

# Depletion of $^{13}\text{C}$ in seawater $\Sigma\text{CO}_2$ on modern carbonate platforms: Significance for the carbon isotopic record of carbonates

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## ABSTRACT

Seawater  $\Sigma\text{CO}_2$  from modern carbonate platforms (Bahama Banks and Florida) is depleted in  $^{13}\text{C}$  by as much as 4‰ relative to open-ocean water. Depletion in  $^{13}\text{C}$  is caused by isotopically light  $\text{CO}_2$  input from respiration of marine and terrestrial organic matter during water-mass residence on the bank. As such, depletion in  $^{13}\text{C}$  is related to changes in water chemistry driven by evaporation, freshwater discharge, and  $\text{CaCO}_3$  withdrawal. Deviation of modern platform seawater  $\delta^{13}\text{C}$  values away from those of surface seawater suggests that  $\delta^{13}\text{C}$  values of ancient cratonic carbonate must be cautiously interpreted. Initial depositional environment, as well as alteration during diagenesis, must be considered in extracting valid secular trends for oceanic  $\delta^{13}\text{C}$  variation.

## INTRODUCTION

As chemical precipitates, marine carbonate rocks are an archive of information on ancient oceanic and atmospheric chemistry. Although shallow-marine carbonate composes only 20%–30% of modern oceanic carbonate, it dominates the geologic record during periods of higher global sea level (e.g., Hay and Southam, 1977; Opdyke and Wilkinson, 1988). Prior to the evolution of planktonic carbonate-secreting organisms, platform carbonate was the main component of the carbonate budget, regardless of relative global sea level (e.g., Milliman, 1974).

$\delta^{13}\text{C}$  of ancient carbonate can provide a primary record of oceanic and atmospheric chemical variation and has been used to model C, O, and S cycles (e.g., Schidlowski and Junge, 1981; Berner, 1987, 1989). Shifts in  $\delta^{13}\text{C}$  recorded in shelf-carbonate sequences also are used as a proxy for the isotopic composition of surface ocean water to establish paleocean chemistry and circulation patterns (e.g., Veizer et al., 1986; Margaritz and Holser, 1990; Grossman et al., 1993). However, modern seawater overlying carbonate platforms is significantly modified by evaporation, dilution, and carbon transfer (e.g., Broecker and Takahashi, 1966; Morse et al., 1984), which may affect  $\delta^{13}\text{C}$ . Indeed, Lloyd (1964) showed that shells of recent molluscs from the Florida platform exhibit progressive depletion in  $^{13}\text{C}$  with increasing environmental restriction.

Previous studies of bank seawater chemistry have not determined the  $\delta^{13}\text{C}$  of  $\Sigma\text{CO}_2$ , although extensive data exist on  $\delta^{13}\text{C}$  values of open-marine seawater (e.g., Kroopnick, 1985; Broecker and Maier-Reimer, 1992).  $\delta^{13}\text{C}$  values of surface seawater range from +1.5‰ to +2.0‰ (relative to Pee Dee belemnite—PDB). Oxidation of organic mat-

ter causes progressive enrichment in  $^{12}\text{C}$  with increasing depth and age of water mass, resulting in  $\delta^{13}\text{C}$  values as low as -0.5‰ in oldest deep-water masses of the North Pacific (Kroopnick, 1985).

We determined the  $\delta^{13}\text{C}$  values of platform-carbonate seawater as part of a larger study on the C-exchange dynamics among sediment, organic matter, and pore water. In this paper, we show that organic-matter respiration and isotopic exchange between inorganic and organic C reservoirs signifi-

cantly affect the composition of  $\Sigma\text{CO}_2$ , producing an even wider range of isotopic compositions than observed in the global deep ocean. Isotopic variation is related to salinity changes and carbonate-system evolution during the “aging” of surface seawater on these semirestricted platforms. We discuss the implications of our findings for interpretation of the  $\delta^{13}\text{C}$  record in ancient shelf carbonate.

## STUDY AREA, METHODS, AND RESULTS

Seawater and bottom sediments were sampled adjacent to and on carbonate platforms in south Florida (United States) and the Bahamas (Fig. 1). Sediment is metastable carbonate (aragonite and Mg-bearing calcite), produced by breakdown of skeletal and algal carbonates. Sampling was conducted during different seasons to encompass the variable influence of freshwater discharge and evaporation. Water tempera-

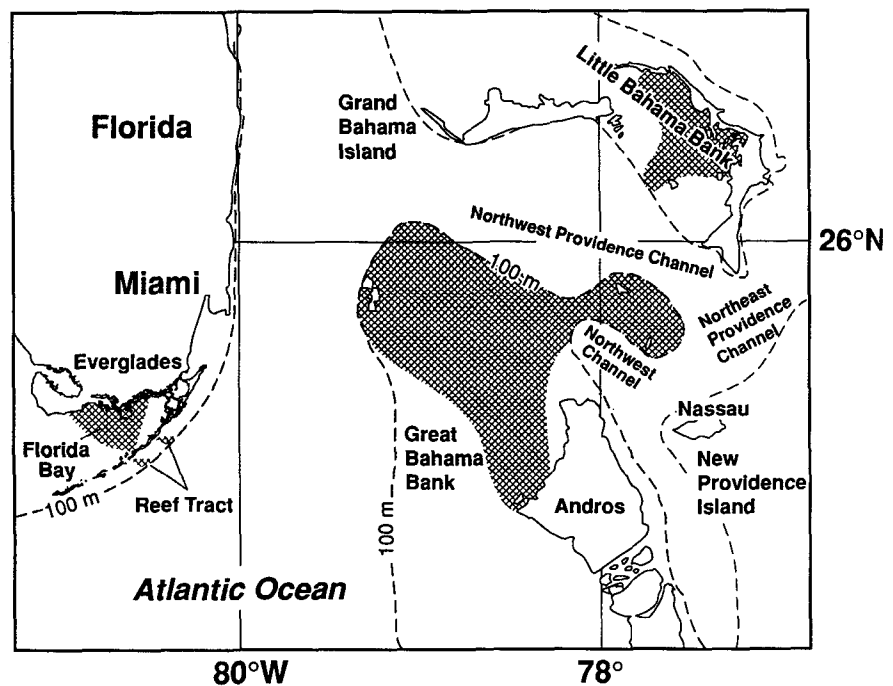


Figure 1. Map of south Florida and the Bahama Banks. Pattern shows sampling areas of Florida Bay, Atlantic reef tract, and Great and Little Bahama Banks. Most samples were obtained in water depths of <10 m. Florida Bay is most hydrographically isolated of the banks and also has greatest freshwater influx from the Everglades. Less protected, but broader, platforms of Great and Little Bahama Banks have less freshwater input but still undergo significant evaporation.

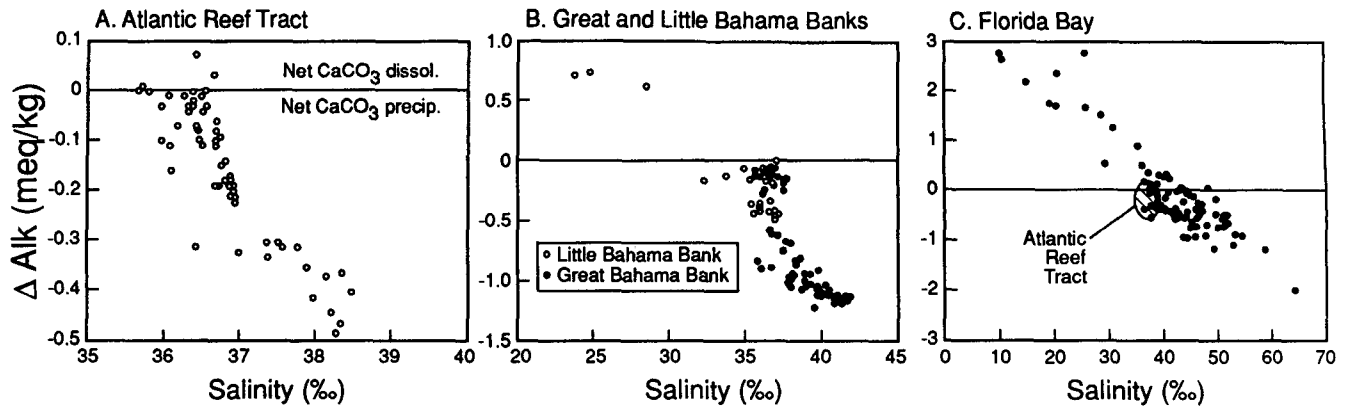


Figure 2. Titration alkalinity and salinity of bank seawater. Samples from south Florida platform were collected in May 1990, January 1991, and August 1991. Samples from Bahama platform were collected in January 1992 and July 1992. Because salinity is variable, alkalinity change is normalized to salinity (standard seawater value used is 2.4 meq/kg at salinity of 35‰ [Morse et al., 1984]). Most bank waters exhibit decreases in normalized titration alkalinity by carbonate precipitation, but Little Bahama Bank and Florida Bay exhibit increases in normalized alkalinity at low salinity due to carbonate dissolution. Conservative mixing and evaporation behavior would fall on horizontal line at normalized alkalinity of zero. Analytical uncertainty is  $\pm 0.05\%$  for salinity and  $\pm 0.025$  meq/kg for titration alkalinity.

tures ranged from 20 to 33 °C, most measurements being between 26 and 29 °C.

Water samples were analyzed for temperature (*T*), pH, Cl, titration alkalinity,  $\Sigma\text{CO}_2$ , Ca, Mg, and Sr.  $\delta^{13}\text{C}$  of  $\Sigma\text{CO}_2$  was determined for a representative subset of water samples as well as for sediment from representative cores. Filtered seawater samples were preserved for isotopic analysis in serum vials prepoisoned with  $\text{HgCl}_2$ , capped with Teflon septa. Offline extractions for both  $\Sigma\text{CO}_2$  and  $\text{CaCO}_3$  used a  $\text{N}_2$ -purged syringe and subsequent addition of phosphoric acid in vacuo. Yield for  $\text{CO}_2$  in waters was verified by pressure-transducer comparison to coulometric titration. Analyses were performed on a Finnegan Delta-S Ratio mass spectrometer with analytical uncertainty of  $\pm 0.1\%$  (relative to PDB).

Evaporation and progressive  $\text{CaCO}_3$  withdrawal occur during seawater residence time on the platform (Fig. 2). Commonly, waters with salinities below 35‰ display elevated salinity-normalized alkalinity, indicating that dilution adds nonmarine  $\Sigma\text{CO}_2$ . This is a consequence of meteoric discharge

from carbonate aquifers and surface runoff, which has dissolved Pleistocene carbonate. Freshwater discharge and evaporative concentration are most apparent for waters from Florida Bay (Fig. 2C). These results may in part represent more detailed sampling, but they likely also reflect discharge from the Everglades watershed and the more restricted character of this platform relative to the Bahama Banks.

$\Sigma\text{CO}_2$  in all samples is significantly depleted in  $^{13}\text{C}$  relative to the  $+2\%$  value typical of surface "blue" ocean water, regardless of whether salinity has increased or decreased (Fig. 3). Samples from the Atlantic reef tract (Fig. 3A) have undergone the smallest change in salinity and alkalinity, as well as the smallest isotopic depletion ( $+0.5\%$  to  $+1.7\%$ ). Samples from the Bahama Banks (Fig. 3B) that have evolved compositionally via evaporation and meteoric dilution are more variable and isotopically depleted; values range from about  $-2.2\%$  to  $+1.2\%$ . Florida Bay waters (Fig. 3C) exhibit greatest variation in salinity and  $\delta^{13}\text{C}$ . Depletion in  $^{13}\text{C}$  is common, per-

haps characteristic, and is associated with seawater residence time on the platform.

Processes involved in  $^{13}\text{C}$  depletion of seawater overlying these platforms are best illustrated by the Florida data set. There,  $\delta^{13}\text{C}$  of "normal-salinity" seawater from the reef tract is close to that predicted in equilibrium with the atmosphere (Mook et al., 1974). However, at salinity values above or below this "normal" value, the C reservoir becomes increasingly depleted (Fig. 3C). Data from other locations (Fig. 3 A and B) fall within the domains defined by Florida Bay waters. Depletion of  $^{13}\text{C}$  in low-salinity water results from  $\text{CO}_2$  input from terrestrial organic-matter oxidation buffered by dissolution of Pleistocene limestone. In evaporatively concentrated waters, depletion in  $^{13}\text{C}$  may be driven by progressive carbonate precipitation, photosynthesis, and respiration, all of which occur as the water mass "ages."

Isotopic fractionation of the C reservoir by carbonate precipitation contributes to, but cannot account for, the  $-4\%$  to  $-5\%$  isotopic depletion. Alkalinity data indicate

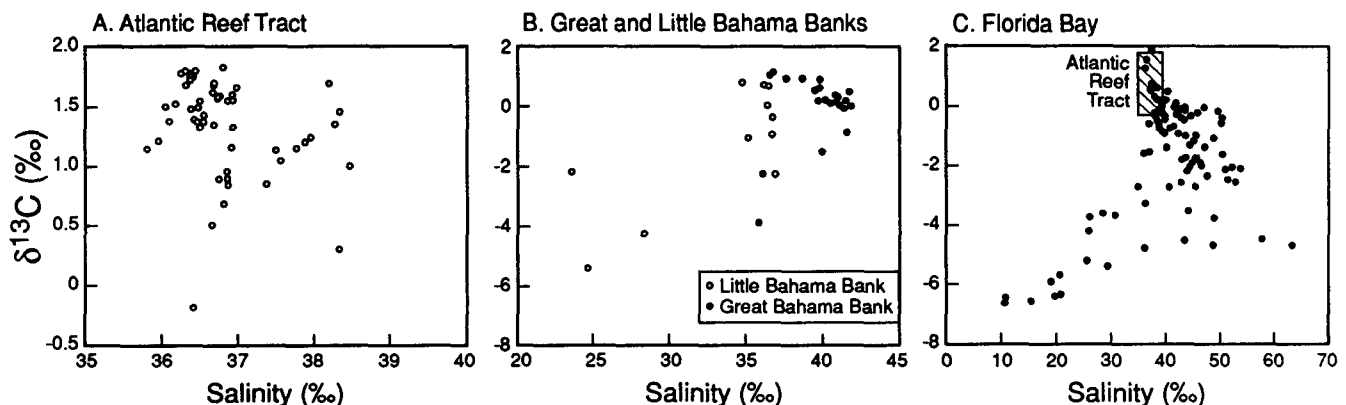


Figure 3.  $\delta^{13}\text{C}$  of  $\Sigma\text{CO}_2$  of platform seawater relative to salinity.

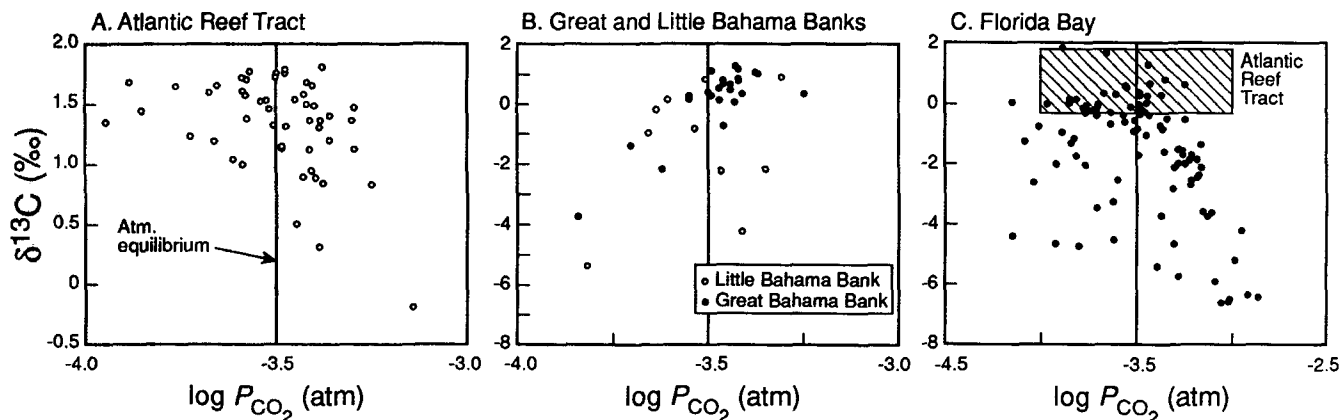


Figure 4. Plot of  $\delta^{13}\text{C}$  of  $\Sigma\text{CO}_2$  for platform seawater relative to calculated equilibrium  $\text{CO}_2$  partial pressure.  $\log P_{\text{CO}_2}$  was calculated using carbonic acid system constant algorithms in Millero (1979) with pH measured on NBS scale, titration alkalinity, temperature, and salinity. Uncertainty in  $\log P_{\text{CO}_2}$  is  $\pm 0.05$  log units.

that no more than half the  $\Sigma\text{CO}_2$  is removed by precipitation. Assuming isotopic enrichment of  $+2.7\text{‰}$  relative to water during precipitation of aragonite, and  $+1.0\text{‰}$  during precipitation of calcite (Romanek et al., 1992), the residual  $\Sigma\text{CO}_2$  is depleted by at most  $\sim 1\text{‰}$ .

Photosynthesis preferentially removes isotopically light C, generating  $^{13}\text{C}$  enrichment of the water reservoir rather than the observed depletion. Alternatively, rapid disequilibrium invasion of atmospheric  $\text{CO}_2$  ( $\sim -9\text{‰}$  relative to PDB) can occur in waters of unusually high pH and low  $\Sigma\text{CO}_2$  (Herczeg and Fairbanks, 1987; Lazar and Erez, 1992). Marine brines ( $S = 70\text{‰}$  to  $120\text{‰}$ ) associated with algal mats exhibit significant depletion in  $\Sigma\text{CO}_2$  and can attain  $\delta^{13}\text{C}$  values as low as  $-6\text{‰}$  (Lazar and Erez, 1992). Because these platforms have not experienced such extreme chemical evolution, an alternative explanation is required for the depleted  $^{13}\text{C}$  values we observe.

Most bank waters have  $P_{\text{CO}_2}$  values out of equilibrium with respect to the atmosphere. Rates of  $\text{CaCO}_3$  precipitation and organic-matter remineralization must be sufficiently rapid to maintain disequilibrium (Fig. 4). The photosynthetic  $\text{CO}_2$ -fractionation mechanism invoked for marine brines (Lazar and Erez, 1992) is incompatible with the variable isotopic depletion for bank waters, many of which are supersaturated with respect to the atmosphere. Net respiration elevates  $P_{\text{CO}_2}$  in many waters of normal salinity and hypersalinity, as well as those diluted by meteoric water (see Fig. 2 for distribution of salinity). Even bank waters with  $P_{\text{CO}_2}$  values less than those of the atmosphere display no relation between  $^{13}\text{C}$  depletion and  $P_{\text{CO}_2}$ .

The simplest explanation for  $^{13}\text{C}$  depletion, first advanced by Lloyd (1964), is the input of isotopically light C from respiration. This explains the  $^{13}\text{C}$  depletion in bank waters unaffected by freshwater discharge.

The less pronounced  $^{13}\text{C}$  depletion in hypersaline Florida Bay water is consistent with the less depleted  $^{13}\text{C}$  in marine organic matter ( $\delta^{13}\text{C} \approx -10\text{‰}$  for grasses and algae; Mitterer et al., 1988; and our own data) relative to terrestrial organic matter ( $\delta^{13}\text{C} \approx -25\text{‰}$ ). The most restricted waters of Florida Bay can, in fact, have near-normal salinity because of the dilution of hypersaline water by meteoric discharge from the Everglades, which complicates the  $^{13}\text{C}$  budget.

The mechanism of  $^{13}\text{C}$  depletion in surface waters on carbonate banks is similar to that of the global ocean, although depletion is manifested in a lateral, rather than vertical, orientation. Deep, open-ocean water masses exhibit progressive depletion in  $^{13}\text{C}$  with increasing  $\Sigma\text{CO}_2$  and increasing oxygen utilization (e.g., Kroopnick, 1985). However, processes affecting the budget and isotopic composition of C and water inputs to carbonate platforms are temporally and spatially more variable, leading to a less regular relation between  $\delta^{13}\text{C}$  and chemistry.

The spatial variability in  $\delta^{13}\text{C}$  in Florida Bay water is similar to that illustrated by Lloyd (1964) for gastropod shells in this area. Figure 5 shows  $\delta^{13}\text{C}$  values of bulk sediment in two representative cores from Florida Bay (Captain Key) and the inner Atlantic reef tract (Tavernier bank). Predicted  $\delta^{13}\text{C}$  values from our water measurements agree well with observed  $\delta^{13}\text{C}$  values in the sediment. The data indicate that sediment accumulated in areas of restricted exchange is significantly depleted in  $^{13}\text{C}$  relative to that in areas of more open exchange.

#### IMPLICATIONS FOR THE PHANEROZOIC $\text{CaCO}_3$ RECORD

During the Paleozoic, most carbonate accumulated in epeiric seaways and on continental shelves. Likewise, in the Mesozoic and Cenozoic, a high percentage of carbon-

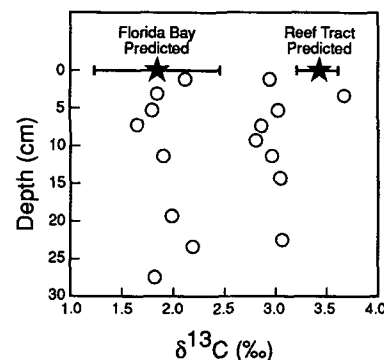


Figure 5. Measured  $\delta^{13}\text{C}$  of sediment from two representative cores agrees well with that calculated from water composition. Predicted sediment values are calculated by using  $\delta^{13}\text{C}$  of  $\Sigma\text{CO}_2$  in overlying water from each area and for carbonate-water equilibrium values from Romanek et al. (1992) with sediment composed of 65% aragonite and 35% calcite (Patterson, 1992). Mean  $\delta^{13}\text{C}$  of  $\Sigma\text{CO}_2$  for Florida Bay samples adjacent to Captain Key is  $-0.28\text{‰}$  ( $n = 9$ ), and reef tract values for Tavernier Key average  $1.31\text{‰}$  ( $n = 17$ ) relative to PDB. Error bars represent 1 standard deviation for each population.

ate was precipitated in such restricted environments. Phanerozoic carbonate  $\delta^{13}\text{C}$  values have been considered a record of variation in seawater composition (e.g., Veizer and Hoefs, 1976; Lindh, 1983). These secular trends assume that the  $\delta^{13}\text{C}$  composition of epeiric seas approximates that of global surface seawater. However, if epeiric seas experienced the restriction and compositional evolution away from open-marine values that we observe on modern platforms, this assumption becomes questionable. The entire  $\delta^{13}\text{C}$  variation over Phanerozoic time is about  $8\text{‰}$ , too large a shift to be a simple function of environment. However, many variations oscillate over smaller ranges, with changes of several per

mil considered significant (e.g., Magaritz and Stemmerik, 1989; Föllmi et al., 1994).

Biogeochemical models utilize  $\delta^{13}\text{C}$  of seawater as recorded in carbonate rocks to partition C into "reduced" and "oxidized" C reservoirs and to model variation of atmospheric  $\text{CO}_2$  and  $\text{O}_2$  levels through time. The compilation of Lindh (1983) has been applied to biogeochemical models (e.g., Berner, 1987, 1989). Although diagenetic alteration has been recognized as a potential problem, our results show that depositional environment also must be considered before the  $\delta^{13}\text{C}$  of carbonate can be assumed to represent the  $\delta^{13}\text{C}$  of global surface seawater.

Isotopic analyses of stable C in well-preserved skeletal carbonate (i.e., brachiopods) have been used in conjunction with O isotopic composition to estimate Paleozoic seawater depth and temperature, respectively (e.g., Grossman et al., 1993). However, stable isotopic composition and chemistry of modern platform seawater vary laterally, and  $^{13}\text{C}$  depletion can be produced by freshwater runoff or by evaporation. Similarly, the usual response of seawater to freshwater input is  $^{18}\text{O}$  depletion whereas evaporation normally results in  $^{18}\text{O}$  enrichment (e.g., Adlis et al., 1988). Thus, carbonate depleted in  $^{13}\text{C}$  could be produced by increasing water depth (by analogy with modern oceans), freshwater input, and meteoric diagenesis. Correspondingly, carbonate depleted in  $^{18}\text{O}$  can be produced by increasing temperature, freshwater input, and meteoric diagenesis, whereas  $^{18}\text{O}$  enrichment could indicate either lower temperature or evaporation. These results greatly complicate the mutual interpretation of  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  in the rock record.

An illustrative example of these mutual relations is found in well-preserved Paleozoic brachiopods from established shallowing-upward sequences (Adlis et al., 1988) that nevertheless display  $^{13}\text{C}$  depletion and  $^{18}\text{O}$  enrichment. Our data, however, suggest that depleted  $^{13}\text{C}$  and enriched  $^{18}\text{O}$  values can readily be explained by restriction and evaporative concentration. Although diagenetic alteration also can result in depleted  $^{13}\text{C}$ , it would likely result in depleted rather than enriched  $^{18}\text{O}$  (e.g., Magaritz and Stemmerik, 1989).

The strong lateral, environmentally driven change in  $\delta^{13}\text{C}$  of surface seawater likely has analogues in the ancient carbonate rock record, which accumulated predominately in epeiric seas. An important fact is that extreme salinity excursions are not required for significant depletion in seawater  $^{13}\text{C}$ . Even within a "near-normal" salinity range of 34‰ to 38‰, isotopic depletion relative to surface open-ocean water can be as great as 4‰. The focus on vari-

ation of  $\delta^{13}\text{C}$  with depth in the modern ocean cannot be simply applied to isotopic shifts in ancient platform carbonates, which likely experienced strong lateral gradients and restricted circulation. Ancient carbonate deposited in lower energy lagoonal facies is most likely to be associated with chemically evolved seawater. Facies least likely to be affected are those that occupy shelf breaks and margins such as oolite and organic reef facies.

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