ORGANOGENIC DOLOMITIZATION IN PERITIDAL TO DEEP-SEA SEDIMENTS

S.J. MAZZULLO

Department of Geology, Wichita State University, Wichita, Kansas 67260, U.S.A.
e-mail: mazzullo@twsuvm.uc.twsu.edu

ABSTRACT: Presumed barriers to early dolomitization in normal sea-water-derived pore fluids at earth-surface temperatures appear to be overcome within some anoxic, organic-rich sediments as a result of bacterial sulfate reduction and methanogenesis. These processes may promote early dolomitization, particularly during methanogenesis and late stages of sulfate reduction, by concurrently raising and sustaining high pH and high total alkalinity and CO_3^{2-} concentrations in pore fluids, and by simultaneously either decreasing Mg and Ca hydration or by promoting crystal surface reactions with less hydrated Mg–Ca neutral ion pairs. Volumetrically significant quantities of dolomite are associated with sulfate reduction and/or methanogenesis within peritidal, shallow-marine, and deep-sea deposits. Average concentrations of organogenic dolomite are as much as 70% in some Holocene peritidal deposits, and 28% in Mesozoic to Quaternary deep-sea sediments.

Organogenic dolomites are mainly cements, and contain relatively low concentrations of Sr and Mn. Sulfate-reduction dolomites generally are Fe-deficient because of concurrent pyrite precipitation, whereas methanogenetic dolomites may be somewhat more ferroan as Fe substitutes for depleting Mg. Sources of Mg and Ca for dolomite are diffusion from overlying seawater and/or dissolution of precursor carbonate sediments. Dolomites are characterized by a wide range in $\delta^{13}C$ values wherein those of sulfate reduction versus methanogenetic origin typically are ^{13}C-depleted and ^{13}C-enriched, respectively. The extent of ^{13}C depletion or enrichment, however, depends on the extent of organodiagenetic reactions and amount of ^{13}C contributed by seawater diffusion, and commonly results in overlap of $\delta^{13}C_{dolomite}$ values. The range of $\delta^{18}O_{dolomite}$ values is somewhat more restricted, and generally reflects differences in pore-fluid temperature and salinity. Some of the unresolved issues in organogenic dolomitization are: the relative efficiencies of sulfate reduction versus methanogenesis in promoting dolomitization, depths of dolomite formation inferred on the basis of $\delta^{18}O_{dolomite}$ values and probable sources of Mg and Ca, and the mode of dolomitization with progressive burial into methanogenetic zones.

INTRODUCTION

The origin of dolomite has been a subject of scientific scrutiny for more than 200 years, and the many depositional and geochemical models that have been proposed are reviewed by Land (1980), Zenger et al. (1980), Machel and Mountjoy (1986, 1987), Hardie (1987), Morrow (1990b), Braithwaite (1991), and Purser et al. (1994). Yet, an important aspect of the ''dolomite problem'' remains: how barriers to dolomite nucleation may be overcome at earth-surface temperature. This problem applies particularly to modern and ancient dolomites that precipitated essentially syndepositionally in marine or marine-derived pore fluids within peritidal, shallow-marine, and deep-sea deposits. Such a timing is referred to as ''early dolomitization'' in this paper. The pioneering studies of deep-sea deposits by workers such as Bramlette (1946), Russel et al. (1967), Murata et al. (1969), Murata et al. (1972), Gieskes (1975), Irwin et al. (1977), Pisciotto (1981), Pisciotto and Mahoney (1981), and Kelts and McKenzie (1982), for example, crystallized the concept of organic-matter diagenesis—''*organodiagenesis*''—and its possible relevance to the early formation of ''organogenic dolomites'' (Compton 1988a). Organodiagenesis relates specifically to the role of bacterial sulfate reduction and methanogenesis in overcoming barriers to dolomite nucleation within anoxic, organic-rich sediments at earth-surface temperatures. These processes have been invoked to explain early dolomitization in many deep-sea deposits, and more recently, in shallow-marine and peritidal deposits. In fact, there appears to be growing consensus that sulfate reduction and methanogenesis may be a long-sought-after ''holy grail'' of at least initial dolomitization in diverse depositional environments.

The literature on organogenic dolomitization is voluminous and complex because it draws from the fields of sedimentology, carbonate geochemistry, organic chemistry, and bacteriology. This paper summarizes this vast literature and evaluates the important attributes of the organogenic dolomitization model, including the petrology and geochemistry of early dolomites whose formation may have been promoted by sulfate reduction and/or methanogenesis. It assesses the validity of the model on the basis of the geochemical dynamics of sulfate reduction and methanogenesis, and the occurrence and extent of organogenic dolomites, in modern sediments and ancient rocks.

PROPOSED BARRIERS TO DOLOMITIZATION

Several factors have been proposed to explain why dolomite does not readily precipitate from seawater that is otherwise supersaturated with respect to this mineral in typical marine carbonate environments (Kitano and Hood 1965; Gaines 1980; Mirsal and Zankl 1985; Hardie 1987; Morrow 1990a; Tucker and Wright 1990; Braithwaite 1991; Chai et al. 1995). Three of these factors commonly are considered to be the most critical barriers to dolomitization. The first is hydration of Mg and Ca ions, which is relatively strong at the typically low concentrations of both total dissolved carbonate, and particularly at the low concentrations of CO_3^{2-}, in seawater of normal pH (Fig. 1; Lippmann 1973). Hydrated Mg and Ca constitute 89.2% and 88.5%, respectively, of the total concentration of these ions in normal-pH seawater (Pytkowicz and Hawley 1974). To a lesser extent Mg and Ca also bond with CO_3^{2-} and HCO_3^{-}, sulfate, and perhaps with Cl in brines (Machel and Mountjoy 1986). Related to Mg and Ca hydration is the second presumed barrier, the relatively low alkalinity and low concentrations of dissolved CO_3^{2-} relative to HCO_3^{-}, and also relative to total dissolved Mg and Ca, at typical values of pH in normal seawater (Fig. 1). It is commonly believed that under such conditions there is insufficient energy for available CO_3^{2-} to break through hydration barriers surrounding Mg and Ca ions on the surfaces of growing dolomite crystals (Lippmann 1973; Machel and Mountjoy 1986; Morrow 1990a). Although increase in the pH of the fluids would increase CO_3^{2-} activity, and presumably, reduce Mg and Ca hydration, it is difficult to raise the pH of normal (i.e., surface) seawater (Lippmann 1973). Third, low concentrations of dissolved SO_4^{2-} are believed to inhibit dolomite formation (Baker and Kastner 1981; Kastner 1984). Magnesium also may combine with available dissolved SO_4^{2-} to form $MgSO_4^{o}$, which can be adsorbed on growing crystal surfaces, thereby reducing dolomitization rates (Slaughter and Hill 1991).

ORGANODIAGENESIS

Most of these presumed barriers to dolomitization can be overcome at high temperatures, and also in some terrestrial alkaline groundwaters (Morrow 1990a). Neither scenario, however, is readily applicable to early dolomitization in most modern and ancient peritidal, shallow-marine, and deep-sea deposits. Sulfate reduction and methanogenesis, however, have been proposed as two processes whereby these barriers to early dolomiti-
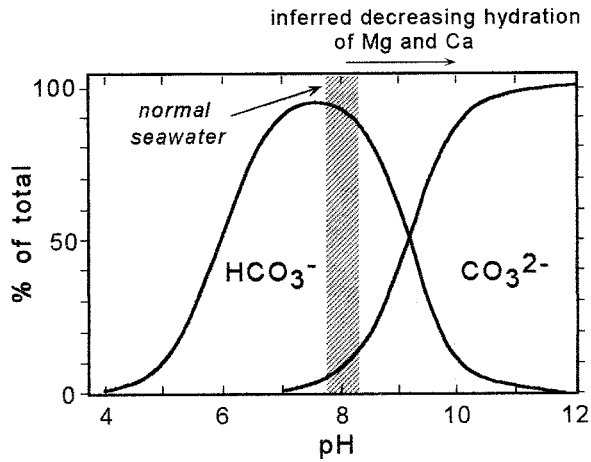
Fig. 1.—Speciation of bicarbonate and carbonate in seawater at 25°C at different values of pH (after Slaughter and Hill 1991). Dissolved CO_3^{2-} and HCO_3^- constitute 8% and 81.3%, respectively, at normal seawater pH (Pytkowicz and Hawley 1974). Boric acid ($H_2BO_3^-$) is a minor component above a pH of ~7.8, and CO_2 and H_2CO_3 are also components below a pH of ~7.7; phosphate also contributes to total alkalinity. Hydration of Mg and Ca presumably decreases with increasing pH (Lippmann 1973).

zation can be overcome in pore fluids in such deposits at earth-surface temperatures. Sulfate reduction and methanogenesis are mediated by bacteria in anoxic, organic-rich sediments (Fig. 2A). In these processes various bacteria oxidize organic matter as food sources and, in doing so, they modify the chemistry of pore fluids (Fig. 2B).

Controls on Bacterial Sulfate Reduction and Methanogenesis

Depth ranges and extent of sulfate reduction and methanogenesis, and their effects on pore-fluid geochemistry, depend on several interrelated factors such as the concentration, type, and reactivity of organic carbon in the sediments, sedimentation rate and degree of bioturbation, rate of diffusion of dissolved O_2 and SO_4 into the sediment from the seawater, and the geothermal gradient (Claypool and Kaplan 1974; Berner 1978, 1980; Pisciotto and Mahoney 1981; Gieskes et al. 1982; Kelts and McKenzie 1982; Baker and Burns 1985). The presence of highly reactive, proteinaceous (nitrogen-rich) organic matter, common in marine sediments, is required for either process to operate in anoxic environments (Berner 1980). High contents of organic carbon enhance bacterial degradation (Berner 1978; Jorgensen 1979), and high geothermal gradients increase the rate of organic reactions (Pisciotto and Mahoney 1981; Kelts and McKenzie 1982). Both processes operate from a few centimeters to several hundred meters and, perhaps, as much as about 1000 m sub-bottom depths within sediments in contact with circulating marine pore fluids (Claypool and Kaplan 1974; Martens and Berner 1974; Oremland and Taylor 1978; Kelts and McKenzie 1982; Burns et al. 1988). Many deep-sea, shallow-marine, and peritidal deposits progressively pass through the sulfate reduction zone and into the methanogenetic zone with increasing burial (Fig. 2B). Depths of these organodiagenetic zones, however, are much less in modern platform deposits than in deep-sea deposits because of the relatively limited thicknesses of the former.
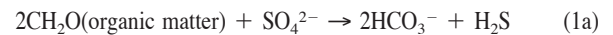
Relatively high sedimentation rates and low rates of bioturbation limit O_2 diffusion, thereby preserving organic matter and promoting anaerobic bacterial activity. Sulfate reduction dominates where sedimentation rates are relatively low and when diffusion from seawater provides enough SO_4 to maintain the process. Methanogenesis normally replaces sulfate reduction as burial depth and/or sedimentation rates increase and when SO_4 is not replenished by diffusion. Extreme sulfate reduction, especially in very

organic-rich sediments, may shift the system to methanogenesis at sub-bottom depths of only a few centimeters to several tens of meters in both platform and deep-sea deposits (Claypool and Kaplan 1974; Oremland 1975; Oremland and Taylor 1978; Compton 1988a). Methanogenesis ceases when suitable organic matter is exhausted or, in deep-sea sediments, when the system enters the higher-temperature zone of thermocatalytic decarboxylation (Fig. 2B; Irwin et al. 1977). Diagenetic systems can revert from methanogenesis back to sulfate reduction as sulfate is resupplied by diffusion.
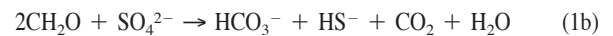
Sulfate Reduction

Sulfate-reducing bacteria utilize the oxygen in dissolved SO_4 as an oxidant in a respiratory process that decomposes organic matter, mainly lactic acid and 4-C dicaroxylic acids. Concentrations of these acids are low in sediments (Berner 1980), hence, active sulfate reduction requires both a symbiotic association with fermenting anaerobes, which provide this source of oxidizable carbon substrate, and a continuous supply of dissolved SO_4^{2-}. Sulfate reducers produce a steady source of H_2 (Fig. 2A) on which they may rely for respiration when concentrations of dissolved SO_4 are high and organic substrates are limited (Oremland and Taylor 1978).
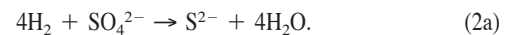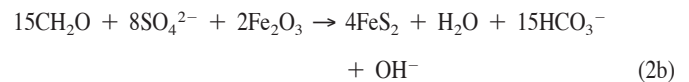
Sulfate reduction is variously expressed as

$$2CH_2O(\text{organic matter}) + SO_4^{2-} \rightarrow 2HCO_3^- + H_2S \qquad (1a)$$

or

$$2CH_2O + SO_4^{2-} \rightarrow HCO_3^- + HS^- + CO_2 + H_2O \qquad (1b)$$

depending on the pH of the system, with the overall process commonly represented by

$$2CH_2O + SO_4^{2-} \rightarrow S^{2-} + 2CO_2 + 2H_2O \qquad (1c)$$

(Claypool and Kaplan 1974; Irwin et al. 1977) and at the same time

$$4H_2 + SO_4^{2-} \rightarrow S^{2-} + 4H_2O. \qquad (2a)$$

Pyrite and, to a lesser extent, marcasite or pyrrhotite, are typical by-products of these reactions in the presence of available Fe^{2+} (Berner 1980) via

$$15CH_2O + 8SO_4^{2-} + 2Fe_2O_3 \rightarrow 4FeS_2 + H_2O + 15HCO_3^-$$
$$+ OH^- \qquad (2b)$$

or

$$CH_2O + 3SO_4^{2-} + 2FeOOH \rightarrow FeS_2 + FeS + 4H_2O$$
$$+ 6HCO_3^-. \qquad (2c)$$
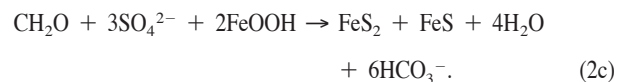
Most pyrite in anoxic deposits typically forms in the zone of sulfate reduction as available iron is quickly fixed, although the concentration of remaining iron can build up into the methanogenetic zone, where it may be incorporated into authigenic carbonates (Irwin 1980).

Methanogenesis

Methanogenic bacteria ferment carbohydrates by stripping oxygen directly from organic matter, which results in methane generation. Methanogenesis and sulfate reduction are usually considered to be mutually exclusive processes because methanogens ordinarily do not thrive in the presence of dissolved SO_4, and perhaps also because H_2S generated during sulfate reduction may be toxic to them (Claypool and Kaplan 1974; Martens and Berner 1974). Both processes may operate in SO_4-rich pore waters, however, although sulfate reduction would dominate, and the activity of methanogens in fact may not be inhibited by the presence of dissolved sulfide (Oremland and Taylor 1978). Methanogenesis typically dominates when at least 90% of dissolved SO_4 is removed from pore fluids (Martens and Berner 1974; Oremland 1975). In any case the presence of free hy-
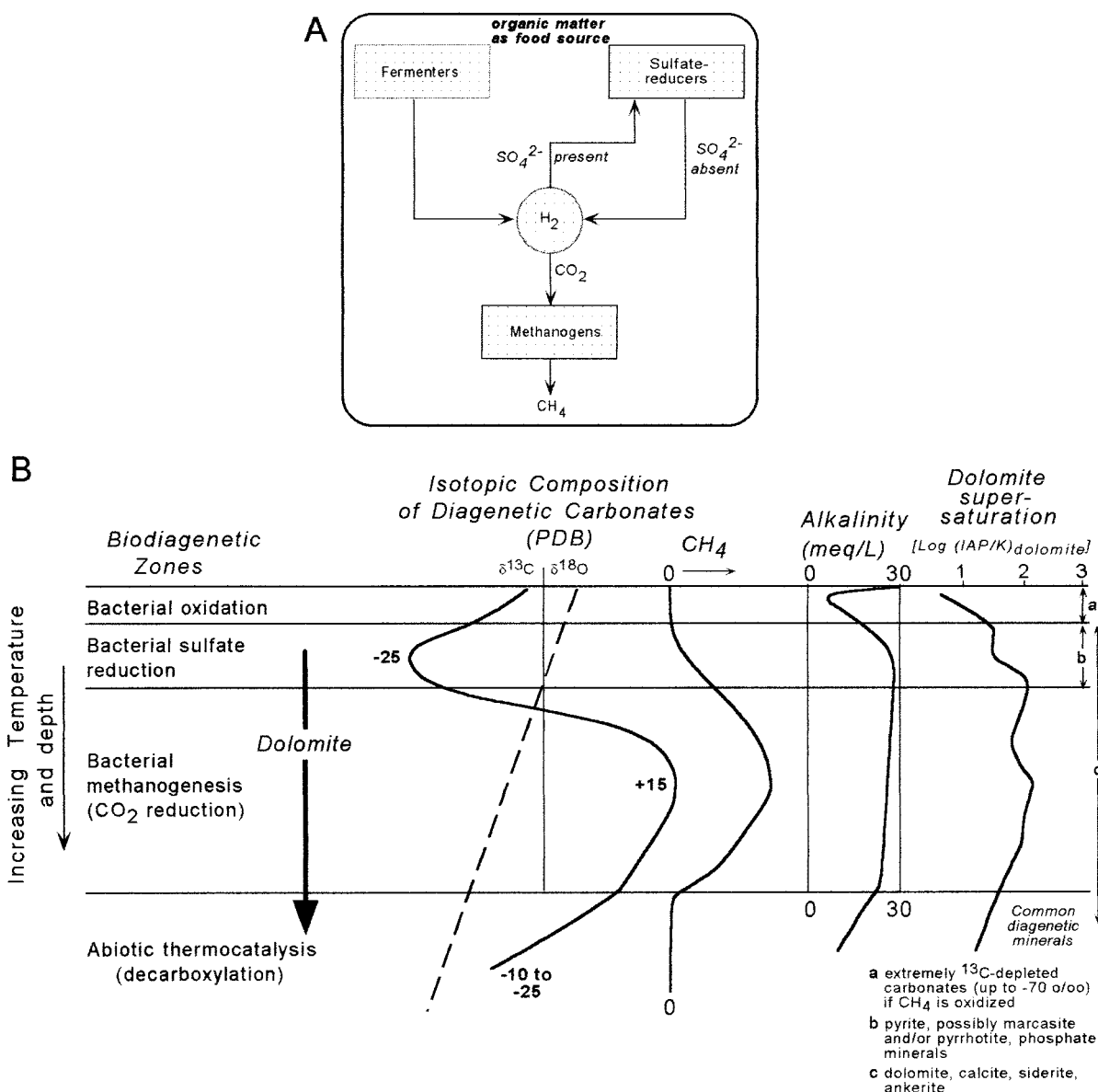
Fig. 2.—**A)** Sulfate reduction and methanogenesis in marine sediments (after Oremland and Taylor 1978). Methanogens obtain H_2 from organic matter degraded by fermentative bacteria, although sulfate-reducing bacteria can generate H_2 from oxidation of organic matter in the absence of sulfate. Sulfate reducers can compete for H_2 when supplies of organic matter are limited and dissolved sulfate and H_2 are abundant. **B)** Diagenetic zones in anoxic, organic-rich (proteinaceous) marine sediments and general geochemical trends (variously after Irwin et al. 1977; Pisciotto and Mahoney 1981; Kelts and McKenzie 1982); calculated trend of dolomite supersaturation (saturation = 0) is from DSDP Site 467 (from Compton 1988a), and mirrors that at other DSDP sites. Isotopic compositions of pore fluids follow the same trends as those for diagenetic carbonates.

drogen, derived from sulfate-reducing bacteria and/or inorganic sources (Fig. 2A), is essential to methanogens and methane production (Oremland and Taylor 1978).

Most of the methane produced is believed to be the product of bacterial reduction of evolved CO_2 by reaction with the H_2 produced by sulfate reducers (Eq 2a) via "carbonate reduction" (Claypool and Kaplan 1974)

$$2CH_2O + 2H_2O \rightarrow 2CO_2 + 4H_2$$

$$4H_2 + HCO_3^- + H^+ \rightarrow CH_4 + 3H_2O \qquad (3)$$
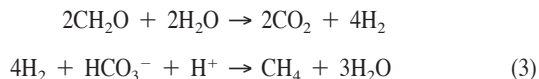
wherein the second line represents carbonate reduction. Some amount of methane also may be generated through the intermediate formation of acetate (Friedman and Murata 1979) via the reaction

$$CH_3COOH \rightarrow CH_4 + CO_2. \qquad (4)$$

Methane can be produced so rapidly that, at least in slowly deposited sediments, it may diffuse upward into the oxic zone, where it then can be utilized by aerobic bacteria. Evolved methane can be oxidized at the bases of sulfate reduction zones in anoxic marine sediments, in a process wherein bacteria utilize the O_2 in SO_4 as an oxidant in the reaction

$$CH_4 + SO_4^{2-} + 2H^+ \rightarrow H_2S + CO_2 + 2H_2O \qquad (5)$$

thus further depleting concentrations of dissolved sulfate (Reeburgh 1980).

Overcoming Barriers to Dolomite Nucleation

The following discussions focus on dolomitic deep-sea deposits to illustrate current thought as to how sulfate reduction and methanogenesis may

overcome barriers to early dolomitization. Similar processes and geochemical trends also have been described in some dolomitic platform deposits.

Sulfate, Alkalinity and pH, and Dolomite Supersaturation.—Sulfate concentrations in pore waters decrease rapidly at relatively shallow sub-bottom depths accompanying bacterial sulfate reduction, and also, oxidation of evolved methane at greater depth, and concentrations of methane generated mainly during methanogenesis increase thereafter in dolomitic sediments (Fig. 3A, B). Pore-fluid alkalinity commonly increases during sulfate reduction or methanogenesis (Fig. 3B, C) as a result of CO_2 generation (which reacts with water to form HCO_3^- and/or CO_3^{2-}, depending on pH), H_2S, H^+, and OH^- (Eqs 1c, 2a–c, and 3). Carbon dioxide is also generated in zones of bacterial methane oxidation (Reeburgh 1980). Alkalinity increases as long as these evolved species do not diffuse upward and as long as enough Fe^{2+} is present to prevent buildup of excess S^{2-} via iron sulfide precipitation (Claypool and Kaplan 1974; Compton 1988a), but it can decrease as diagenetic carbonates are precipitated (Fig. 3A, C). Evolved pore waters initially can be supersaturated to highly supersaturated with respect to dolomite (Fig. 2B) and calcite as a result of organodiagenesis (Compton 1988a; Middelburg et al. 1990), while maintaining essentially nearly normal salinity (Fig. 3B, C; Pisciotto and Mahoney 1981; Gieskes et al. 1982). Decreasing dolomite supersaturation with depth may reflect slow equilibration of pore fluids with respect to nearly ideal dolomite stoichiometry with increasing temperature (Hardie 1987; Compton 1988a).

According to Slaughter and Hill (1991), however, both high pH *and* high alkalinity may be critical in promoting dolomitization in large part because high pH increases the concentration and activity of dissolved CO_3^{2-} (Fig. 1), thereby increasing dolomite supersaturation and reaction rates. They suggested that both high pH and high CO_3^{2-} alkalinity can increase and be maintained only by increasing concentrations of dissolved NH_3 produced bacterially during sulfate reduction and, mainly, during methanogenesis, because it is the only natural base produced in sufficient quantities to affect pH and alkalinity via generation of hydroxide in the reaction

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^-. \qquad (6)$$
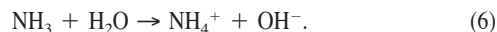
The possible significance of ammonia in dolomitized deep-sea deposits was suggested earlier by several workers (Berner 1980; Baker and Kastner 1981; Gieskes et al. 1982; Kelts and McKenzie 1982; Compton 1988a; Suess et al. 1988). They noted that high pore-fluid CO_3^{2-} alkalinity, high pH, and high concentrations of ammonia in many deep-sea cores correlated with minimum concentrations of SO_4 and increasing amounts of dolomite in methanogenetic zones (e.g., Fig. 3). Ammonium can be bound to clays, however, reducing its contribution to increase in alkalinity and pH.

Hydration and Proposed Mechanisms of Ion Supply to Growing Dolomite Crystals.—It is generally thought, but by no means proven, that reduction in Mg and Ca hydration, and also of relatively less hydrated CO_3^{2-}, can occur in evolved pore fluids of high pH and high CO_3^{2-} alkalinity (e.g., Usdowski 1968; Lippmann 1973; Morrow 1990a), which may be critical in dolomite nucleation (Fig. 4A). Increasing concentrations of dissolved CO_3^{2-} and fluid Mg/Ca ratios are thought to promote dolomitization by increasing dolomite saturation and the number of Mg ions relative to Ca that are energetic enough to shed their water of hydration, which presumably would favor uptake of Mg into dolomite crystal lattices, respectively.

Slaughter and Hill (1991) proposed instead that it is the transfer of the neutral ion pairs $MgCO_3^\circ$ and $CaCO_3^\circ$ to and from crystal surfaces, and not hydrated Mg and Ca, that is involved in (replacive) dolomitization under conditions of high pH or ionic strength, high CO_3^{2-} activity, and elevated ammonia concentrations in interstitial fluids during organodiagenesis. In this model ammonia also preconditions the surface chemistry of precursor carbonate sediments, which they believed otherwise generally retards dolomitization in relatively low-pH solutions. Their model suggests that the dominant Mg and Ca species in solution in normal seawater (Fig. 1), for example, are Mg^{2+} and Ca^{2+} and some $MgHCO_3^+$ and $CaHCO_3^+$,

which may not be able to approach the surfaces of substrate calcite crystals, which are dominantly positively charged because of adsorbed H^+ (Fig. 4B). At elevated pH or ionic strength and high CO_3^{2-} activity, however, H^+ would be expelled from crystal surfaces, making them negatively charged (Fig. 4C); hydration of all ions and ion pairs in solution would be reduced; and the total energy required to overcome the effects of hydration would be reduced. The dominant Mg and Ca species in such solutions would become $MgCO_3^\circ$ and $CaCO_3^\circ$ because the reactions

$$Mg^{2+} + HCO_3^- + OH^- \rightarrow MgCO_3^\circ + H_2O$$

and $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (7)$

$$Ca^{2+} + HCO_3^- + OH^- \rightarrow CaCO_3^\circ + H_2O$$

are promoted by the hydroxide generated during ammonia formation, and these ions could more readily approach crystal surfaces (Fig. 4C). Some amount of unhydrated Mg also could be liberated from bacterially degraded organic matter during ammonia formation.

The role of ammonia in promoting early dolomitization has been suggested for the formation of regionally widespread peritidal to shallow-marine dolomites in some ancient rocks (Wright 1997), but it has not yet been evaluated for dolomites formed in analogous modern environments.

Discussion of the Model

The specific roles of sulfate reduction, Mg and Ca hydration, and alkalinity and pH as barriers to dolomite nucleation are uncertain. For example, some studies (e.g., Morrow 1990a) have suggested that levels of dissolved SO_4 necessary to inhibit dolomitization at earth-surface temperature may be considerably higher than indicated by experiments at 200°C (Baker and Kastner 1981; Kastner 1984), which may partly explain the presence of dolomite associated with fluids of normal to elevated SO_4 concentrations (Hardie 1987). The results of some experiments at >145°C have also suggested that dissolved SO_4 retards dolomitization if it proceeds via dissolution of precursor carbonates (Morrow and Ricketts 1988; Morrow and Abercrombie 1994). However, differences in the saturation of fluids with respect to calcite or aragonite resulting from variations in the concentration of dissolved SO_4 may not be a factor in dolomitization rates at earth-surface temperatures (Morrow and Abercrombie 1994).

Likewise, the effects of high CO_3^{2-} alkalinity and pH on Mg and Ca hydration and dolomitization rates (e.g., Lippmann 1973; Slaughter and Hill 1991) are merely speculative, because there are little data that substantiate the claims that Mg–Ca hydration actually retards dolomite nucleation or that high alkalinity and pH increase dolomitization rates. Furthermore, the sensitivities of pore-fluid pH and CO_3^{2-} activity to increasing concentrations of ammonia have not been adequately evaluated. Interestingly, pore-water pH in most deep-sea and platform deposits that presumably are being affected by sulfate reduction or methanogenesis generally has been shown to either increase or decrease only slightly rather than increase dramatically (Fig. 3B, C). Although CO_2 evolved during sulfate reduction and methanogenesis can act to lower the pH of pore fluids as this reaction shifts to the right because

$$CO_2 + H_2O \leftrightarrow H^+ + HCO_3^- \qquad (8)$$

pH instead can increase as the reaction shifts to the left because of the OH^- produced as a result of iron sulfide precipitation and/or by methane generated during methanogenesis (Eq. 3) via

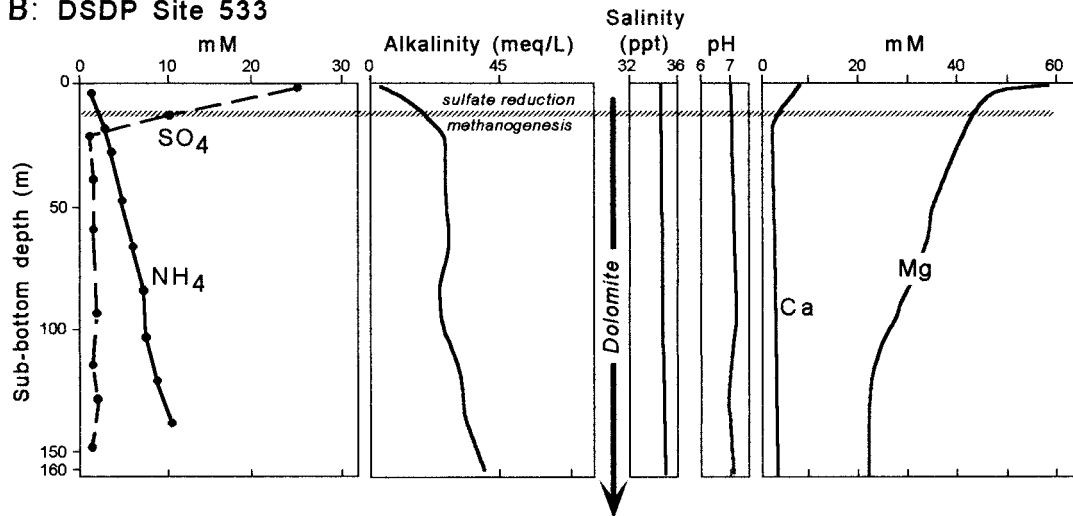$$OH^- + HCO_3^- \rightarrow H_2O + CO_3^{2-}. \qquad (9)$$
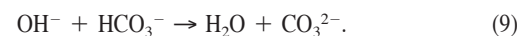
Evolving pH depends to a great extent on, among other factors: (1) type and amount of organic matter present, and amount of CO_2 and organic acids relative to amounts of nitrogenous bases produced during organodiagenesis; and (2) rate of bacterial consumption of organic matter (Berner
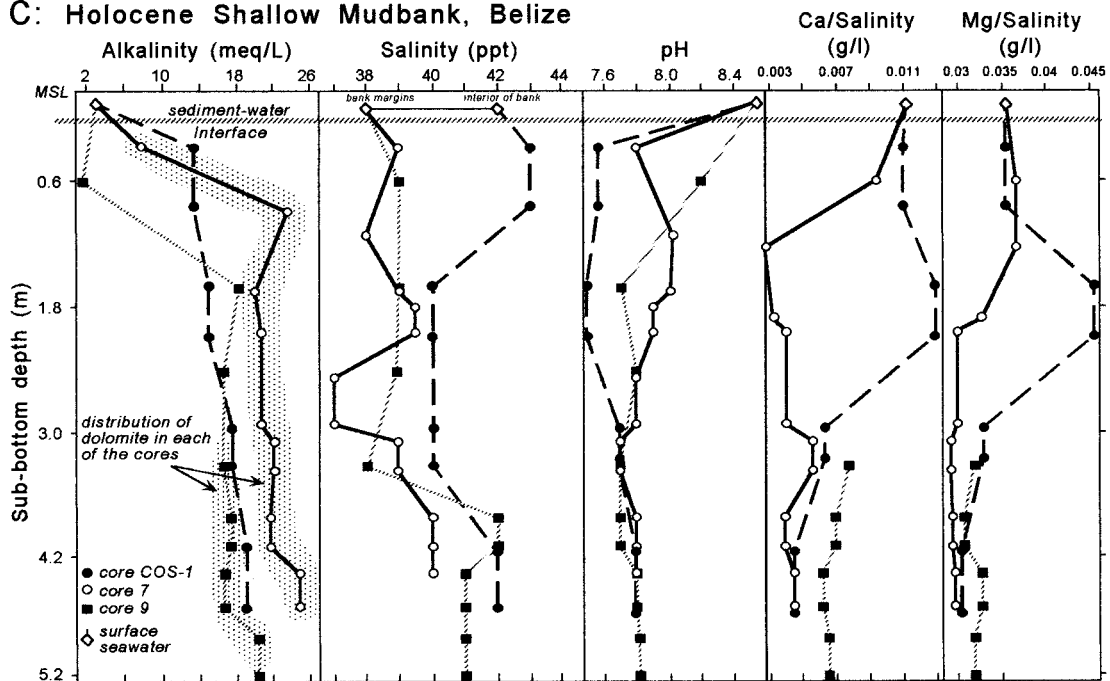
A: DSDP Site 479
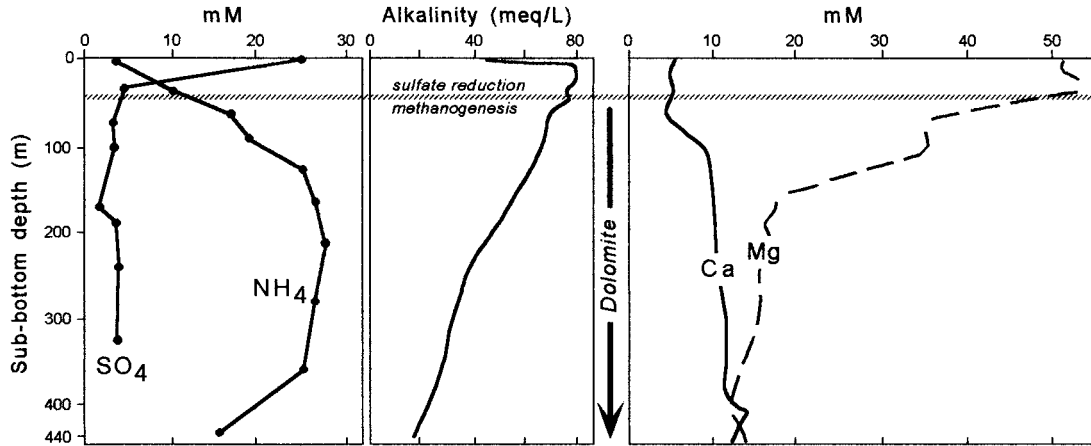
B: DSDP Site 533

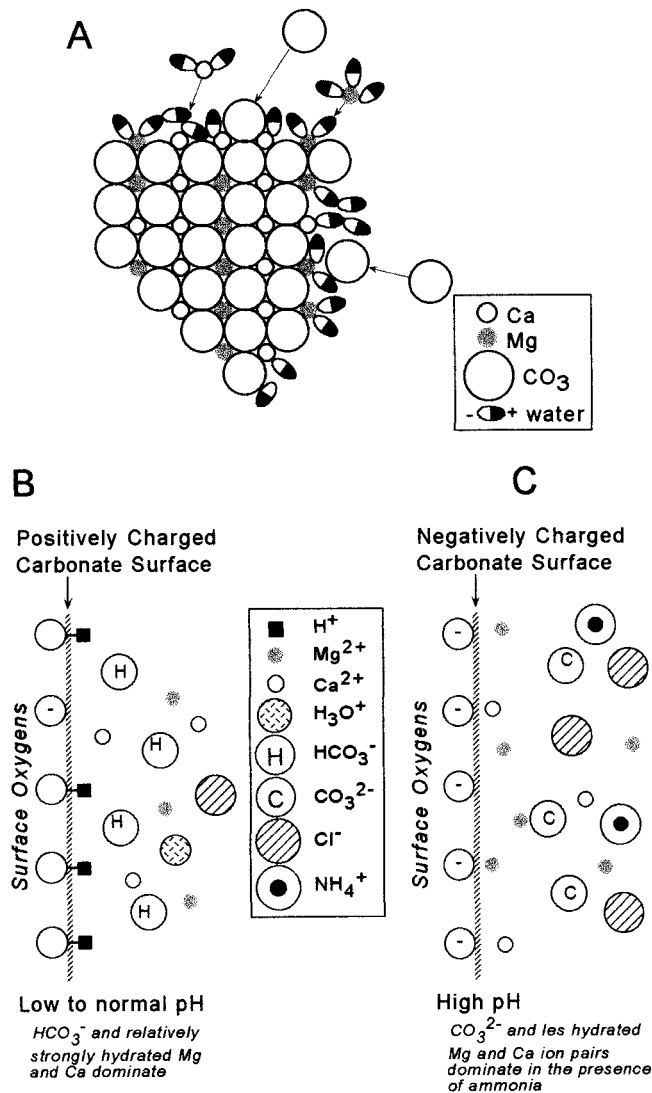## C: Holocene Shallow Mudbank, Belize

FIG. 4.—**A)** Crystal structure showing conceptual bonding of water dipoles to cations on the crystal surface (after Lippmann 1973 and Morrow 1990b). Carbonate ions are relatively unhydrated but need sufficient energy to displace water molecules adjacent to cation layers at normal seawater pH. Hydrated Ca ions can be incorporated into Mg layer positions, resulting in formation of calcic, poorly ordered dolomite. **B, C)** Schematic of (replacive) dolomitization of calcitic nuclei at low to normal and high pH (after Slaughter and Hill 1991). Hydrogen attaches to non-bonding electrons of the otherwise negatively charged oxygens of CO_3 molecules at crystal surfaces, resulting in positive crystal surface charges at low to normal seawater pH when bicarbonate dominates. Hydrated Mg^{2+} and Ca^{2+} therefore cannot attach to crystal surfaces, and dolomitization is retarded. At high pH, crystal surfaces instead are negatively charged because surface oxygens have free bonding electrons, and CO_3^{2-} instead dominates; hydrogen is exchangeable with other ions. Mg and Ca are present mostly as less hydrated free ion pairs, and can more readily interact with crystal surface to produce dolomite.

1980). Pore-fluid pH also can be rapidly buffered in carbonate-rich sediments (Berner 1980; Pisciotto and Mahoney 1981).

If reported dolomite $\delta^{13}C$ values are indeed indicative of different organodiagenetic processes (e.g., Irwin et al. 1977; discussed below), then despite such geochemical uncertainties it appears that dolomitization has in fact attended both sulfate reduction and/or methanogenesis in Tertiary to Holocene deep-sea deposits (e.g., Bramlette 1946; Murata et al. 1972; Claypool and Kaplan 1974; Gieskes 1975; Irwin et al. 1977; Friedman and Murata 1979; Irwin 1980; McKenzie et al. 1980; Pisciotto 1981; Pisciotto and Mahoney 1981; Gieskes et al. 1982; Kelts and McKenzie 1982, 1984; Baker and Burns 1985; Hennessy and Knauth 1985; Burns and Baker 1987; Burns et al. 1988; Compton 1988a, 1988b; Suess et al. 1988; Middelburg et al. 1990; Soussi and M'Rabet 1994; Dix 1997). Dolomitization attending sulfate reduction has also been inferred in many modern and ancient shallow-marine and peritidal deposits (e.g., Davies et al. 1975; Brown and Farrow 1978; Gebelein et al. 1980; Gunatilaka et al. 1984; Gunatilaka et al. 1985; Lyons et al. 1984; Mazzullo et al. 1987; Lasemi et al. 1989; Burns and Swart 1992; Baltzer et al. 1994; Perkins et al. 1994; Whitaker et al. 1994; Mazzullo et al. 1995; Mitchell and Horton 1995a; Mitchell and Horton 1995b; Bischoff and Mazzullo 1996; Budd 1997; Nielsen et al. 1997; Vasconcelos and McKenzie 1997; Wright 1997; Bailey et al. 1998; Mazzullo et al. 1999). The only known occurrence of bacterial methanogenetic dolomite in modern shallow-marine deposits was described by Mazzullo et al. (1995), Mazzullo et al. (1999), Teal (1998), and Teal et al. (1998). Hence, these organodiagenetic processes apparently *can and do* promote early dolomitization and precipitation of other minerals in many depositional and diagenetic environments by obviously overcoming generally acknowledged barriers to dolomite nucleation, if not also others that at present are poorly understood or not yet identified. In this regard two specific aspects of the organodiagenetic dolomitization model are relevant: (1) what is the relative role of sulfate reduction versus methanogenesis in dolomitization, and (2) why is dolomite *not* present in some anoxic, organic-rich sediments within which pore waters are or were modified by these processes?

Relative Efficiency of Sulfate Reduction versus Methanogenesis in Early Dolomitization.—Some workers (e.g., Baker and Burns 1985; Burns and Baker 1987) have suggested that more dolomite can form in zones of sulfate reduction than in methanogenic zones, although this contention has been disputed and, in fact, the efficiency of sulfate reduction relative to methanogenesis in promoting dolomite nucleation has been questioned for two main reasons.

First, some organic-rich sediments that are, or that are presumed to have been, in the zone of sulfate reduction contain little or no dolomite (e.g., Kelts and McKenzie 1982; Burns and Baker 1987; Mazzullo et al. 1995). Several interrelated factors may preclude dolomite formation during sulfate reduction, however, for example: (1) Perhaps pH and CO_3^{2-} alkalinity are low when limited amounts of ammonia are generated (Slaughter and Hill 1991). In this regard not only high pH and high alkalinity (Slaughter and Hill 1991) but perhaps sustained high pH and alkalinity may be more effective in promoting dolomite nucleation than merely sulfate reduction. (2) Sediments may be less organic-rich, or they may contain dominantly protein-poor terrestrial organic matter, than those in which dolomite is present.

←

FIG. 3.—Pore-fluid chemistry in anoxic sediments deep-sea and shallow subtidal sediments with organogenic dolomite. **A)** Alkalinity, and concentrations of dissolved ammonia, sulfate, Ca, and Mg in pore fluids within Upper Pliocene to Upper Pleistocene deposits at DSDP Site 479 (data from Gieskes et al. 1982; Kelts and McKenzie 1982; Slaughter and Hill 1991). **B)** Similar geochemical parameters, and salinity and pH, in pore fluids within Quaternary deposits at DSDP Site 533 (data from Gieskes 1975; Pisciotto and Mahoney 1981; Claypool and Threlkeld 1983; Matsumoto 1983; Baker and Burns 1985; Slaughter and Hill 1991). According to Baker and Burns (1985), this site is typical of DSDP Sites 102, 147, 262, 362, 440, 467, and 532. Dolomite appears to be of methanogenetic origin at both sites, and is associated with high levels of dissolved ammonia and depleted sulfate. Drop in alkalinity at Site 479 is due to dolomite precipitation. **C)** Similar geochemical parameters in pore fluids within Holocene shallow subtidal deposits in Belize (data from Mazzullo et al. 1995; Teal et al. 1998). Dolomites are of both sulfate-reduction and methanogenetic origin as suggested by their carbon-isotope compositions. Ca and Mg here likely are supplied by diffusion from seawater.

Hence, levels of sulfate reduction necessary for dolomitization may not be reached or are not maintained for sufficiently long periods of time (Baker and Burns 1985; Austin et al. 1986). (3) Insufficient supplies of dissolved Mg and Ca are available for dolomitization (Kelts and McKenzie 1982; Baker and Burns 1985; Burns and Baker 1987; Burns et al. 1988). (4) The degree of saturation of pore waters with respect to dolomite may not be great enough to overcome the inhibiting effects of dissolved sulfate (Compton 1988a). (5) Supersaturation possibly can be maintained without dolomite precipitation because of the presence of organic matter dissolved in the pore water (Berner 1980). Conversely, these same reasons also may explain the absence or limited amounts of dolomite formed during methanogenesis.

Second, early dolomite is present in organic-rich sediments wherein concentrations of dissolved sulfate in pore fluids are presumed to have been normal or even elevated (Hardie 1987; Mullins et al. 1988; Ruppel and Cander 1988; Graber and Lohmann 1989; Morrow and Abercrombie 1994; Perkins et al. 1994; Zenger 1996; Budd 1997). There is always uncertainty, however, as to the timing of dolomitization in the sense of whether or not ambient fluids actually are those that precipitated the dolomite (Cooper and Evans 1983; Slaughter and Mathews 1984; Perkins et al. 1994), which also may explain the relatively low pH of pore waters in many dolomitic deep-sea and platform sediments (Fig. 3B, C). Regardless, bacterial sulfate reduction relies upon a steady source of dissolved sulfate, hence, SO_4^{2-} might under certain conditions actually be a catalyst to dolomite formation at earth-surface temperature (Eugster and Hardie 1978; Oremland and Taylor 1978; Vasconcelos and McKenzie 1997).

Whereas some dolomites apparently have formed as a result of sulfate reduction, other workers instead have suggested, strictly following the model of Baker and Kastner (1981) and Kastner (1984), that dolomitization in some deep-sea deposits actually may have begun *after* much of the dissolved sulfate was depleted, and hence that the dolomites are mostly of methanogenetic and possibly also of late sulfate-reduction origin. Examples of dolomites that presumably formed under such conditions have been described by Irwin (1980), Pisciotto and Mahoney (1981), Kelts and McKenzie (1982, 1984), Claypool and Threlkeld (1983), Mertz (1984), Kushnir and Kastner (1984), Baker and Burns (1985), Hennessy and Knauth (1985), Burns and Baker (1987), Burns et al. (1988), Compton (1988a), Suess et al. (1988), Malone et al. (1994), and Wright (1997). Dolomitization attending methanogenesis in shallow-marine deposits has been described by Mazzullo et al. (1995), Teal (1998), Teal et al. (1998), and Mazzullo et al. (1999). Dolomitization in such cases may be promoted by sustained, higher pH and alkalinity that may attend methanogenesis and late stages of sulfate reduction, when according to Slaughter and Hill (1991) there are maximum concentrations of dissolved ammonia in pore fluids (Fig. 3A, B). In this regard it is interesting to note that $\delta^{13}C$ values of the majority of presumed sulfate-reduction dolomites reported are only slightly depleted (Fig. 5), which possibly suggests the formation of such dolomites during the transition to methanogenesis or during methane oxidation rather than during the early or main stages of sulfate reduction. Unfortunately, it is not possible to compare the percentages of dolomites presumably formed only in sulfate reduction zones versus those presumably formed only in methanogenetic zones on the basis of published references.

ORGANOGENIC DOLOMITES

Dolomite Petrography and Chemistry

Most organogenic dolomites in modern and ancient deep-sea, shallow-marine, and peritidal deposits are cements (e.g., Gebelein et al. 1980; Pisciotto 1981; Pisciotto and Mahoney 1981; Baker and Burns 1985; Burns et al. 1988; Lasemi et al. 1989; Middelburg et al. 1990; Baltzer et al. 1994; Mazzullo et al. 1995; Mitchell and Horton 1995a; Mitchell and Horton 1995b; Dix 1997; Vasconcelos and McKenzie 1997; Teal et al. 1998; Mazzullo et al. 1999), although some replacive dolomites also have been de-

scribed (e.g., Kelts and McKenzie 1982; Gunatilaka et al. 1984; Lyons et al. 1984; Mazzullo et al. 1987; Suess et al. 1988; Whitaker et al. 1994). They typically are fine crystalline, generally less than 10 μm, and most are calcic and poorly ordered. Many Neogene and Quaternary dolomites appear to be somewhat more stoichiometric than older dolomites (Fig. 6A), which may reflect limited Ca availability in, for example, precursor carbonate-poor sediments (e.g., Burns et al. 1988), slower rates of precipitation (Hardie 1987; Morrow 1990a; Nielsen et al. 1997), or other factors (e.g., Searl 1994). It is not likely that these more stoichiometric dolomites are more recrystallized relative to the older dolomites (e.g., Sperber et al. 1984). Conversely, a general trend toward increased stoichiometry in progressively more deeply buried deep-sea dolomites is not apparent in the dataset shown in Figure 6; exceptions are discussed later in this paper.

Concentrations of Sr, Fe, and Mn in organogenic dolomites typically are about 300–500 ppm, 2–3 mole%, and 850 ppm, respectively, and there are no specific trends in these concentrations with depth in either deep-sea or shallow platform dolomites (Fig. 6B–D). Relatively high Sr contents may reflect increasing Sr/Ca ratios in pore fluids during dolomitization because $Sr/Ca_{seawater}$ is greater than $Sr/Ca_{dolomite}$ (Burns et al. 1988). Sulfate-reduction dolomites generally are Fe-poor, because available Fe is rapidly incorporated into sulfide minerals and/or because of bonding to organic substrate (Elderfield 1981). Some methanogenic dolomites may be Fe-enriched because of substitution of Fe for Mg in pore fluids with low Mg concentrations (Burns and Baker 1987). The Mn concentration in dolomite usually correlates with Fe concentration and also is a function of rates of input of terrestrial siliciclastics. Sodium in dolomites likely is present mainly as inclusions within dolomite crystals rather than substituting for metal ions (Land 1980).

Carbon-Isotope Compositions

Organogenic dolomites are characterized by wide range in $\delta^{13}C$ values (Fig. 5), reflecting relative amounts of carbon incorporated into the dolomite from the different bacterial zones of organodiagenesis (Fig. 2B), from dissolution of precursor carbonate sediments, or from seawater bicarbonate (Claypool and Kaplan 1974; Irwin et al. 1977). $\delta^{13}C_{PDB}$ values of sulfate-reduction dolomites typically are depleted to varying degrees relative to that of ambient seawater because of addition to pore fluids of ^{12}C-enriched CO_2 derived mainly from bacterially degraded organic matter. Dolomite $\delta^{13}C$ values are known to be as light as -20 to $-21‰$, and less depleted compositions may reflect dolomite precipitation either: (1) during early sulfate reduction, prior to maximum ^{12}C enrichment in pore fluids, or (2) in sediments with relatively little organic matter, wherein much of the dissolved carbon is derived from seawater. $\delta^{13}C$ values can in some cases approach that of unmodified seawater if precipitation occurred in precursor carbonate-rich sediments or within sediments with little organic matter (Fig. 5; e.g., Compton 1988a). Lyons et al. (1984) suggested that $\delta^{13}C$ values of some Holocene sulfate-reduction dolomites may be slightly heavier than expected because of incorporation of relatively ^{13}C-enriched bicarbonate ($-5‰$) from anomalously ^{13}C-enriched organic matter.

In contrast, $\delta^{13}C_{PDB}$ values of methanogenetic dolomites typically are enriched to varying degrees relative to seawater (Fig. 5) because of addition to pore fluids of ^{13}C-enriched CO_2 generated by carbonate reduction attending methanogenesis. Isotopically heavy $\delta^{13}C$ values of dissolved CO_2 result from the strong fractionation between CH_4 and the HCO_3^- produced during methanogenesis. The process results in ^{12}C-enriched methane and leaves ^{13}C-enriched bicarbonate because $H^{12}CO_3^-$ is removed about 7‰ faster than $H^{13}CO_3^-$ during methane formation (Bottinga 1969) via

$$^{12}CO_2 + {}^{13}CH_4 \rightarrow {}^{13}CO_2 + {}^{12}CH_4. \qquad (10)$$
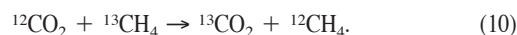
$\delta^{13}C$ values of dolomites precipitated during early methanogenesis may be less enriched than those precipitated during the main stage of methanogenesis (Figs. 2B, 5; e.g., Pisciotto and Mahoney 1981; Kelts and McKenzie
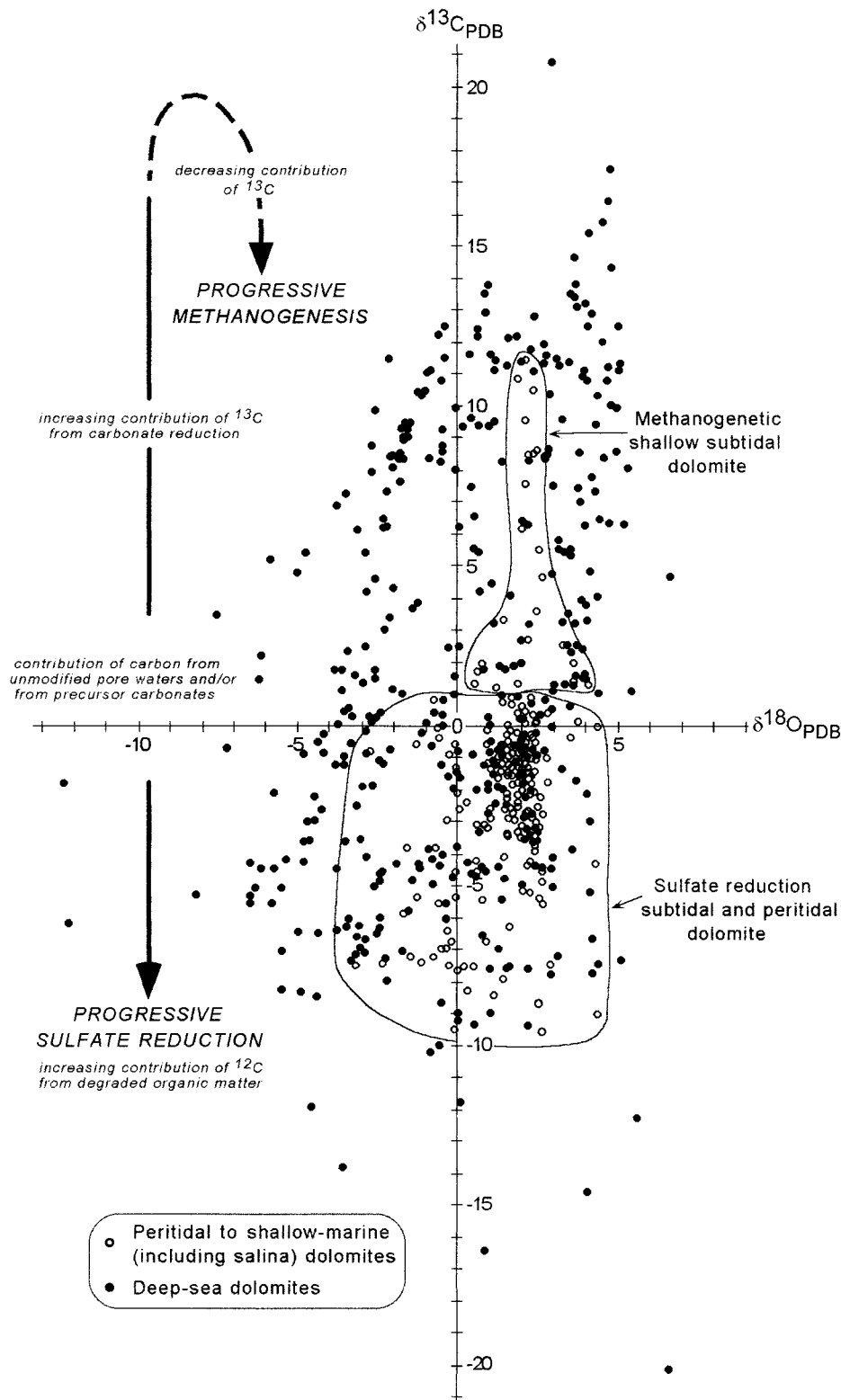
FIG. 5.—Stable carbon–oxygen isotopic composition of organogenic dolomites. Sources of deep-sea data: Murata et al. (1969), Irwin et al. (1977), Hein et al. (1979), Irwin (1980), Pisciotto and Mahoney (1981), Kelts and McKenzie (1982, 1984), Mertz (1984), Hennessy and Knauth (1985), Burns and Baker (1987), Burns et al. (1988), Lumsden (1988), Suess et al. (1988), Malone et al. (1994), Soussi and M'Rabet (1994), and Dix (1997). Field of methanogenetic shallow-subtidal dolomite from Mazzullo et al. (1995), Teal (1998), and Teal et al. (1998); field of sulfate reduction peritidal and shallow-subtidal dolomite from Mazzullo et al. (1987), Gregg et al. (1992), Baltzer et al. (1994), Perkins et al. (1994), Whitaker et al. (1994), Mitchell and Horton (1995a, 1995b), and Vasconcelos and McKenzie (1997).

1982; Suess et al. 1988). Decrease in the influx of ^{13}C-enriched pore-water CO_2 during latest methanogenesis can result in a return to less ^{13}C-enriched or even ^{13}C-depleted dolomite compositions (Fig. 2B), possibly because of continued degradation of organic matter at a rate faster than CO_2 removal by carbonate reduction and methane formation (Claypool and Kaplan

1974). Average $\delta^{13}C$ values of dolomites formed during the main phase and latest phase of methanogenesis in some deep-sea deposits, for example, are $+15.3‰$ and $-4.7‰$, respectively (Pisciotto and Mahoney 1981). Such trends are not always apparent during methanogenesis, however, because the pore-water carbon-isotope system is sensitive, particularly in pre-
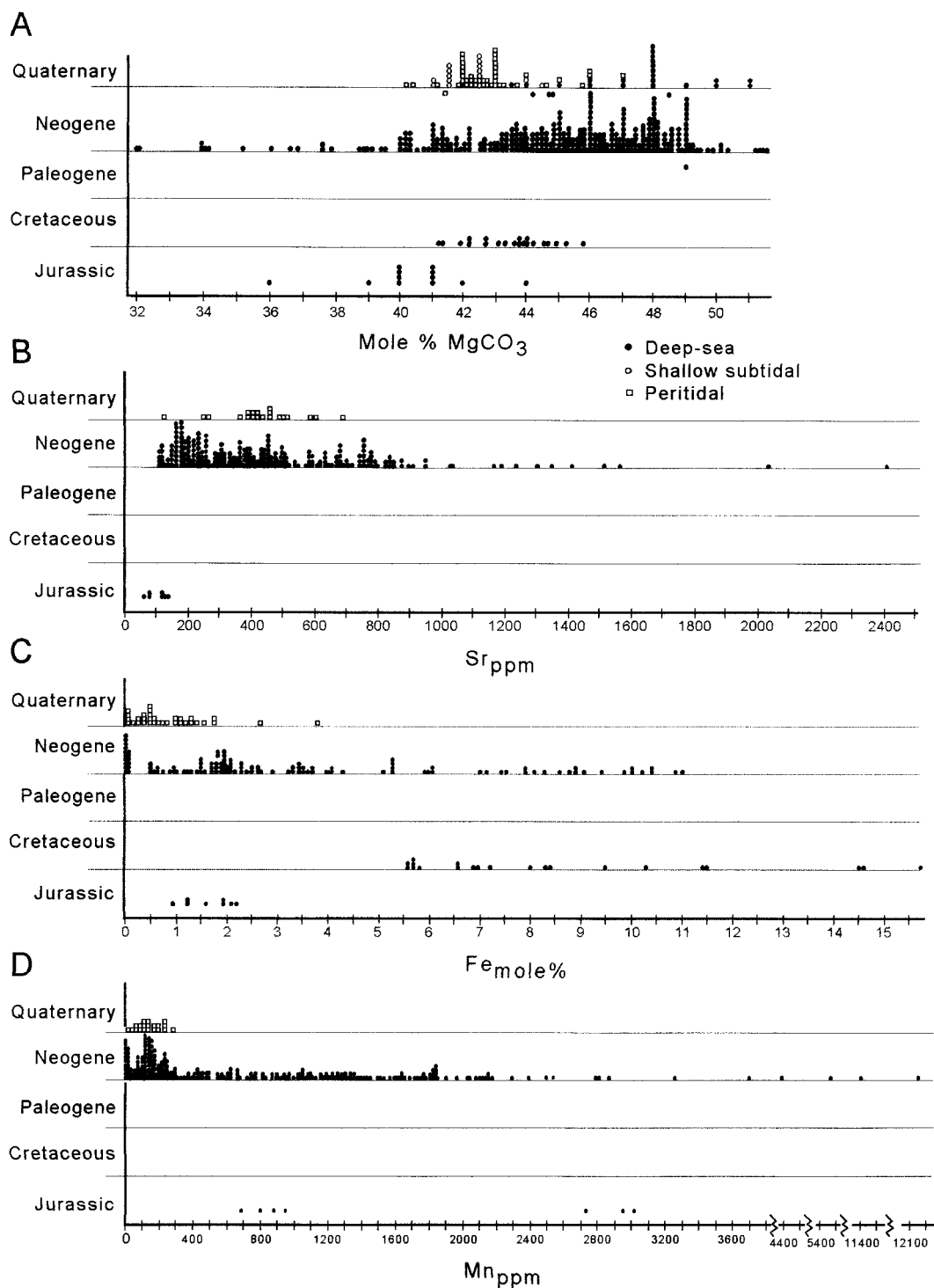
A

Mole % MgCO$_3$

• Deep-sea
○ Shallow subtidal
□ Peritidal

B

Sr$_{ppm}$

C

Fe$_{mole\%}$

D

Mn$_{ppm}$

FIG. 6.—Minor-element and trace-element chemistry of some organogenic dolomites. **A)** Stoichiometry of dolomite. Data on deep-sea dolomites are from Murata et al. (1969), Irwin (1980), Pisciotto and Mahoney (1981), Kelts and McKenzie (1982, 1984), Mertz (1984), Hennessy and Knauth (1985), Burns and Baker (1987), Burns et al. (1988), Compton (1988b), Suess et al. (1988), Malone et al. (1994), Soussi and M'Rabet (1994), and Dix (1997); data on shallow-marine and peritidal dolomites are from Mazzullo et al. (1987), Gregg et al. (1992), and Mazzullo et al. (1995). **B)** Sr in dolomite. Deep-sea data are from Burns and Baker (1987), Burns et al. (1988), Malone et al. (1994), and Soussi and M'Rabet (1994); peritidal data are from Gregg et al. (1992). **C, D)** Fe and Mn in dolomite. Deep-sea data are from Irwin (1980), Burns and Baker (1987), Burns et al. (1988), Compton (1988b), Malone et al, (1994), and Soussi and M'Rabet (1994); peritidal data are from Gregg et al. (1992).

cursor carbonate-rich deposits, to other factors such as the rate and extent of carbonate precipitation and/or dissolution (Claypool and Kaplan 1974).

Significance of Oxygen-Isotope Compositions

The range of $\delta^{18}O_{PDB}$ values of most organogenic dolomites defines a somewhat more restricted field than their $\delta^{13}C$ values, and does not appear to depend on whether the dolomites precipitated in zones of sulfate reduction or methanogenesis. In fact, there is overlap in the $\delta^{18}O$ values of dolomites formed under the influence of these processes (Fig. 5). Rather, $\delta^{18}O_{dolomite}$ values depend mainly on temperature and salinity, and also the $\delta^{18}O$ value, of the fluids from which the dolomites precipitated. $\delta^{18}O$ values further appear to suggest that organogenic dolomites form in a wider range of geochemical environments in shallow buried platform deposits than in deep-sea sediments, although the $\delta^{18}O$ values of dolomites in these disparate environments also overlap. Holocene, shallow-marine dolomites in Belize, for example, appear to have precipitated in zones of sulfate reduction and methanogenesis, whereas peritidal dolomites here are associated only with sulfate reduction (Mazzullo et al. 1987; Gregg et al. 1992; Mazzullo et al. 1995; Teal et al. 1998). Yet, the mean $\delta^{18}O$ value of all of these dolomites is 2‰ (standard deviation 0.3‰), which suggests precipitation from near-normal-salinity pore fluids (Fig. 3C) at about 28°C. In contrast, the $\delta^{18}O$ values of some Holocene shallow-marine and peritidal, sulfate-reduction dolomites in the Bahamas range from −3.2‰ to 3.6‰, and they were variously interpreted to have precipitated from slightly hypersaline (and relatively high-temperature) to normal-salinity marine and mixed meteoric–marine fluids (Mitchell and Horton 1995a, 1995b). $\delta^{18}O$ values of Holocene sulfate-reduction dolomites in sabkha deposits in Abu Dhabi (Baltzer et al. 1994) and salina deposits on West Caicos Island (Perkins et al. 1994) range from 1.5‰ to 4.3‰, and were interpreted as having precipitated from interstitial fluids of variably elevated salinity and temperature. Dolomites precipitated from marine groundwaters beneath Andros Island have a mean $\delta^{18}O$ value of 3.5‰, and are believed to have precipitated from relatively cool water affected by minor sulfate reduction (Whitaker et al. 1994).

The $\delta^{18}O$ values of deep-sea dolomites range from about −12.5‰ to +7‰ (Fig. 5), a scatter that partly represents temporal variations in the isotopic composition of pore fluids from which the dolomites precipitated in the Mesozoic to Holocene deposits that have been examined. There is no convincing evidence that any of these dolomites precipitated from fluids of other than near-normal-marine salinity (Fig. 3B). Preferential removal of ^{18}O during carbonate precipitation does not appear to cause its depletion in pore waters, which might otherwise result in subsequent precipitation of ^{18}O-depleted carbonates (Burns 1998). Some workers have suggested that reduced sulfate ions (Aharon et al. 1977) can supply anomalous isotopically light oxygen to pore waters and diagenetic carbonates during sulfate reduction. Anaerobic oxidation of methane, wherein bacteria utilize dissolved sulfate as an oxidant, is known in anoxic marine sediments (Reeburgh 1980). Other workers have suggested that isotopically light oxygen can be provided from organic-matter degradation (Coleman and Raiswell 1981; Sass et al. 1991). Regardless, the range in $\delta^{18}O$ values of deep-sea dolomites commonly has been ascribed mainly to variations in depth and temperature. Judging by temperatures estimated from $\delta^{18}O$ values, for example, it appears that deep-sea dolomites formed at sub-bottom depths of a few meters to as much as 1000 m (see Burns et al. 1988), with increasing decrease in of $\delta^{18}O_{dolomite}$ values with depth mainly reflecting increasing temperature. Burns et al. (1988), however, suggested that $\delta^{18}O_{dolomite}$ values may be misleading, and that this inferred depth range of dolomitization may be too great because more depleted $\delta^{18}O$ values of some dolomites instead may indicate re-equilibration of prior-formed dolomite with increasing burial and temperature. Although they did not provide isotopic evidence for this contention, nevertheless they alternatively proposed that some deep-sea dolomites may have initially nucleated at depths of 100 m or less and

then recrystallized at greater depths (see also Kelts and McKenzie 1982; Baker and Burns 1985; Burns and Baker 1987; Malone et al. 1994).

Source of Mg and Ca

Although Mg also may be supplied from degraded organic matter (Friedman et al. 1973; Gebelein and Hoffman 1973), exchange of ammonia for Mg in smectitic clays (Kelts and McKenzie 1982), or release of Mg adsorbed on clay-mineral surfaces (Baker and Kastner 1981), amounts are negligible (Baker and Burns 1985). Many workers instead believe that the dominant source of Mg and Ca attending organogenic dolomitization, particularly in precursor carbonate-poor deposits, is diffusion from overlying seawater (Irwin 1980; Pisciotto 1981; Hennessy and Knauth 1985; Burns and Baker 1987; Burns et al. 1988; Compton 1988b; Mitchell and Horton 1995a; Mitchell and Horton 1995b; Dix 1997). Modeling studies and mass-balance calculations indicate that diffusion can supply enough Mg and Ca to account for the amounts of dolomite present in some deep-sea deposits only if the sediments are buried just a few tens of meters below the sediment/water interface (Compton and Siever 1986; Burns et al. 1988), which supports Burns et al.'s (1988) contention that maximum depths of dolomite nucleation inferred from $\delta^{18}O_{dolomite}$ values in deep-sea dolomites (1000 m) are too great. Both sulfate reduction and methanogenesis can occur at such depths. Limited concentrations of Mg and Ca supplied by diffusion therefore might be rate-limiting factors in continued dolomitization of more deeply buried sediments, as suggested by Burns et al. (1988) and Compton (1988a). Adequate supply of ions by diffusion would not be a problem in most shallowly buried platform deposits.

In contrast, other workers believe that Mg and Ca are supplied mainly by dissolution in precursor carbonate-rich sediments (Irwin 1980; Baker and Burns 1985; Burns et al. 1988; Compton 1988a; Baltzer et al. 1994). Limited rates of dissolution and, particularly, supply of Ca (Burns et al. 1988; Compton 1988b; Middelburg et al. 1990) therefore might be rate-limiting factors in continued dolomitization of such deposits. Dolomites formed in such sediments conceptually should be dominantly of replacement origin, although dolomite cement likely could be present as well. Essentially constant down-hole concentrations of dissolved Ca in many deep-sea pore waters, particularly those that are depleted relative to near-surface waters (Fig. 3B), are often interpreted as evidence that Ca is supplied from dissolution rather than diffusion (Baker and Burns 1985). A similar trend in Ca depletion is noted in dolomitic shallow-marine mudbank sediments in Belize (Fig. 3C), however, wherein Ca and Mg instead are believed to be supplied by diffusion and dolomites are cements (Mazzullo et al. 1995).

Many issues obviously still need to be resolved in regard to depths of dolomitization versus mode of supply of Mg and Ca, particularly considering that the amounts of these ions available for dolomitization depend on depth of dolomite nucleation, rates of precipitation, and sedimentation rates (Compton 1988a). Limited rates of Mg and Ca diffusion or of dissolution of precursor carbonates, however, may partly explain one aspect of the dolomite problem—that is, why only minor amounts of dolomite are present in some deposits despite evidence of sulfate reduction and/or methanogenesis.

DISCUSSIONS

Amount of Organogenic Dolomite

It is difficult to estimate and compare the amount of dolomite present per unit thickness of sediment in platform and deep-sea deposits from published accounts. Nevertheless, reported amounts of organogenic dolomite in shallow platform and deep-sea deposits are volumetrically significant, and such newly formed dolomites can be nuclei for later, more pervasive dolomitization. Organogenic dolomites appear to be particularly abundant in Holocene peritidal and shallow-marine deposits, especially considering

that the dolomites and host sediments are very young (<10 ka) and dolomite has had less time to form than in most reported deep-sea occurrences. Dolomite constitutes an average of 70% (range 35–100%) of the 1-m-thick section of peritidal deposits (<3 ka) in Belize, for example, and is present throughout this section (Mazzullo et al. 1987; Gregg et al. 1992). Rapid rate of dolomitization here could be an analog of pervasive early dolomitization in some analogous ancient deposits. Dolomite constitutes as much as 30% and 100% of peritidal sediments in the Bahamas (Gebelein et al. 1980; Mitchell and Horton 1995b) and on Abu Dhabi sabkhas (Baltzer et al. 1994), respectively, although it is concentrated mainly in some thin crusts rather than throughout these sediments. The 8-m-thick, shallow-marine mudbank deposits at Cangrejo Shoals in Belize (<6 ka) contain an average of 12% dolomite present throughout most of the section, although as much as 30% dolomite is present in some thin zones therein (Mazzullo et al. 1995). In fact, significant amounts (up to 40%) of inferred organodiagenetic dolomite are present in Holocene shallow-marine sediments throughout a large area of northern Belize (Mazzullo et al. 1999). Hopefully, these occurrences may compel other workers to reexamine similar deposits elsewhere in the world. Dolomite constitutes 7–32% in some relatively thin sections of shallow-marine carbonates in the Bahamas (Mitchell and Horton 1995a).

Amounts of dolomite in Mesozoic to Quaternary deep-sea sediments also vary greatly but are highest within nodules and thin beds, although some dolomite is present throughout many of these sections. Amounts vary from 1 to 5% in Miocene to Quaternary deposits (Pisciotto and Mahoney 1981; Kelts and McKenzie 1982, 1984; Baker and Burns 1985), 1 to 20% and 58 to 89% in some Miocene deposits (Burns and Baker 1987; Burns et al. 1988), 50 to 95% in Miocene and Pliocene deposits (Compton 1988b), and 5 to 20% in Pliocene deposits (Dix 1997). According to data in Lumsden (1988), dolomite averages about 28% in dolomitic deep-sea deposits. There is some evidence that dolomite abundance increases as the amount of precursor carbonate sediments and organic matter increases (Baker and Burns 1985; Compton 1988a, 1988b), but dolomite amount does not generally increase systematically with depth in deep-sea deposits (Lumsden 1985).

Mode of Progressive Dolomitization

Although at least initial dolomitization attending sulfate reduction and/or methanogenesis can occur in sediments, specific mechanisms of dolomitization during progressive burial into the methanogenetic zone remain uncertain. Several studies of deep-sea organogenic dolomites, for example, have documented initial dolomitization via sulfate reduction as identified by ^{13}C-depleted dolomites, followed by later methanogenetic dolomitization wherein the dolomites are ^{13}C-enriched (Murata et al. 1969; Murata et al. 1972; Pisciotto and Mahoney 1981; Kelts and McKenzie 1982, 1984; Burns et al. 1988; Suess et al. 1988). End-member depleted (sulfate reduction) and enriched (methanogenetic) $\delta^{13}C_{dolomite}$ compositional subpopulations are readily recognizable, although the range of intermediate $\delta^{13}C_{dolomite}$ values that is common in many datasets (Fig. 5) is most equivocal. These intermediate compositions may be inherent in a population of dolomites formed within a given organodiagenetic zone (sulfate reduction or methanogenesis) because of temporal and/or spatial differences in several parameters, including the extent of bacterial activity, amount of organic matter, and degree of interaction of evolved pore fluids with circulating marine fluids. If so, then is dolomite formation continuous as sediments pass progressively from zones of sulfate reduction into methanogenetic zones, or is it episodic? If it is continuous, then it follows that such $\delta^{13}C_{dolomite}$ compositional ranges may indicate that dolomitization proceeds by the development of new nucleation sites because there are no published data that might unequivocally suggest that core crystals of early-formed, relatively ^{13}C-depleted dolomite are overgrown by later-formed ^{13}C-enriched dolomite. Some workers (Compton 1988b; Vahrenkamp et al. 1991; Dix 1997) have suggested that organogenic dolomitization in some Neo-

gene deep-sea deposits may be episodic, or even cyclic, insofar as temporal variations in sedimentation rates, the residence time of the dolomitizing environment below the sediment/water interface, and changes in paleoceanography, eustasy, and tectonics may exert controls on dolomitization. Compton (1988b) also suggested that climatic cycles, possibly on the order of Milankovitch periodicities, also may influence the progress of dolomitization by affecting some of these factors. All of these aspects of organogenic dolomitization remain to be more fully evaluated.

Another issue is whether initial nucleation proceeds with or without the existence of prior diagenetic carbonate phases. Several workers have indicated, for example, that high-magnesium calcite may form first and later revert to dolomite in some deep-sea deposits (Kelts and McKenzie 1982, 1984; Burns et al. 1988). Similar precursor phases have not been noted in other deep-sea or in peritidal or shallow-marine organogenic dolomites.

Dolomite Recrystallization or Geochemical Alteration?—Kelts and McKenzie (1982) and Burns et al. (1988) suggested that progressively depleted $\delta^{18}O_{dolomite}$ values with depth in some deep-sea deposits, presumably with attendant increase in crystal size and ordering, are indicative of geochemical alteration and recrystallization as pore fluids passed from sulfate-reduction zones into deeper methanogenetic zones. Unfortunately, they did not provide convincing data that might have substantiated this idea. In this vein Suess et al. (1988) described ^{13}C-depleted calcite cements in deep-sea deposits which presumably precipitated in the zone of sulfate reduction but which now reside in the deeper methanogenetic zone. They found no obvious change in at least the carbon-isotope composition of these cements with increased burial and, hence, no evidence of geochemical alteration. Malone et al. (1994) suggested that, as a result of deeper burial and exposure to higher temperatures in the zone of thermal decarboxylation, the $\delta^{18}O$ and $\delta^{13}C$ values of prior-formed methanogenetic dolomites in the Miocene Monterey Formation (mean $\delta^{18}O$ and $\delta^{13}C$ = 4.3‰ and 10.2‰, respectively) were reequilibrated to more depleted mean values of −1.9‰ and −4.5‰, respectively. Increased stoichiometry and cation ordering, and depletion of Sr, in the dolomite attended such isotopic reequilibration. Swart (1993) also suggested that increase in dolomite stoichiometry with depth in some deep-sea deposits may be indicative of alteration attending deeper burial. Compton (1988b) suggested that increase in dolomite crystal size with depth in some Miocene deep-sea deposits, from 0.1–5 m to 10–40 m, may indicate recrystallization. Interestingly, dolomite stoichiometry does not increase with age (depth) in the database of deep-sea dolomites shown in Figure 6A.

Vasconcelos and McKenzie (1997) also inferred ''ageing'' of Holocene, shallow subtidal dolomites of sulfate-reduction origin, which presumably involved reequilibration of $\delta^{18}O$ compositions and increase in crystal size and stoichiometry with depth. Critical inspection of their data, however, indicates that such claims are not at all warranted. There also was no evidence of recrystallization or geochemical alteration of Holocene subtidal dolomites from 0 to 8 m sub-bottom depths in shallow-marine mudbank deposits in Belize (Mazzullo et al. 1995; Teal 1998; Teal et al. 1998). Recrystallization of Holocene peritidal dolomites of sulfate-reduction origin in Belize was suggested by Gregg et al. (1992) on the basis of slight increase in crystal size and log-normality of crystal size distributions with depth. There was no significant isotopic reequilibration of these dolomites. The extent of early recrystallization or geochemical alteration of newly formed organogenic dolomites therefore remains uncertain.

CONCLUSIONS

Organodiagenesis, involving bacterial sulfate reduction and methanogenesis in anoxic, organic-rich sediments, apparently has promoted early dolomitization in peritidal and marine deposits by overcoming barriers that otherwise may retard the process in seawater-derived fluids of normal pH, alkalinity, and dissolved-sulfate concentration at earth-surface temperature. Organogenic dolomites are volumetrically significant in a variety of de-

positional and geochemical environments in many modern and ancient sediments and, hence, they can be templates for later, more pervasive dolomitization. Sulfate reduction and methanogenesis may promote early dolomitization by resulting in concurrent increase in pH and total alkalinity, specifically, concentrations of dissolved CO_3^{2-}, and decrease in Mg and Ca hydration There is some indication, however, that dolomite nucleation may be promoted more effectively during methanogenesis and late stages of sulfate reduction when both higher pH and CO_3^{2-} concentrations in pore fluids are sustained by evolved methane, which also may result in the involvement in dolomitization of less hydrated Mg and Ca neutral ion pairs.

Organogenic dolomites typically are fine crystalline and nonstoichiometric (calcic) cements and, to a lesser extent, of replacement origin and generally contain relatively low concentrations of Sr, Fe, and Mn. Magnesium and calcium are variously believed to be derived by dissolution of precursor carbonate sediments and/or by diffusion from overlying seawater. Hence, supply of these ions is the rate-limiting factor in early dolomitization, and modeling studies suggest that dolomite formation may be limited to shallow sub-bottom depths (100 m or less) if ions are supplied mainly by diffusion. Organogenic dolomites are characterized by a wide range in $\delta^{13}C$ values that reflect the carbon-isotope composition of pore-water-dissolved CO_2 evolved in the different bacterial diagenetic zones in which they have formed. Sulfate reduction typically results in ^{13}C-depleted dolomites whereas methanogenesis results in ^{13}C-enriched dolomites. There is considerable range in, and overlap of, the $\delta^{13}C$ and $\delta^{18}O$ values of dolomites formed in each of these zones, however, which can complicate interpretations of their origin.

Many unanswered questions remain regarding early organogenic dolomitization, notably: (1) the specific role of presumed barriers to its nucleation—sulfate concentrations, pH and alkalinity, and ion hydration; (2) the relative efficiency of sulfate reduction versus methanogenesis, and of ammonia generation, in promoting dolomite formation; (3) depth limits of initial dolomitization, particularly regarding probable sources of Mg and Ca and the significance of $\delta^{18}O_{dolomite}$ values; (4) the extent of possible recrystallization and/or geochemical alteration of dolomites as they are progressively buried into the methanogenetic zone; (5) whether progressive organogenic dolomitization involves continually new nucleation sites or overgrowth of prior-formed crystals; and (6) whether dolomitization is episodic or continuous during progressive burial into methanogenetic zones.

ACKNOWLEDGMENTS

REFERENCES

AHARON, P., KOLODNY, Y., AND SASS, E., 1977, Recent hot brine dolomitization in the ''Solar Lake'', Gulf of Elat, isotopic, chemical and mineralogical study: Journal of Geology, v. 85, p. 27–48.

AUSTIN, J.A., AND SHIPBOARD SCIENTIFIC PARTY, 1986, Site 627: southern Blake Plateau; Initial Reports of the Ocean Drilling Project, v. 101, p. 111–212.

BAILEY, A.M., ROBERTS, H.H., AND BLACKSON, J.H., 1998, Early diagenetic minerals and variables influencing their distributions in two long cores (> 40 m), Mississippi River delta plain: Journal of Sedimentary Research, v. 68, p. 185–197.

BAKER, P.A., AND BURNS, S.J., 1985, Occurrence and formation of dolomite in organic-rich continental margin sediments: American Association of Petroleum Geologists, Bulletin, v. 69, p. 1917–1930.

BAKER, P.A., AND KASTNER, M., 1981, Constraints on the formation of sedimentary dolomite: Science, v. 213, p. 214–216.

BALTZER, F., KENIG, F., BOICHARD, R., PLAZIAT, J.C., AND PURSER, B.H., 1994, Organic matter distribution, water circulation and dolomitization beneath the Abu Dhabi sabkha (United Arab Emirates), in Purser, B., Tucker, M., and Zenger, D., eds., Dolomites, A Volume in

Honour of Dolomieu: International Association of Sedimentologists, Special Publication 21, p. 409–427.

BERNER, R.A., 1978, Sulfate reduction and the rate of deposition of marine sediments: Earth and Planetary Science Letters, v. 37, p. 492–498.

BERNER, R.A., 1980, Early Diagenesis; A Theoretical Approach: Princeton, New Jersey, Princeton University Press, 241 p.

BISCHOFF, W.D., AND MAZZULLO, S.J., 1996, Contrasting styles of peritidal and subtidal dolomitization in near-normal marine pore fluids, Belize (abstract): Geological Society of America, Annual Convention, Abstracts, v. 28, no. 7, p. A336.

BOTTINGA, Y., 1969, Calculated fractionation factors for carbon and hydrogen isotope exchange in the system calcite–carbon dioxide–graphite–methane–hydrogen–water vapor: Geochimica et Cosmochimica Acta, v. 33, p. 49–64.

BRAITHWAITE, C.J.R., 1991, Dolomites, a review of origins, geometry and textures: Royal Society of Edinburgh, Transactions, Earth Science, v. 82, p. 99–112.

BRAMLETTE, M.N., 1946, The Monterey Formation of California and the origin of its siliceous rocks: U.S. Geological Survey, Professional Paper 212, 57 p.

BROWN, B.J., AND FARROW, G.E., 1978, Recent dolomitic concretions of crustacean burrow origin from Loch Sunart, west coast of Scotland: Journal of Sedimentary Petrology, v. 48, p. 825–833.

BUDD, D.A., 1997, Cenozoic dolomites of carbonate islands: their attributes and origin: Earth-Science Reviews, v. 42, p. 1–47.

BURNS, S.J., 1998, Can diagenetic precipitation of carbonate nodules affect pore-water oxygen isotope ratios?: Journal of Sedimentary Research, v. 68, p. 100–103.

BURNS, S.J., AND BAKER, P.A., 1987, A geochemical study of dolomite in the Monterey Formation, California: Journal of Sedimentary Petrology, v. 57, p. 128–139.

BURNS, S.J., AND SWART, P.K., 1992, Diagenetic processes in Holocene carbonate sediments: Florida Bay mudbanks and islands: Sedimentology, v. 39, p. 285–304.

BURNS, S.J., BAKER, P.A., AND SHOWERS, W.J., 1988, The factors controlling the formation and chemistry of dolomite in organic-rich sediments: Miocene Drakes Bay Formation, California, in Shukla, V., and Baker, P.A., eds., Sedimentology and Geochemistry of Dolostones: SEPM, Special Publication 43, p. 41–52.

CHAI, L., NAVROTSKY, A., AND REEDER, R.J., 1995, Energetics of calcium-rich dolomite: Geochimica et Cosmochimica Acta, v. 59, p. 939–944.

CLAYPOOL, G.E., AND KAPLAN, I.R., 1974, The origin and distribution of methane in marine sediments, in Kaplan, I.R., ed., Natural Gases in Marine Sediments: New York, Plenum Press, p. 99–139.

CLAYPOOL, G.E., AND THRELKELD, C.N., 1983, Anoxic diagenesis and methane generation in sediments of the Blake Outer Ridge, DSDP Site 533, Leg 76: Initial Reports of the Deep Sea Drilling Project, v. 76, p. 391–402.

COLEMAN, M.L., AND RAISWELL, R., 1981, Carbon, oxygen and sulphur isotope variations in concretions from the Upper Lias of N.E. England: Geochimica et Cosmochimica Acta, v. 45, p. 329–340.

COMPTON, J.S., 1988a, Degree of supersaturation and precipitation of organogenic dolomite: Geology, v. 16, p. 318–321.

COMPTON, J.S., 1988b, Sediment composition and precipitation of dolomite and pyrite in the Neogene Monterey and Sisquoc Formations, Santa Maria Basin, California, in Shukla, V., and Baker, P.A., eds., Sedimentology and Geochemistry of Dolostones: SEPM, Special Publication 43, p. 53–64.

COMPTON, J.S., AND SIEVER, R., 1986, Diffusion and mass balance of Mg during early dolomite formation, Monterey Formation: Geochimica et Cosmochimica Acta, v. 50, p. 125–136.

COOPER, J.E., AND EVANS, W.S., 1983, Ammonium-nitrogen in Green River Formation oil shale: Science, v. 219, p. 492–493.

DAVIES, P.J., FERGUSON, J., AND BUBELA, B., 1975, Dolomite and organic material: Nature, v. 255, p. 472–474.

DIX, G.R., 1997, Stratigraphic patterns of deep-water dolomite, Northeast Australia: Journal of Sedimentary Research, v. 67, p. 1083–1096.

ELDERFIELD, H., 1981, Metal-organic associations in interstitial waters of Narragansett Bay sediments: American Journal of Science, v. 281, p. 1184–1196.

EUGSTER, H.P., AND HARDIE, L.A., 1978, Saline lakes, in Lerman, A., ed., Lakes: Chemistry, Geology, Physics: New York, Springer-Verlag, p. 237–297.

FRIEDMAN, G.M., AMIEL, A.J., BRAUN, M., AND MILLER, D.S., 1973, Generation of carbonate particles and laminites in algal mats—examples from sea-marginal hypersaline pool, Gulf of Aqaba, Red Sea: American Association of Petroleum Geologists, Bulletin, v. 57, p. 541–557.

FRIEDMAN, I., AND MURATA, K., 1979, Origin of dolomite in Miocene Monterey shale and related formations in the Temblor Range, California: Geochimica et Cosmochimica Acta, v. 43, p. 1357–1365.

GAINES, A.M., 1980, Dolomitization kinetics: recent experimental studies, in Zenger, D.H., Dunham, J.B., and Ethington, R.L., eds., Concepts and Models of Dolomitization: Society of Economic Paleontologists and Mineralogists, Special Publication 28, p. 81–86.

GEBELEIN, C.D., AND HOFFMAN, P., 1973, Algal origin of dolomite laminations in stromatolitic limestone: Journal of Sedimentary Petrology, v. 43, p. 603–613.

GEBELEIN, C.D., STEINEN, R.P., GARRETT, P., HOFFMAN, E.J., QUEEN, J.M., AND PLUMMER, L.N., 1980, Subsurface dolomitization beneath the tidal flats of central west Andros Island, Bahamas, in Zenger, D.H., Dunham, J.B., and Ethington, R.L., eds., Concepts and Models of Dolomitization: SEPM, Special Publication 28, p. 31–49.

GIESKES, J.M., 1975, Chemistry of interstitial waters of marine sediments: Annual Review of Earth and Planetary Sciences, v. 3, p. 433–453.

GIESKES, J.M., ELDERFIELD, H., LAWRENCE, J.R., JOHNSON, J., MEYERS, B., AND CAMPBELL, A., 1982, Geochemistry of interstitial waters and sediments, Leg 64, Gulf of California: Initial Reports of the Deep Sea Drilling Project, v. 64, p. 675–694.

GRABER, E.R., AND LOHMANN, K.C., 1989, Basinal marine dolomicrite from the Pennsylvanian/

Wolfcampian Horquilla Formation, New Mexico: Journal of Sedimentary Petrology, v. 59, p. 4–12.

GREGG, J.M., HOWARD, S.A., AND MAZZULLO, S.J., 1992, Early diagenetic recrystallization of Holocene (< 3000 years old) peritidal dolomites, Ambergris Cay, Belize: Sedimentology, v. 39, p. 143–160.

GUNATILAKA, A., SALEH, A., AL-TEMEEMI, A., AND NASSAR, N., 1984, Occurrence of subtidal dolomite in a shallow hypersaline lagoon, Kuwait: Nature, v. 311, p. 450–452.

GUNATILAKA, A., SALEH, A., AND AL-TEMEEMI, A., 1985, Sulfate reduction and dolomitization in a Holocene lagoon, Kuwait (abstract): SEPM, Midyear Meeting, Abstracts, v. 2, p. 38.

HARDIE, L.A., 1987, Dolomitization: a critical view of some current views: Journal of Sedimentary Petrology, v. 57, p. 166–183.

HEIN, J.R., O'NEIL, J.R., AND JONES, M.G., 1979, Origin of authigenic carbonates in sediment from the deep Bering Sea: Sedimentology, v. 26, p. 681–705.

HENNESSY, J., AND KNAUTH, L.P., 1985, Isotopic variations in dolomite concretions from the Monterey Formation, California: Journal of Sedimentary Petrology, v. 55, p. 120–130.

IRWIN, H., 1980, Early diagenetic carbonate precipitation and pore fluid migration in the Kimmeridge Clay of Dorset, England: Sedimentology, v. 27, p. 577–591.

IRWIN, H., CURTIS, C., AND COLEMAN, M., 1977, Isotopic evidence for source of diagenetic carbonates formed during burial of organic-rich sediments: Nature, v. 269, p. 209–213.

JORGENSEN, B.B., 1979, A comparison of methods for the quantification of bacterial sulfate reduction in coastal marine sediments. 2. Calculations from mathematical models: Journal of Geomicrobiology, v. 1, p. 29–51.

KASTNER, M., 1984, Control of dolomite formation: Nature, v. 311, p. 410–411.

KELTS, K., AND McKENZIE, J.A., 1982, Diagenetic dolomite formation in Quaternary anoxic diatomaceous muds of DSDP Leg 64, Gulf of California: Initial Reports of the Deep Sea Drilling Project, v. 64, p. 553–569.

KELTS, K., AND McKENZIE, J.A., 1984, A comparison of anoxic dolomites from deep sea sediments: Quaternary Gulf of California and Messinian Tripoli Formation of Sicily, in Garrison, R.E., Kastner, M., and Zenger, D.H., eds., Dolomites of the Monterey Formation and Other Organic-Rich Units: SEPM, Pacific Section, Publication 41, p. 19–28.

KITANO, Y., AND HOOD, J.D.W., 1965, The influence of organic material on the polymorphic crystallization of calcium carbonate: Geochimica et Cosmochimica Acta, v. 29, p. 29–41.

KUSHNIR, J., AND KASTNER, M., 1984, Two forms of dolomite occurrences in the Monterey Formation, California: concretions and layers; a comparative mineralogical, geochemical and isotope study, in Garrison, R.E., Kastner, M., and Zenger, D.H., eds., Dolomites in the Monterey Formation and Other Organic-Rich Units: SEPM, Pacific Section, Publication 41, p. 171–1837.

LAND, L.S., 1980, The isotopic and trace element geochemistry of dolomite: the state of the art, in Zenger, D.H., Dunham, J.B., and Ethington, R.L., eds., Concepts and Models of Dolomitization: Society of Economic Paleontologists and Mineralogists, Special Publication 28, p. 87–110.

LASEMI, Z., BOARDMAN, M.R., AND SANDBERG, P.A., 1989, Cement origin of supratidal dolomite, Andros Island, Bahamas: Journal of Sedimentary Petrology, v. 59, p. 249–257.

LIPPMANN, F., 1973, Sedimentary Carbonate Minerals: Berlin, Springer-Verlag, 228 p.

LUMSDEN, D.N., 1985, Secular variations in dolomite abundance in deep marine sediments: Geology, v. 13, p. 766–769.

LUMSDEN, D.N., 1988, Characteristics of deep-marine dolomite: Journal of Sedimentary Petrology, v. 58, p. 1023–1031.

LYONS, W.B., LONG, D.T., HINES, M.E., GAUDETTE, H.E., AND ARMSTRONG, P.B., 1984, Calcification of cyanobacterial mats in Solar Lake, Sinai: Geology, v. 12, p. 623–626.

MACHEL, H.G., AND MOUNTJOY, E.W., 1986, Chemistry and environments of dolomitization—a reappraisal: Earth-Science Reviews, v. 23, p. 175–222.

MACHEL, H.G., AND MOUNTJOY, E.W., 1987, General constraints on extensive pervasive dolomitization and their application to the Devonian carbonates of Western Canada: Bulletin of Canadian Petroleum Geology, v. 35, p. 143–158.

MALONE, M.J., BAKER, P.A., AND BURNS, S.J., 1994, Recrystallization of dolomite: evidence from the Monterey Formation (Miocene), California: Sedimentology, v. 41, p. 1223–1239.

MARTENS, C.S., AND BERNER, R.A., 1974, Methane production in the interstitial waters of sulfate-depleted marine sediments: Science, v. 185, p. 1167–1169.

MATSUMOTO, R., 1983, Mineralogy and geochemistry of carbonate diagenesis of the Pliocene and Pleistocene hemipelagic muds in the Blake Outer Ridge, Site 533, Leg 76: Initial Reports of the Deep Sea Drilling Project, v. 76, p. 411–428.

MAZZULLO, S.J., REID, A.M., AND GREGG, J.M., 1987, Dolomitization of Holocene Mg-calcite supratidal deposits, Ambergris Cay, Belize: Geological Society of America, Bulletin, v. 98, p. 224–231.

MAZZULLO, S.J., BISCHOFF, W.D., AND TEAL, C.S., 1995, Holocene shallow-subtidal dolomitization by near-normal seawater, northern Belize: Geology, v. 23, p. 341–344.

MAZZULLO, S.J., TEAL, C.S., WILHITE, B.W., AND BISCHOFF, W.D., 1999, Reversible sulfate reduction and methanogenesis reactions in dolomitization of Holocene shallow-marine carbonate sediments, Belize (abstract): American Association of Petroleum Geologists, Annual Convention, Abstracts, v. 8, p. A-91.

McKENZIE, J.A., JENKYNS, H.C., AND BENNET, G.G., 1980, Stable isotope study of the cyclic diatomite-claystones from the Tripoli Formation, Sicily: a prelude to the Messinian salinity crisis: Palaeogeography, Palaeoclimatology, Palaeoecology, v. 29, p. 125–141.

MERTZ, K.A., 1984, Diagenetic aspects, Sandholdt Member, Miocene Monterey Formation, Santa Lucia Mountains, California: implications for depositional and burial environment, in Garrison, R.E., Kastner, M., and Zenger, D.H., eds., Dolomites in the Monterey Formation and Other Organic-Rich Units: SEPM, Pacific Section, Publication 41, p. 49–74.

MIDDELBURG, J.J., deLANGE, G.S., AND KREULEN, R., 1990, Dolomite formation in anoxic sediments of Kau Bay, Indonesia: Geology, v. 18, p. 399–402.

MIRSAL, I.A., AND ZANKL, H., 1985, Some phenomenological aspects of carbonate geochemistry. The control effect of transition metals: Geologische Rundschau, v. 74, p. 367–377.

MITCHELL, S.W., AND HORTON, R.A., 1995a, Dolomitization of modern subtidal sediments, New Providence Island, Bahamas, in Curran, H.A., and White, B., eds., Terrestrial and Shallow-Marine Geology of the Bahamas and Bermuda: Geological Society of America, Special Paper 300, p. 189–199.

MITCHELL, S.W., AND HORTON, R.A., 1995b, Dolomitization of modern tidal flat, tidal creek, and lacustrine sediments, Bahamas, in Curran, H.A., and White, B., eds., Terrestrial and Shallow-Marine Geology of the Bahamas and Bermuda: Geological Society of America, Special Paper 300, p. 201–221.

MORROW, D.W., 1990a, Dolomite—Part 1: The chemistry of dolomitization and dolomite precipitation: Geoscience Canada, Reprint Series 4, p. 113–123.

MORROW, D.W., 1990b, Dolomite—Part 2: Dolomitization models and ancient dolostones: Geoscience Canada, Reprint Series 4, p. 125–139.

MORROW, D.W., AND ABERCROMBIE, H.J., 1994, Rates of dolomitization: the influence of dissolved sulfate, in Purser, B., Tucker, M., and Zenger, D., eds., Dolomites, A Volume in Honour of Dolomieu: International Association of Sedimentologists, Special Publication 21, p. 377–386.

MORROW, D.W., AND RICKETTS, B.D., 1988, Experimental investigation of sulfate inhibition of dolomite and its mineral analogues, in Shukla, V., and Baker, P.A., eds., Sedimentology and Geochemistry of Dolostones: SEPM, Special Publication 43, p. 25–38.

MULLINS, H.T., DIX, G.R., GARDULSKI, A.F., AND LAND, L.S., 1988, Neogene deep-water dolomite from the Florida–Bahamas platform, in Shukla, V., and Baker, P.A., eds., Sedimentology and Geochemistry of Dolostones: SEPM, Special Publication 43, p. 235–243.

MURATA, K.J., FRIEDMAN, I., AND MADSEN, B.M., 1969, Isotopic composition of diagenetic carbonates in marine Miocene formations of California and Oregon: U.S. Geological Survey, Professional Paper 614-B, 24 p.

MURATA, K.J., FRIEDMAN, I., AND CREMER, M., 1972, Geochemistry of diagenetic dolomites in Miocene marine formations of California and Oregon: U.S. Geological Survey, Professional Paper 724-C, p. C1–C12.

NIELSEN, P., SWENNEN, R., DICKSON, J.A.D., FALLICK, A.E., AND KEPPENS, E., 1997, Spheroidal dolomites in a Visean karst system—bacterial induced origin?: Sedimentology, v. 44, p. 177–195.

OREMLAND, R.S., 1975, Methane production in shallow-water, tropical marine sediments: Applied Microbiology, v. 30, p. 602–608.

OREMLAND, R.S., AND TAYLOR, B.F., 1978, Sulfate reduction and methanogenesis in marine sediments: Geochimica et Cosmochimica Acta, v. 42, p. 209–214.

PERKINS, R.D., DWYER, G.S., ROSOFF, D.B., FULLER, J., BAKER, P.A., AND LLOYD, R.M., 1994, Salina sedimentation and diagenesis: West Caicos Island, British West Indies, in Purser, B., Tucker, M., and Zenger, D., eds., Dolomites, A Volume in Honour of Dolomieu: International Association of Sedimentologists, Special Publication 21, p. 37–54.

PISCIOTTO, K., 1981, Review of secondary carbonates in the Monterey Formation, California, in Garrison, R.E., and Douglas, R.G., eds., The Monterey Formation and Related Siliceous Rocks of California: Society of Economic Paleontologists and Mineralogists, Pacific Section, Special Publication, p. 273–283.

PISCIOTTO, K.A., AND MAHONEY, J.J., 1981, Isotopic survey of diagenetic carbonates, Deep Sea Drilling Project Leg 63: Initial Reports of the Deep Sea Drilling Project, v. 63, p. 595–609.

PURSER, B., TUCKER, M., AND ZENGER, D., EDS., 1994, Dolomites, A Volume in Honour of Dolomieu: International Association of Sedimentologists, Special Publication 21, 451 p.

PYTKOWICZ, R.M., AND HAWLEY, J.E., 1974, Bicarbonate and carbonate ion pairs and a model of seawater at 25°C: Limnology and Oceanography, v. 19, p. 223–232.

REEBURGH, W.S., 1980, Anaerobic methane oxidation: rate depth distributions in Skan Bay sediments: Earth and Planetary Science Letters, v. 47, p. 345–352.

RUPPEL, S.C., AND CANDER, H.S., 1988, Dolomitization of shallow-water platform carbonates by sea water and seawater-derived brines: San Andres Formation (Guadalupian), west Texas, in Shukla, V., and Baker, P.A., eds., Sedimentology and Geochemistry of Dolostones: SEPM, Special Publication 43, p. 245–262.

RUSSEL, K.L., DEFFEYES, K.S., FOWLER, G.A., AND LLOYD, R.M., 1967, Marine dolomite of unusual isotopic composition: Science, v. 155, p. 189–191.

SASS, E., BEIN, A., AND ALMOGI-LABIN, A., 1991, Oxygen-isotope composition of diagenetic calcite in organic-rich rocks: evidence for ¹⁸O depletion in marine anaerobic pore water: Geology, v. 19, p. 839–842.

SEARL, A., 1994, Discontinuous solid solution in Ca-rich dolomites: the evidence and implications for the interpretation of dolomite petrographic and geochemical data, in Tucker, M., Purser, B., and Zenger, D., eds., Dolomites, A Volume in Honour of Dolomieu: International Association of Sedimentologists, Special Publication 21, p. 361–376.

SLAUGHTER, M., AND HILL, R.J., 1991, The influence of organic matter in organogenic dolomitization: Journal of Sedimentary Petrology, v. 61, p. 296–303.

SLAUGHTER, M., AND MATHEWS, A., 1984, Mineralogy and geochemistry of the Green River Formation, Colorado Core Hole No. 1, Piceance Creek Basin, Colorado: U.S. Department of Energy, Report of Investigation no. 7234, 904 p.

SOUSSI, M., AND M'RABET, A., 1994, Burial dolomitization of organic-rich and organic-poor carbonates, Jurassic of central Tunisia, in Purser, B., Tucker, M., and Zenger, D., eds., Dolomites, A Volume in Honour of Dolomieu: International Association of Sedimentologists, Special Publication 21, p. 429–445.

SPERBER, C.M., WILKINSON, B.H., AND PEACOR, D.R., 1984, Rock composition, dolomite stoichiometry and rock/water reactions in dolomitic carbonate rocks: Journal of Geology, v. 92, p. 609–622.

SUESS, E., VON HUENE, R., AND LEG 112 SHIPBOARD SCIENTISTS, 1988, Ocean Drilling Program Leg 112, Peru continental margin: Part 2, sedimentary history and diagenesis in a coastal upwelling environment: Geology, v. 16, p. 939–943.

SWART, P.K., 1993, The formation of dolomite in sediments from the continental margin of northeastern Queensland: Proceedings of the Ocean Drilling Project, Scientific Results Leg 133, College Station, Texas, p. 705–722.

Teal, C.S., 1998, Holocene Sedimentation and Dolomitization at Cangrejo Shoals Mudbank, Northern Belize [unpublished M.S. thesis]: Wichita State University, Wichita, Kansas, 240 p.

Teal, C.S., Mazzullo, S.J., and Bischoff, W.D., 1998, Syndepositional marine dolomitization in shallow subtidal deposits, northern Belize (abstract): American Associastion of Petroleum Geologists–SEPM Annual Convention, Salt Lake City, Abstracts, p. A652.

Tucker, M., and Wright, V.P., 1990, Carbonate Sedimentology: Oxford, U.K., Blackwell, 482 p.

Usdowski, H.E., 1968, The formation of dolomite in sediments, in Muller, G., and Friedman, G.M., eds., Recent Developments in Carbonate Sedimentology in Central Europe: New York, Springer-Verlag, p. 21–32.

Vahrenkamp, V.C., Swart, P.K., and Ruiz, J., 1991, Episodic dolomitization of Late Cenozoic carbonates in the Bahamas: evidence from strontium isotopes: Journal of Sedimentary Petrology, v. 61, p. 1002–1014.

Vasconcelos, C., and McKenzie, J.A., 1997, Microbial mediation of modern dolomite precipitation and diagenesis under anoxic conditions (Lagoa Vermelha, Rio de Janeiro, Brazil): Journal of Sedimentary Research, v. 67, p. 378–390.

Whitaker, F.F., Smart, P.L., Vahrenkamp, V.C., Nicholson, H., and Wogelius, R.A., 1994, Dolomitization by near-normal seawater? Field evidence from the Bahamas, in Purser, B., Tucker, M., and Zenger, D., eds., Dolomites, A Volume in Honour of Dolomieu: International Association of Sedimentologists, Special Publication 21, p. 111–132.

Wright, D.T., 1997, An organogenic origin for widespread dolomite in the Cambrian Eilean Dubh Formation, northwestern Scotland: Journal of Sedimentary Research, v. 67, p. 54–64.

Zenger, D.H., 1996, Dolomitization patterns in widespread ''Bighorn facies'' (Upper Ordovician), western craton, USA: Carbonates and Evaporites, v. 11, p. 219–225.

Zenger, D.H., Dunham, J.B., and Ethington, R.L., eds., 1980, Concepts and Models of Dolomitization: Society of Economic Paleontologists and Mineralogists, Special Publication 28, 320 p.