

Syndepositional diagenesis of modern platform carbonates: Evidence from isotopic and minor element data

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ABSTRACT

Physical, elemental, and stable isotopic evidence documents significant syndepositional diagenesis of biogenic carbonate in modern sediment pore water. *Halimeda* (aragonite) and *Neogoniolithon* (high-Mg calcite) fragments from sediment cores and experimental substrates were compared with fresh samples to determine the magnitude of minor element (Sr, Mg), and stable isotopic (C and O) compositional shifts. Although no significant shift in bulk sediment mineralogy is apparent, experimental substrates and natural biogenic grains exhibit significant diagenetic changes. These changes include dissolution textures, net loss of mass, changes in minor element composition, and progressive evolution toward carbon and oxygen isotopic equilibrium with pore water. Our results demonstrate that carbonate sediment can undergo rapid syndepositional dissolution and reprecipitation. Pore waters likely are buffered chemically and isotopically by most abundant carbonate grain types. In turn, compositions of less abundant carbonate grains may shift toward equilibrium with respect to pore water. Therefore, many components of shelf limestone have compositions controlled by chemically evolved pore waters rather than by seawater from which the biotic carbonate originally precipitated.

INTRODUCTION

Modern tropical carbonates are in contact with seawater highly supersaturated with respect to all carbonate minerals. Nevertheless, acids released during decomposition of organic matter within surface sediment produce undersaturation in pore waters (e.g., Morse et al., 1985; Walter and Burton, 1990). Elevated Ca/Cl in pore waters of platform carbonate sediment suggests that net dissolution is an important process (e.g., Morse et al., 1985; Walter and Burton, 1990). Moreover, data on minor elements (Sr, F; Rude and Aller, 1991) and carbon isotopes (Walter et al., 1993) in pore water suggest that dissolution can be accompanied by reprecipitation of more stable carbonate phases.

Coupled dissolution and reprecipitation could promote significant diagenetic alteration of biogenic grains. On the basis of mineralogical and scanning electron microscopy textural studies, Reid et al. (1992) suggested that carbonate shelf sediment of Belize was massively recrystallized. As a complement to a detailed investigation of pore-water chemistry, we conducted a physical and geochemical study of the sediment. We present stable isotopic and minor element data on green and red calcareous algae, including living specimens, fragments recovered from sediment, and experimental substrates exposed to natural pore water which documents significant syndepositional diagenesis of biogenic carbonate.

STUDY SITE

Investigations of bulk and fine-fraction sediment mineralogy, isotopic and elemen-

tal chemistry of several biogenic carbonate producers and sediment grains, and carbonate substrate implantation experiments were made for sedimentary environments of the South Florida platform, Florida Bay, and the Atlantic reef tract (Fig. 1). Florida Bay sites include Crab, Captain, and Shell keys; reef tract sites focused on Rodriguez, Tavernier, and Indian keys. Descriptions of these environments and their pore water chemistry can be found in Walter and Burton (1990).

Carbonate sediment of the Florida platform is un lithified wackestone to packstone composed almost exclusively of metastable

aragonite and high-Mg calcite (HMC), with minor low-Mg calcite (LMC). Typically, aragonite composes 60%–80% of the sediment. Calcareous green algae are important sediment producers throughout the platform. The sediment-pore water system is geochemically open because of intense bioturbation (e.g., Shinn, 1968; Enos and Perkins, 1979). Pore waters have near-normal sulfate concentrations despite rapid sulfate reduction rates, attesting to open exchange with overlying seawater (Walter and Burton, 1990; Walter et al., 1993).

METHODS

We sampled green and red calcareous algae (*Halimeda*, aragonite; *Neogoniolithon*, 18 mol% Mg calcite) because of their significance to sediment budgets, coherence as fragments in sediment, and physical integrity as experimental substrates. Sediment from 30-cm-long box cores was sampled at depth intervals of 2 cm resolution and analyzed for bulk and size fraction (<63 μm) mineralogy. Living specimens were collected proximate to each sample site to determine initial appearance and composition. Biogenic fragments recovered from cores were compared with fresh skeletal materials to quantify changes in elemental and isotopic composition.

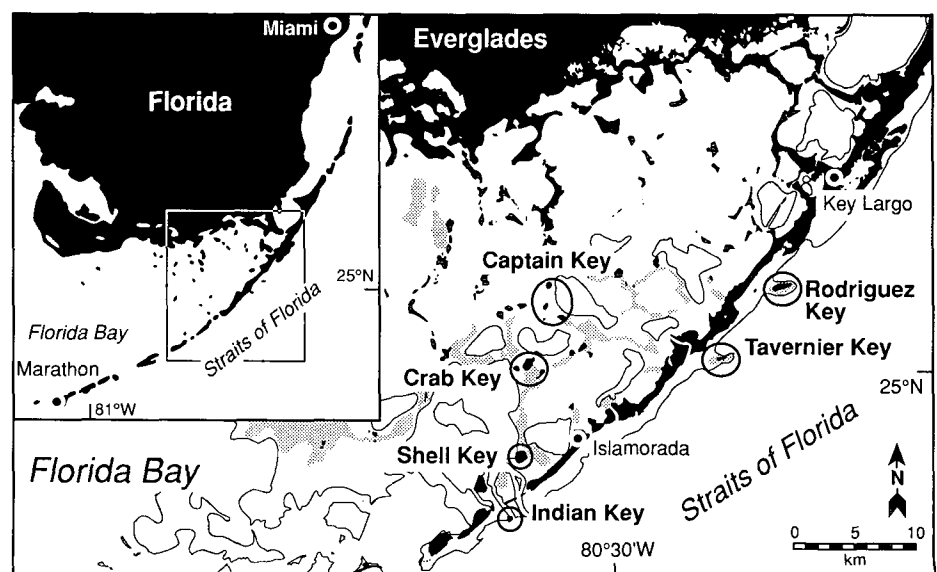


Figure 1. Map of south Florida study locations, including Florida Bay and Atlantic reef tract. Labeled circles indicate sampling locations. Stippled areas denote location of mudbanks.

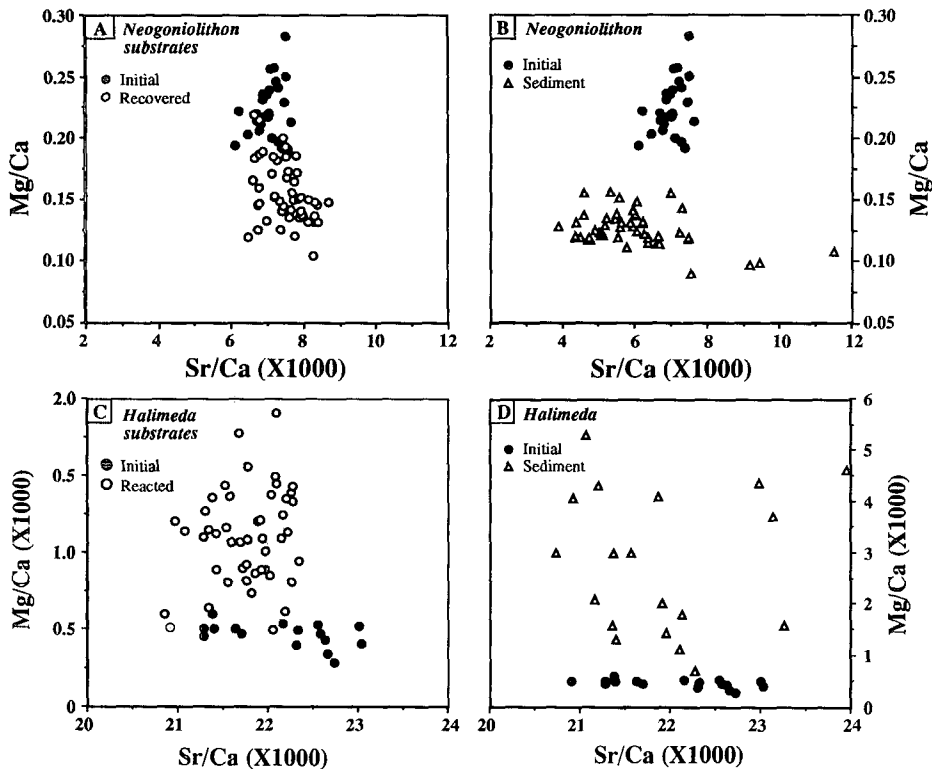


Figure 4. A: Recovered *Neogoniolithon* substrate grains lose substantial percentage of original Mg, whereas Sr content remains relatively constant. B: *Neogoniolithon* sediment grains lose much more Mg than do initial and reacted substrates. C: Mg content of *Halimeda* substrates increases up to 400% relative to initial values, likely due to precipitation of secondary Mg calcite. (Note change in scale.) D: Mg/Ca of sediment grains is up to ten times greater than Mg/Ca of initial grains. (Note change in scale.) This indicates that as much as 15 wt% of some grains may be secondary carbonate.

net dissolution rates determined from change in mass of carbonate substrates after exposure to pore water for 500 days (d) are presented in Figure 2. *Neogoniolithon* substrates show significant net dissolution of 2%–8%/yr (Fig. 2A). *Halimeda* substrates (Fig. 2B) show small weight losses, or even weight increases. The greater instability of 18 mol% Mg calcite relative to aragonite, as well as reactive surface area differences, doubtless affect weight changes in substrates. Mass loss appears independent of sediment depth; rapid bioturbation rates likely blur any potential trends. Moreover, pore-water concentration profiles show little variation with depth over the depth interval (Walter and Burton, 1990, and unpublished data).

SEM examination of the reacted substrates, however, reveals both dissolution and reprecipitation features. Comparison of fresh *Halimeda* grains from reef tract surface sediments with substrates (Fig. 3, A and B) reveal striking differences. Exposed *Halimeda* substrates commonly have rhombohedral calcite overgrowths (Fig. 3B). Dissolution features include rounding of crystal termini. *Neogoniolithon* substrates (Fig. 3, C and D, respectively) exhibit prom-

inent dissolution features, preferentially affecting cell walls and surfaces.

CHEMICAL CHANGES WITHIN SUBSTRATES AND NATURAL SEDIMENT GRAINS

Despite the short contact time between incubated substrates and pore waters (500 days), significant chemical shifts are observed (Fig. 4). The decrease in Mg content for *Neogoniolithon* (Fig. 4, A and B) suggests that differential dissolution of HMC and/or a brucite phase has occurred. Brucite can comprise up to several weight percent of red algae (e.g., Milliman et al., 1971) and is rapidly removed during exposure to pore water (Walter and Burton, 1990). Less stable, higher magnesium phases may reside in or between the walls, which appear to undergo dissolution most rapidly (see SEM image in Fig. 2D). The lower Sr/Ca ratios of reacted *Neogoniolithon* grains are consistent with precipitation of a lower Mg calcite (with lower Sr content) or dissolution of the higher Mg calcite, which would contain relatively more Sr (Carpenter and Lohmann, 1992).

As would be expected from longer contact time with pore water, *Neogoniolithon* fragments from natural sediment are even more

extensively altered than are substrates (Fig. 4B). The compositional data suggest a continued differential dissolution process (preferential loss of Mg), because the Mg/Ca of sediment fragments is even lower than that of recovered substrates.

Analyses of Mg/Ca and Sr/Ca of reacted *Halimeda* substrates are compared with fresh specimen values in Figure 4C. The Mg/Ca of reacted substrates is up to four times greater than that of the initial biogenic material, consistent with precipitation of a secondary Mg calcite. Mass balance calculations indicate that precipitation of 5 wt% of a 12 mol% Mg calcite could produce the compositions in the reacted substrates. Compositions of *Halimeda* initial and reacted sediment grains shown in Figure 4D clearly indicate much greater accumulation of Mg-rich secondary carbonate. These more extreme elemental changes require that secondary Mg calcite comprise 15 wt%, on average, of recovered sediment grains.

If carbonate dissolution and reprecipitation is as extensive as suggested by elemental shifts, the stable isotopic composition could be affected. Carbon and oxygen isotopic composition of unreacted *Halimeda* substrates, shown in Figure 5A, vary by about 1‰ in $\delta^{18}\text{O}$ value and 3‰ in $\delta^{13}\text{C}$. Reacted *Halimeda* substrates, moreover, are more variable (2‰ in $\delta^{18}\text{O}$ and 4‰ in $\delta^{13}\text{C}$), possibly reflecting heterogeneity in pore-water composition (Fig. 5A). The initial variation identified in unreacted *Halimeda* substrates and proximity to equilibrium with pore-water isotopic compositions preclude a simple trend in the isotopic composition of reacted substrates. Any secondary calcite precipitated on *Halimeda* substrates should have an isotopic composition close to equilibrium with respect to pore water, which in turn is indistinguishable from the original biogenic composition. Thus, for aragonitic *Halimeda* substrates, changes in Mg content are more sensitive indicators of precipitation of secondary Mg calcite than are stable isotopic shifts.

Neogoniolithon initial substrates have a narrow range of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values and are substantially out of equilibrium with the pore water (Fig. 5). Isotopic shifts in *Neogoniolithon* grains would therefore be expected to be better tracers of diagenesis. Secondary calcium carbonate precipitated from pore waters would be approximately 6‰ heavier in $\delta^{18}\text{O}$ and 8‰ heavier in $\delta^{13}\text{C}$ than original biogenic values. The $\delta^{18}\text{O}$ values of recovered *Neogoniolithon* substrates (Fig. 5C) are up to 2‰ more positive after 500 d exposure, whereas $\delta^{13}\text{C}$ values are nearly unchanged. Mass balance requires that about 25 wt% of the exposed substrate is converted to secondary Mg calcite per year.

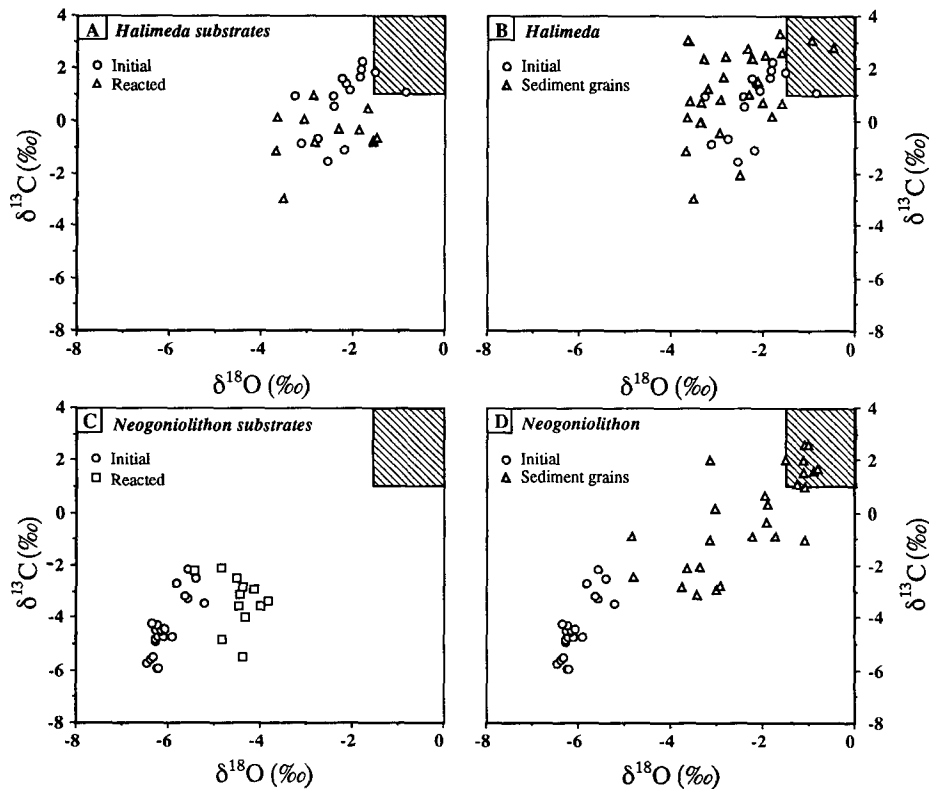


Figure 5. A: Initial *Halimeda* compositions are close to values predicted for carbonate precipitated in carbon and oxygen isotopic equilibrium with pore waters (compositions from Walter et al. [1993], represented by box at upper right). **B:** As in A, secondary carbonate precipitated from pore water is similar in composition to that of initial carbonate. **C:** Reacted *Neogoniolithon* substrates are up to 2‰ heavier in oxygen, with no significant change in carbon isotopic composition from initial composition. Precipitation of secondary carbonate in equilibrium with pore water is responsible for observed shifts in isotopic composition. **D:** Isotopic composition of grains is significantly enriched for both carbon and oxygen, more than 6‰ and 8‰, respectively.

Evolution of the stable isotopic composition of natural sediment grains is more extensive than are changes in experimental substrates, presumably because of the longer residence time in the sediment-pore water system (see Fig. 5, B and D). *Neogoniolithon* Mg calcite stable isotopic composition approaches equilibrium with respect to pore-water values, nearly 7‰ enriched in $\delta^{18}\text{O}$ and 8‰ enriched in $\delta^{13}\text{C}$ (Fig. 5D). Therefore, dissolution of original HMC and precipitation of lower Mg calcite and aragonite are reflected in the elemental and isotopic compositional shifts between original specimens and sediment fragments.

SUMMARY

Early marine diagenesis of metastable carbonates is driven by chemical evolution of pore water during oxidation of organic matter. Dissolution and reprecipitation occur rapidly and can produce significant isotopic and elemental exchange. The magnitude of the change depends on the original elemental and isotopic composition of the biogenic carbonate relative to that precipi-

tated in equilibrium with the pore water, as well as grain abundance and reactivity.

Comparison of initial chemical and isotopic compositions of biogenic carbonates investigated with that of experimentally implanted substrates of the same material indicate that significant alteration occurs within 500 d. *Neogoniolithon* substrates evolve rapidly from values near 30 mol% Mg to values as low as 15 mol%. *Neogoniolithon* fragments from sediment, owing to greater exposure time, lose even more Mg than the experimental substrates. *Halimeda* substrates are encrusted with up to 15% secondary Mg calcite after only 500 d in the sediment, even though substrates experienced little net weight change.

Isotopic analyses of initial *Halimeda* grains are close to those in isotopic equilibrium with chemically evolved pore water, making it difficult to distinguish between original and secondary carbonate on the basis of isotopic composition alone. Isotopic analyses of *Neogoniolithon* substrates demonstrate precipitation of secondary carbonate equivalent to 25% of the total grain mass per year, despite up to 10% net loss of mass.

Neogoniolithon grains from the sediment are enriched in ^{18}O and ^{13}C by up to 7‰ and 8‰, respectively. Thus, significant shifts in elemental and stable isotopic compositions away from those initially acquired in seawater can occur in the dynamic environment of chemically evolved sediment pore waters.

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