A re-evaluation of facies on Great Bahama Bank II: variations in the $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ and mineralogy of surface sediments

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ABSTRACT

In order to investigate the spatial distribution of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of modern carbonate sediments on Great Bahama Bank, ~290 surface samples were collected from a grid of stations approximately 10 km apart between 2001 and 2004. These samples were classified using a modified Dunham scheme, physically separated into six size fractions and subsequently analysed for their mineralogy (aragonite, low-Mg calcite and high-Mg calcite) and $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values. A striking feature of these data is the relatively positive $\delta^{13}\text{C}$ values of all the samples. Based on measurements of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of the dissolved inorganic carbon and the water, most of the sediments can be considered to be in C and O isotopic equilibrium with the ambient waters. The high $\delta^{13}\text{C}$ values are suggested to arise from isotopic enrichment of the dissolved inorganic carbon pool by photosynthesis of seagrasses, benthic algae and cyanobacteria on the platform and through the fractionation of HCO_3^- during the precipitation of calcium carbonate. Sediments that are not in C and O isotopic equilibrium are dominated more by skeletal material. The data showed an absence of significant spatial variation in $\delta^{13}\text{C}$ of the sediments on the Great Bahama Bank and no clear spatial patterns relative to the margin of the platform. The $\delta^{18}\text{O}$ of the sediment showed more variation, with the interior sediments being isotopically enriched relative to the platform margin. The absence of significant variations in the $\delta^{13}\text{C}$ in the modern surface sediments of Great Bahama Bank irrespective of facies type suggests that in the case of Great Bahama Bank, downcore variations in $\delta^{13}\text{C}$ cannot be related to changes in facies.

Keywords Stable isotope, shallow-water carbonates, Bahamas, grain-size, carbonate platforms, salinity.

INTRODUCTION

The descriptions of Great Bahama Bank (GBB) and its surface sediments (Illing, 1954; Newell *et al.*, 1959; Purdy, 1963a, 1963b; Traverse & Ginsburg, 1966; Enos, 1974) made between 1950 and 1970 are widely used for modern biological and geological studies on GBB. In addition, GBB is often applied as an analogue for the study of ancient carbonate platforms. This paper together

with a companion study (Reijmer *et al.*, 2009) examines spatial variations in the facies and geochemistry of surface sediments on GBB. Although there have been several papers that provided some general geochemical characteristics on the sediments on GBB (Lowenstam & Epstein, 1957; Shinn *et al.*, 1989), there have been no studies which have described spatial variation in the inorganic and organic mineralogy of the sediments on the same scale as the original sedimentary facies were investigated. Such data are important as changes in the $\delta^{13}\text{C}$ of platform and periplatform carbonates are increasingly being used for stratigraphic purposes (Vahrenkamp, 1996; Saltzman *et al.*, 2004) and for providing information on the global CO_2 cycle in periods prior to the

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existence of pelagic records (Berner, 1987; Kump & Arthur, 1999). It is well documented that global changes in the $\delta^{13}\text{C}$ of platform carbonates can be correlated between various strata during certain periods of the geological record (Föllmi *et al.*, 1994; Vahrenkamp, 1996; Valladares *et al.*, 1996; Weissert *et al.*, 1998; Kump & Arthur, 1999; Veizer *et al.*, 1999; Immenhauser *et al.*, 2002; Saltzman, 2002a,b; Saltzman *et al.*, 2004; Saltzman & Young, 2005) as well as related to the pelagic record of $\delta^{13}\text{C}$ change (Gale, 1993; Weissert *et al.*, 1998). Such variations are normally interpreted as reflecting changes in the partitioning of the global carbon cycle, with elevated values indicating the increased burial of organic carbon (Berner *et al.*, 1983; Kump & Arthur, 1999). However, it is well established that changes in $\delta^{13}\text{C}$ can also reflect diagenesis (Allan & Matthews, 1982; Immenhauser *et al.*, 2003) as well as variations in the relative

proportion of periplatform and pelagic material (Swart & Eberli, 2005; Reuning *et al.*, 2006). In this paper the origin of the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ and mineralogy of ~290 samples collected from Great Bahama Bank on a regular grid spacing of ~10 km between 2001 and 2004 are reported.

SAMPLES

Samples were collected using a Shipek sampler during four cruises aboard the RV *Bellows* between 2001 and 2004 (Fig. 1). The Shipek sampler differs from the Van-Veen sampler used during earlier studies (Purdy, 1963a,b) in that it is better at retaining the mud material. In total 291 bulk samples were analysed. Of these approximately 120 were separated into size fractions (>1000, 500–1000, 250–500, 125–250, 125–63 and

Fig. 1. Location map of the Bahamas and position of sample collection points (black diamonds).

<63 μm) and the relative percentages of aragonite, high-Mg calcite (HMC) and low-Mg calcite (LMC) were determined together with their carbon and oxygen-isotopic compositions. Each sample was also separated into a modified Dunham facies classification. At the same time water samples were taken for salinity and stable oxygen and hydrogen measurements. Samples for carbon isotopic analysis of the dissolved inorganic carbon (DIC) were filtered using a 1 μm filter and preserved in sealed crimped vials with excess mercuric chloride.

METHODS

X-ray mineralogy

The percentages of aragonite, HMC and LMC were determined using the method of Swart & Melim (2000). In this method the sample is assumed to be completely composed of aragonite, HMC and LMC. Areas of the appropriate peaks for each mineral are determined using a scan between 23 and 32° 2 θ (CuK α radiation). These are then compared with standard relationships between peak area and percentage mineral and the percentage of the mineral in the sample determined.

Stable isotopes carbonates

The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of the carbonate materials was determined using dissolution in phosphoric acid using the common acid bath method (Swart *et al.*, 1991) at 90°C. The gas produced was analysed using a Finnigan-MAT 251. Later some samples were also analysed using a Kiel III device attached to a Finnigan Delta plus. Data produced in both methods were corrected for isobaric interferences using the procedures (Craig, 1957) modified for a triple collector mass spectrometer. Data are reported relative to Vienna Pee Dee Belemnite (V-PDB) using the conventional notation. Average standard deviation based on replicate analyses of internal standards is <0.1‰.

Water samples

The oxygen and hydrogen-isotopic composition ($\delta^{18}\text{O}$ and δD) were determined using the methods of Epstein & Mayeda (1953) and Coplen *et al.* (1991) respectively. All $\delta^{18}\text{O}$ and δD data for waters are reported relative to Vienna Standard Mean Ocean Water (VSMOW). Average standard

deviation, based on replicate analyses of internal standards is <0.1‰ for $\delta^{18}\text{O}$ and 2.0‰ for δD . The $\delta^{13}\text{C}$ of the dissolved inorganic carbon (DIC) was determined by acidification of the sample followed by extraction using a flowing stream of He and analysis in a stable isotope ratio mass spectrometer (Europa 20–20). Data are reported relative to V-PDB using the conventional notation. Average standard deviation based on replicate analyses of internal standards is <0.1‰.

Facies classification

Immediately after collection, samples were assigned to a modified Dunham scheme (Dunham, 1962). In order to supplement the classification divisions were added between wackestone and mudstone (mud-rich wackestone), between a packstone and wackestone (mud-rich packstone) and finally between packstone and grainstone (mud-lean packstone). For display purposes the mudstone, wackestone, packstone, grainstone and rudstone classification were assigned numbers from 1 to 5, with the intermediary categories being assigned values of 1.5, 2.5 and 3.5. Samples from all cruises were preserved in cold storage and after the 2004 cruise all samples were re-examined to ensure consistency between cruises (Reijmer *et al.*, 2009).

RESULTS

Stable isotopes of carbonates

The mean $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values for the carbonate sediments and the various size fractions are shown in Tables 1 and 2 and Fig. 2. The $\delta^{18}\text{O}$ of all fractions are statistically the same, but the $\delta^{13}\text{C}$ of the coarser material (>1000 μm) is statistically significantly more negative than the finer fraction and the bulk. Relative to the modified Dunham classification there is no statistically significant difference between the mean $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of the coarser and finer sediment types (Table 3; Figs 3 and 4). However, the range of values of the modified Dunham categories increases with grain size (Table 3). The spatial distribution of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ are shown in Figs 5 and 6.

Water samples

The $\delta^{18}\text{O}$ of the waters are shown in Fig. 7 and range between +0.75 and +2.93‰. There is an approximate positive correlation with salinity,

Table 1. Carbon isotopic composition of size fractions.

	Bulk	>1000 μm	1000–500 μm	500–250 μm	250–125 μm	125–63 μm	<63 μm
Mean	+4.8	+4.0	+4.6	+4.8	+4.9	+4.9	+4.4
SD	0.3	0.7	0.5	0.4	0.5	0.3	0.5
Minimum	+3.2	+2.0	+3.4	+3.3	+3.5	+3.9	+3.4
Maximum	+5.5	+5.1	+5.6	+5.9	+5.9	+5.4	+5.5

Table 2. Oxygen isotopic composition of size fractions.

	Bulk	>1000 μm	1000–500 μm	500–250 μm	250–125 μm	125–63 μm	<63 μm
Mean	+0.4	+0.3	+0.4	+0.5	+0.4	+0.5	+0.4
SD	0.4	0.4	0.3	0.4	0.44	0.4	0.4
Minimum	–0.8	–0.5	–0.5	–0.40	–0.3	–0.3	–0.5
Maximum	+1.8	+1.5	+2.0	+2.0	+1.7	+1.3	+2.0

Table 3. The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in different modified Dunham classification.

	1.5 Mud-rich wackestone	2 Wackestone	2.5 Mud-rich packstone	3 Packstone	3.5 Mud-lean packstone	4 Grainstone	5 Rudstone
$\delta^{13}\text{C}$	+4.8	+4.8	+4.8	+4.8	+5.0	+4.9	+3.7
SD	0.1	0.2	0.2	0.2	0.3	0.3	0.1
$\delta^{18}\text{O}$	+0.5	+0.6	+0.6	+0.6	+0.4	+0.2	–0.1
SD	0.3	0.4	0.4	0.3	0.5	0.4	0.2

Fig. 2. Stable $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of all samples and size fractions from 2001 to 2004 cruises: (a) data from <63, 63–125 and 125–250 μm size fractions, (b) data from bulk, 250–500, 500–1000 and >1000 μm size fractions.

Fig. 3. Relationship between $\delta^{13}\text{C}$ and facies type (1 = mud, 1.5 = mud-rich wackestone, 2 = wackestone, 2.5 = mud-rich-packstone, 3 = packstone, 3.5 = mud-lean packstone, 4 = grainstone, 5 = rudstone).

similar to that shown previously (Lowenstam & Epstein, 1957; Shinn *et al.*, 1989). The $\delta^{13}\text{C}$ values of the DIC range from +0.4 to +2.4‰ and show no specific relationship with salinity (Fig. 8).

Sediment classification

The descriptions and distribution of these facies are fully described in a companion

Fig. 4. Relationship between $\delta^{18}\text{O}$ and facies type (1 = mud, 1.5 = mud-rich wackestone, 2 = wackestone, 2.5 = mud-rich-packstone, 3 = packstone, 3.5 = mud-lean packstone, 4 = grainstone, 5 = rudstone).

paper (Reijmer *et al.*, 2009). The majority of the sediments are dominated by non-skeletal material (mud, pellets, peloids, ooids and grapestones), although all samples contained small amounts of skeletal debris. The percentage of mud in the samples increases rapidly moving away from the bank margin towards the interior of the platform with samples completely composed of skeletal material only present near the bank margin. The facies distribution pattern found is fairly similar to that shown in the facies distribution map of Purdy (1963a,b) and roughly agrees with the map of Traverse & Ginsburg (1966).

Fig. 5. Spatial composition map of the $\delta^{13}\text{C}$ of bulk carbonate sediments from GBB.

Fig. 6. Spatial composition map of $\delta^{18}\text{O}$ of bulk carbonate sediments from GBB.

DISCUSSION

Previous work on the variation of $\delta^{13}\text{C}$ on modern carbonate platforms

There have been relatively few previous studies on the distribution of $\delta^{13}\text{C}$ of sediments on modern carbonate platforms (Lowenstam & Epstein, 1957; Weber, 1967; Weber & Schmalz, 1968; Weber & Woodhead, 1969; Shinn *et al.*, 1989; Dix *et al.*, 2005). Studies such as the one carried out at Heron Island (Weber & Woodhead, 1969) examined variations over a relatively small area, a coral atoll approximately $5 \times 20\text{ km}$. The Heron Island study showed substantial variation in $\delta^{13}\text{C}$ progressing across the reef, with the margins being

significantly more negative (up to 2‰) in $\delta^{13}\text{C}$ compared with portions of the interior (Fig. 9a). These changes are strongly correlated with the percentage of aragonite and arise because carbonate materials produced from the decomposition of algae, such as the various calcareous green algae commonly found on coral reefs (*Halimeda* sp., *Penicillus* sp., *Acetabularia* sp. and others), have very positive $\delta^{13}\text{C}$ values (typically $> +4\text{‰}$). In contrast, the $\delta^{13}\text{C}$ of most LMC and HMC components is close to or below 0‰ (Keith & Weber, 1965; Weber, 1965; Milliman, 1974; Land, 1989). Hence, a mixing line between aragonite and LMC or HMC will produce a covarying trend. However, a close inspection of the data (Fig. 9) shows two apparent trends, one at concentrations of

Fig. 7. Relationship between $\delta^{18}\text{O}$ and salinity for water samples from GBB measured by Shinn *et al.* (1989), Lowenstam & Epstein (1957) and this study. The line shows a model result of the evaporation of a water body with an initial salinity of 32 and $\delta^{18}\text{O}$ of 0‰ using the equations outlined by Gonfiantini (1986) and the model of Craig & Gordon (1965).

aragonite higher than 60%, where there is a strong positive association between percentage aragonite and $\delta^{13}\text{C}$, and one at concentrations below 60%, where there is apparently no correlation between the percentage of aragonite and $\delta^{13}\text{C}$ (Fig. 9b). This apparent difference probably arises because there are at least two sources of aragonite with very different $\delta^{13}\text{C}$ values on GBB. One source is the calcareous green algae exhibiting high $\delta^{13}\text{C}$ values, mentioned above. The other source is the aragonite produced by scleractinian corals and red calcareous algae which possess much lower $\delta^{13}\text{C}$ values (−1 to +1‰) (Keith & Weber, 1965; Milliman, 1974; Land, 1989). Hence, increasing the concentration of aragonite by adding material derived from corals and red calcareous algae will not result in a corresponding $\delta^{13}\text{C}$ increase and will not produce a correlation between the concentration of aragonite and $\delta^{13}\text{C}$. A similar result was found at Enewetok, with relationships between aragonite and $\delta^{13}\text{C}$ being either positive or negative depending upon the location sampled (Weber & Schmalz, 1968). Another significant study which examined a much larger spatial area was that by Dix *et al.* (2005). Here workers examined approximately 100 samples collected over an approximate 600 km² area on the North West Australian Shelf and also identified a positive relationship between the percentage of aragonite and $\delta^{13}\text{C}$, again produced by a mixing between isotopically positive aragonite and more depleted LMC. A similar explanation has been invoked for different correlations

Fig. 8. Relationship between $\delta^{13}\text{C}$ of DIC and salinity for samples collected in this study. There is no statistically significant correlation in these data between $\delta^{13}\text{C}$ of DIC and salinity.

between C and O found in modern sediments collected from Belize and the Persian Gulf (Gischler *et al.*, 2007).

RELATIONSHIPS ON GREAT BAHAMA BANK

Salinity and stable isotopes

There have been no systematic temporal or spatial investigations of the water chemistry of Great Bahama Bank, but the analyses that have been made show waters increasing in salinity as one progresses across Great Bahama Bank from west to east (Black, 1933; Smith, 1940b; Lowenstam & Epstein, 1957; Cloud Jr., 1962; Shinn *et al.*, 1989). Very close to Andros Island, salinities have been shown to decrease as a result of runoff (Cloud Jr., 1962).

Oxygen-isotopic analyses of the waters generally show a weak positive relationship with salinity as do the data measured in this study (Lowenstam & Epstein, 1957; Shinn *et al.*, 1989) (Fig. 7). However, as a result of exchange between atmospheric water vapour and the water on GBB, the maximum $\delta^{18}\text{O}$ that can be attained is limited (Lloyd, 1964; Craig & Gordon, 1965; Gonfiantini, 1986) and therefore there is no clear relationship between salinity and $\delta^{18}\text{O}$. In fact the maximum $\delta^{18}\text{O}$ value measured in this study was ~+2.8‰ at a salinity of 35.75. Waters with higher salinity values had actually lower $\delta^{18}\text{O}$ values. The δD data also show clear evidence of a strong evaporative trend (Fig. 10) with original source water close to 0‰. As the samples were collected over a four-year time period during which the salinity and $\delta^{18}\text{O}$ of

Fig. 9. (a) Sediment $\delta^{13}\text{C}$ data from Heron Island, Australia showing the $\delta^{13}\text{C}$ values in a south to north transect (low numbers to high numbers) across the reef. See Weber & Woodhead (1969) for sample location. Changes in $\delta^{13}\text{C}$ correspond to changes in facies with elevated values corresponding to areas dominated by calcareous green algae and lower values in areas where there are abundant red algae and scleractinian corals (Weber & Woodhead, 1969). (b) Sediment $\delta^{13}\text{C}$ data shown in (a) correlated with the percentage of aragonite.

the water varied as a result of weather conditions, it is not possible to combine the data and make a generalization about the distribution of $\delta^{18}\text{O}$ on GBB. However, it is probable that waters further from the margin might have elevated $\delta^{18}\text{O}$ values on a consistent basis. Hence carbonates formed further from the margin might also be expected to have higher $\delta^{18}\text{O}$ values than carbonates found on or near the margin.

Previous studies on the $\delta^{13}\text{C}$ of waters on GBB are limited to one, which showed large ranges in $\delta^{13}\text{C}$ ranging from ~ -5 to $+1\text{‰}$ (Patterson & Walter, 1994). It was suggested that these variations were related to oxidation of organic material, photosynthesis and precipitation of aragonite and LMC. The $\delta^{13}\text{C}$ of the DIC measured in this study were significantly higher and varied from $\sim +0.5$ to $+2.5\text{‰}$ (Fig. 8). In no instance over five years of analyses were waters with $\delta^{13}\text{C}$ values less than $+0.5\text{‰}$ recorded. The lower values measured in this study are typical of open marine values (Weber & Woodhead, 1971; Kroopnick, 1974; Swart *et al.*, 2005), while the higher ones suggest both fractionation of CO_2 during photosynthesis and/or fractionation of

Fig. 10. Relationship between $\delta^{18}\text{O}$ and δD in the data measured in this study relative to the meteoric water line (dashed line). The solid line shows the evaporative trend of a water body using the same conditions as used in Fig. 7.

the HCO_3^- pool as CO_2 is produced during the precipitation of CaCO_3 . Photosynthesis by the abundant algae and seagrasses on GBB preferentially removes the lighter isotope of carbon, causing the residual bicarbonate pool to become enriched in the heavier isotope of carbon, while precipitation of calcium carbonate lowers the pH, converting HCO_3^- into CO_2 . As there is an isotopic fractionation of approximately 8%

in this process (Emrich *et al.*, 1970; Romanek *et al.*, 1992), the residual bicarbonate becomes isotopically enriched.

Sediments

Perhaps the most startling results arising from this study are (i) the absence of significant patterns in the $\delta^{13}\text{C}$ across the GBB (Fig. 5) and (ii) the lack of a relationship between facies type and $\delta^{13}\text{C}$ (Fig. 3). The only exception to the latter is that very large grains ($>1000\mu\text{m}$) are slightly less positive (+4.2 vs. +4.9‰). The relatively depleted values are a result of the fact that these grains are more likely to be composed of skeletal material, which generally have lower $\delta^{13}\text{C}$ values (see previous discussion). The origin of relatively high $\delta^{13}\text{C}$ values of the sediments compared with pelagic LMC arises from two phenomena. First, as mentioned above the $\delta^{13}\text{C}$ of the DIC averages +1.5‰ ranging from +0.4 to +2.4‰. Second, enrichment of $\delta^{13}\text{C}$ in aragonite is about $2.7 \pm 0.6\text{‰}$ relative to only about 1‰ for LMC (Romanek *et al.*, 1992). Hence equilibrium values for aragonite precipitated directly from surface waters of GBB should range from $\sim +2.6$ to $\sim +5.8\text{‰}$ (this range is calculated using the error of 0.6‰ and the $\delta^{13}\text{C}$ values measured on the surface water DIC (Fig. 8). This corresponds to a measured range of +3.6 to +5.5‰ (see Tables 1 and 2).

As regards the $\delta^{18}\text{O}$, the variation in water temperatures on GBB probably exceeds 10°C , but averages 25°C . Using the standard palaeotemperature equation (Epstein *et al.*, 1953) and the values reported in Table 2, the sediments if formed at equilibrium should lie between -1.2 and $+0.8\text{‰}$. This is a little more negative than the range of the sediments (-0.8 to $+1.8\text{‰}$) but still within the errors of the temperature estimate (Fig. 11). So if the predominantly aragonite sediments on GBB are in equilibrium with the ambient waters, then why do all the sediments, from the mud-dominated wackestones to the grainstones, have similar $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ compositions? The simple answer is that the majority of the sediments are genetically related; the exception being the small amount of skeletal material mentioned previously.

The origin of the finest carbonate sediment on GBB has been the subject of speculation for over 50 years (Black, 1933; Smith, 1940a,b; Cloud Jr., 1962). Authors have proposed that the material is either a result of direct or algal induced precipitation from seawater (Cloud Jr., 1962; Morse *et al.*, 1984; Shinn *et al.*, 1989; Robbins &

Blackwelder, 1992), or that they are stirred up bottom sediments, ultimately originating from the decomposition of calcareous algae (Broecker & Takahashi, 1966; Stockman *et al.*, 1967; Morse *et al.*, 1984). This debate has been heated over the years, but regardless of the ultimate origin of the mud component, this fine-grained sediment seems to be the building material for most of the other sedimentary particles on GBB. Mud becomes ingested by benthic organisms forming faecal pellets which harden to form peloids, some of which become coated to form ooids or clumped together to form grapestones. This process is supported by the fact that the finest sediments have the narrowest range of C and O isotopic compositions (Fig. 2a), gradually increasing in range as diagenetic and cementation processes add carbonate material of differing generations and isotopic compositions to the grains.

RELATIONSHIPS BETWEEN $\delta^{13}\text{C}$ AND $\delta^{18}\text{O}$

The relationships between the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in the bulk samples and the separated size fractions are shown in Fig. 2a and b. In $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ space, the data define a triangle with the samples possessing the most positive $\delta^{18}\text{O}$ values also containing the narrowest range and the most elevated $\delta^{13}\text{C}$ values. These samples tend to be mud-rich wackestones. This pattern (Fig. 11) probably reflects the relationships between those areas on GBB where the water consistently possesses the highest $\delta^{13}\text{C}$ (DIC) and $\delta^{18}\text{O}$ values. These areas are probably fairly restricted in geographical extent. In contrast, the areas where there are wider ranges in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ are more prevalent and account for the majority of the samples. The largest sized samples ($500\text{--}1000\mu\text{m}$ and $>1000\mu\text{m}$) have a much shallower relationship between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ reflecting a larger proportion of skeletal material in the samples (Fig. 11).

IMPLICATIONS FOR CARBON ISOTOPE STRATIGRAPHY

This study on the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of surface sediments of GBB shows that in spite of a large range in sediment sizes, there is a relatively small spread in the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values. The elevated $\delta^{13}\text{C}$ values are a result of a combination of isotopic

Fig. 11. Ranges of equilibrium estimates of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of sediments based on data shown in Figs 5 and 6 (region enclosed by cross-hatched symbol), compared with the mean $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values measured on carbonates in this study (area enclosed by blue rectangular area). Carbonate data are the same as shown in Fig. 2. Estimates for skeletal data (red rectangular area) are taken from the literature (Weber, 1965; Milliman, 1974; Swart, 1983; Land, 1989).

fractionation of the DIC during photosynthesis and the natural enrichment of aragonite relative to LMC (see above). These sediments are exported from the platform and form periplatform sediments (Schlager & Ginsburg, 1981; Eberli *et al.*, 1997; Eberli, 2000) that drape the flanks of the platform and extend into the pelagic realm. It has been shown that the $\delta^{13}\text{C}$ of such sediments can be correlated between units of equivalent age, but that these $\delta^{13}\text{C}$ values are not related to pelagic $\delta^{13}\text{C}$ values (Swart & Eberli, 2005). The reason for the correlation between units of similar age arises as varying amounts of surface sediments enriched in $\delta^{13}\text{C}$, mix with more depleted carbonate derived from pelagic sources. As all sediment size fractions have similar $\delta^{13}\text{C}$ values, the mixing does not appear to change as a function of distance from the platform. This pattern may not be present surrounding carbonate buildups with high percentages of aragonite derived from calcareous organisms such as corals.

The question posed by this study is whether the results are at all applicable to carbonate

platforms in previous geological time periods. For example, it has been proposed that the normal form of calcium carbonate precipitated from marine seawater has changed throughout geological time as a function of the Mg/Ca ratio of the oceans varying between 'calcite' and 'aragonite' seas (Sandberg, 1983; Hardie, 2003; Lowenstein *et al.*, 2003). During periods of 'calcite' seas, clearly the $\delta^{13}\text{C}$ of carbonates formed on the platform would probably not be as isotopically positive today because the only mechanisms that would enrich the platform carbonates would be the influences of photosynthesis and fractionation during the precipitation of calcium carbonate. The platform-derived carbonate would nevertheless be more isotopically positive than pelagic material formed at the same time, although not as enriched that as today. Hence it is proposed that there still might be a carbon isotopic effect as a result of precipitation on carbonate platforms during periods of 'calcite' seas, but that this might be reduced compared with periods of 'aragonite' seas.

CONCLUSIONS

- 1 The positive $\delta^{13}\text{C}$ values of surface sediments arises from a combination of the large fractionation between aragonite and bicarbonate ($\sim 2.7\%$) and the elevated $\delta^{13}\text{C}$ of the DIC caused by the fractionation during photosynthesis of benthic algae, seagrasses and cyanobacteria and fractionation during the conversion of HCO_3^- into CO_2 during the precipitation of calcium carbonate.
- 2 All sediments formed upon GBB have similar $\delta^{13}\text{C}$ values suggesting a common origin. Mud, whether formed by direct precipitation or breakdown from algal carbonate, is ingested by benthic organisms forming pellets, which harden to produce peloids, which in turn are coated to form coated grains, grapestones and/or ooids. As a result of this paragenetic sequence, the range of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of the sediments increases with increasing grain size.
- 3 Skeletal material only forms a small proportion of sediment on GBB, but has more negative $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values.
- 4 The $\delta^{18}\text{O}$ of the carbonate sediment is elevated in the interior bank relative to the margin as a result of the persistent elevated salinity and $\delta^{18}\text{O}$ of the water.

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