Dissolution and Recrystallization in Modern Shelf Carbonates: Evidence from Pore Water and Solid Phase Chemistry [and Discussion]

Lynn M. Walter, Steven A. Bischof, William P. Patterson, Timothy W. Lyons, R. K. O'Nions, M. Gruszczynski, B. W. Sellwood and M. L. Coleman

Phil. Trans. R. Soc. Lond. A 1993 **344**, 27-36
doi: 10.1098/rsta.1993.0072

Dissolution and recrystallization in modern shelf carbonates: evidence from pore water and solid phase chemistry

By Lynn M. Walter, Steven A. Bischof, William P. Patterson and Timothy W. Lyons

The Department of Geological Sciences, Room 1006 C.C. Little Building, The University of Michigan, Ann Arbor, Michigan 48109-1063, U.S.A.

We present an overview of geochemical data from pore waters and solid phases that clarify earliest diagenetic processes affecting modern, shallow marine carbonate sediments. Acids produced by organic matter decomposition react rapidly with metastable carbonate minerals in pore waters to produce extensive syndepositional dissolution and recrystallization. Stoichiometric relations among pore water solutes suggest that dissolution is related to oxidation of H_2S which can accumulate in these low-Fe sediments. Sulphide oxidation likely occurs by enhanced diffusion of O_2 mediated by sulphide-oxidizing bacteria which colonize oxic/anoxic interfaces invaginating these intensely bioturbated sediments. Buffering of pore water stable isotopic compositions towards values of bulk sediment and rapid ^{45}Ca exchange rates during sediment incubations demonstrate that carbonate recrystallization is a significant process. Comparison of average biogenic carbonate production rates with estimated rates of dissolution and recrystallization suggests that over half the gross production is dissolved and/or recrystallized. Thus isotopic and elemental composition of carbonate minerals can experience significant alteration during earliest burial driven by chemical exchange among carbonate minerals and decomposing organic matter. Temporal shifts in palaeo-ocean carbon isotope composition inferred from bulk-rocks may be seriously compromised by facies-dependent differences in dissolution and recrystallization rates.

1. Introduction

Modern calcium carbonate sediment volumes in the world ocean are roughly equally distributed between deep marine and shallow shelf depositional environments (e.g. Milliman 1974). Although early investigations of chemical alteration of carbonate sediments were focused on dissolution in undersaturated deep ocean waters, there is a growing body of evidence from pore water studies that early diagenetic modification of shallow marine carbonates is important (Morse *et al.* 1985; Walter & Burton 1990; Rude & Aller 1991). In addition, the role of grain recrystallization in developing classical 'micritic' textures in modern sediments has been recognized by carbonate petrologists (Reid *et al.* 1992).

Tropical shelf carbonate sediments are typically comprised of metastable minerals, aragonite and Mg-calcite. Association with abundant, reactive organic matter is common, as is intense sediment bioturbation (Shinn 1968; Aller & Dodge 1974). Although overlying surface seawater is highly supersaturated with respect to calcium

Phil. Trans. R. Soc. Lond. A (1993) **344**, 27–36

Printed in Great Britain

carbonate, organic decomposition and concomitent CO_2 release within sediment pore waters often produces a chemical environment near equilibrium, or slightly undersaturated, with respect to these minerals (Berner 1966; Morse *et al.* 1985; Walter & Burton 1990).

Importantly, carbonate mineral undersaturation can be maintained in pore waters of low-Fe sediments during microbial sulphate reduction (Walter & Burton 1990). When FeS_2 precipitation is precluded the weak acid, H_2S, accumulates in pore water, buffering the pH at values slightly below 7 (e.g. Ben Yaakov 1973). Carbonate dissolution is evident in shelf carbonate pore waters from observations of Ca/Cl ratios significantly greater than those of overlying seawater (Walter & Burton 1990). Also, release of F and Sr during aragonite recrystallization to F- and Sr-poor low-Mg calcite has been invoked to explain increases in shelf carbonate pore water F/Ca and Sr/Ca ratios (Rude & Aller 1991).

We present here geochemical evidence from interrelated, ongoing studies of sediment and pore water compositions from a wide range of modern shelf carbonate environments of South Florida (U.S.A.) and the Bahama Banks. Our results demonstrate that carbonate mineral dissolution and reprecipitation (recrystallization) are significant processes in the upper 10s of cm of the sediment column. The evidence presented includes relations among pore water solutes, pore water and solid phase stable isotopic compositions, and isotope exchange experiments. More complete and detailed presentations of these data sets are forthcoming. Our goal in this brief overview paper is to integrate the body of evidence for syndepositional diagenesis of platform carbonates, develop a predictive model for carbonate dissolution, and provide updated estimates of rates of recrystallization and dissolution.

2. Methodology

Pore water and sediment samples were obtained from the upper 20 cm of recent carbonate sediments of the South Florida and Bahama platforms using diver-collected boxcores. Water depths were typically less than 4 m. Sediments ranged from muds to muddy sands (wackestones) from environments with highly variable degrees of infaunal activity (bioturbation and bioirrigation of burrow networks). Sediments were dominantly comprised of aragonite (60 %) and Mg-calcite (40 %), with minor low-Mg calcite.

Boxcores were processed (2 cm intervals) under a N_2-atmosphere to prevent oxidation. Pore waters were extracted from sediments by centrifugation. Established analytical techniques (Grasshoff *et al.* 1983) were used for pore water analyses which included: pH, titration alkalinity, SO_4 (ion chromatography), Ca and Cl by potentiometric titration, TCO_2 (total dissolved CO_2: coulometric titration), and H_2S (coulometric titration).

Boxcores taken with overlying seawater were used as time series experiments to determine fluxes of dissolved Ca from a known sediment volume. Overlying seawater was gently stirred to prevent disturbance of the sediment–water interface and maintained in oxic state by bubbling with an aquarium pump. Closed system sediment incubation experiments under anoxic conditions were performed to determine rates of microbial sulphate reduction, uptake rates of ^{45}Ca onto sediment from spiked solutions, and carbonate dissolution rates under anoxic conditions.

Degree of equilibration between sediment and pore water was determined by C and O isotope measurements. Isotopic compositions of fresh specimens of living carbonate

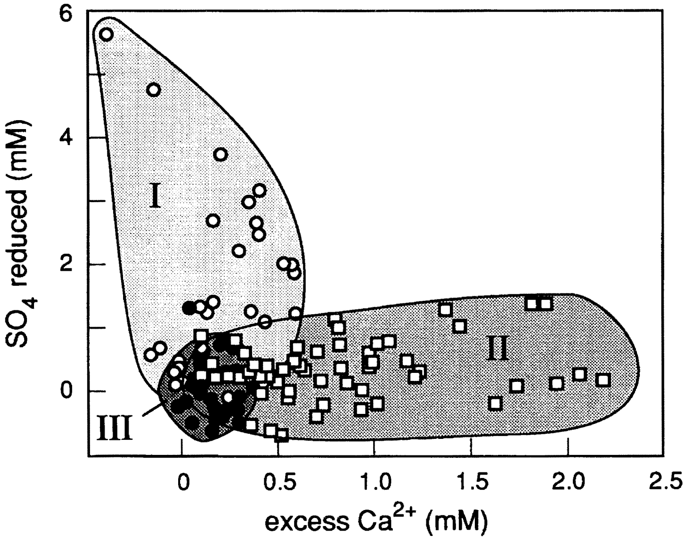

Figure 1. Amount of SO_4 reduced against amount of excess Ca in pore waters from the upper 20 cm of carbonates from the South Florida platform (Florida Keys reef tract and Florida Bay). Each point represents a 2 cm sediment depth interval. As seawater has about 30 mM sulphate and 10 mM Ca, amount of sulphate reduction or carbonate dissolution is most clearly expressed as a deviation from original marine values. Analytical precisions for sulphate analyses are $\pm 0.5\%$, or about ± 0.25 mM sulphate reduced. Groups I, II, and III are in part divided on sediment fabric and burrowing. Group I sediment is muddy and least bioturbated. Group II sediments are muds to sandy muds with intense bioturbation and burrowing activity. Group III sediments are muddy sands with pore waters largely unevolved chemically relative to overlying seawater.

secreting organisms (aragonitic green algae, *Halimeda*; 18 mol% Mg-calcite red algae, *Neogoniolithon*) were compared with those of recognizable algal fragments from the same species picked from boxcored sediment. These compositions were compared with the C isotope composition of TCO_2 from coexisting sediment pore waters.

3. What supplies the acid for carbonate dissolution?

(*a*) *Pore water chemistry*

Although elevation of pore water Ca/Cl ratios above that of overlying seawater has been established in earlier studies (Morse *et al.* 1985; Walter & Burton 1990), the acid source for carbonate dissolution has proven difficult to identify. In low-Fe carbonate sediments, the most extensive reactions occurring in sediment pore waters are sulphate reduction and carbonate dissolution. Identifying acid sources and reaction stoichiometries in carbonate pore waters is hindered by low extents of reaction and the generally 'unevolved' chemistry of pore water relative to overlying seawater. It is rare to encounter degrees of sulphate reduction in excess of 3 mM SO_4^{2-} reduced, less than a 10% reduction in the original amount of sulphate contained in seawater (Morse *et al.* 1985; Walter & Burton 1990).

Although CO_2 can be generated in principle via oxic respiration, the amount generated is limited by the solubility of oxygen in seawater (about 0.3 mM O_2; see Walter & Burton 1990). Instead, Walter and Burton (1990) suggested CO_2 generated during sulphate reduction as an alternative acid source based on the tendency for porewater excess Ca values to increase with increasing degrees of sulphate reduction (up to 10% reduction of original sulphate). The low excess Ca, to even slightly

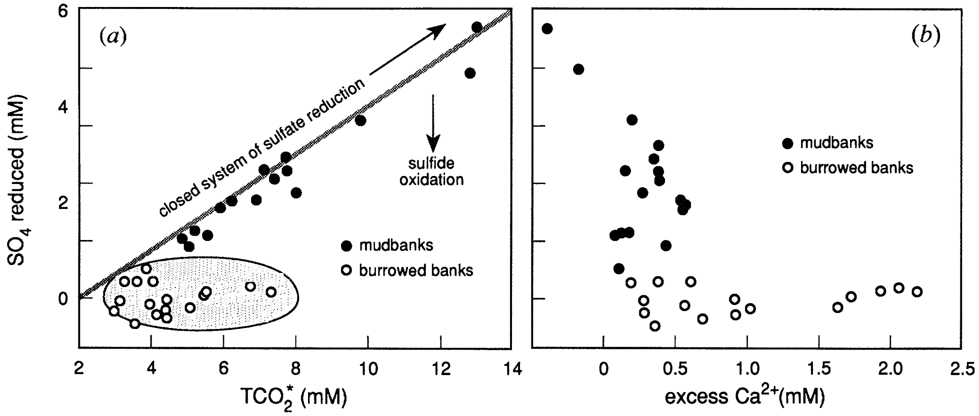

Figure 2. (*a*) Amount of SO_4 reduced against corrected total CO_2 (TCO_2). TCO_2^* is corrected for CO_2 added by dissolution of $CaCO_3$ by the amount of excess Ca in each pore water sample. In this way, TCO_2 excursions can be directly related to amount of organic matter decomposed. Closed circles represent data from mudbank sediments (Group I) which have little bioturbation. Open circles represent well-burrowed bank sediments (Group II). Mudbank pore waters largely follow the trend for closed system sulphate reduction, with 2 mM CO_2 produced per mM SO_4 reduced. Burrowed bank sediments exhibit little or no net reduction of SO_4, but the large excess of TCO_2 suggests that additional organic matter decomposition has occurred in these pore waters. (*b*) Amount of SO_4 reduced against excess Ca. Data points are as in (*a*), showing trajectories of evolution for Group I (mudbanks) and Group II (burrowed banks) as established in figure 1.

depleted Ca, values observed in pore waters with greater than 10% sulphate reduction were attributed to carbonate reprecipitation driven by carbonate saturation increases as alkalinity continues to accumulate.

Our recent results for degree of sulfate reduction and amounts of excess Ca in pore waters are shown in figure 1. There is no strong trend between amount of excess Ca and the degree of sulphate reduction, except at the extremes of the plot. Pore waters with the highest extent of sulphate reduction tend to have little or no excess Ca, while pore waters with significant amounts of excess Ca tend to have low degrees of sulphate reduction. The relatively unevolved pore waters of group I have neither large degrees of sulphate reduction nor significant amounts of excess Ca.

These data suggest that sulphate reduction alone cannot provide the source of acid for carbonate mineral dissolution. This was confirmed by closed system anoxic incubation experiments where no excess Ca was generated in sediment pore waters.

The theoretical closed-system relation between moles of sulphate reduced and increase in TCO_2 of pore water is shown in figure 2*a* for two end-member environments (highly burrowed bank sediment against undisturbed mudbank sediment). Calcium data for pore waters from the same sites are shown in figure 2*b*. Mudbank sediments have TCO_2 values in agreement with closed system sulphate reduction, but display little increase in Ca. Data from pore waters in burrowed bank sediments, in contrast, fall well off the closed system trend, suggesting that sulphide oxidation has occurred. Pore water TCO_2 in these burrowed sediments is thus too high for the 'apparent' degree of sulphate reduction. Importantly, it is in these sediment pore waters that significant elevation of Ca values are observed (figure 2*b*).

(*b*) *Stoichiometry of reactions*

The trends of natural pore waters in figure 2*a* can be explained most simply by sulphide oxidation. In this case, the TCO_2 generated during sulphate reduction may remain in the pore water although the sulphide generated by the reaction has been transformed back to sulphate. Previous studies of carbonate sediment pore waters have not determined completely and precisely the S and C systems. Our data suggest that it is important to make these coupled measurements to accurately understand the amount of organic matter decomposition that has occurred in the sediment pore water system.

The difference between the degree of sulphate reduction indicated from *measured* sulphate concentrations and those indicated from mass balance from the TCO_2 data can be related to the amount of H_2S oxidized to SO_4^{2-}. This follows simply from the following reaction stoichiometries:

1. $SO_4^{2-} + 2CH_2O \Rightarrow 2HCO_3^- + H_2S$ (+2 TCO_2 units),
2. $H_2S + 2O_2 \Rightarrow SO_4^{2-} + 2H^+$ (no change in TCO_2).

For pore waters in our study, reaction stoichiometries suggest that large amounts of sulphide oxidation have occurred, as great as 1–2 mM S. As discussed by Coleman (1985), isotopically distinctive SO_4^{2-} from oxidation of sulphide is preserved in phosphate minerals in ancient rocks.

Finally, and perhaps most importantly, 2 mol of dissolved O_2 are required per mole of H_2S to regenerate SO_4^{2-} in the pore water. The amount of dissolved oxygen required to accomplish this oxidation is as much as 4 mM. This is nearly 10 times the equilibrium concentration of dissolved O_2 in seawater (0.3 mM, as mentioned earlier).

Because oxygen demand by sulphide oxidation exceeds the amount that can be supplied by advection of oxygenated seawater, it is reasonable to turn to a non-stoichiometric supply mechanism such as enhanced diffusion of O_2 by films of sulphide-oxidizing bacteria at oxic–anoxic sediment–water interfaces. This mechanism has been invoked for near surface algal mats by Jørgensen & Revsbeck (1983) and may find application in the invaginated, burrowed layers of disturbed platform carbonate sediments.

Rapid and selective mass transport of oxygen is required to maintain natural pore waters at near-normal sulphate concentrations in the face of rapid sulphate reduction rates observed in sediment incubation studies. Walter & Burton (1990) determined that sulphate reduction rates in long-term (weeks) sediment incubation ranged between 40–100 mM a^{-1}. Our recent measurements using shorter-term ^{35}S incubation experiments yield values within this range; average sulphate reduction rates over the upper 20 cm of sediment are about 70 mM a^{-1}.

Stoichiometrically, the oxidation of H_2S or HS^- back to SO_4^{2-} in pore water yields between 1 and 2 mol of hydrogen ion. This, in turn, can dissolve between 1 and 2 mol $CaCO_3$. This relation is shown schematically in figure 3 where pore waters from the three sediment types are depicted in coordinate space of excess Ca and amount of H_2S oxidized. Pore waters with high excess Ca values (burrowed sediments of Group II) range widely on the plot.

Although data trends suggest a relation between dissolution and sulphide oxidation, Group II pore waters in figure 3 have significantly less excess Ca than expected for the H^+ generated by sulphide oxidation. Reprecipitation of more stable carbonate phases (‘recrystallization’) could explain lower amounts of excess Ca

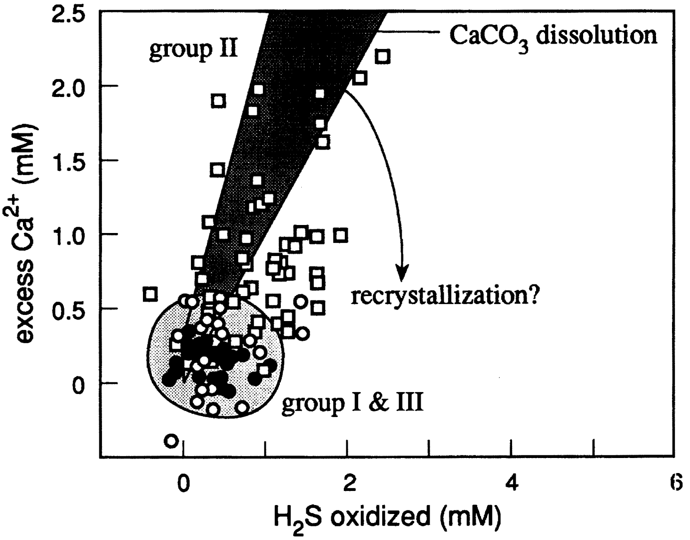

Figure 3. Amount of excess Ca generated by carbonate dissolution against H_2S oxidized, a calculated parameter. Amount of H_2S oxidized back to SO_4 is calculated assuming that the difference between the amount of excess TCO_2 due to sulphate reduction and measured amount of sulphate reduction equals amount of H_2S oxidized. The shaded region represents the speciation of sulphide: H_2S, producing two H^+, or HS^- producing one H^+. The H^+ produced by sulphide oxidation may then drive $CaCO_3$ dissolution, increasing Ca concentrations.

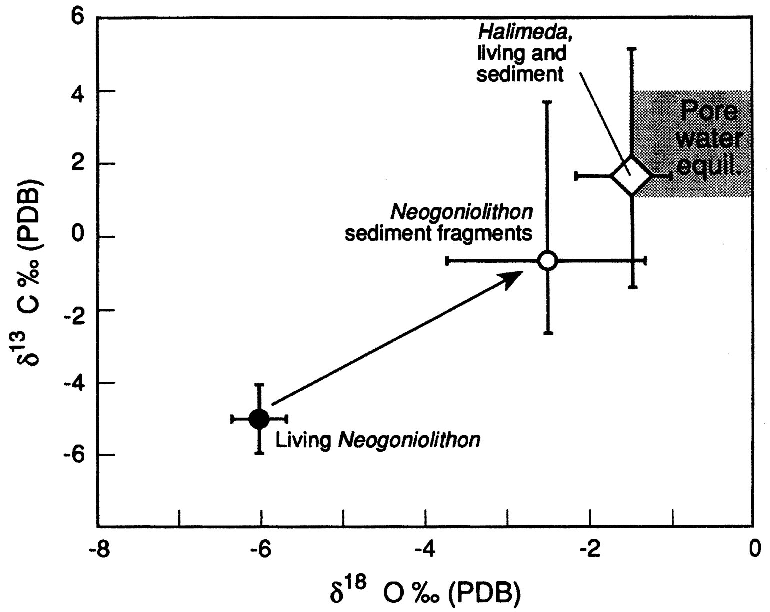

Figure 4. Mean ^{18}O and ^{13}C compositions for live specimens and sediment grains of *Neogoniolithon* (red) and *Halimeda* (green) calcareous algae. Living *Neogoniolithon* compositions ($n = 14$) evolve toward the composition predicted by the equilibrium precipitation of Mg-calcite and aragonite from measured pore water isotopic compositions in our field areas ($\delta^{18}O = -1.0$ to 0.0 SMOW, $\delta^{13}C = -2.0$ to -1.0 PDB). *Neogoniolithon* grains recovered from the sediment ($n = 29$) have increased by 4–5 permil in $\delta^{18}O$ and 5 permil in $\delta^{13}C$. *Halimeda* grains show little variation between living ($n = 46$) and sediment grain ($n = 27$) composition, and act as a buffer for the carbon isotopic composition of pore water. Error bars represent 1 standard deviation for each population.

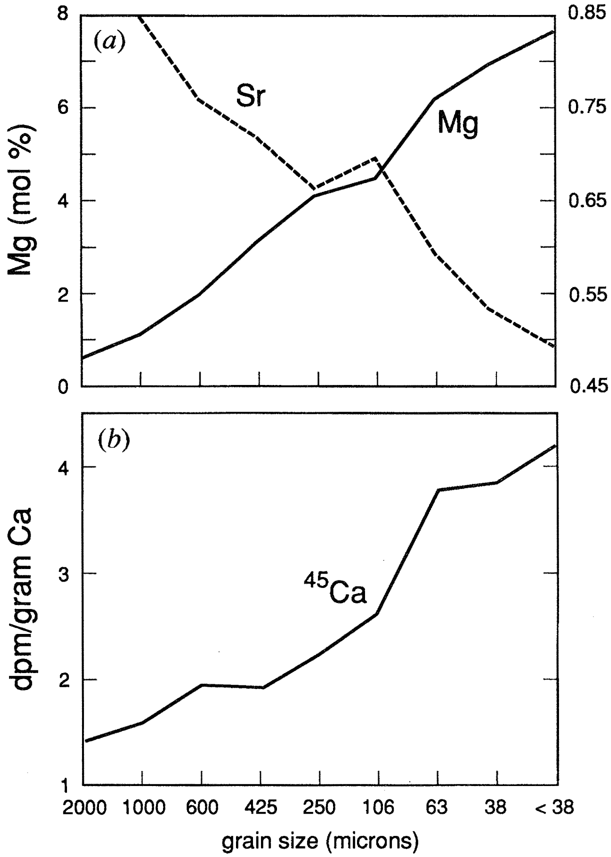

Figure 5. These data represent solid phase compositions of carbonate muds collected on Little Bahama Bank, incubated after an addition of ^{45}Ca: (*a*) mol % Mg and mol % Sr, and (*b*) decays per minute per gram plotted against grain size. Addition of ^{45}Ca is greatest in the smaller size fractions and correlates positively with Mg content and inversely with Sr content, indicating precipitation of Mg-calcite.

observed in most pore waters. It is important to bear in mind for overall budget calculations that the 'net' dissolution rate of $CaCO_3$ is the difference between 'gross' dissolution rate and rate of recrystallization (back precipitation of a more stable $CaCO_3$ phase).

4. Dissolution and recrystallization: how significant?

Rude & Aller (1991) recently invoked carbonate mineral recrystallization to explain elevated pore water Sr/Ca and F/Ca ratios in carbonate muds from South Florida. Sr and F both increase in pore water relative to Ca due to dissolution of high Sr and F aragonite, coupled with precipitation of more stable low-Mg calcite with lower F and Sr content. This possibility can be evaluated from the stable isotope systematics depicted schematically in figure 4. The carbon isotopic composition of aragonite from live and sediment grains of *Halimeda*, a dominant sediment contributor, is very close to ambient pore water TCO_2 carbon isotopic composition. This suggests buffering of pore water carbon isotope composition by equilibration with algal aragonite. In turn, the less abundant grain type, high Mg-calcite red algae,

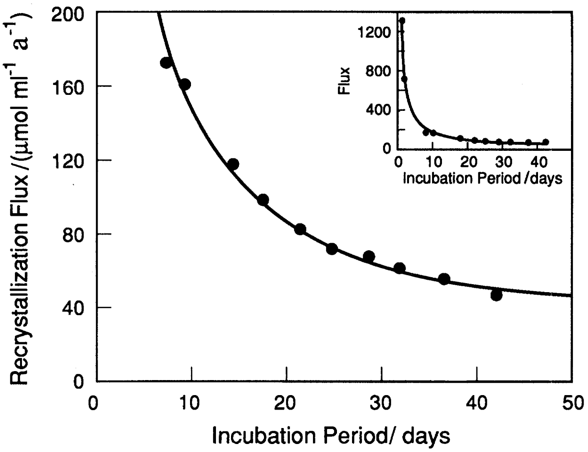

Figure 6. Recrystallization flux against incubation period. The recrystallization flux is calculated from loss of ^{45}Ca from pore water during the duration of the isotope exchange experiment. The rate of Ca exchange from pore water to solid is proportional to rate of ^{45}Ca loss as there is no isotope effect during $CaCO_3$ precipitation due to the ionic nature of the bond. $F = 1033t^{-0.8187}$ ($r = 0.993$).

evolves from relatively negative C isotope compositions in live specimens to values approaching those of pore water TCO_2 (and aragonitic algae) once exposed to the pore water environment.

Isotopic exchange via recrystallization is also manifested in ^{45}Ca isotope exchange experiments. Finer sediment grain sizes tend to have higher Mg contents (figure 5*a*) and higher ^{45}Ca activities (figure 5*b*). Isotopic exchange appears most extensive in finer sediment size fractions, although exchange has influenced to some extent the entire spectrum of grain sizes in the sample.

Figure 6 depicts the recrystallization rate, expressed for the upper 20 cm of a natural sediment, based on the ^{45}Ca exchange rates between the spiked solution and the incubated carbonate mud. There was no net dissolution in this experimental series of closed system incubations and pore water Ca contents remained constant over the course of the experiment. Thus, the uptake of the radioisotope can be directly related to a recrystallization rate. The long-term rate approaches a value of about 400 µmol cm^{-2} a^{-1}, very close to the value reported by Rude & Aller (1991).

Rate of recrystallization can be compared with estimates of both total biogenic carbonate production and the net dissolution flux from these sediments. Gross carbonate production estimates for South Florida and Bahama carbonate environments are between 700 and 1200 µmol cm^{-2} a^{-1} (Milliman 1974; Bosence *et al.* 1985). Combining estimates of recrystallization (400 µmol cm^{-2} a^{-1}) and net dissolution (200 and 350 µmol cm^{-2} a^{-1}) suggests that a significant fraction of the gross carbonate production can be dissolved. Moreover, a significant fraction of the accumulated carbonate is recrystallized in pore waters within the uppermost layers of shallow marine sediments.

These results, taken together with supporting evidence from previous work, show that shelf carbonate deposits can undergo extensive early diagenetic modification. These modifications must affect net carbonate accumulation rates, mineralogy, grain microstructure, texture, and elemental/isotopic composition. As such, it is important to consider the possibility that analyses of altered components of ancient shelf carbonates may tell us more about the composition of pore water than about overlying seawater. Ultimately, chemical and isotopic exchange among carbonate sediments, pore water, and decomposing organic matter may be important to consider in evaluating global mass balances and in interpreting shifts in the C isotope age curve for marine carbonates.

This research was supported by NSF Oceanography (Grants OCE 8811058 and OCE 9102543). S.A.B. was supported by a U.S. Department of Energy Graduate Fellowship for Global Change. We acknowledge the laboratory and field assistance of many colleagues; Jeff Alt, Linda Bonnell, Karlis Muehlenbachs, Eva Moldovanyi, Sheila Murphy, Charles Bukowski, and Ted Huston.

References

Aller, R. C. & Dodge, R. E. 1974 Animal sediment relations in a tropical lagoon, Discovery Bay, Jamaica. *J. mar. Res.* **32**, 209–231.

Ben Yaakov, S. 1973 pH buffering of pore water of recent anoxic marine sediment. *Limnol. Oceanogr.* **18**, 86–94.

Berner, R. A. 1966 Chemical diagenesis of some modern carbonate sediments. *Am. J. Sci.* **264**, 1–36.

Bosence, D. W. J., Rowlands, R. J. & Quine, M. L. 1985 Sedimentology and budget of a Recent carbonate mound, Florida Keys. *Sedimentology* **32**, 317–342.

Coleman, M. L. 1985 Geochemistry of diagenetic non-silicate minerals: kinetic considerations. *Phil. Trans. R. Soc. Lond.* A **315**, 39–56.

Grasshoff, K., Ehrhardt, M. & Kremling, K. 1983 *Methods of seawater analysis*. (419 pages.) Weinheim: Verlag-Chemie.

Jørgensen, B. B. & Revsbech, N. P. 1983 Colorless sulfur bacteria, *Beggiatoa* spp. and *Thiovulum* spp. in O_2 and H_2S microgradients. *Appl. envir. Microbiol.* **45**, 1261–1270.

Milliman, J. D. 1974 *Marine carbonates*. (375 pages.) Berlin: Springer-Verlag.

Morse, J. W., Zullig, J. J., Bernstein, L. D., Millero, F. J., Milne, P., Mucci, A. & Choppin, G. R. 1985 Chemistry of calcium carbonate-rich shallow water sediments in the Bahamas. *Am. J. Sci.* **285**, 147–185.

Reid, R. P., Macintyre, I. G. & Post, J. E. 1992 Micritized skeletal grains in northern Belize lagoon: a major source of Mg-calcite mud. *J. Sed. Petrol.* **62**, 145–156.

Rude, P. D. & Aller, R. C. 1991 Fluorine mobility during early diagenesis of carbonate sediment: an indicator of mineral transformations. *Geochim. cosmochim. Acta* **55**, 2491–2509.

Shinn, E. A. 1968 Burrowing in recent lime sediment of Florida and the Bahamas. *J. Paleont.* **42**, 879–894.

Walter, L. M. & Burton, E. A. 1990 Dissolution of recent platform carbonate sediments in marine pore fluids. *Am. J. Sci.* **290**, 601–643.

Discussion

R. K. O'Nions. What about the organic carbon burial rates? Are the isotopic age curves for carbonate sound?

L. M. Walter. In carbonate sediments, the organic carbon sequestering rates are similar to those in high-carbon, low-sulphur sediments.

M. Gruszczynski. Is it possible to release Ca^{2+} and precipitate gypsum/halite, as in hardgrounds?

L. M. Walter. Gypsum may precipitate, perhaps, if over-saline and sediment pore waters mix (hence high Ca^{2+}), but not in open marine systems.

B. W. Sellwood. Would Dr Walter expect to see significant differences in response if the host sediment consisted of low Mg-calcite rather than aragonite and high-Mg calcite? Predictable differences could have significant consequences in terms of the expected early burial response in Mesozoic and Palaeozoic carbonates and, indeed, in temperate water carbonates.

L. M. Walter. You would probably get more dissolution (sulphide oxidation). The sulphate reduction rate can be related to dissolution rate but not back to precipitation. Fine grained calcite can reprecipitate as coarser grained calcite.

M. L. Coleman. Is the negative δ^{34}S a result of sulphide oxidation as opposed to positive values from closed system sulphate reduction? I had hoped to see modern examples to confirm inferred processes which gave negative δ^{34}S in phosphates (francolite).

L. M. Walter. No negative values have been seen.