The stable carbon isotopic composition of organic material in platform derived sediments: implications for reconstructing the global carbon cycle

AMANDA M. OEHLERT*, KATHRYN A. LAMB-WOZNIAK†, QUINN B. DEVLIN*, GRETA J. MACKENZIE*, JOHN J. G. REIJMER‡ and PETER K. SWART*

*Rosenstiel School of Marine and Atmospheric Sciences (RSMAS/MGG), University of Miami, 4600 Rickenbacker Causeway, Miami, FL 33149, USA (E-mail: aoehlert@rsmas.miami.edu)
†ExxonMobil Exploration, 222 Benmar Drive, Houston TX 77060, USA
‡Faculty of Earth and Life Sciences, Sedimentology and Marine Geology Department, VU University Amsterdam, de Boelelaan 1085, 1081 HV Amsterdam, the Netherlands

Associate Editor – Tracy Frank

ABSTRACT

In pelagic carbonate sediments, the degree to which the $\delta^{13}C$ values of inorganic and organic fractions co-vary has been used to interpret rates of production, burial and decomposition of organic carbon. This relationship is relatively consistent through time, permitting estimates of organic carbon production and preservation. However, as the majority of pelagic sediments older than 200 Myr have been subducted, carbonate sediments deposited in epeiric seas and platforms are often substituted for pelagic carbonates in analyses of ancient global carbon cycling. There are well-known pitfalls to using shallow marine carbonate materials, including diagenesis, semi-isolation of depositional environments and input of different types of sediments with varying inorganic $\delta^{13}C$ ($\delta^{13}C_{\text{inorganic}}$) values, which can obscure any global signatures. One method used to assess whether global changes in $\delta^{13}C$ are accurately represented by $\delta^{13}C_{\text{inorganic}}$ records is to examine variations in the $\delta^{13}C$ of co-occurring organic material ($\delta^{13}C_{\text{organic}}$). If a $\delta^{13}C_{\text{organic}}$ record co-varies with a co-occurring $\delta^{13}C_{\text{inorganic}}$ record, it is argued that the signals must be related to variations in the global carbon cycle. This assumption has been investigated by analysing the isotopic composition of the organic carbon preserved in the uppermost 150 m of periplatform sediments recovered during ODP Leg 166 from the western margin of Great Bahama Bank. The $\delta^{13}C_{\text{organic}}$ values measured in this study were compared to previously published $\delta^{13}C_{\text{inorganic}}$ records measured on identical samples, thus allowing a study of the correlation between the two records through time. These analyses showed that the correlation coefficient between $\delta^{13}C_{\text{inorganic}}$ and $\delta^{13}C_{\text{organic}}$ increased from the proximal location (Site 1005, $r^2 = 0.1$), to the distal site (Site 1006, $r^2 = 0.63$). The importance of platform-derived carbonate and organic material at the proximal location, Site 1005, is reflected in the absence of a co-variation between inorganic and organic $\delta^{13}C$ records, which exhibit no correlation on the platform itself. In contrast, the co-variance in $\delta^{13}C$ values at the basinal location, Site 1006, is explained by a two-point mixing model, which demonstrates the importance of both pelagic and platform-derived carbonate and organic carbon in generating the positive correlation between the organic and inorganic $\delta^{13}C$ values; this results in a correlation between $\delta^{13}C_{\text{inorganic}}$ and $\delta^{13}C_{\text{organic}}$ records at Site 1006 that is unrelated to global carbon cycling. Such data question the applicability of using $\delta^{13}C_{\text{organic}}$ values...
to support the ability of $\delta^{13} C_{\text{inorganic}}$ values to record global carbon cycling in carbonates recovered from environments where multiple sources of carbonate and organic carbon contribute to the bulk $\delta^{13} C$ signal.

**Keywords** Carbon cycle, carbon isotopes, carbonate platforms, organic matter, pCO$_2$.

**INTRODUCTION**

Changes in the $\delta^{13} C$ of carbonate sediments through geological time have been interpreted to represent variations in the rate of organic carbon production relative to rates of organic carbon burial and preservation (Hayes *et al*., 1999). In a general sense, elevated $\delta^{13} C$ values in carbonates reflect increased production and/or burial of organic material, while depletions in the $\delta^{13} C$ values indicate increased oxidation of organic material and hence a lower proportion of organic carbon burial (Veizer & Hoefs, 1976; Schidlowski, 1979; Shackleton, 1985). In reconstructions of global carbon cycling over the past ca 200 Myr, the preferred types of carbonate for obtaining $\delta^{13} C$ values are oceanic carbonate sediments and fossils, specifically foraminifera; these are believed to accurately reflect variations in the $\delta^{13} C$ values of the dissolved inorganic carbon (DIC) in the oceans (Zachos *et al*., 2001). For example, over the past 50 Myr the $\delta^{13} C$ values of foraminifera and bulk oceanic sediments have become increasingly more negative (Shackleton & Hall, 1980; Broecker & Woodruff, 1992). This negative trend is interpreted to be the result of a transfer in the order of 10$^{20}$ g of carbon from an organic to the inorganic carbon reservoir (Shackleton, 1985).

As a result of the absence of pelagic records older than 200 Myr, either macrofossils, like brachiopods and belemnites, or bulk sediments have to be analysed to obtain $\delta^{13} C$ records. These sediments and organisms were often deposited in more restricted environments, such as epeiric seas, ramps or carbonate platforms. While these records can be correlated in some instances with trends in the oceanic $\delta^{13} C$ record (Vahrenkamp, 1996), skeletal and bulk $\delta^{13} C$ records from such environments can present significant interpretive problems, in that true open ocean conditions may not have been present at these locations, there may have been vital or mineralogical effects which produced carbonates with different $\delta^{13} C$ values, or the sediments and fossils may have been diagenetically altered. A common test to verify the global nature of $\delta^{13} C_{\text{inorganic}}$ records from carbonates older than 200 Ma is to correlate coeval $\delta^{13} C$ records from several basins. If the $\delta^{13} C$ trends are comparable, it is assumed that the record represents an accurate global signal, especially when the basins are geographically distant. In a recent study, Holocene to Middle Miocene $\delta^{13} C$ values measured in periplatform sediments from Great Bahama Bank (GBB) were compared with $\delta^{13} C$ values measured in a pelagic sequence off the coast of Africa (Swart & Eberli, 2005). Five cores on a proximal to distal transect were analysed for the $\delta^{13} C$ values of the carbonate sediments. The cores reached the latest Oligocene, and time equivalent sequences were compared across the transect. The sites sampled upper slope to basin depositional environments and are composed of a mixture of oceanic and platform materials (periplatform sediments; Schlager & Ginsburg, 1978). While the $\delta^{13} C$ values measured in the bulk carbonate sediments of each sequence were correlatable between the various sites, the values showed no relationship to the global carbon cycle as represented in other deep-sea records (Shackleton, 1985; Zachos *et al*., 2001; Swart & Eberli, 2005). In fact, the $\delta^{13} C$ values of these periplatform sediments showed an opposite trend, becoming more enriched over the past 25 Myr. It was proposed that carbonate from the platform surface with relatively heavy $\delta^{13} C$ values (+4.5 to +6‰; Swart *et al*., 2009) mixed with oceanic carbonate with relatively light $\delta^{13} C$ values (0 to +1‰; Milliman, 1974).

As the $\delta^{13} C$ values were found to be correlated at each of the GBB sites (Swart & Eberli, 2005), it was concluded that stratigraphic changes observed at all sites are controlled by sea-level changes. During periods of high sea-level, abundant amounts of surface platform sediments and organic material are contributed to the slope, whereas during sea-level lowstands, there is a greater contribution from pelagic material. This phenomenon was recognized globally in $\delta^{13} C$ records measured in sediments adjacent to other carbonate platforms and margins in the Indian Ocean (Maldives), Great Barrier Reef (Queensland Plateau) and the South Australian Bight (Swart, 2008). These findings demonstrate that globally synchronous changes in inorganic $\delta^{13} C$ values
Carbon isotopes in organic material from carbonate platforms

exist; however, they are unrelated to the secular changes in the global carbon cycle preserved in pelagic-derived carbonates deposited in the deep sea. Consequently, the existence of similar $\delta^{13}C$ records at globally disparate locations cannot be used to confirm that the $\delta^{13}C_{\text{inorganic}}$ values are representative of variations in the global carbon cycle (Swart, 2008).

The importance of platform sediment contributions to the periplatform environment is not limited to the Pleistocene sequence that experiences high amplitude, high frequency sea-level variations. In older sediments, such as the Late Jurassic of the Vocontian Basin, it has been clearly demonstrated that carbonate mud accumulating in the basin was largely dependent on sediment export related to cyclical variations in carbonate production in the shallow-marine settings of the Swiss Jura (Colombie & Strasser, 2005). Similar relationships were observed for the Toarcian in the Umbria–Marche and Lusitanian Basins (Pittet & Mattioli, 2002; Mattioli & Pittet, 2004), the Oxfordian–Kimmeridgian of the South-west German Basin (Pittet et al., 2000; Pittet & Mattioli, 2002), the Nahr Umr Basin in Oman (Aptian–Albian; Immemhauser et al., 1999) and the Middle–Upper Triassic hemipelagites of the Dolomites (Preto et al., 2009). These results show that a model describing the dependence of $\delta^{13}C_{\text{inorganic}}$ values on sea-level change is applicable in ancient as well as modern shallow marine settings.

Determining whether or not an inorganic $\delta^{13}C$ record ($\delta^{13}C_{\text{inorganic}}$) from platform-derived sediments accurately records global carbon cycling is problematic. Often, the $\delta^{13}C$ of co-occurring organic material ($\delta^{13}C_{\text{organic}}$) is used to corroborate changes in the $\delta^{13}C_{\text{inorganic}}$ signal. Typically, if both the $\delta^{13}C$ of the inorganic and organic portions co-vary in a sedimentary sequence, it is assumed that the variations in the $\delta^{13}C_{\text{inorganic}}$ values are robust and indicate a real change in the $\delta^{13}C_{\text{inorganic}}$ of the environment (Margaritz et al., 1986; Gale, 1993; Underwood et al., 1997; Jarvis et al., 2006). In addition, differences between the $\delta^{13}C$ of the organic and inorganic fractions have been suggested to be indicative of the pCO$_2$ of the depositional environment (Popp et al., 1989). Although it is widely recognized that the origin of the organic material exerts an overriding control over the $\delta^{13}C_{\text{organic}}$ value (and thus the $\delta^{13}C$ of diagnostic organic compounds is preferred to that of bulk organic material; Hayes et al., 1990), there are still numerous studies which report only the bulk organic $\delta^{13}C$ values. These studies use bulk $\delta^{13}C_{\text{organic}}$ values to support their interpretation of secular changes in $\delta^{13}C_{\text{inorganic}}$ values from carbonates, as well as changes in global pCO$_2$. In doing so, these studies make the inherent assumption that the $\delta^{13}C$ of the bulk organic and inorganic fractions are correlated from inception and that this relationship is consistent through time.

These assumptions are tested in this paper by comparing published records of $\delta^{13}C_{\text{inorganic}}$ (Swart & Eberli, 2005) to measurements of bulk $\delta^{13}C_{\text{organic}}$ records in identical samples. In addition, published $\delta^{13}C_{\text{inorganic}}$ distributions are compared with $\delta^{13}C_{\text{organic}}$ analyses of sedimentary organic material in the surface sediments of GBB, as well as the various individual organic components (algae, sea grasses, etc.) which degrade to form the sedimentary organic matter. The measurements and comparisons performed in this study have been used to test two assumptions currently applied in research on the global carbon cycle. The first assumption suggests that co-variation between $\delta^{13}C_{\text{organic}}$ and $\delta^{13}C_{\text{inorganic}}$ in sediments derived from shallow carbonate platforms indicate that variations in the $\delta^{13}C_{\text{inorganic}}$ are related to variations in the global carbon cycle. The second assumption is that differences between $\delta^{13}C_{\text{organic}}$ and $\delta^{13}C_{\text{inorganic}}$ are related to the partial pressure of CO$_2$ in the atmosphere when the organic material and sediments were formed.

**SAMPLES**

The samples analysed in this study were collected during Leg 166 of the Ocean Drilling Program and cruises aboard the RV Bellows.

**Leg 166**

Ocean Drilling Program Leg 166 drilled seven cores off the western margin of GBB (Eberli et al., 1997). Five of the seven cores were drilled along an extension of the Western Seismic Line (Eberli & Ginsburg, 1987; Fig. 1), and sediments recovered from Sites 1003, 1005, 1006 and 1007 have been utilized in this study. The location, water depth and age of the oldest sediments reached are listed in Table 1 for each of the cores. Seventeen seismic sequences were recognized in the Leg 166 transect, and correlated to the sediments using a vertical seismic profile. Age dates for the sequence boundaries were calculated using biostratigraphic and magnetostratigraphic methods (Eberli et al., 1997; Eberli, 2000). The $\delta^{13}C$ of the inorganic fraction was found to be correlated in
sequences of equivalent age between sites, but did not correlate with global changes in $\delta^{13}$C (Swart & Eberli, 2005).

The average sampling resolution for each of the sites varied from 1 to 1.6 m. Sampling resolution at Site 1003 ranged from 0.4 to 8.1 m, and averaged...
1.6 m between samples. Site 1005 sampling resolutions ranged from 0.1 to 24.5 m, and averaged 1.6 m. Sample intervals at Site 1007 ranged from 0.3 to 19.5 m, and averaged 1.2 m. Larger sampling intervals are the result of lost core material during the drilling process. Site 1006 sample intervals ranged from 0.8 to 5.8 m, and averaged 1.6 m coverage. Site 1006 represents the most continuous coverage of Pleistocene sea-level changes and was the least influenced by the deposition of turbidites.

**Shallow water carbonates**

During four cruises on the *RV Bellows* between 2001 and 2004, 291 samples were recovered from the surface of GBB (Fig. 1) and analysed for bulk $\delta^{13}C_{\text{inorganic}}$ values (Swart *et al.*, 2009). The samples range from mud-rich wackestone, in the lee of Andros Island, to rudstone at the margin of the platform (Reijmer *et al.*, 2009). Although the distribution of the samples was similar to that shown in previous work (Purdy, 1963a,b; Traverse & Ginsburg, 1966), the higher resolution sampling density allowed for an improved facies resolution and a geochemical study of the sediments. Two end-member facies types were recognized, grainstones and mud-rich wackestones, with a clear distinction between the outer and inner platform. Coarse-grained sediments along the margin surround a mud-dominated realm positioned on the western leeward side of Andros Island (Fig. 2). This distribution reflects the relative importance of currents and protected areas in controlling sediment deposition on the platform. The mineralogy of the sediments shows a clear dominance of aragonite mixed with minor high-magnesium calcite and low-magnesium calcite. The difference in mineralogy between the bulk and fine fractions suggests a preferential transport of aragonite-rich muds from the platform to the surrounding basins (Reijmer *et al.*, 2009). The $\delta^{13}C_{\text{inorganic}}$ values of all the samples were fairly positive, ranging from +4.0 to +6.0‰ ($m = +4.5\%$), and showed no relationship to facies (Swart *et al.*, 2009).

**METHODS**

**Organic $\delta^{13}C$ composition of sediments**

Approximately 400 mg of sediment from each of the locations was treated with 10% hydrochloric

---

**Fig. 2.** Map of facies distribution on top of Great Bahama Bank, from Reijmer *et al.* (2009). Facies characterizations are based upon a modified Dunham Scheme, detailed in Reijmer *et al.* (2009).
acid (HCl) overnight, and filtered through glass microfibre filters using a vacuum pump. The filters were subsequently dried for at least 48 h in a desiccator or until a constant weight was attained. The material collected on the filters was split and placed in tin capsules for analysis of $\delta^{13}$C$_{\text{organic}}$ composition.

Organic $\delta^{13}$C composition of algae and sea grasses

Samples were rinsed with deionized water (DI) to remove salts and then dried. Dry samples were treated with 5% HCl to remove any epifaunal inorganic carbonate. Samples were subsequently rinsed in DI water and dried in an oven at 40°C until a constant dry weight was reached. Samples were then weighed and packed individually into tin capsules.

Isotopic analyses

The tin capsules were combusted using Dumas type combustion (ANCA, Europa Scientific, Crewe, UK or ECS 4010 CHNSO Analyzer, Costech Analytical Technologies Inc., Valencia, CA, USA) and the resultant CO$_2$ analysed using a continuous flow isotope-ratio mass spectrometer (CFIRMS 20-20, Europa Scientific, Crewe, UK or a Delta V Advantage, ThermoFisher Scientific, Bremen, Germany). Data have been corrected for the usual isobaric interferences and are reported relative to Vienna Pee Dee Belemnite (V-PDB) for $\delta^{13}$C using the conventional notation. Reproducibility assessed from repeated analyses of internal standards of known weight and composition is ±0.1‰. Concentrations of organic carbon in the samples were estimated by using a standard of known carbon content, and a calibration line defining the relationship between peak area, measured by the elemental analyzer (ANCA or Costech), versus the carbon content of the standard. The weights of standards were chosen to bracket the range of organic carbon concentrations expected in the samples. The reproducibility of this method assessed from repeated analyses of standards is ±1.5%.

RESULTS

ODP Leg 166 Sites 1003 to 1007

The $\delta^{13}$C values of the organic material ($\delta^{13}$C$_{\text{organic}}$) recovered from the periplatform sediments of Leg 166 averages −15.4‰ (maximum = −14.4‰, minimum = −16.8‰; Fig. 3). The most depleted values are found at Site 1006, furthest from the platform margin, with values becoming progressively heavier closer to the margin (Table 2). The relationship between the $\delta^{13}$C$_{\text{organic}}$ and $\delta^{13}$C$_{\text{inorganic}}$ ranges from no correlation at Site 1005 ($r^2 = 0.09$, $P > 0.1$) to a statistically significant positive correlation at Site 1006 ($r^2 = 0.64$, $P < 0.01$; Table 2 and Fig. 4). The Pleistocene portion of Site 1006 (the only site at which there is a reasonably continuous Pleistocene record recovered) shows a general pattern in which the heavier $\delta^{13}$C$_{\text{organic}}$ values are correlated with heavy $\delta^{13}$C$_{\text{inorganic}}$ values. These positive values occurred during interglacial periods, as defined by negative $\delta^{18}$O values of the foraminifera Globigerinoides ruber and high concentrations of aragonite (Kroon et al., 2000; Fig. 5).

Surface of Great Bahama Bank

Platform sediments

The $\delta^{13}$C of the sedimentary organic material from the bank top averages −12.2‰, and ranges from −10.9 to −14.3‰ (Table 3). Relatively enriched $\delta^{13}$C values are found in the lee of Andros Island. Towards the platform margins and the areas to the north and south of Andros, the $\delta^{13}$C$_{\text{organic}}$ values become more depleted (−14.0 to −23.0‰, Fig. 6A). This spatial pattern correlates with published grain-size distributions (Reijmer et al., 2009; Fig. 6B). Total sedimentary organic carbon averages 0.10%, and ranges from 0.002 to 0.97% (Table 3). The total organic carbon in the sediments showed a spatial pattern similar to the distribution of the $\delta^{13}$C of the sedimentary organic material, in which samples with the highest total organic carbon are found in the lee of Andros Island (Fig. 6C). A non-parametric statistical test (Kruskal–Wallis) showed statistical differences between each of the five facies described by Reijmer et al. (2009) and total organic carbon content ($P < 0.01$), and $\delta^{13}$C$_{\text{organic}}$ value ($P < 0.01$). However, the correlation between the $\delta^{13}$C$_{\text{organic}}$ and $\delta^{13}$C$_{\text{inorganic}}$ fractions shows no statistically significant relationship in any of the facies on the bank top ($r^2 = 0.02$, $P > 0.1$), with the exception of the mud-rich wackestone facies ($r^2 = 0.70$, $P < 0.01$; Fig. 7).

Green algae

Samples of the green algae Halimeda sp., Penicillus sp., Acetabularia sp., Udotea sp., Rhipo-
Fig. 3. (A) Graphs of the correlation between the $\delta^{13}C_{\text{inorganic}}$ and $\delta^{13}C_{\text{organic}}$ values measured in identical samples in the ODP Leg 166 cores from 0 to 150 metres below sea floor (m b.s.f.). Symbols represent measured data points and the line is a four-point moving average for each of the cores in the transect. (B) Schematic depiction of cores with respect to the bathymetry and distance from the platform margin. ODP Site 1006 is the most basinward of the sites, located ca. 30 km from the platform margin.
Table 2. The average isotopic composition of periplatform sediments from ODP Leg 166. Sites are listed from most proximal (1005) to most distal (1006). Inorganic data are taken from Swart and Eberli (2005). The $r^2$ column represents the linear correlation coefficient calculated for the correlation between the $\delta^{13}$C$_{\text{inorganic}}$ and the $\delta^{13}$C$_{\text{organic}}$. The %OC is the percentage organic carbon preserved in the sediment and was calculated by taking the average weight of organic carbon measured through analysis divided by the original weight of the sediment dissolved. The % Insoluble is calculated by dividing the weight of the material that remained after filtration divided by the original weight.

<table>
<thead>
<tr>
<th>Site</th>
<th>$\delta^{13}$C$_{\text{inorganic}}$</th>
<th>$\delta^{13}$C$_{\text{organic}}$</th>
<th>$r^2$</th>
<th>%OC$_{\text{total}}$</th>
<th>% Insoluble</th>
</tr>
</thead>
<tbody>
<tr>
<td>1005</td>
<td>4.4 ± 0.5%</td>
<td>−14.4% ± 0.5</td>
<td>0.09 ($P &gt; 0.1$)</td>
<td>0.5</td>
<td>1.4</td>
</tr>
<tr>
<td>1003</td>
<td>3.7 ± 0.8%</td>
<td>−14.7% ± 0.9</td>
<td>0.04 ($P &gt; 0.1$)</td>
<td>0.4</td>
<td>1.5</td>
</tr>
<tr>
<td>1007</td>
<td>4.2 ± 1.0%</td>
<td>−15.6% ± 0.4</td>
<td>0.41 ($P &lt; 0.02$)</td>
<td>0.3</td>
<td>1.6</td>
</tr>
<tr>
<td>1006</td>
<td>2.8 ± 0.9%</td>
<td>−16.8% ± 0.2</td>
<td>0.64 ($P &lt; 0.01$)</td>
<td>0.2</td>
<td>9.1</td>
</tr>
</tbody>
</table>

**Correlation between organic and inorganic $\delta^{13}$C values**

**ODP Leg 166**

Fig. 4. Graph of the correlation between the inorganic and organic $\delta^{13}$C values at each ODP Leg 166 Site (1003 to 1007).

**DISCUSSION**

**Modern platform variations**

Organic $\delta^{13}$C values on Great Bahama Bank

The $\delta^{13}$C$_{\text{organic}}$ of organic material produced by sea grasses and macroalgae growing on GBB is not only substantially heavier than organic material produced in the pelagic environment, but shows heavier $\delta^{13}$C$_{\text{organic}}$ values compared with similar species growing in other tropical shallow-water marine environments (Fig. 9). For example, the $\delta^{13}$C$_{\text{organic}}$ of *Thalassia sp.* is on average 2 to 5‰ heavier.

**Sea grasses**

Samples of the sea grasses *Thalassia testudinum* and *Halodule sp.* were analysed for the $\delta^{13}$C$_{\text{organic}}$ values of the organic material. The $\delta^{13}$C$_{\text{organic}}$ values of sea grasses average −6.4‰ and range from −4.2 to −8.7‰ (Table 4).
more enriched on GBB (mean value = \(-5.7\%\) ; this study) when compared with Florida Bay and the Atlantic side of the Florida Reef Tract (\(-7.2\) to \(-10.4\%\); Anderson & Fourqurean, 2003), Laguna Madre, Texas (\(-10.8 \pm 0.3\); Jones et al., 2003), Port Aransas, Texas (\(-9.0\%\); Benedict & Scott, 1976) and the Dominican Republic (\(-8.5 \pm 0.3\%\); Tewfik et al., 2005). The \(\delta^{13}C_{\text{organic}}\) values of Thalassia sp. measured in this study fall within the range of another study from St. Croix that reports values of \(-4\) to \(-11\%\) (Fry et al., 1982). The enrichment in the \(\delta^{13}C_{\text{organic}}\) values of the algae and sea grasses is mirrored by the relatively heavy values observed in the inorganic components of the sediments collected from the top of GBB (Swart et al., 2009). These workers postulated that the enrichment in the \(\delta^{13}C\) values of DIC resulted from a relatively restricted circula-

![Fig. 5. Plot of the \(\delta^{13}C_{\text{organic}}\) (blue triangles) and \(\delta^{13}C_{\text{inorganic}}\) (red circles) values measured at Site 1006. The record of \(\delta^{18}O\) (yellow diamonds) was measured in foraminifera by Kroon et al. (2000) and several hiatuses in the core were observed. The grey bars mark highstands as indicated by negative \(\delta^{18}O\) values.](image)

Table 3. Facies type, number of samples in analysis, values of \(\delta^{13}C\) for the inorganic and organic fractions, percentage of the sample that is organic carbon and percentage of the sample that is insoluble in the bank top sediments.

<table>
<thead>
<tr>
<th>Facies Type</th>
<th>Samples</th>
<th>(\delta^{13}C_{\text{inorganic}})</th>
<th>(\delta^{13}C_{\text{organic}})</th>
<th>%OC\text{total}</th>
<th>% Insoluble</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mud-rich wackestone</td>
<td>21</td>
<td>(-4.5 \pm 0.5%)</td>
<td>(-10.9 \pm 1.4%)</td>
<td>0.41 ± 0.40</td>
<td>1.59 ± 0.6</td>
</tr>
<tr>
<td>Wackestone</td>
<td>34</td>
<td>(-4.7 \pm 0.2%)</td>
<td>(-10.9 \pm 1.8%)</td>
<td>0.27 ± 0.26</td>
<td>1.27 ± 0.5</td>
</tr>
<tr>
<td>Mud-rich packstone</td>
<td>11</td>
<td>(-4.8 \pm 0.2%)</td>
<td>(-11.3 \pm 1.9%)</td>
<td>0.14 ± 0.08</td>
<td>1.04 ± 0.3</td>
</tr>
<tr>
<td>Packstone</td>
<td>47</td>
<td>(-4.8 \pm 0.2%)</td>
<td>(-12.1 \pm 1.8%)</td>
<td>0.09 ± 0.07</td>
<td>0.63 ± 0.3</td>
</tr>
<tr>
<td>Mud-lean packstone</td>
<td>41</td>
<td>(-5.0 \pm 0.3%)</td>
<td>(-13.2 \pm 2.1%)</td>
<td>0.06 ± 0.06</td>
<td>0.63 ± 0.5</td>
</tr>
<tr>
<td>Grainstone</td>
<td>109</td>
<td>(-4.9 \pm 0.3%)</td>
<td>(-14.3 \pm 2.6%)</td>
<td>0.04 ± 0.03</td>
<td>0.47 ± 0.4</td>
</tr>
<tr>
<td>Rudstone</td>
<td>2</td>
<td>(-3.7 \pm 0.1%)</td>
<td>(-12.9 \pm 3.0%)</td>
<td>0.23 ± 0.27</td>
<td>0.79 ± 0.5</td>
</tr>
</tbody>
</table>

The sedimentary \(\delta^{13}C_{\text{organic}}\) values reflect the input of the degraded organic material of the marine plants and organisms inhabiting the shallow waters of GBB. The most enriched \(\delta^{13}C_{\text{organic}}\) values for sedimentary organic materials are found in the area of GBB corresponding to the smallest grain sizes (<125 µm) in the lee of Andros Island. The \(\delta^{13}C_{\text{organic}}\) composition of the sedimentary organic material is more depleted at the margins and in the open areas to the north and south of Andros. This pattern is similar to the grain-size distribution described on the surface of GBB.
Fig. 6. Surface maps of the Great Bahama Platform top. (A) Distribution of δ13Corganic values measured in surface sediments collected on the bank top. Orange shading denotes heavier carbon isotopic compositions, while green is indicative of lighter carbon isotopic compositions. (B) Map of the distribution of the inorganic δ13C values on the platform top. Darker colours indicate heavier isotopic compositions and lighter greys are representative of relatively depleted inorganic δ13C values, modified from Swart et al. (2009). (C) Map of the concentration of organic carbon preserved in the surface sediments collected on the platform. Darker colours indicate higher concentrations, while lighter colours represent lower concentrations of sedimentary organic carbon.
Reijmer et al. (2009) and show that the finer grain-size sediments have a higher concentration of organic carbon which is isotopically enriched compared with the sedimentary organic material recovered from facies with larger average grain sizes (Table 3). In the more open areas, fine-grained sediments and associated organic material are probably removed by stronger current regimes, and the concentration of organic material is lower. As the sedimentary $\delta^{13}C_{\text{organic}}$ values on the platform top result from the contributions of organic material from a variety of sources and the $\delta^{13}C_{\text{inorganic}}$ is relatively homogeneous, there is no correlation between the $\delta^{13}C_{\text{organic}}$ and $\delta^{13}C_{\text{inorganic}}$ records. The exception to this is the mud dominated facies (Fig. 7) where there is a positive correlation between the two fractions ($r^2 = 0.70$, $P < 0.01$).

During active sediment production, the sediment and organic material constituents are transported off the bank as a result of storm action, tidal energy and trade winds (Wilber et al., 1990; Reijmer et al., 2009). The sediment that is exported from the platform top has relatively enriched $\delta^{13}C_{\text{organic}}$ and $\delta^{13}C_{\text{inorganic}}$ values ($-12.2 \pm 1.3_{\%/oo}$ and $+4.6 \pm 0.4_{\%/oo}$, respectively). Sediments deposited on the slopes of GBB would

![Fig. 7. Plots of the correlation between $\delta^{13}C_{\text{inorganic}}$ and $\delta^{13}C_{\text{organic}}$ values measured in the sediments collected from the platform top: (A) mud-rich wackestone; (B) wackestone; (C) mud-rich packstone; (D) packstone; (E) mud-lean packstone; and (F) grainstone. The relationships between the $\delta^{13}C_{\text{inorganic}}$ and $\delta^{13}C_{\text{organic}}$ values are only statistically significant ($P < 0.01$) in the case of the mud-rich wackestones.]

### Table 4. Average $\delta^{13}C_{\text{organic}}$ composition of sediment and organic material producers collected from the surface of Great Bahama Bank. The averaged sediment $\delta^{13}C$ values were calculated using all grain sizes collected from the bank top.

<table>
<thead>
<tr>
<th>Type</th>
<th>$\delta^{13}C_{\text{organic}}$ (SD, n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Averaged Sediment</td>
<td>$-12.9_{%/oo}$ ($\pm2.6$, 277)</td>
</tr>
<tr>
<td>Sea Grass</td>
<td>$-5.7_{%/oo}$ ($\pm1.0$, 90)</td>
</tr>
<tr>
<td>Thalassia sp.</td>
<td>$-7.0_{%/oo}$ ($\pm1.7$, 30)</td>
</tr>
<tr>
<td>Halodule sp.</td>
<td>$-11.4_{%/oo}$ ($\pm3.2$, 24)</td>
</tr>
<tr>
<td>Green Algae</td>
<td>$-10.5_{%/oo}$ ($\pm2.3$, 11)</td>
</tr>
<tr>
<td>Halimeda sp.</td>
<td>$-11.2_{%/oo}$ ($\pm1.5$, 4)</td>
</tr>
<tr>
<td>Penicillus sp.</td>
<td>$-11.9_{%/oo}$ ($\pm2.5$, 8)</td>
</tr>
<tr>
<td>Acetabularia sp.</td>
<td>$-10.3_{%/oo}$ ($\pm1.2$, 4)</td>
</tr>
<tr>
<td>Udotea sp.</td>
<td>$-23.6_{%/oo}$ ($\pm3.3$, 3)</td>
</tr>
<tr>
<td>Rhipocephalus sp.</td>
<td>$-21.1_{%/oo}$ ($\pm3.0$, 18)</td>
</tr>
<tr>
<td>Caulerpa sp.</td>
<td>$-21.1_{%/oo}$ ($\pm3.0$, 19)</td>
</tr>
</tbody>
</table>

© 2011 The Authors. Journal compilation © 2011 International Association of Sedimentologists, *Sedimentology*
exhibit $\delta^{13}C_{\text{organic}}$ values that reflect mixtures of platform-derived ($ca -12\%_{oo}$; this study) and pelagic-derived organic carbon ($ca -21\%_{oo}$; Laws et al., 1995). The correlation between the organic and inorganic components would be expected to vary relative to the distance from the platform margin. For example, if the majority of the sediments in the cores were derived from the surface of the platform, the $\delta^{13}C_{\text{organic}}$ records and $\delta^{13}C_{\text{inorganic}}$ records should not be expected to co-vary in the cores because they do not demonstrate this relationship in the surface sediments. However, as the proportion of platform-derived sediment decreases with distance from the platform margin, a positive correlation between $\delta^{13}C_{\text{inorganic}}$ and $\delta^{13}C_{\text{organic}}$ should be recognized, resulting from the mixture of isotopically heavy carbon produced on the platform, with relatively light pelagic derived carbon.

**Downcore variation in $\delta^{13}C$ of organic material**

The average $\delta^{13}C_{\text{organic}}$ values for each core become more negative with increasing distance from the platform margin (Table 2). The most distal core, Site 1006, exhibits the most depleted average $\delta^{13}C_{\text{organic}}$ value ($-16.8\%_{oo}$), while the core closest to the platform, Site 1005, has a measured $\delta^{13}C_{\text{organic}}$ value of $-14.4\%_{oo}$. These data suggest that there is a higher percentage contribution from the pelagic material at the most basinward Site 1006 and, conversely, a lower percentage contribution from pelagic organic material at the site nearest the platform, Site 1005 (Fig. 4).

The correlation between the $\delta^{13}C_{\text{organic}}$ and $\delta^{13}C_{\text{inorganic}}$ records also changes substantially with increasing distance from the platform margin. In the proximal cores, Sites 1003 and 1005, there is either a very weak or a not statistically significant correlation between $\delta^{13}C_{\text{organic}}$ and $\delta^{13}C_{\text{inorganic}}$ values. Conversely at the toe of the slope, Site 1007, and the basin core, Site 1006, there is a strong positive correlation between the organic and inorganic $\delta^{13}C$ records (Fig. 4). The influence of sea-level changes, which dictates these spatial differences, is particularly well-manifested at Site 1006, which has a reasonably continuous Pleistocene record. Highstands are characterized by relatively heavy $\delta^{13}C_{\text{organic}}$ and $\delta^{13}C_{\text{inorganic}}$ values, while the lowstands are isotopically depleted (Fig. 5). Such observations were consistent with other studies which have shown that marginal settings receive significant amounts of sediment derived from the platform surface during highstands (Schlager et al., 1994; Roth & Reijmer, 2004, 2005).

**Systematic deposition sourced within the GBB system**

Within a 30 km transect of platform to basin cores of the same ages, varying correlations between $\delta^{13}C_{\text{inorganic}}$ and bulk $\delta^{13}C_{\text{organic}}$ records were observed. This finding is contrary to the assumption that the two records should be correlated throughout time, with co-occurring variations representing changes in the global carbon cycle. These results suggest that sea-level controlled contributions of platform-derived carbonates which control the relationship between $\delta^{13}C_{\text{inorganic}}$ and $\delta^{13}C_{\text{organic}}$ records. Modelling can be used to confirm the importance of these two separate (pelagic and platform) contributions of carbonate and organic carbon. If the surface of GBB is considered to be the source of isotopically heavy organic material, and the pelagic contribution is a source of isotopically light organic material, then the bulk $\delta^{13}C_{\text{organic}}$ values in peri-platform sediments can be explained by a simple mixing model between the two sources. This

---

**Fig. 8.** Box and whisker plot of the range of $\delta^{13}C$ values measured in this study for sea grasses and green algae sampled from Great Bahama Bank. Oceanic plankton values were analysed by Laws et al. (1995). The range (maximum and minimum values) of the dataset is defined by the error bars, while the coloured box represents the lower and upper quartiles. The line inside the box denotes the median value of the dataset.
Carbon isotopes in organic material from carbonate platforms

Fig. 9. Box and whisker plot of Thalassia sp. values of δ\textsuperscript{13}C\textsubscript{organic} from other Caribbean locations. The range (maximum and minimum values) of the dataset is defined by the error bars, while the coloured box represents the lower and upper quartiles. The line inside the box denotes the median value of the dataset. Great Bahama Bank (GBB) Thalassia sp. values were measured in this study. Florida Bay and the Florida Reef Tract values were measured by Anderson and Fourqurean (2003). The Laguna Madre, TX, USA Thalassia sp. values were analysed by Jones et al. (2003). Port Aransas, TX, USA δ\textsuperscript{13}C\textsubscript{organic} values were reported in Benedict and Scott (1976). Dominican Republic δ\textsuperscript{13}C\textsubscript{organic} values were analysed by Tewfik et al. (2005). and the St. Croix, U.S. Virgin Islands and Cayos Miskitos, Nicaragua δ\textsuperscript{13}C values were reported by Fry et al. (1982). If just one value was reported, the data was plotted as a bar. For all other instances, the standard deviation and range were used to plot the ‘whiskers’.

model would predict that: (i) sediments closer to the platform should be isotopically heavier than those further away; (ii) there should be higher concentrations of organic carbon in sediments closer to the platform; and (iii) there should be an increase in the correlation between δ\textsuperscript{13}C\textsubscript{organic} and δ\textsuperscript{13}C\textsubscript{inorganic} in cores further away from the platform. These patterns are observed along four sites off GBB. The average δ\textsuperscript{13}C\textsubscript{organic} value changes from −14.4‰, nearest the platform at Site 1005 to −16.8‰, at basin Site 1006, the total organic carbon average value decreases from 0.5 to 0.2%, and the correlation between δ\textsuperscript{13}C\textsubscript{organic} and δ\textsuperscript{13}C\textsubscript{inorganic} increases from r\textsuperscript{2} = 0.1 near the platform to r\textsuperscript{2} = 0.6 in the most basinward site (Site 1006). The observed trend can be adequately simulated using a simple mixing model (Fig. 10). In this model, it is assumed that the pelagic sediment has δ\textsuperscript{13}C\textsubscript{inorganic} values between 0‰ and 1‰, and δ\textsuperscript{13}C\textsubscript{organic} values of –20 to –22‰, while the platform component displays δ\textsuperscript{13}C\textsubscript{inorganic} values between +3‰ and +6‰, and δ\textsuperscript{13}C\textsubscript{organic} values between −7‰ and −16‰. The percentage of input from each respective source is then varied to fit the observed correlation (Fig. 10). In the case of Site 1006, sediment composition varies between 10% and 80% material derived from the platform. This relationship changes and contributions between 40% and 90% are identified at the toe of the slope (Site 1007), and 75 to 99% at Site 1005, which is situated closest to the platform margin.

Other possible sources of variation

In addition to this explanation for the varying correlation between δ\textsuperscript{13}C\textsubscript{organic} and δ\textsuperscript{13}C\textsubscript{inorganic} records, there are at least two other possibilities which might lead to variability in the δ\textsuperscript{13}C\textsubscript{organic} record. First, the sediments deposited at Sites 1006 and 1007 might be sourced from another platform, on which the organic and inorganic fractions co-vary in the bank top sediment and organic material. Potential sources of such shallow water sediments include Cay Sal Bank and the carbonate margin surrounding Cuba (Fig. 1). Although environmental processes similar to those on GBB might take place on Cay Sal Bank, or the Cuban carbonate margin, there are no published data on the distribution of δ\textsuperscript{13}C\textsubscript{organic} and δ\textsuperscript{13}C\textsubscript{inorganic} at these locations. Secondly, the correlation between δ\textsuperscript{13}C\textsubscript{organic} and δ\textsuperscript{13}C\textsubscript{inorganic} found at Sites 1006 and 1007 could have been overwhelmed at Sites 1003 and 1005 by migrated bitumen from deeper in the section at sites closer to the Bahama platform. During the drilling of the marginal sites, evidence of migrated bitumen was detected (Eberli et al., 1997). This bitumen could have the potential to raise the amount of organic material in the sediments, as well as alter its δ\textsuperscript{13}C value. However, such evidence was not present in the uppermost 150 m at any of the cores analysed in this study. While the importance of these sources cannot be assessed at the present time, the available evidence is consistent with a simple two component mixing between pelagic and platform-derived sediments.

Application to ancient shallow marine carbonate platform systems

Through a wide range of events and geological time periods, co-occurring excursions in organic and inorganic δ\textsuperscript{13}C values have been used to assess
Fig. 10. Modelling of the $\delta^{13}$C$_{\text{inorganic}}$ and $\delta^{13}$C$_{\text{organic}}$ values of the sediments at Sites 1006 (A) and 1005 (B). In each case, it is assumed that there is a mixture of pelagic material component with a range of $\delta^{13}$C$_{\text{inorganic}}$ values between $0\%_\text{oee}$ and $+1\%_\text{oee}$ and $\delta^{13}$C$_{\text{organic}}$ values of $-20.0$ to $-22.0\%_\text{oee}$ and a platform material component with $\delta^{13}$C$_{\text{inorganic}}$ values ranging between $+3.0\%_\text{oee}$ and $+6.0\%_\text{oee}$ and $\delta^{13}$C$_{\text{organic}}$ values of $-7.0$ to $-16.0\%_\text{oee}$. The model randomly selects $\delta^{13}$C$_{\text{inorganic}}$ and $\delta^{13}$C$_{\text{organic}}$ values from the pelagic and the platform components. (A) For distal Site 1006, the model results (blue circles) are plotted on the same axes as the values measured from the sediments (blue diamonds). The observed correlation at Site 1006 ($r^2 = 0.64$) can be simulated by a platform contribution of organic material and sediments that range from $20$ to $90\%$ through time (model correlation = 0.66, dashed line). (B) For proximal Site 1005, the model results (large green circles) are plotted on the same axes as the measured values (green diamonds). At Site 1005, the observed correlation ($r^2 = 0.07$, solid line) was simulated through a platform contribution that ranges from $95$ to $99\%$ through time (model correlation = 0.04, dashed line). Neither of these correlations suggests a statistically significant relationship between the two $\delta^{13}$C records at proximal Site 1005.

Several aspects of the global carbon cycle, providing information about changes in productivity and preservation, environmental conditions and atmospheric concentrations of CO$_2$. This principle has been applied to the Permian–Triassic interval and has been used to generate reconstructions of ancient pCO$_2$ and to understand the conditions leading up to the extinction event at the boundary (Margaritz et al., 1992; Krull et al., 2004). Also, co-occurring variations in both the $\delta^{13}$C$_{\text{inorganic}}$ and $\delta^{13}$C$_{\text{organic}}$ have been used to interpret global carbon cycling and generate estimates of the buffering capacity of the DIC pool during the ice ages of the Ediacaran and Proterozoic time periods (Kaufman et al., 1997; Swanson-Hysell et al., 2010). Factors affecting the decoupling of the $\delta^{13}$C$_{\text{inorganic}}$ and $\delta^{13}$C$_{\text{organic}}$ records have been used to generate assessments of the oxygenation of Earth’s oceans and the subsequent effects on the carbon cycle through the oxidation of organic material (Karhu & Holland, 1996; Fike et al., 2006). The correlation between the $\delta^{13}$C$_{\text{inorganic}}$ and $\delta^{13}$C$_{\text{organic}}$ records has been a widely used tool in the reconstruction of fluctuations in the global carbon cycle through geological time.

Previous work has suggested that correlations between the $\delta^{13}$C values of the organic and inorganic carbon measured in pelagic sequences reflect changes in the burial of organic carbon on a global scale (Popp et al., 1989; Hayes, 1993; Hayes et al., 1999; Zachos et al., 2001). As deep marine sequences older than 200 Myr are not available for study, many workers substitute carbonates deposited in marginal settings, including carbonate platforms, epeiric seas and ramps (Hotinski et al., 2004; Saltzman, 2002; Saltzman et al., 2004a,b; Underwood et al., 1997). The main assumptions for this substitution are that: (i) the DIC pool is in isotopic equilibrium with the inorganic carbonate precipitated by organisms derived from shallow carbonate platforms or ramps; and (ii) the nature of the $\delta^{13}$C of the organic material is similar to that found in the deep sea. However, the results of this study have generated some alternative conclusions. The co-variance between the $\delta^{13}$C$_{\text{inorganic}}$ and $\delta^{13}$C$_{\text{organic}}$ in the periplatform sediments from GBB do not exhibit a consistent co-variance between the two records at every location. Ludvigson et al. (1996) suggested several methods by which the records might be decoupled at one location, including increased organic productivity, high preservation potential, changes in circulation, temperature, salinity and pCO$_2$, diagenetic alteration and sea-level changes. The results of this study support some of the suggestions of Ludvigson et al., but have gener-
ated a more specific model describing how sea-level fluctuations can initiate or terminate the carbonate factory on shallow marine platforms. At proximal locations such as Sites 1005 and 1003, decoupled δ13C_{inorganic} and δ13C_{organic} records are observed because the cores consist primarily of platform material which does not demonstrate a co-variation between δ13C_{inorganic} and δ13C_{organic} on the modern platform top. Distal locations such as Sites 1006 and 1007 demonstrate appreciable covariances between the δ13C_{inorganic} and δ13C_{organic} values because they are the result of a two point mixing system between pelagic and platform-produced material. As a result, an understanding of the depositional environment from which the sediment is sampled, and local sea-level history are the required contextual information necessary to generate interpretations about the coupling or decoupling of δ13C_{inorganic} and δ13C_{organic} records in ancient shallow marine carbonate platforms.

The important question in relating the results of this study to older deposits, and interpretations of ancient global carbon cycling, is whether the Neogene is really the key to the past. It is not known what the isotopic nature of the types of organic material was during older time periods. Were there differences in the δ13C of the organic material between the deep sea and shallow water in these time periods such as there are now? Were there differences in the δ13C of the inorganic components? While the answers to these questions are unknown, the possibility that a variety of organisms contributed both organic and inorganic carbon to these ancient shallow marine carbonate deposits, such as shown in the Bahamas, cannot be dismissed in explaining past patterns in the relationship of δ13C_{organic} and δ13C_{inorganic} records.

SUMMARY AND CONCLUSIONS

The results of this study question the use δ13C_{organic} values from shallow marine carbonate environments as a method to corroborate changes in the δ13C values of inorganic carbonates. The data presented in this paper show that within a relatively short distance from the platform margin there are completely different patterns in the association of δ13C_{inorganic} and δ13C_{organic} values. Close to the margin, where the periplatform sediments are dominated by platform-derived materials, there is no correlation between the δ13C_{organic} and δ13C_{inorganic} records; this is the result of a lack of correlation between δ13C_{organic} and δ13C_{inorganic} values in the platform-derived sediment. Further away from the margin, there is a strong co-variation between δ13C_{organic} and δ13C_{inorganic} records. This pseudo-correlation is actually a mixing line between platform sediments, which are more enriched in both δ13C_{organic} and δ13C_{inorganic}, and pelagic material, which is more depleted in both δ13C_{organic} and δ13C_{inorganic} values. As a result, when interpretations of organic carbon burial, pCO2 or other fluctuations in the global carbon cycle are analysed in shallow marine settings like platforms, ramps and epeiric seas, they should be accompanied by the understanding that bulk records are sourced from a variety of producers in the shallow marine and pelagic environment. However, it is not known how applicable these results are to ancient materials consisting of inorganic and organic materials that might have been produced by different organisms or processes than the Tertiary sediments analysed in this study. Nonetheless, it is important to recognize that equally complicated isotopic relationships could have existed in shallow marine environments during earlier time periods. In addition, contextual information about the depositional setting and sea-level history of the ancient environment is crucial in accurately interpreting ancient relationships between δ13C_{inorganic} and δ13C_{organic} records.

ACKNOWLEDGEMENTS

This paper was greatly improved by comments from Tracy Frank, Lee Kump and Karl Föllmi. The authors thank the members of the Stable Isotope Laboratory at the University of Miami for assistance in the analysis of these samples. The crew and participants of the RV Bellows and the JOIDES Resolution expeditions are also thanked for collecting the samples. In addition, the manuscript was improved through discussions with Martin Kennedy and Gregor P. Eberli. Work on this paper was partially supported by NSF grant EAR 0825577, the Stable Isotope Laboratory at the Rosenstiel School of Marine and Atmospheric Science and the sponsors of the Comparative Sedimentology Laboratory.

REFERENCES


Manuscript received 7 September 2010; revision accepted 6 June 2011

© 2011 The Authors. Journal compilation © 2011 International Association of Sedimentologists, Sedimentology