects a higher proportion of hydrolyzed lipids in coral reef sediments. The high $S_3$ value most likely results from the degradation of carbonate minerals in a low temperature range.

Associated with the CaCO₃ increase towards the offshore area, the C/N ratio decreased, $S_1$ and $S_2$ values increased, and total fatty acid and phytol concentrations increased. The changes have
negative correlations with the branched/total fatty acid ratio, implying that the degree of eubacterial activity during early diagenesis is reflected.

The occurrence of lignin phenols was independent of the distance from the land, suggesting that it was controlled by the preservation rate of organic matter rather than the supply of terrigenous matter.

The higher preservation of lipids and lignin phenols in CaCO₃-rich sediments is attributable to their higher preservation effect by impermeable carbonate matrix.

Both a-15/i-15 and a-17/i-17 ratios have significant negative correlations with total fatty acid concentration and have positive correlations with branched/total fatty acid ratio, indicating that a-15/i-15 and a-17/i-17 ratios are closely related to the degree of eubacterial degradation of organic matter. This suggests that a-15/i-15 and a-17/i-17 ratios can be potentially used as the indicator of eubacterial activity.

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