METHANE IN THE REEF FLAT POREWATERS OF DAVIES REEF, GREAT BARRIER REEF (Australia)

PRESENCE DE METHANE DANS LES EAUX INTERSTITIELLES DU PLATIER RECIFAL DE DAVIES REEF, GRANDE BARRIERE (Australie)

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ABSTRACT

Dissolved methane was detected in the interstitial porewater from three of four wellholes sampled in the reef flat of Davies Reef, Great Barrier Reef, Australia; this is apparently the first report of methane in such an environment.

Porewater was collected at depths of 0.5 - 5.3 m into the reef framework, where methane concentrations ranged between 60 - 370 nM. These waters were anoxic, and contained highly elevated nutrient levels, but, surprisingly, contained sulfate concentrations which were not depleted from seawater values.

The presence of methane in these sulfate-containing porewaters is hypothesized to result from one or more of the following processes: a) methane production in sulfate-depleted microzones (visible porosity of reef framework is 5-10%); b) methane production in deeper, possibly sulfate-depleted zones of the reef framework, with upward transport of the produced methane; c) methane production from the oxidation of short-chain amines or other organic compounds for which methanogens can out-compete sulfate reducers.

These results, when combined with data from other reef systems, suggest that anaerobic oxidation of organic material, and the subsequent oxidation of reduced decomposition products, may play an important role in controlling geochemical processes such as carbonate dissolution and cementation in the internal porewaters of the reef.

This research was conducted as a part of the US-Australian MECOR (Microbial Ecology of Coral Reefs) project.

RESUME

Du méthane dissous a été décelé dans l'eau interstitielle provenant de trois de quatre puits forés sur le platier du récif de Davies. Il s'agit semble-t-il de la première référence à la présence de méthane dans ce type de milieu.

De l'eau interstitielle a été récoltée à des profondeurs de 0,5 à 5,3 m dans la masse récifale, avec une concentration en méthane variant de 60 à 370 nM. L'eau de ces échantillons était anoxique et présentait des concentrations très élevées en sels nutritifs. Cependant, et de façon quelque peu surprenante, les concentrations en sulfate n'étaient pas différentes des valeurs normales pour l'eau de mer.

On peut admettre que la présence de méthane dans ces eaux interstitielles riches en sulfates est la conséquence de l'un (ou d'une combinaison) des processus suivants : a) -production de méthane dans des microzones appauvries en sulfates (la porosité apparente du substrat récifal est de 5 à 10%); b) -production de méthane dans des zones plus profondes peut-être appauvries en sulfates, avec transport vers le haut du méthane produit. c) -production de méthane résultant de l'oxydation d'amines à chaîne courte ou d'autres composés organiques pour lesquels les méthanogènes l'emportent sur les sulfatoréducteurs.

Ces résultats, lorsqu'on les ajoute à des données obtenues dans d'autres systèmes récifaux, indiquent que l'oxydation anaérobie de matière organique, ainsi que l'oxydation subséquente des produits de décomposition réduits, pourrait jouer un rôle important dans la régulation de processus géochimiques tels que la dissolution des carbonates et la cimentation, dans l'eau interstitielle de la masse récifale.

Ce travail de recherche a été conduit dans le cadre du projet australo-américain MECOR (Microbial Ecology of Coral Reefs).
This paper reports the measurement of dissolved methane in the internal pore waters of a coral reef flat. The presence of methane in these waters, along with the associated elevated levels of inorganic nutrients and the absence of oxygen, indicates that anaerobic decomposition reactions may occur in modern carbonate frameworks. The occurrence of methane is of particular interest because it indicates the presence of the highly reducing conditions necessary for methanogenesis.

Although geologists and geochemists have traditionally viewed carbonate reef frameworks as sites for the deposition of fine-grained material and the precipitation of carbonate cements (Macintyre, 1977; Marshall, 1983a, 1983b), interest has generally focused on the involvement of aerobic inorganic processes. The data presented here, however, suggest that organic inputs and transformations within reef frameworks may be more important than previously thought. Anaerobic conditions, presumably the result of decomposition of structural, sedimented, and/or dissolved organic matter, were found within Davies Reef (Great Barrier Reef, Australia) and may be a common occurrence in the internal cavities of other carbonate frameworks. It is possible that the end products of these anaerobic organic matter transformations may significantly influence the occurrence and kinetics of inorganic geochemical processes such as carbonate cementation and dissolution.

There have been several reports of anaerobic processes in intertidal and lagoonal carbonate sediments (Skyring and Chambers, 1976; Hines and Lyons, 1982; Skyring et al., 1983), but only a few such reports exist for carbonate framework environments. Very low oxygen concentrations have been measured in the pore waters of both dead coral rubble (DiSalvo, 1971) and intact carbonate frameworks (DiSalvo, 1971; Zankl and Multer, 1977; Risk and Muller, 1983); in these cases it has been assumed that the depletion of oxygen was due to the oxidation of organic material associated with fine-grained sediment that is commonly trapped in the internal cavities (Ginsburg and Schroeder, 1973; Ginsburg, 1983). These processes have also been reflected by the elevated nutrient concentrations (Andrews and Muller, 1983; Risk and Muller, 1983) and changes in pH and alkalinity (Zankl and Multer, 1977; Risk and Muller, 1983) with respect to overlying seawater that have been reported for carbonate framework porewaters.

Direct evidence for anaerobic organic matter oxidation within carbonate framework sediments was provided by the presence of sulfide-producing grey-black voids in coral frameworks (DiSalvo, 1971), and the observation that methane concentrations increase in seawater as it passes over the reef flat at Kaneohe Bay, Hawaii (Webb, 1977).

Previous analyses of Davies Reef porewater (Buddemeier and Oberdorfer, 1983) indicated that these waters were anoxic and contained elevated levels of sulfide and nutrients as compared to overlying seawater (Table 1). These results suggested that anaerobic decomposition of organic material was occurring within the reef framework, which led to my investigation of the possibility of methane accumulation.

### FIELD LOCATION AND METHODS

Samples of pore water for this study were collected from the windward reef flat of Davies Reef, Great Barrier Reef, Australia (18°48'S, 147°39'E) using bore holes which had been drilled, cased, and equipped with sampling tubes; the tubes allowed samples to be collected from the bottom of each hole by means of a battery-operated peristaltic pump operated from a small boat anchored above the reef. These wells were constructed in 1983 by M. Sandstrom and coworkers, Australian Institute of Marine Science, Townsville, Qld.

Samples for this study came from depths of 0.5 to 5.3 m below the reef flat/seawater interface, at sites near the front and middle of the flat (Fig. 1). Initial processing of samples was conducted on shipboard at the field.

**Table 1.** Arithmetic means of analyses for Davies Reef porewaters obtained from wells shown in Fig. 1, and for seawater overlying the reef flat. NA = data not available. O₂, NH₄, NO₃+NO₂, PO₄, and Si data are from samples collected 12-13 Feb 1983 (n=13); S²⁻ data are from samples collected 7 Mar 1983 (n=2); pH, alkalinity (Alk), and ECₐO₂ data are from samples collected 11-12 Mar 1983 (n=3). Data from M.W. Sandstrom and R.W. Buddemeier (reported by Buddemeier and Oberdorfer, 1983).

<table>
<thead>
<tr>
<th>Site</th>
<th>O₂ (µM)</th>
<th>NH₄ (µM)</th>
<th>NO₃+NO₂ (µM)</th>
<th>PO₄ (µM)</th>
<th>S²⁻ (µM)</th>
<th>pH (meq/l)</th>
<th>Alk (meq/l)</th>
<th>ECₐO₂ (µM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Front-shallow (FS)</td>
<td>1.9</td>
<td>63</td>
<td>0.01</td>
<td>1.1</td>
<td>9.8</td>
<td>7.76</td>
<td>2.27</td>
<td>2.16</td>
</tr>
<tr>
<td>Front-deep (FD)</td>
<td>4.5</td>
<td>32</td>
<td>0.37</td>
<td>1.2</td>
<td>9.3</td>
<td>7.74</td>
<td>2.32</td>
<td>2.21</td>
</tr>
<tr>
<td>Middle-shallow (MS)</td>
<td>4.5</td>
<td>7.4</td>
<td>0.32</td>
<td>0.74</td>
<td>2.2</td>
<td>7.76</td>
<td>2.20</td>
<td>2.05</td>
</tr>
<tr>
<td>Middle-deep (MD)</td>
<td>0.64</td>
<td>56</td>
<td>0.07</td>
<td>1.1</td>
<td>24</td>
<td>7.75</td>
<td>2.41</td>
<td>2.30</td>
</tr>
<tr>
<td>Overlying seawater</td>
<td>170</td>
<td>0.34</td>
<td>0.57</td>
<td>0.18</td>
<td>NA</td>
<td>8.23</td>
<td>2.35</td>
<td>1.99</td>
</tr>
</tbody>
</table>
Methane samples were analyzed by gas-phase extraction and gas chromatography (Kipphut and Martens, 1982). Samples were collected in 10 ml gas-tight glass syringes and then extracted with He in the field; the extracted gases were returned to the shore-based laboratory for analysis by gas chromatography and flame ionization detection (Tracor 222). Sulfate was measured gravimetrically as BaSO$_4$ (Hartens and Klump, 1980).

**Fig. 1. Location of sample wells on the windward reef flat of Davies Reef.** The sampling depths of the wells (the distances into the reef flat from which samples were pumped) are given in meters.

### RESULTS AND DISCUSSION

Measurable levels of dissolved methane were found in the porewaters of three of the four wells sampled (Table 2) despite the existence of sulfate concentrations that were not measurably depleted from surface seawater values (ca. 28.5 mM). These sulfate levels were surprising because previous studies have indicated that, in general, sulfate-reducing bacteria can out-compete methane-producing bacteria for most of the available sources of reduced compounds in marine sediments containing more than ca. 1 mM sulfate (e.g., Martens and Berner, 1974; Nedwell and Benat, 1981; Sansome and Martens, 1981).

The presence of methane in these sulfate containing porewaters is hypothesized to be the result of one or more of the following possible processes: a) methane production in nearby sulfate-depleted microzones; b) methane production in sulfate-depleted zones deeper in the reef, with upward diffusion of the produced methane; c) methane production from the decomposition of organic compounds that are not utilized by sulfate-reducing bacteria (e.g., short-chain methylated amines or dimethylsulfide (Oremland and Polcin, 1982; King, 1984)).

### Table 2. Methane and sulfate data for samples collected 20 August 1984, and estimates of the concentrations in the overlying surface seawater. Numbers in parentheses are standard deviations; n = the number of replicate samples analyzed (two methane replicates were analyzed per sample container; five or six containers were analyzed per site); nd = not detectable (detection limit = ca. 25 nM methane).

<table>
<thead>
<tr>
<th>Site</th>
<th>Sulfate (mM)</th>
<th>Methane (nM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FS</td>
<td>28.3</td>
<td>150</td>
</tr>
<tr>
<td></td>
<td>(0.4)</td>
<td>(10)</td>
</tr>
<tr>
<td></td>
<td>n=2</td>
<td>n=10</td>
</tr>
<tr>
<td>FD</td>
<td>29.2</td>
<td>373</td>
</tr>
<tr>
<td></td>
<td>(0.6)</td>
<td>(14)</td>
</tr>
<tr>
<td></td>
<td>n=3</td>
<td>n=9</td>
</tr>
<tr>
<td>MS</td>
<td>27.4</td>
<td>nd</td>
</tr>
<tr>
<td></td>
<td>(1.3)</td>
<td>n=12</td>
</tr>
<tr>
<td></td>
<td>n=2</td>
<td></td>
</tr>
<tr>
<td>MD</td>
<td>30.1</td>
<td>62</td>
</tr>
<tr>
<td></td>
<td>(0.4)</td>
<td>(8)</td>
</tr>
<tr>
<td></td>
<td>n=3</td>
<td>n=11</td>
</tr>
<tr>
<td>Surface South Pacific Tropical Seawater</td>
<td>28.5$^a$</td>
<td>1.6-2.0$^b$</td>
</tr>
</tbody>
</table>

$^a$ - Salinity = 35 0/oo.

$^b$ - Data from Lamontagne et al. (1974).

It is likely that anaerobic processes in reef matrices occur in environments with restricted circulation; these environments may possibly range in size from sub-millimeter microzones to cavities with diameters of up to tens of centimeters (Garrett et al., 1971; Scoffin, 1972; W.J. Wiebe, pers. comm., 1984). However, it has been shown that methane, if in sufficient concentration, can be transported moderate distances in sediments (at least several meters) before oxidation and incorporation into carbonate cements (Allen et al., 1969; Roberts and Whelan, 1975; Nelson and Lawrence, 1984). Thus, it is possible that the effects of anaerobic decomposition on carbonate dissolution/cementation may be significant some distance from the actual site of organic matter oxidation.

Methane oxidation has been fairly well studied in marine systems, and the residence time of methane in sediments and coastal waters has been measured to range from 0.3 to 0.9 years (Sansome and Martens, 1978; Scranton and Brewer, 1978; Iverson and Blackburn, 1981; Griffiths et al., 1982; Devol, 1983; Lin, 1983; Alperin and Reeburgh, 1984). Because the residence time of porewater in the reef flat of Davies Reef has been estimated to be approximately one year (Oberdorfer and Buddemeier, 1983), it is reasonable to hypothesize that much of the methane produced in this reef flat is oxidized within the reef framework.

Measurement of cement $^{13}C/^{12}C$ ratios should provide information on the importance of methane in cementation, because methane-derived cements...
have very "light" stable carbon isotopic compositions compared to that of seawater inorganic carbon (Allen et al., 1969; Roberts and Whelan, 1975; Nelson and Lawrence, 1984). However, isotopically light cements will ultimately be converted by diagenesis to isotopic ratios resembling the bulk solid phase (Friedman, 1975).

Methane that is not utilized in the reef framework may leave the interior of the reef flat for the overlying water column, where it may be oxidized or released to the atmosphere. This hypothesis is supported by the observation that the methane concentration in seawater increases as it passes over a reef flat in Kaneohe Bay, Hawaii (Wehrl, 1977). The flux into the overlying seawater was estimated to be 2.6 μmol/m²/hr, with the flux to the atmosphere approximately 10% of that value.

In conclusion, the existence of elevated methane concentrations demonstrates the presence of active anaerobic organic matter decomposition within the reef flat studied. Further research will determine the ubiquity and importance of these processes in other carbonate frameworks and should provide a better understanding of the specific roles and effects of anaerobic diagenesis on geochemical processes such as carbonate cementation and/or dissolution.

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REFERENCES


