

Global synchronous changes in the carbon isotopic composition of carbonate sediments unrelated to changes in the global carbon cycle

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The carbon isotopic ($\delta^{13}\text{C}$) composition of bulk carbonate sediments deposited off the margins of four carbonate platforms/ramp systems (Bahamas, Maldives, Queensland Plateau, and Great Australian Bight) show synchronous changes over the past 0 to 10 million years. However, these variations are different from the established global pattern in the $\delta^{13}\text{C}$ measured in the open oceans over the same time period. For example, from 10 Ma to the present, the $\delta^{13}\text{C}$ of open oceanic carbonate has decreased, whereas platform margin sediments analyzed here show an increase. It is suggested that the $\delta^{13}\text{C}$ patterns in the marginal platform deposits are produced through admixing of aragonite-rich sediments, which have relatively positive $\delta^{13}\text{C}$ values, with pelagic materials, which have lower $\delta^{13}\text{C}$ values. As the more isotopically positive shallow-water carbonate sediments are only produced when the platforms are flooded, there is a connection between changes in global sea level and the $\delta^{13}\text{C}$ of sediments in marginal settings. These data indicate that globally synchronous changes in $\delta^{13}\text{C}$ can take place that are completely unrelated to variations in the global carbon cycle. Fluctuations in the $\delta^{13}\text{C}$ of carbonate sediments measured during previous geological periods may also be subject to similar processes, and global synchronicity of $\delta^{13}\text{C}$ can no longer necessarily be considered an indicator that such changes are related to, or caused by, variations in the burial of organic carbon. Inferences regarding the interpretation of changes in the cycling of organic carbon derived from $\delta^{13}\text{C}$ records should be reconsidered in light of the findings presented here.

isotope | organics | shallow-water platform

Variations in the stable carbon isotopic composition ($\delta^{13}\text{C}$) of calcium carbonate sediments throughout geological time have been an invaluable aid in unraveling changes in the global carbon cycle (1, 2). In addition, such variations in $\delta^{13}\text{C}$ have provided information on the transfer of carbon between reservoirs during major geological events such as bolide impacts or catastrophic climate changes (3, 4). Generally speaking, increases in the $\delta^{13}\text{C}$ of carbonates are considered indicative of increased burial and preservation of isotopically negative organic carbon, whereas decreases in the $\delta^{13}\text{C}$ suggest transfer of carbon from the organic into the inorganic reservoir (5–7). Hence, variation in the $\delta^{13}\text{C}$ of carbonate material should be a proxy for the amount of buried organic carbon. For example, the $\delta^{13}\text{C}$ of the oceanic record has become increasingly more negative over the past 50 million years (Myr) (8, 9), suggesting that as much as 10^{20} g of organic carbon have been transferred from the organic to the inorganic carbon reservoir (6).

The most reliable archives of changes in the $\delta^{13}\text{C}$ of the oceans over the past 100 Myr to 200 Myr are contained in the skeletons of planktic and benthic foraminifera (9, 10). Not only are these organisms relatively diagenetically stable, but the $\delta^{13}\text{C}$ values can be corrected for any species-specific isotopic effects. However, for older time periods, geologists are forced to use records from macrofossils such as brachiopods, belemnites, and mollusks (11, 12) as well as the $\delta^{13}\text{C}$ of bulk sediments associated with

carbonate ramps or platforms (13–15) and from epicontinental seas (16). Shallow water carbonate sediments deposited *in situ* are not reliable recorders of global $\delta^{13}\text{C}$ as they are known to be affected by short-term changes in sea level, which subject the deposits to the influences of meteoric diagenesis during which time the $\delta^{13}\text{C}$ can be altered substantially (17, 18). A more diagenetically stable environment is found on the slopes of carbonate platforms, at depths below glacio-eustatic sea-level changes, where mixtures of pelagic and platform-derived sediments are deposited [so-called periplatform sediments (19)]. In these locations the $\delta^{13}\text{C}$ values of carbonate sediments, although subjected to closed-system diagenesis, are not substantially altered from their original $\delta^{13}\text{C}$ values.

Despite the assumption made by numerous workers that the $\delta^{13}\text{C}$ values of these sediments are related to the global carbon cycle, and that they can be used both as a proxy for the burial of organic material (15) and as a stratigraphic tool (20), several studies have proposed that changes in the $\delta^{13}\text{C}$ of carbonate rocks might not be related to variations in the global organic carbon cycle. For example, it has been suggested that variations in the $\delta^{13}\text{C}$ of carbonate sediments deposited in epeiric seas are related to local recycling of organic material, rather than to changes in the global carbon cycle (18, 21–23). Another study has shown that variations in the $\delta^{13}\text{C}$ of carbonate sediments surrounding the Bahamas, an oceanic dominated platform, are not related to global changes in the organic carbon cycle, at least over the past 25 Myr. Instead the $\delta^{13}\text{C}$ changes recorded in the Bahamian sediments were shown to be related to variations in the amount of sediments produced in the shallow waters of the platforms themselves (23). The study presented in this article tests the hypothesis that the patterns seen in the Bahamas are also present globally, adjacent to other carbonate platforms such as the Maldives (Site 716), Queensland Plateau (Site 817), and the Great Australian Bight (Site 1126) (Fig. 1). If true, the results would challenge the widely held assumption that global synchronicity in $\delta^{13}\text{C}$ variations implies a connection to the global carbon cycle.

Results

Although the absolute $\delta^{13}\text{C}$ values of the sediments are different at each of the localities studied, all of the sites show the same basic trends with respect to age and depth, that is a decrease in the $\delta^{13}\text{C}$ of the bulk sediments from the Holocene to the late Miocene (Fig. 2). The percentage of aragonite also decreases over the same interval at each site and therefore the concentration of aragonite is inversely correlated with the $\delta^{13}\text{C}$ of the

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mineralogy precipitated inorganically and by organisms inhabiting shallow-carbonate platforms. It has been proposed that there has been a change in the dominant type of calcium carbonate precipitated inorganically and by shallow-water carbonate secreting organisms from LMC to aragonite (50) related to the changing Mg/Ca of the oceans (51). Modern oceans have a Mg/Ca ratio of ≈ 5 , which favors the precipitation of aragonite over LMC. As this ratio is lowered, LMC becomes the preferred form of calcium carbonate precipitation. As aragonite is $\approx 2\text{--}3\text{‰}$ enriched in $\delta^{13}\text{C}$ relative to LMC at standard temperatures and pressures, the pattern of decreasing $\delta^{13}\text{C}$ with age over periods >10 Myr, which is evident at Site 1006 (23), may partially reflect a change from predominantly aragonite to calcite deposition by shallow-water organisms.

Previous work has suggested that global changes in sea level during the Paleozoic could cause local variation in the recycling of organic carbon, also leading to changes in $\delta^{13}\text{C}$ in epeiric seas unrelated to the global carbon cycle (21, 22). During high stands of sea level it was suggested that circulation of water would be increased, hence reducing the influence of oxidized organic material. During sea-level falls circulation would be restricted and the $\delta^{13}\text{C}$ would decrease. Such changes would be manifested as a decrease in the $\delta^{13}\text{C}$ of carbonates toward the more restricted portions of the shelf (52). The mechanism proposed by those workers (21, 22, 52) could easily complement the model presented here during certain geological time periods, thus making the interpretation of changes in the $\delta^{13}\text{C}$ of carbonates even more problematic.

Regardless of the mechanisms accounting for the synchronous variations in $\delta^{13}\text{C}$ between these four locations, this study has

shown that a major assumption regarding changes in the $\delta^{13}\text{C}$ of periplatform carbonate sediments is flawed. Although some previous researchers (14, 53) argued that synchronous changes in the $\delta^{13}\text{C}$ of sediments had to indicate global changes in the carbon cycle, clearly the results of this study show that in addition to changes in the global carbon cycle, other factors may also be important. One of these factors is the input of different types of sediments with varying $\delta^{13}\text{C}$ values.

Methods

Samples of sediment (5 cm³) from the cores were freeze-dried, and a portion of the bulk sample was analyzed for $\delta^{13}\text{C}$ by using a Finnigan-MAT 251 after dissolution in phosphoric acid by using a common-acid bath technique (54). Data were corrected for the usual isobaric interferences (55) modified for a triple collector mass spectrometer. Data are reported relative to Vienna Pee Dee Belemnite by using the conventional notation. Data from a previous study (56) were also analyzed by using the identical procedure and the same mass spectrometer at the University of Miami. For comparative purposes, isotopic data were interpolated into 100-ka intervals by using a rectangular interpolation method (57). The proportion of aragonite and calcite in the sediments was determined by x-ray diffraction using a model that assumed that the sample was composed only of aragonite, LMC, high-Mg calcite, and dolomite (58). The ages of the samples were calculated by using published age vs. depth relationships (27–30).

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