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Organic matter diagenesis in shallow water carbonate sediments

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Abstract—Muddy carbonate deposits near the Dry Tortugas, Florida, are characterized by high organic carbon remineralization rates. However, approximately half of the total sedimentary organic matter potentially supporting remineralization is occluded in $CaCO_3$ minerals (intracrystalline). While a portion of nonintracrystalline organic matter appears to cycle rapidly, intracrystalline organic matter has an approximately constant concentration with depth, suggesting that as long as its protective mineral matrix is intact, it is not readily remineralized. Organic matter in excess of intracrystalline organic matter that is preserved may have a variety of mineral associations (e.g., intercrystalline, adsorbed or detrital). In surface sediment, aspartic acid contributed ~22 mole % and ~50 mole % to nonintracrystalline and intracrystalline pools, respectively. In deeper sediment (1.6–1.7m), the composition of hydrolyzable amino acids in both pools was similar (aspartic acid ~40 mole %). Like amino acids, intracrystalline and nonintracrystalline fatty acids have different compositions in surface sediments, but are indistinguishable at depth. These data suggest that preserved organic matter in the nonintracrystalline pool is stabilized by its interactions with $CaCO_3$. Neutral lipids are present in very low abundances in the intracrystalline pool and are extensively degraded in both the intracrystalline and nonintracrystalline pools, suggesting that mineral interactions do not protect these compounds from degradation. The presence of chlorophyll-*a*, but absence of phytol, in the intracrystalline lipid pool demonstrates that chloropigments are present only in the nonintracrystalline pool. Sedimentary chloropigments decrease with depth at similar rates in Dry Tortugas sediments as found in alumino-silicate sediments from the Long Island Sound, suggesting that chloropigment degradation is largely unaffected by mineral interactions. Overall, however, inclusion and protection of organic matter by biominerals is a major pathway for organic matter preservation in this low-organic carbon, biomineral-rich regime.

1. INTRODUCTION

Biomineral-rich deposits contain organic matter that is both intracrystalline and nonintracrystalline in nature. The influence of the mineral matrix on these two pools of organic matter during diagenesis is not well known. Here we investigate changes in the concentration and composition of organic matter associated with the mineral matrix in a $CaCO_3$-rich sedimentary deposit.

$CaCO_3$ that is precipitated in the presence of organic matter incorporates some of this organic material into its crystal structure (Mitterer, 1971; Mitterer, 1972; Ramseyer et al., 1997). In the case of biogenic $CaCO_3$, glycoproteins that are produced by the organism to aid mineral precipitation are incorporated into the mineral during calcification (Abelson, 1955; Constantz and Weiner, 1988; Lowenstam and Weiner, 1989). Incorporated organic matter is in two operationally defined pools: "intracrystalline" organic matter is within biogenic $CaCO_3$ crystals, and "intercrystalline" organic matter surrounds individual biogenic $CaCO_3$ crystals (Towe, 1980; Endo et al., 1995; Sykes et al., 1995). Intercrystalline organic matter is accessible to strong oxidants while intracrystalline organic matter is not (Gaffey and Bronnimann, 1993). Thus, intracrystalline organic matter tends to remain associated with the $CaCO_3$ for very long timescales, or until the mineral dissolves (King and Hare, 1972; King, 1977; Weiner and Lowenstam, 1980; Collins et al., 1991; Collins et al., 1992). The concentration and composition of glycoproteins are largely genetically determined and species specific (King, 1977), but are often highly enriched in aspartic acid (Mitterer, 1978; Constantz and Weiner, 1988).

In addition to incorporating organic matter during precipitation, $CaCO_3$ can adsorb organic matter onto its surface. Adsorbed organic matter may come from surrounding sediment, from pore waters, or from the organic matter originally produced by the organism that precipitated the $CaCO_3$. The sorptive capacity of a mineral is proportional to its surface area and potential for ionic interactions with dissolved constituents (Suess, 1973). Compared to other minerals, $CaCO_3$ preferentially adsorbs more acidic organic compounds onto its surface (Müller and Suess, 1977; Carter, 1978). Amino acids adsorbed to $CaCO_3$ are usually enriched in the acidic amino acid aspartic acid relative to the source of adsorbed organic matter (Jackson and Bischoff, 1971; Mitterer, 1972). The composition of organic matter (OM) associated with fine-grain $CaCO_3$ sediments is often dominated by adsorbed compounds due to their large surface area to volume ratio (Carter and Mitterer, 1978). Larger grain sizes (>250 μm) tend to have bulk organic compound compositions that resemble intracrystalline material because the small surface area to volume ratio increases the importance of intracrystalline organic matter (Carter and Mitterer, 1978).

As mentioned above, there has been considerable work on intracrystalline, intercrystalline, and adsorbed amino acids in $CaCO_3$. However, most studies have not separated intracrys-

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talline from nonintracrystalline (which includes both intercrystalline, adsorbed as well as organic matter in discrete particles) amino acids to determine their individual compositions and behavior during early diagenesis. In addition, other compounds have not been as well studied as amino acids. Here we investigate the reactivity and preservation of chloropigments, lipids, amino acids, and total organic carbon (TOC) in biogenic sediments by analyzing intracrystalline and nonintracrystalline organic matter concentration and composition with depth in carbonate-rich sediments in the Dry Tortugas, Florida. Intercrystalline, adsorbed, and discrete organic matter sources are not distinguished in this study because our method for separating organic matter pools (bleach treatment) is not capable of doing so. Amino acids and lipids can be in each of these pools (Isa and Okazaki, 1987; Lowenstam and Weiner, 1989). Chloropigments are highly labile compounds that are closely associated with algal organic matter and are not expected to be intracrystalline or intercrystalline due to their location, normally within chloroplasts. In the case of Chl-*a*, we calculated degradation rate constants from core profiles and from laboratory experiments with carbonate sediment conducted under oxic and anoxic conditions. These results are compared with similar studies of Chl-*a* degradation in alumino silicate-rich sediments (Leavitt and Carpenter, 1990; Sun et al., 1993a). Organic matter preservation mechanisms are discussed in the context of other marine sediments and carbonate matrices. In particular, we compare organic matter degradation in these carbonate sediments with previous results from the more closed system found in coral heads (Ingalls et al., 2003). This study suggests that occlusion within biominerals is a major pathway for the preservation of organic matter in this low-organic carbon, biomineral-rich environment.

2. STUDY SITE AND SAMPLING

Sediment cores (<20 cm) were collected near the Dry Tortugas, small islands 110 km west of Key West, Florida (Fig. 1). The area is a fine-grained carbonate shelf environment where the sediments are up to 97% $CaCO_3$ (the remainder is primarily quartz and biogenic silica), and are composed primarily of fragments of the aragonitic green alga *Halimeda* sp. with smaller quantities of coral, mollusc, and foraminifera remains (Furukawa et al., 1997; Mallinson et al., 1997; Veyera et al., 2001). Biologic mixing in the vicinity of Southeast Channel (Fig. 1) is intense, and biogenic sedimentary fabrics dominate over those deposited by storm activity (Bentley and Nittrouer, 1997). Biologic mixing is primarily carried out by molluscs, polychaetes (0–4 cm), carnivores (upper 10 cm), and burrowing *Callianassa* shrimp (≥30 cm) (D'Andrea and Lopez, 1997). Total organic carbon content is low (0.4–0.7 wt.%) compared to other coastal sediments (Furukawa et al., 2000). Dissolved oxygen penetration into the sediment away from irrigated burrow structures is 2 to 3 mm (Furukawa et al., 2000). Benthic algae are common to the area, but bioturbation and frequent storms result in destabilization of algal mats (D'Andrea and Lopez, 1997). Salinity was 36.3 ppt and water temperature 28°C during sampling. Sediment porosities ranged from 0.6 to 0.8.

Cores were collected aboard the R/V Armagnac by SCUBA with a Plexiglas corer on April 19–20, 1997. Cores (~20 cm) were collected at Middle Key (MK; 24°39.484′N, 82°49.722′W, water depth 13.5 m), North Key Harbor (NKH; 24°40.759′N, 82°48.592′W, water depth 10.5 m), and East Key (EK; 24°39.544′N, 82°48.381′W, water depth 12 m). Surface sediment (top 0.5 cm) for the incubation experiments was collected in North Key Harbor by scooping up sediment with a plastic container. This sediment was refrigerated for ~48 h before beginning the experiment. One 180-cm gravity core (Left Key Harbor [LFK]: 24°36.973N, 82°50.761W, water depth 23 m) was collected from the R/V Pelican in June 1997 in the North Key Harbor area as part of the Coastal Benthic Boundary Layer Special Research Project sponsored by the Office of Naval Research. Short sediment cores were sectioned into 0.5-cm (surface) or 2.0-cm (deeper) intervals on board ship and frozen in dry ice until analysis. The gravity core was sectioned into 10-cm intervals and frozen.

2.1. Depositional Environment

Throughout the study, the diagenetic status of organic matter in sediment from 1.0 to 1.5 cm interval of MK (shallow sediment) is compared with that from 160 to 170 cm interval of LFK (deep sediment) assuming that the LFK sediment is "older" than the MK sediment. These two cores were collected from different locations that may have different depositional histories, perhaps compromising this assumption. For example, sediments in the Dry Tortugas are subject to redistribution from bioturbation, sea level rise, strong currents, and storm events (Davis and O'Neill, 1979; Bentley and Nittrouer, 1997; Wright et al., 1997). Despite possible differences, several factors suggest that the organic matter in deep sediment at North Key Harbor is generally older than organic matter in regional surface sediments.

While the ^{14}C age of the carbon in the $CaCO_3$ and organic matter pools has not been measured, the incorporation of ^{210}Pb ($t_{1/2}$ = 22 yr) and ^{234}Th ($t_{1/2}$ = 24 d) into the seabed suggests that sediments are accumulating steadily at a rate of ~0.3 to 0.4 cm/yr (Bentley and Nittrouer, 1997; Bentley, 1998). These authors conclude that some modern sediment is being deposited onto the seabed from surrounding *Halimeda* beds. Other sedimentological and geochemical evidence suggests that vertical changes with depth in sediment cores taken in North Key Harbor reflect progressive diagenesis and micritization (Furukawa et al., 1997; Furukawa et al., 2000). As argued subsequently, a variety of organic geochemical properties such as the presence of chlorophyll-*a* in surface, but not deep samples, are also consistent with sedimentological observations of steady diagenesis and an overall increasing age with depth.

3. MATERIAL AND METHODS

3.1. Sediment Analysis

Organic matter in sediment samples from various depth intervals was separated operationally into "intracrystalline" and "nonintracrystalline" pools. Intracrystalline organic matter was isolated after destruction of nonintracrystalline (intercrystalline, adsorbed and discrete) organic matter by exposing sediment to bleach (5% NaOCl) for eight days at room temperature (Gaffey and Bronnimann, 1993; Ingalls et al., 2003). We analyzed total organic carbon (TOC), intracrystalline organic carbon (CaTOC), total hydrolyzable amino acids (THAA), and intracrystalline total hydrolyzable amino acids (CaTHAA). We measured both

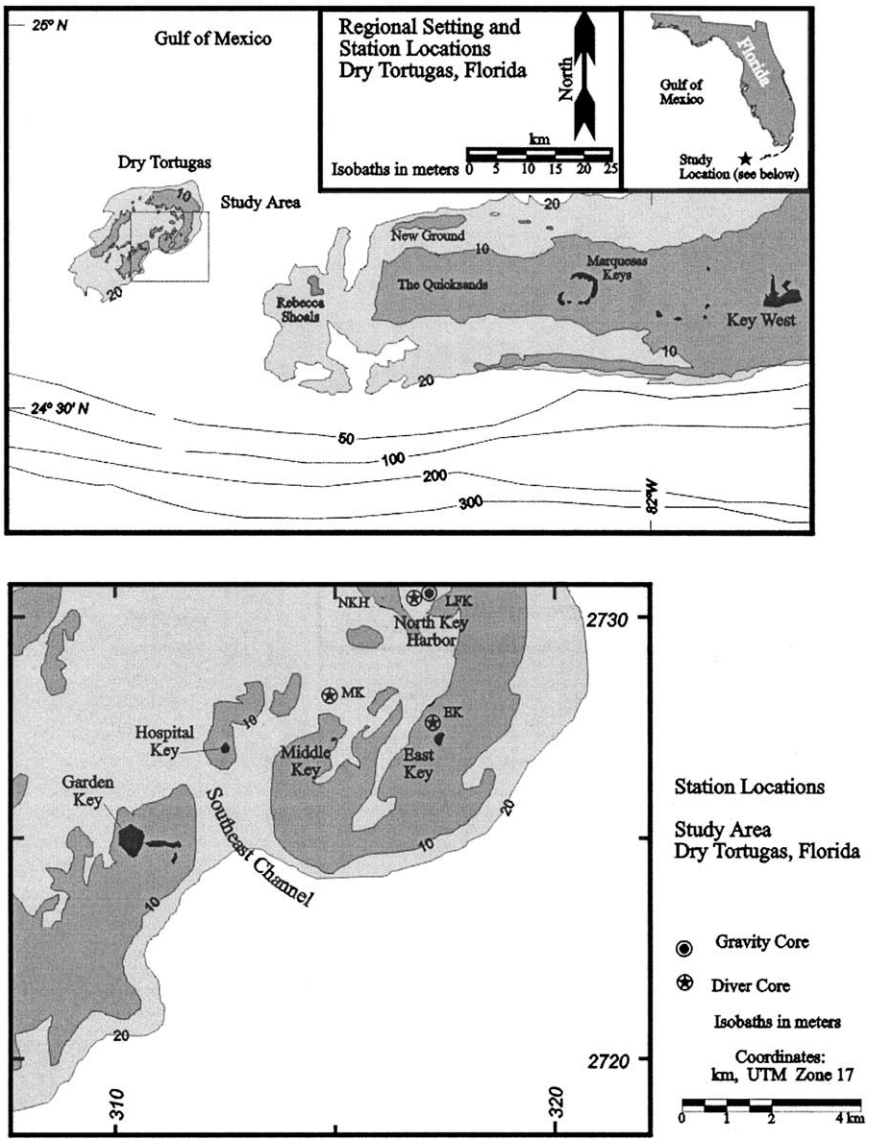

Fig. 1. Map of study area with core locations (after Bentley; 1998). Dry Tortugas National Park, Florida, USA.

nonintracrystalline and intracrystalline lipids, but only nonintracrystalline chloropigments.

As stated above, one surface and one deep sediment sample was chosen for comprehensive analysis to compare intracrystalline and nonintracrystalline organic matter concentration and composition in relatively fresh and aged sediment. Both the 160 to 170 cm LFK sediment and the 1.0 to 1.5 cm MK sediment were analyzed for TOC, CaTOC, THAA, CaTHAA, nonintracrystalline lipids, intracrystalline lipids, and surface area. In addition, TOC was measured in every depth interval of LFK. Chloropigments were measured in every depth interval collected from the MK, EK, NKH, and LFK cores. THAA were measured in every depth interval sampled from MK and EK, and in 2 depth intervals in the LFK gravity core (120–130 cm and 170–180 cm). CaTHAA were measured on depth intervals between 50 to 180 cm in LFK and 0 to 12 cm in MK. Surface area measurements were made by L. Mayer on five samples between 0 and 13 cm and two samples between 160 to 190 cm using the BET (Brunauer-Emmett-Teller) method after a 150°C outgassing, but without removal of organic matter (Brunauer et al., 1938; Mayer, 1994).

3.2. Degradation Experiments

Degradation rates of chloropigments and TOC in surface NKH sediment were determined by incubating homogenized, sieved (1-mm mesh, under N_2 in a glove bag) sediment at room temperature (~22°C) for 64 d under three conditions: diffusively open oxic (oxic), diffusively open anoxic (open anoxic), and diffusively closed anoxic (closed anoxic). The experimental setup has been described previously (Sun et al., 1993a; Aller, 1994). Briefly, thin layers of sediment were placed into a circular mold or "plug" (23 mm diameter and 2 mm thick) and incubated in a tank of filtered Long Island Sound surface seawater. In both oxic and open anoxic incubations, pore waters in the sediment plug were able to exchange diffusively with the overlying water, preventing metabolite buildup in the sediment plug. Oxic conditions were maintained by bubbling overlying water with air. Anoxia and constant pH were maintained in open anoxic incubations by continual purging of the overlying water with N_2/CO_2 gas. In closed anoxic incubations, plastic vials were filled with sediment and sealed and buried in mud, preventing exchange of metabolites and O_2 with the sediment in the vial. In each of the incubation experiments, samples were removed every 1 to 4 d during the first 64 d. The closed anoxic

sediments were incubated for a total of 500 d. Three samples were removed from the closed anoxic incubations between 64 and 500 d. All samples were analyzed for their chloropigment composition. Pore water for ΣCO_2 analysis was separated by centrifugation and analyzed by flow injection gas diffusion (Hall and Aller, 1992).

3.3. Analytical Methods

3.3.1. Total organic carbon (TOC)

Typically, before performing TOC analyses, sediments are acidified to remove traces of $CaCO_3$ (Verardo et al., 1990). Samples with low $CaCO_3$ concentrations can usually be acidified in the same Ag cup that carries the sample into the elemental analyzer. For highly $CaCO_3$-rich samples with low OC concentrations, this is impractical. Because of the large sample size necessary, the cups typically used are too small to hold the acid needed to dissolve the sample; analysis of samples prepared in this way resulted in inconsistent results. Therefore, TOC and CaTOC were measured after dissolving unbleached or bleached sediment (~1 g) in trace-metal grade 6N HCl overnight in a combusted glass vial. In both cases, organic matter insoluble in 6 N HCl was removed from the dissolved sediment by filtration through a combusted Whatman GFF filter (0.7 μm nominal pore size). The filter was rinsed with 1 mL of 1% HCl to remove any acid-soluble organic matter left on the filter, and filtrates were combined. HCl-soluble organic carbon in filtrates was analyzed using a Shimadzu DOC analyzer. Precision of replicate samples was ±5%. Measurements were standardized using potassium hydrogen phthalate and standard DOC reference material (courtesy of Jon Sharp). HCl-insoluble organic C and total N on filters from bleached and unbleached samples were analyzed using a Carlo-Erba elemental analyzer. Precision of replicate samples was ±5%. Measurements were standardized with sulfanilamide and intercalibration reference materials from NIST (Standard Coal) and NRC-Canada (BCSS-1 Estuarine Sediment). Soluble and insoluble fractions of unbleached samples were summed to obtain TOC. Nonintracrystalline OC was calculated as the difference between TOC and intracrystalline OC.

3.3.2. Amino acids (THAA and CaTHAA)

For amino acid analyses, bleached or unbleached sediment (~200 mg) was dissolved in enough 12N HCl to result in a 6N HCl solution after $CaCO_3$ dissolution. Additional 6 N HCl was added and the samples hydrolyzed at 150°C for 90 min (Cowie and Hedges, 1992). Total hydrolyzable amino acids (THAA) and intracrystalline amino acids (CaTHAA) were analyzed by high-pressure liquid chromatography (HPLC) using precolumn OPA derivatization (Lindroth and Mopper, 1979; Lee et al., 2000). Precision of replicate samples averaged ±15%. A protein amino acid hydrolyzate standard (Pierce Chemical) was used to identify and quantify individual compounds. The nonprotein amino acids β-alanine and γ-aminobutyric acid (Sigma Chemical) were added to the standard mixture during dilution.

3.3.3. Lipids

Nonintracrystalline and intracrystalline lipids were extracted from ~1 g of unbleached sediment using CH_2Cl_2 before and after dissolution of the $CaCO_3$ mineral, respectively. Strong acid cannot be used to dissolve $CaCO_3$ for lipid analysis as it can cause substantial alteration of lipids. Therefore, methods for dissolution of $CaCO_3$ were adapted from studies of intact skeletal organic matrices that result in minimal alteration of organic matter (Weiner and Erez, 1984). Preextracted (CH_2Cl_2) sediment was dissolved in a commercially prepared 0.1N HCl/EDTA solution (Polysciences Inc). Intracrystalline lipids were then extracted from the HCl/EDTA solution with CH_2Cl_2 (Ingalls et al., 2003).

Lipids in both CH_2Cl_2 extracts were analyzed using methods described by Wakeham et al. (1997a). Neutral (sterols, fatty alcohols, hydrocarbons, and alkenones) and acidic (hydrolysis products of wax ester, triacylglycerols, steryl esters, and phospholipids) lipids were derivatized as the trimethylsilyl and methyl esters, respectively, quantified by gas chromatography (GC), and identified by gas chromatography-mass spectrometry (GC-MS). Analytical precision is usually ±10 to 15% (Wakeham et al., 1997a).

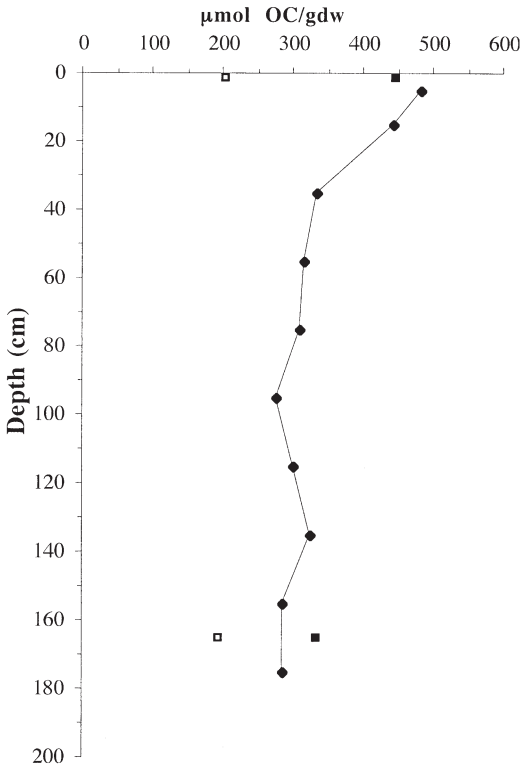

Fig. 2. Organic carbon concentration (μmol OC/gdw) in North Key Harbor. Diamonds are TOC data from Alan Shiller (gravity core, LFK). Squares are data from this study. Filled squares are TOC and open squares are CaTOC (intracrystalline). Surface sediment is the 1.0 to 1.5 cm interval of the diver-collected MK core and deep sediment is the 160 to 170 cm interval of the LFK gravity core.

3.3.4. Chloropigments

Chloropigments were extracted from ~1 g of sediment with 5 mL HPLC-grade, 100% acetone following Sun et al. (1991). Two successive extracts were combined and filtered. Chloropigments were not measured in acidified sediment samples; but since no phytol was detected in the intracrystalline lipid analyses, Chl-*a* could not have been present there. Chl-*a* and its immediate degradation products (phaeophorbide, phaeophytin, and pyrophaeophorbide) were determined by ion-pairing, reverse-phase HPLC (Mantoura and Llewellyn, 1983; Sun et al., 1991). The precision for replicate samples extracted over a several month period was ±15%. A Chl-*a* standard of known concentration (Turner Designs) was used to identify and quantify Chl-*a*. Standards for Chl-*a* phaeopigment degradation products were produced in the lab from purified Chl-*a* (King, 1993), and their concentrations determined spectrophotometrically using known extinction coefficients.

4. RESULTS

4.1. Total Organic Carbon (TOC)

TOC in the gravity core from North Key Harbor (LFK) was 483 μmol C gdw^{-1} in the 0 to 10 cm interval and 283 μmol C gdw^{-1} below 150 cm (Fig. 2a, Shiller data). These values are in good agreement with previous reports of 300 to 600 μmol C gdw^{-1} (0.36–0.72 wt.% C) in the upper 20 cm of NKH sediment (Furukawa et al., 2000). The 42% decrease in organic carbon content of sediments occurred in the upper 30 cm. Below this, the TOC concentration was relatively constant. In

Table 1. Total and intracrystalline organic carbon (μmol C/g dry sediment) in the acid-soluble and acid-insoluble pools of 1.0—1.5 cm sediment (MK) and 160—170 cm sediment (LFK) from North Key Harbor.

Sample Depth (cm)	Pool	Insoluble OC μmol/g	Soluble OC μmol/g	OC μmol/g	Pool % TOC	% Pool soluble	% Pool insoluble	% Pool decrease w/ depth
1—1.5	Total	306	141	447	100	32	68	
160—170	Total	220	114	334	100	34	66	25
1—1.5	Intracrystalline	64	138	202	45	68	32	
160—170	Intracrystalline	78	115	192	57	60	41	5
1—1.5	Non intracrystalline*	242	3	245	55	1	99	
160—170	Non intracrystalline*	142	−1	142	43	−1	100	42

* = total − intracrystalline

MK surface sediment, the TOC concentration was slightly lower (447 μmol C gdw^{-1}) than at LFK (Fig. 2 and Table 1), and 45 ± 4% of the TOC was intracrystalline (CaTOC). The CaTOC concentration was the same in surface MK sediment and deep LFK sediment, but the decrease in TOC (from the loss of nonintracrystalline organic carbon) with depth resulted in an increase in the proportion of CaTOC to 57 ± 6% in deep LFK sediment (Fig. 2 and Table 1). The intracrystalline organic carbon pool was dominated by acid-soluble organic carbon (60 and 68 ± 6% in shallow and deep sediments, respectively), while the nonintracrystalline pool was composed entirely of acid-insoluble OC (Table 1).

4.2. Amino Acids

THAA concentrations in the upper ~18 cm of EK and MK were between 50 to 85 μmol THAA C gdw^{-1} (average = 66 μmol THAA C gdw^{-1}). Depth profiles indicate variability in the amino acid concentration with depth in the upper 18 cm (Fig. 3a). In the 120 to 180 cm sediment interval from LFK, the average THAA concentration was 39 μmol C gdw^{-1}, ~41% less than the average in the upper 18 cm (Table 2, Fig 3b). In contrast, calcium carbonate-bound amino acids (CaTHAA) in NKH sediments were similar (~15 μmol C gdw^{-1}) in both surface and deep sediments (Table 2, Fig. 3b).

Amino acid compositional data were averaged over 0 to 18 cm in sediments from MK and EK and over 120 to 180 cm in sediments from LFK to compare the composition of THAA and CaTHAA in shallow and deep sediments (Fig. 4). In shallow sediment, the compositions of THAA and CaTHAA were distinct, and mole % aspartic acid was 2 times higher in CaTHAA (~50 mole %) than THAA (~22 mole %). In deep sediment, both THAA and CaTHAA had similar compositions of ~39

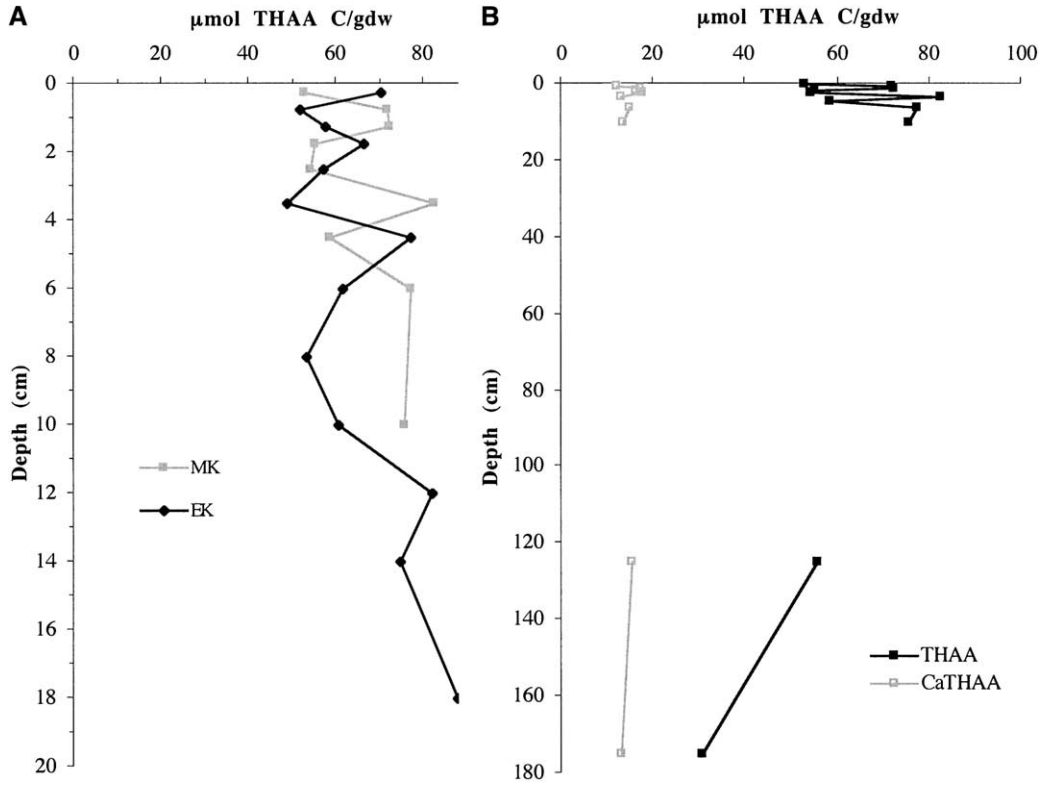

Fig. 3. (a) Total THAA concentration (μmol C/gdw) in cores from Middle Key (MK) and East Key (EK); (b) THAA and CaTHAA from MK (0–20 cm) and LFK (120–180 cm).

Table 2. THAA, CaTHAA and nonintracrystalline amino acid concentrations (μmol C g^{-1}) and aspartic acid composition of surface sediment (0—18 cm average from MK and EK) and deep sediment (120—180 cm average from LFK).

Sample Depth (cm)	Pool	Amino acid μmol C/g	% of Total amino acid pool	OC pool μmol C/g	Amino acids as % OC pool	% Amino acid pool decrease with depth	Aspartic acid mole %
0—18	THAA	66	100	440	15		22
120—180	THAA	39	100	300	13	41	40
0—18	CaTHAA	15	23	214	7		50
120—180	CaTHAA	15	38	188	8	0	40
0—18	Nonintracrystalline THAA*	51	77	226	23		14
120—180	Nonintracrystalline THAA*	24	62	113	21	53	39

* (THAA − CaTHAA)

mol % aspartic acid. The contribution of aspartic acid to the nonintracrystalline amino acid pool was calculated from the composition of THAA and intracrystalline CaTHAA, and was 14 and 39 mol % in shallow and deep sediment, respectively (Table 2). Aspartic acid-rich glycoproteins are involved in mineral precipitation and are a major component of the acid-soluble fraction of the intracrystalline skeletal organic matrix (Mitterer, 1978; Constantz and Weiner, 1988; Cuif et al., 1999; Dauphin, 2001). In addition, acid-insoluble glycine-rich proteins are also present in intracrystalline $CaCO_3$ pools (Levi et al., 1998). Glycine, glutamic acid, and alanine were also major amino acids in all samples. β-Ala was found only in the nonintracrystalline pool, while γ-aba was in both the THAA and CaTHAA pools. These two nonprotein amino acids are often used to indicate biologic degradation (e.g., Cowie and Hedges, 1994). Aspartic acid is usually the most abundant amino acid in biogenic $CaCO_3$.

4.3. Lipids

Fatty acids concentrations were 30 μg/gdw and neutral lipids were 7.6 μg/gdw. The concentration of both lipid classes was dramatically depleted in deeper sediment relative to shallow sediment (Table 3). The greatest decrease with depth was in the nonintracrystalline pool (~90% loss). However, the intracrystalline pool was also significantly lower at depth (~69% loss). The dominant fatty acids in shallow samples were 16:0 followed by 16:1 and 10-methyl-16:0-*anteiso* (Fig. 5a and b). Odd-chain fatty acids (e.g., 15:0 *iso*, 15:0 *anteiso* and 17:0 *iso*) were present in both the nonintracrystalline and intracrystalline pools; these compounds are usually associated with the presence of bacteria (Wakeham et al., 1997a). 16:0 Fatty acid was the most abundant fatty acid in deep sediments followed by 18:1 and 18:0 fatty acids. Neutral lipids were >90% nonintracrystalline.

In surface sediment, the most abundant neutral lipid was the sterol, 24-ethylcholest-5-en-3β-ol, followed by phytol, the hydrolyzed side chain of Chl-*a* and cholesta-5-en-3β-ol (cholesterol) (Fig. 5c and d). 4α,23,24-Trimethyl-cholest-22-en-3β-ol (dinosterol), a dinoflagellate biomarker, and 24-propylcholest-5-en-3β-ol (gorgosterol), a coral biomarker, were also present (Fig. 5c). Several nonintracrystalline neutral lipids that were present in surface sediments, including 14, 15, 16, and 17 alcohols, phytol, cholesta-22-en-3β-ol, and 24-ethylcholest-22-en-3β-ol, were absent in the deep sediment (Fig. 5d). Five of the twenty neutral lipids identified in the nonintracrystalline pool were found in very low concentrations in the intracrystalline pool.

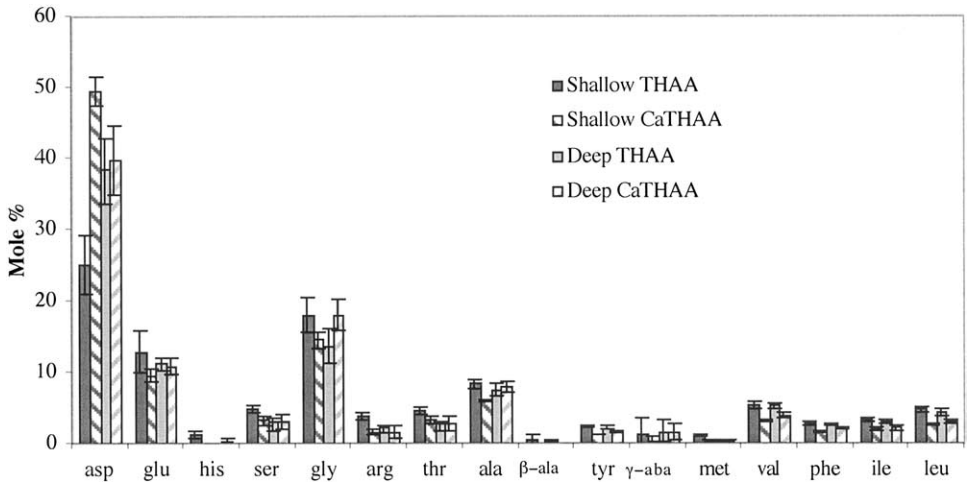

Fig. 4. Total and intracrystalline amino acid composition (mole %). Shallow sediment is the average composition of 0 to 12 cm of MK. Deep sediment is the average composition of 50 to 180 cm sediment of LFK. Error bars are the standard deviations of the averaged samples, not analytical error.

Table 3. Total and intracrystalline lipids (μg/g sediment) in surface sediment (1.0—1.5 cm) and deep sediment (160—170 cm) from North Key Harbor. Values are the sum of all identified peaks.

Sample depth (cm)	Pool	Fatty acids (FA) μg/g	% Total FA pool	% FA pool decrease with depth	Neutral lipid (NL) μg/g	% Total NL pool	% NL pool decrease with depth
1—1.5	Total*	30	100		7.6	100	
160—170	Total*	3.3	100	89	1.0	100	86
1—1.5	Intracrystalline	4.7	16		0.28	4	
160—170	Intracrystalline	1.5	45	68	0.086	8	69
1—1.5	Nonintracrystalline	25	84		7.3	96	
160—170	Nonintracrystalline	1.8	55	93	0.95	92	87

* = (Intracrystalline + Nonintracrystalline)

4.4. Chloropigments

Concentrations of chlorophyll-*a* (Chl-*a*) were between 2 and 6 nmol/gdw (~100–300 nmol C/gdw) in surface sediments of all stations and decreased to background concentrations (<0.2 nmol/gdw) within the upper 10 cm (Fig. 6a). These concentrations are comparable to other coastal areas with similar water depths (Furlong and Carpenter, 1988; Bianchi et al., 1991; Sun, 1994). Chloropigment degradation products were evident at all stations in the 0 to 20 cm depth interval. The concentration of all phaeopigments decreased with depth in all cores (Fig. 6b–d). The ratio of phaeopigments/Chl-*a* generally remained constant or increased with depth in the upper 20 cm. In deeper sediments sampled by gravity core, pheophytin (Ppt) and pyrophaeophorbide (Pyroppb) were undetectable below 20 cm while Chl-*a* was present at very low concentrations (0.005 nmol/gdw) as deep as 80 cm; Chl-*a* was undetectable below that depth. Phaeophorbide (Ppb) was not quantified in the gravity core.

4.5. Component Mass Balance of Total Organic Carbon

THAA made up 15% of the TOC in MK surface sediment and 13% of the TOC in deep LFK sediment (Table 2). CaTHAA made up 7% of the CaTOC in surface sediment and 8% CaTOC in the deep sediment. CaTHAA were 23% of THAA in surface sediment and 38% of THAA in deep sediment. CaTOC was 45% of TOC in surface sediment and 57% of TOC in deep sediment. Lipids were <1% of TOC and CaTOC. Chloropigments made up an insignificant portion of TOC.

4.6. Chlorophyll-*a* Decomposition Experiment

The concentration of Chl-*a* and its degradation products decreased during incubations with the exception of Ppt. Ppt remained constant in the open anoxic plug incubation and increased slightly during the closed anoxic incubation (Fig. 7). First-order decomposition rate constants (k_d) for Chl-*a* were 0.068 d^{-1} ($t_{1/2}$ = 15 d) for oxic, 0.014 d^{-1} ($t_{1/2}$ = 71 d) for open anoxic, and 0.0061 d^{-1} ($t_{1/2}$ = 167 d) for closed anoxic incubations (Table 4). These calculations assume that the nonreactive pool size is equivalent to the concentration remaining at the end of the 70-d incubation. Thus, on short timescales the reactive pool size is smaller under anoxic conditions. However, over longer timescales (500 d), the reactive pool size of Chl-*a* in anoxic incubations is similar to that in oxic incubations (i.e., in both cases the background Chl-*a* was <0.5 nmol/gdw). In addition, both deep LFK sediment and NKH sediment incubated for 3 yr under closed anoxic conditions contained no detectable chloropigments. Previous degradation experiments using low-carbonate sediment yielded similar turnover times of 14 to 55 d (Furlong and Carpenter, 1988; Bianchi et al., 1991; Sun et al., 1993a). With large numbers of macrofauna added, lower turnover times of 5.3 d have been observed (Ingalls et al., 2000).

Pyroppb was the most abundant pheopigment at the start of the incubation and was enriched at t = 0 relative to core top samples that were frozen immediately after sampling. Pyroppb concentrations decreased during the oxic and open anoxic experiments and remained nearly constant in the closed anoxic incubation (Fig. 7 and Table 4). Ppb started at a low-concentration (<0.5 nmol/gdw) and decreased slightly in all incubations. The closed anoxic incubation was carried out for 500 d, and during that time, the degradation rate constants slowed for all compounds except Pyroppb.

ΣCO_2 production during the closed anoxic incubations was ~2 to 3 mM C d^{-1} during the first 3 d of incubation and reached saturating concentrations for $CaCO_3$ within one week (Fig. 8). These rates are comparable to those found in organic-rich coastal environments with high organic carbon remineralization rates (Aller and Aller, 1998).

5. DISCUSSION

5.1. Organic Carbon Reactivity in a Shallow Carbonate Deposit

Despite a very shallow water column, a high sedimentation rate (Bentley, 1998) and the absence of molecular oxygen below 2 to 3 mm in the sediments, the concentration of total organic carbon in Dry Tortugas carbonate sediment is very low (Furukawa et al., 2000), and is comparable to values found in deep sea sediments underlying low-productivity regions (e.g., Degens and Mopper, 1976). Low TOC concentrations in Dry Tortugas deposits may result from a combination of low organic carbon inputs and high degradation rates (Furukawa et al., 2000). The ΣCO_2 production rate measured in our closed anoxic incubation experiments (2–3 mM C d^{-1}) using surface sediment (top 0.5 cm, porosity = 0.59) implies a potential TOC turnover time of ~267 to 404 d, or ~140 to 220 d if applied only to the nonintracrystalline OC pool (~240 μmol g^{-1}). This calculation suggests that in these deposits a high flux of extremely labile material is constantly supplied (~6–9 mmol C

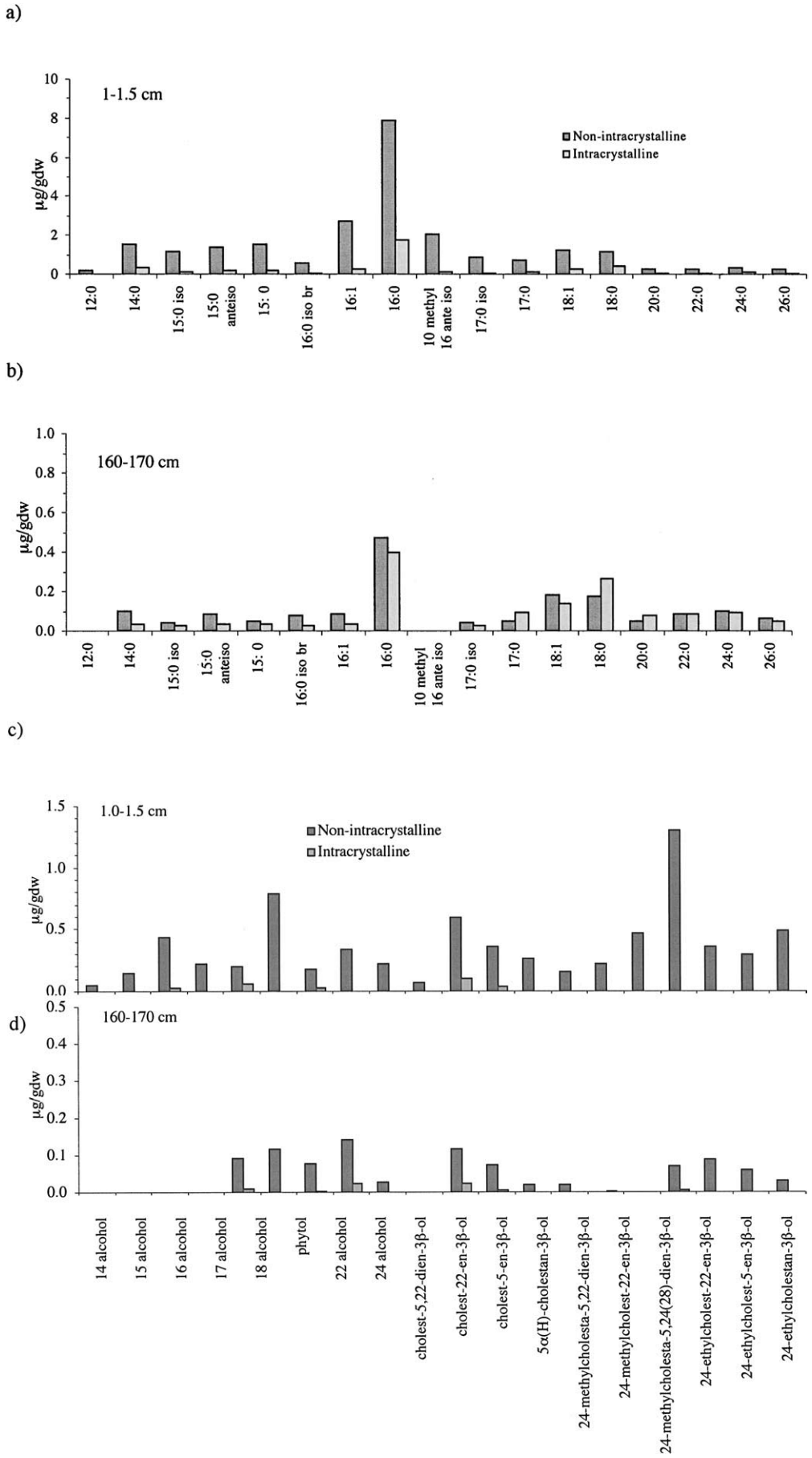

Fig. 5. Nonintracrystalline and intracrystalline lipid concentrations (μg lipid/g sediment) from 1.0 to 1.5 cm interval of Middle Key dive core and 160 to 170 cm interval of North Key Harbor gravity core. (a) Fatty acids in 1.0 to 1.5 cm; (b) fatty acids in 160 to 170 cm; (c) neutral lipid in 1.0 to 1.5 cm; (d) neutral lipids in 160 to 170 cm. Middle Key (MK) and North Key Harbor gravity core (LFK).

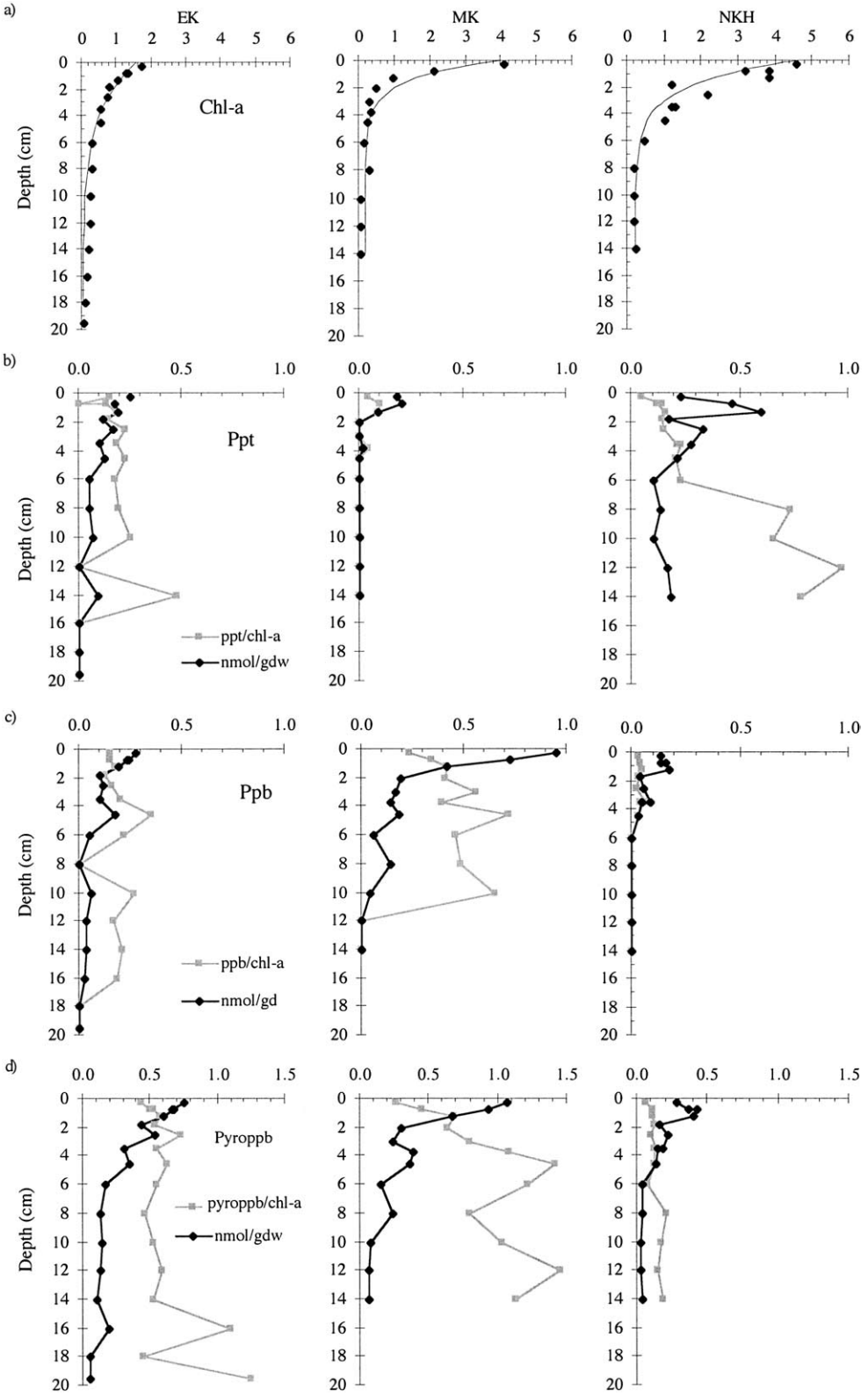

Fig. 6. (a) Chl-*a* (nmol Chl-*a*/gdw) depth profiles (diamond symbols) and model fit from reaction diffusion model (solid line); (b) phaeophytin depth profiles and phaeophytin/Chl-*a* ratio; (c) phaeophorbide (ppb) depth profiles and ppb/Chl-*a* ratio; (d) pyrophaeophorbide (pyroppb) profiles and pyroppb/Chl-*a* ratio.

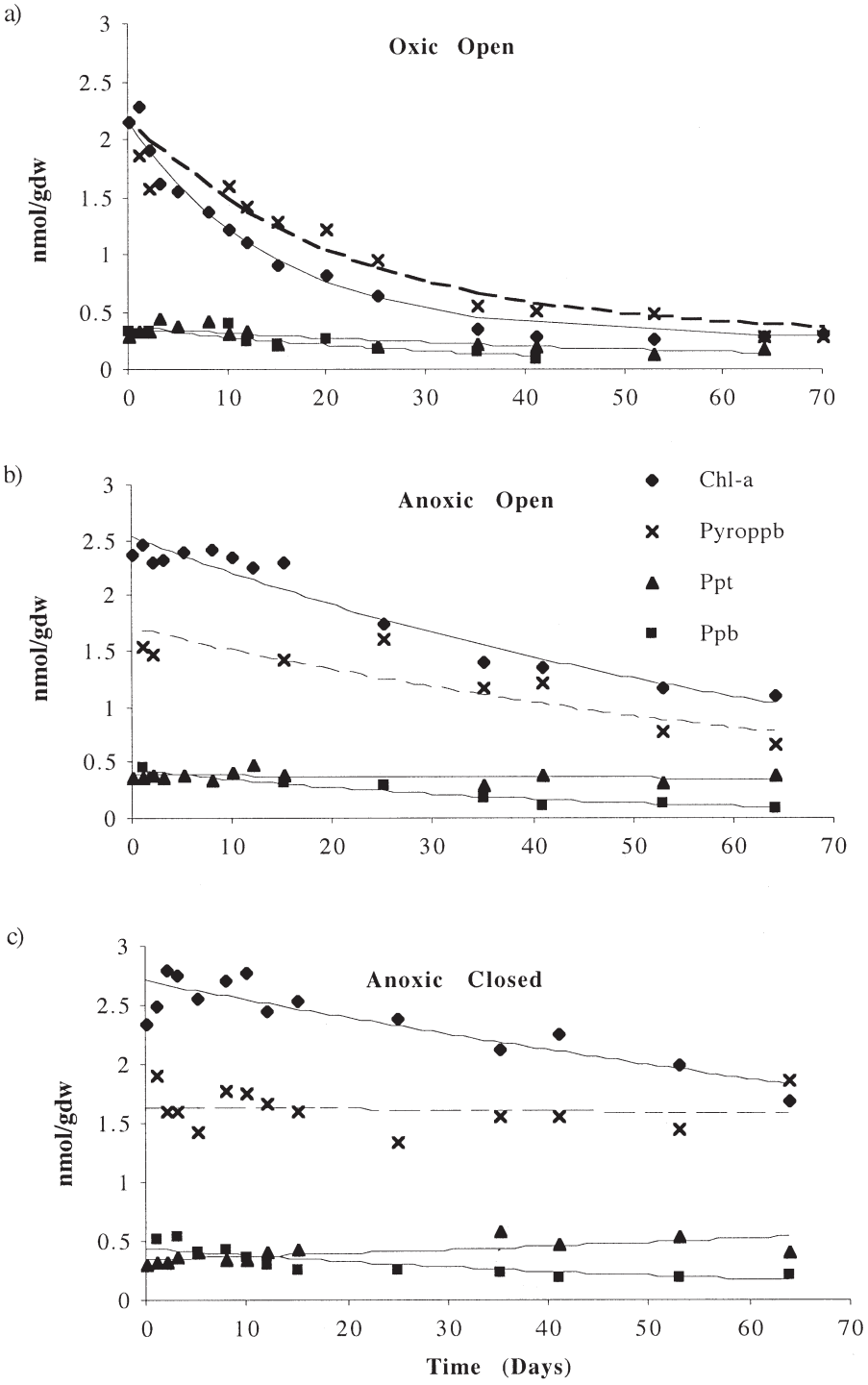

Fig. 7. Pigment concentrations during incubation of surface sediment from North Key Harbor. (a) Oxic plug incubation; (b) anoxic plug incubation; (c) jar incubation.

m^{-2} d^{-1} if only the upper 0.5 cm of sediment is considered), and rapidly turned over compared to larger background concentrations of relatively refractory nonintra and intracrystalline OC. The quantity and composition of the OC eventually buried are determined by factors governing these larger pools, and may be largely independent of the rapidly remineralized labile fraction driving ΣCO_2 fluxes.

The availability of different OC pools to support remineralization depends in part on the physical association between organic carbon and calcium carbonate. Sedimentary organic matter can be stabilized by its interaction with minerals, leading to the preservation of a nearly constant ratio of organic carbon to mineral surface area in many sedimentary regimes (e.g., 0.5–1.0 mg C m^{-2}; Mayer, 1994). However, upwelling areas

Table 4. Decomposition rate constants (k_d) for chlorophyll-*a* and phaeopigments in surface (top 0.5 cm) sediment calculated from incubation experiments.

Treatment	Chl-*a*	Pyroppb	Ppb	Ppt
Oxic Plugs	−0.068	−0.045	−0.023	−0.015
Anoxic Plugs	−0.014	−0.013	−0.022	0
Anoxic Jars	−0.0061	−0.0006	−0.015	0.007

Chl-*a* = chlorophyll-*a*; Ppb = phaeophorbide; Ppt = phaeophytin; Pyroppb = pyrophaeophorbide; Units = d^{-1}.

often have much higher organic carbon loadings, and oligotrophic ocean and delta sediments much lower loadings than predicted by organic matter-mineral surface interactions alone (Mayer, 1994; Hedges and Keil, 1995; Mayer, 1999). Recent work suggests that minerals may protect organic matter by hiding it within mesopores or between clay mineral grains, rendering it relatively inaccessible to microorganisms (Ransom et al., 1998; Bock and Mayer, 2000; Arnarson and Keil, 2001). Organic carbon concentrations in sediments are therefore a function not only of mineral surface area, but also of the particle surface topography and the ability of organic matter to hold particles together (related to its surface charge, stickiness and physical strength). In the case of biomineral-rich sediments, the OC concentration is also a function of the amount of OC locked within the biomineral during biomineralization. In addition to having intercrystalline and intracrystalline OC, $CaCO_3$ surfaces have a high affinity for organic molecules, particularly acidic amino acids. In laboratory experiments, natural sedimentary $CaCO_3$ grains adsorb 1.0 to 1.5 mg C m^{-2} of the protein albumin, 0.0084 mg C m^{-2} of stearic acid (18:0 fatty acid), and 1.32 mgC m^{-2} of dissolved organic carbon (DOC) from seawater onto their surface (Arnold and Pak, 1962; Suess, 1970).

We found that all of the nonintracrystalline organic matter in

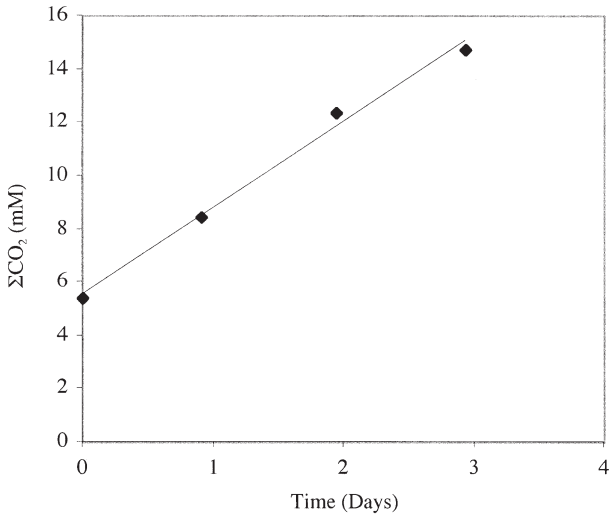

Fig. 8. ΣCO_2 concentration vs. time during the closed anoxic incubation of Dry Tortugas surface sediment. The production rate of ΣCO_2 was calculated using a linear least squares fit to the data and was 3.2 mM/d ($r^2 = 0.99$).

Dry Tortugas sediments was acid-insoluble suggesting that this organic matter pool may not be adsorbed. Nevertheless, we can compare these experimentally observed $CaCO_3$ surface loadings with the nonintracrystalline organic carbon concentration of Dry Tortugas sediments. Shallow sediment (1.0–1.5 cm) at MK had a surface area of 3.3 m^2 g^{-1} and 245 μmol C g^{-1} of nonintracrystalline OC (Table 1, nonintracrystalline = TOC-CaTOC). Thus, these sediments contained 0.89 mg C m^{-2} of nonintracrystalline OC. In the deep sediment (LFK 160–170 cm), the surface area was 5.7 m^2 g^{-1} and the concentration of nonintracrystalline organic carbon was 142 μmol C gdw^{-1}. Thus, the surface loading of OM at this depth was 0.30 mg C m^{-2}.

These calculations suggest that the nonintracrystalline organic carbon concentration was ~42% lower in deep sediment than shallow sediment, probably due to net remineralization of organic matter. However, the surface loading was ~66% lower in deep sediment than shallow sediment. This additional percentage decrease in surface loading is most likely a result of micritization of large sediment grains into smaller grains with depth (Furukawa et al., 1997). Apparently, the new surface area exposed by micritization did not result in additional stabilization of nonintracrystalline organic matter. Instead, decomposition appears to have taken place despite available mineral surfaces, suggesting that nonintracrystalline OC is not necessarily closely associated with $CaCO_3$, or that organic matter that is postdepositionally adsorbed to surfaces is not well protected from degradation. The absence of acid-soluble OC supports the possibility that there is little surface sorption occurring. In addition, micritization could have broken open pores and exposed new organic matter, making it available for remineralization.

The increase in the proportion of aspartic acid in the nonintracrystalline pool suggests that organic matter exposed by micritization may be intercrystalline. It is important to note that the TOC profile of the LFK gravity core (Fig. 2) suggests that nonintracrystalline organic matter that is poor in aspartic acid was primarily remineralized in the upper 30 cm, the zone of very active bioturbation (D'Andrea and Lopez, 1997). Below this depth, even nonintracrystalline organic matter appears to be well preserved. In this environment in which organic matter is rapidly and efficiently remineralized, one mechanism for the preservation of nonintracrystalline organic matter is protection in intercrystalline spaces, that is, between mineral crystals. Thus, nonintracrystalline organic matter derives from multiple sources in surface sediments, but may be primarily intercrystalline at depth. Our analytical method cannot distinguish these organic matter pools.

In contrast to nonintracrystalline TOC, the concentration of CaTOC was not only relatively constant throughout the sediment core, but was similar among all samples analyzed (Table 1). Previous reports of the concentration of intracrystalline organic matter in $CaCO_3$ shells range from 0.1 to 2.0 wt.% in mollusc shells (Hudson, 1967), 0.02 to 0.11 wt.% in coral skeletons (e.g., Wainwright, 1962; Swart, 1981; Ingalls et al., 2003), and <0.1 wt.% in *Halimeda* plates (Gaffey and Bronnimann, 1993). CaTOC in the Dry Tortugas was ~200 μmol C/g (~0.23 wt.%) in both surface and deep sediment intervals (Table 1). Because these values are higher than normally found in *Halimeda* and mound-forming corals, mollusks, and forami-

nifera must be important constituents of the sediment, as previous studies report (Davis and O'Neill, 1979; Furukawa et al., 1997; Bentley, 1998). Alternatively, a preferential loss of $CaCO_3$ relative to intracrystalline OC may occur.

Assuming steady-state diagenesis, the lack of change in CaTOC concentration with depth implies that intracrystalline OM is not remineralized while in the occluded state, even in the highly bioturbated zone. Given a sedimentation rate for this location of 0.3 to 0.4 cm/yr (Bentley and Nittrouer, 1997; Bentley, 1998; Furukawa et al., 2000), the deep sediment examined here was deposited $<$600 yr earlier than surface sediment. The $CaCO_3$ could have been formed before that time if it were resuspended from another location. In either case, occlusion of organic matter in $CaCO_3$ is an important preservation mechanism for organic carbon over at least hundred-yr timescales in this environment.

Although intracrystalline OC is not remineralized as such, the release of intracrystalline OC into the nonintracrystalline OC pool could occur during dissolution, recrystallization, and micritization of the carbonate carrier phase. Respiration and oxidation of secondary metabolites drive dissolution and recrystallization of calcium carbonate in shallow sediments above the lysocline, and these processes are likely occurring in the Dry Tortugas as well (Aller, 1982; Walter and Burton, 1990; Rude and Aller, 1991; Jahnke et al., 1997; Burdige and Zimmerman, 2002). Intracrystalline OC was 60 to 70% acid-soluble, while nearly all nonintracrystalline OC was acid-insoluble (Table 1). Therefore, if dissolution is an important source for reactive organic matter, acid-soluble OM in particular must either be quickly degraded, subject to reactions that render it acid-insoluble, or lost from the system by some physical transport mechanism (e.g., bioturbation, storm activity). In our sediment, most organic matter is degraded through sulfate reduction; and O_2 entering the sediment by diffusion and bioturbation is used up by reoxidation of sulfide to sulfate, largely in the upper 15 cm (Furukawa et al., 2000). The production of sulfuric acid promotes dissolution at oxic-anoxic interfaces near the sediment-water interface and irrigated burrow walls (Walter et al., 1993). Because sulfate reduction produces bicarbonate, completely anoxic organic matter remineralization at depth is not expected to lead to extensive carbonate dissolution.

5.2. Changes in Organic Matter Composition with Depth

Most ($>$80%) sedimentary OM in both the TOC and CaTOC pools was not chemically characterized in this study, as is often the case in studies of sedimentary organic matter (Wakeham et al., 1997b; Hedges et al., 2000). Within the characterizable fraction, the nonintracrystalline and intracrystalline pools showed distinct differences in composition and relative preservation of individual components. Chloropigments were entirely absent in the intracrystalline pool, and nonintracrystalline chloropigments showed dramatic changes in concentration and composition with depth, reaching very low concentrations within the upper 10 cm of sediment (Fig. 6a). While changes in the composition and concentration of chloropigments are good indicators of progressive OM degradation in nonintracrystalline OC, chloropigments are a tiny fraction of TOC, and their degradation does not result in a discernable decrease in the concentration of TOC. The high proportion of Ppb and Pyroppb in sediment cores (with the exception of NKH) suggests that macrofauna are important transformers of organic matter. NKH was dominated by Ppt, suggesting a more important role for anaerobic bacteria at this location and that exposure to oxygen may be less frequent there (Aller, 1994).

5.2.1. Amino acids

THAA are a significant fraction of the characterizable TOC pool and remain a relatively constant proportion of TOC with depth, suggesting that amino acids and TOC degrade at a similar rate (Table 2). Previous studies indicate that CaTHAA are well preserved with respect to remineralization on hundred-yr timescales, but the composition of CaTHAA may change over hundreds of thousands of yrs due to substantial hydrolysis and condensation reactions or slow degradation (Collins et al., 1992; Walton, 1998). In addition, the composition of THAA in carbonate sediments is thought to approach that of CaTHAA with increasing grain size due to the greater contribution of CaTHAA relative to THAA in large grains with low specific surface areas (Müller and Suess, 1977; Carter and Mitterer, 1978). However, these investigators did not report separate analyzes of THAA and CaTHAA to compare the compositions of the two pools.

At our study site, the specific surface area of sediments increased only moderately ($\sim$1.7X) with depth in the sediment suggesting a small decrease in grain size. Over the same depth, the mole % of aspartic acid increased from 22 mol % to 40 mol %, in agreement with earlier studies that suggest that as carbonate sediments age, aspartic acid-rich OM is preferentially preserved in the nonintracrystalline pool. Calculation of the composition of nonintracrystalline aspartic acid mole % clearly shows that aspartic acid is highly enriched in deep sediment (39 mole %) relative to shallow sediment (14 mol %) in this pool (Fig. 4 and Table 2). Aspartic acid is known to adsorb and associate strongly with $CaCO_3$ relative to other amino acids (Jackson and Bischoff, 1971; Mitterer, 1972). In addition, intracrystalline aspartic-acid-rich proteins released during dissolution of minerals subsequently may preferentially adsorb to available mineral surfaces (Jackson and Bischoff, 1971; Mitterer, 1972) and be protected from degradation once in the nonintracrystalline pool. As stated in section 5.1, enrichment of aspartic acid in the nonintracrystalline organic matter pool may be due to a relative enrichment of intercrystalline organic matter compared to organic matter from other sources.

While the increase in aspartic acid mole % with depth in the nonintracrystalline pool is in agreement with previous studies, the reason for the decrease in the mole % of aspartic acid from $\sim$50 mole % to $\sim$40 mole % in CaTHAA is not as obvious and could be a result of several processes. Deep sediments could derive from a different source (species) of $CaCO_3$ either due to selective dissolution of some species of $CaCO_3$ precipitating organisms, or deposition of different $CaCO_3$ precipitating organisms over time. Additionally, precipitation of $CaCO_3$ from supersaturated pore waters could trap dissolved amino acids and result in a different composition than found in the original biogenic $CaCO_3$. The presence of γ-aba in the intracrystalline pool suggests that nonintracrystalline amino acids are a possible source of intracrystalline amino acids during sediment

aging. On the other hand, the absence of β-ala argues against this conclusion. In addition, previous work suggests that bleach treatment itself may produce these amino acid degradation products in biogenic carbonates (Ingalls et al., 2003). The low concentration of β-ala and γ-aba points to relatively fresh organic matter and suggests an important role for intercrystalline organic matter in the preservation of the nonintracrystalline pool of characterized organic matter. Finally, amino acids could be leached from sediment grains after hydrolysis of peptide bonds. Since soluble matrix proteins are enriched in aspartic acid, aspartic acid could be more susceptible to leaching than other amino acids. This process would be more important with depth as grain size decreases with depth.

5.2.2. Lipids

Lipids were not a large fraction of the TOC; however, their composition can be diagnostic of organic matter sources and diagenesis. Fatty acid and neutral lipid concentrations were lower in deep sediment than surface sediment in both intra and nonintracrystalline pools, most likely due to degradation of both pools (Table 3). Although the decrease in intracrystalline lipid concentrations was less than in the nonintracrystalline pool, intracrystalline lipids were not completely protected from loss or alteration. One reason for this could be that alteration of the mineral matrix through micritization, partial dissolution, or recrystallization may allow solvent extraction to be more effective at removing intracrystalline or intercrystalline organic matter in deeper sediments than in shallow sediments. Thus, solvent extraction efficiency of lipids from $CaCO_3$ grains could be related to their age or size. Despite previous work suggesting that fatty acids can adsorb to $CaCO_3$ surfaces (Suess, 1973; Sansone et al., 1987), and can be intra or nonintracrystalline (Isa and Okazaki, 1987; Ingalls et al., 2003), Stern et al. (1999) demonstrate that saponification can release lipids from carbonates that are not removed by solvent extraction. This suggests that lipids are not intracrystalline. It is likely that our operationally defined intracrystalline lipid fraction consists of lipids with a range of mineral associations and susceptibility to degradation.

The composition of lipids suggests the presence of phytoplankton, bacteria, and zooplankton sources (Wakeham and Lee, 1989; Wakeham and Lee 1993; Wakeham et al., 1997a). Several fatty acids found in this study (14:0, 15:0 *anteiso*, 16:0 and 17:0–24:0) were also found in both the nonintracrystalline and intracrystalline pools of coral skeletons (Ingalls et al., 2003). 16:0 fatty acid was the most abundant intracrystalline and nonintracrystalline fatty acid in shallow sediments (Fig. 5). There was a much smaller proportion of this fatty acid in deep sediments in both pools. This difference resulted in a high proportion of 18:0 in the intracrystalline pool in deep sediments. Differences in composition between shallow and deep sediments may reflect differences in biogenic mineral sources. For example, coral skeletons of different species can have different proportions of 16:0 and 18:0 fatty acids (Ingalls et al., 2003). Alternatively, the same processes that are acting on the amino acid pools could be influencing the fatty acid composition as well, resulting in the intracrystalline and nonintracrystalline pools having the same composition at depth. Available data cannot distinguish these two possibilities.

In both intracrystalline and nonintracrystalline pools, the proportion of short chain fatty acids (C_{14}-C_{17}) tended to be greater in shallow samples while the proportion of longer chain compounds (C_{18}-C_{28}) was greater in deep sediments. This difference with depth may be due to differences in the relative rates of degradation. Shorter chain fatty acids have been shown to be lost from sediment incubations more quickly than longer chain compounds (Sun et al., 1997). The overall amount and proportion of bacterially derived fatty acids (odd chain length *iso* and *anteiso* and branched fatty acids) decreased with depth in the sediment with the exception of branched 16:0 *iso*. Again, the preservation of bacterially derived fatty acids in our operationally defined intracrystalline pool suggests that these lipids may not actually be within the $CaCO_3$ crystals. Otherwise they may be incorporated after the mineral is originally formed as suggested for β-ala and γ-aba.

Neutral lipid compositions indicate the presence of primarily phytoplankton, especially dinoflagellate sources. All but a few sterols were absent from the intracrystalline pool (Fig. 5). Several dinoflagellate biomarkers were present in the sediment including trimethyl-5α(H)-cholest-22-en-3β-ol (dinosterol), 24-propylcholest-5-en-3β-ol (gorgosterol), and two stanols including 5α(H)-cholestan-3β-ol (cholestanol) and 24-ethylcholest-3β-ol (ethylcholestanol). Each of these sterols are found in zooxanthellae, the symbiotic dinoflagellates in hermatypic coral polyps of the genus *Symbiodinium* (Withers et al., 1982; Mansour et al., 1999). The dominance of dinoflagellate sterols suggests that dinoflagellates may also be a source of elevated 16:0 fatty acid in surface sediments, which is abundant in these organisms (Mansour et al., 1999). *Halimeda*, a major source of $CaCO_3$ to these sediments, is also enriched in 16:0 fatty acid and also contains 24:0 and 26:0 fatty acid (Carballeira et al., 1999). *Halimeda* contains Δ^5 and 24-methyl sterols as well (Paterson, 1974), suggesting that it could be a source of several of the sterols found here. All of these compounds appear to be rapidly degraded in the sediment (Fig. 5). If $CaCO_3$ recrystallization is occurring (as could be inferred by the similar composition of amino acids and fatty acids in the intracrystalline and nonintracrystalline pools of deep sediments), neutral lipids are not efficiently incorporated into these precipitates.

5.3. Chloropigment Degradation Rates

Chlorophyll-*a* and pheopigments are among the most labile molecules in the marine environment (Lorenzen and Downs, 1986; Furlong and Carpenter, 1988) and are good indicators of sediment diagenesis and bioturbation (Sun et al., 1991). Despite this lability, concentrations of Chl-*a* often reach a nonzero asymptotic background concentration (<1 nmol/gdw in the upper 5–10 cm) in sediment incubation experiments (Sun et al., 1993b; Ingalls et al., 2000), sediment profiles (Sun et al., 1991; Sun et al., 1994; Gerino et al., 1998), and zooplankton feeding experiments (Shuman and Lorenzen, 1975). This residual pool of Chl-*a* degrades very slowly, particularly under anoxic conditions. Various matrix effects have been proposed as possible mechanisms for protection of Chl-*a* in these studies. Chl-*a* derived from endolithic algae in coral heads can be preserved over hundred-yr timescales, suggesting that mineral (calcium carbonate) interactions may stabilize Chl-*a* (Ingalls et al., 2003). Here we model Chl-*a* profiles from sediment cores and

sediment incubations to investigate Ch-*a* reactivity in a carbonate sediment environment and compare it to that of terrigenous sediments and coral skeletons.

We calculated Chl-*a* degradation rate constants in our $CaCO_3$ sediments in two independent ways: by measuring loss of Chl-*a* during sediment incubations, and by modeling natural sediment concentration profiles. The results of our sediment incubations suggest that Chl-*a* turns over rapidly ($t_{1/2}$ = 15 d) in $CaCO_3$ sediments, with a half-life similar to that found previously in $CaCO_3$-poor Long Island Sound sediments under oxic conditions ($t_{1/2}$ = 23 d; Sun et al., 1993a). The rapid degradation and very low background concentration (<0.5 nmol/gdw) of Chl-*a* in our oxic incubations (Fig. 7 and Table 4) suggests that the presence of $CaCO_3$ minerals does not enhance preservation of nonintracrystalline Chl-*a* over other types of matrices.

Previous studies have found that initial rates of Chl-*a* degradation are similar in oxic and anoxic incubations, but that the pool of Chl-*a* available for degradation is smaller under anoxic conditions (Sun et al., 1993a). In our incubations, initial decomposition rates were slower under anoxic (0.014 d^{-1}) than oxic conditions (0.068 d^{-1}) (Table 4). The closed anoxic incubation resulted in an even slower degradation rate constant than oxic or open anoxic incubations over 70 d (Table 4). The eventual complete loss of all Chl-*a* from closed anoxic incubations suggests that on longer timescales, all Chl-*a* is available for degradation under anoxic conditions. These results also imply that, unlike oxic degradation, anoxic degradation of Chl-*a* may be characterized phenomenologically by multiple pools (or evolving associations), resulting in a degradation coefficient that becomes progressively smaller with time (Middelburg, 1989).

Previous work has shown that Ppt can be a stable endproduct of Chl-*a* degradation under anoxic conditions (Sun et al., 1993b). We also found that Ppt was relatively stable, Ppt concentrations remained constant in anoxic plugs, and increased in the closed anoxic experiment. Degradation rate constants for other pheopigments are presented in Table 4. However, these net values are not corrected for production from degradation of Chl-*a*. Since production of all degradation products is likely to occur, these rate constants reflect minimum net values, or "apparent rates." Nevertheless, degradation of pheopigments occurred in all incubations (except Ppt as noted above) and apparent rates were faster under oxic than under anoxic conditions.

Assuming steady state diagenesis, sediment profiles of chloropigment concentrations suggest that the loss of Chl-*a* and pheopigments is more rapid than mixing in the upper 10–20 cm of sediment, thus preventing homogenization of profiles (Fig. 5a). Chl-*a* profiles were modeled assuming steady state, first-order kinetics for Chl-*a* decomposition (Sun et al., 1993a) and diffusive mixing according to Equation 1:

$$\frac{\partial C}{\partial_t} = D_B \frac{\partial^2 C}{\partial x^2} - k_d C \qquad (1)$$

Using the following boundary conditions:

$$x = 0$$

$$x = \infty$$

Table 5. Decomposition rate constants (k_d) assuming 130 cm^2/yr (Bentley and Nittrouer, 1997) and mixing coefficients (D_B) for Chl-*a* in sediment cores assuming k_d from oxic incubation.

Sample	k_d (d^{-1})	D_B (cm^2/yr)
EK	−0.032	150
MK	−0.22	22
NKH	−0.12	41

$$C = C_0$$

$$C = C_\infty$$

The solution simplifies to Equation 2

$$C = (C - C_\infty)\exp\left(-x\sqrt{\frac{k_d}{D_B}}\right) + C_\infty \qquad (2)$$

C = Chl-*a* concentration
C_∞ = background Chl-*a* concentration at 12 cm
x = depth in sediment
D_B = particle mixing coefficient
k_d = decomposition rate constant for Chl-*a*

Assuming that decomposition and bioturbation are the major controls on attenuation of Chl-*a* with depth, plotting $\ln(C\text{-}C_\infty)$ vs depth yields a line with a slope of $(k_d/D_B)^{1/2}$. Assuming a D_B of 130 cm^2/yr (from ^{234}Th and ^{210}Pb profiles; Bentley and Nittrouer, 1997) results in k_d values of 0.03 to 0.22 d^{-1} (Table 5). These values are in good agreement with calculated Chl-*a* degradation rate constants from our incubation experiments (Table 4), and, as mentioned previously, those published for alumino-silicate sediment profiles of 0.07 to 0.18 d^{-1} (Furlong and Carpenter, 1988; Bianchi et al., 1991; Sun et al., 1993b; Ingalls et al., 2000). Although the overall degradation rate of Chl-*a* does not appear to be affected by $CaCO_3$, the partitioning of Chl-*a* into refractory pools and the degradation under anoxic and oxic conditions may differ in the two environments.

Alternatively, we can compare D_B values in different cores by calculating D_B independently assuming the degradation rate constant in the oxic incubations with NKH sediments (Table 4) applies to all cores. The result of these calculations (Table 5) suggests that biologic mixing rates are lowest in the MK core. But, the lack of Ppt in this core suggests that these sediments were exposed to oxygen at some time in the past. In contrast, NKH had high Ppt concentrations, and the Ppt/Chl-*a* ratio increases with depth (Fig. 6b). This is consistent with primarily anoxic degradation and less exposure to oxygen through bioturbation (Sun et al., 1993a; Aller, 1994).

Deeper concentration profiles acquired from gravity cores show that all the chloropigments measured reach undetectable concentrations by 80 cm. At a sedimentation rate of 0.4 cm/yr (Bentley, 1998), undetectable Chl-*a* at 80 cm indicates that complete degradation occurs within 200 yr, and undetectable Ppt and Pyroppb at 30 cm correspond to complete degradation within ~75 yr. Ppt is usually stable relative to Chl-*a* under anoxic conditions; rapid disappearance of Ppt suggests that while the main pathway of degradation in these anoxic sediments is sulfate reduction (Furukawa et al., 2000), periodic oxygen exposure must occur (Sun et al., 1993a; Aller, 1994),

most likely by bioturbation or storm resuspension of sediments. Previous experiments have shown that redox oscillations enhance degradation of organic matter and Chl-*a* relative to permanently anoxic conditions, and that Ppt does not accumulate under oxic conditions (Sun et al., 1993a; Sun et al., 1993b; Aller, 1994). Because degradation of chloropigments does not appear to be specifically affected by $CaCO_3$, previously reported long-term preservation of Chl-*a* in coral heads (Ingalls et al., 2003) is likely due to unique properties of the coral environment such as low diffusion and permanent anoxia (Risk and Müller, 1983), or to protection by the cell walls of algal filaments.

6. CONCLUSIONS

Intracrystalline organic matter made up approximately one half of the organic matter preserved in the upper 2 m of $CaCO_3$-rich sediment, and is preferentially preserved relative to nonintracrystalline OC in the upper 30 cm of sediment. These data suggest that physical protection through occlusion in biominerals appears to be a significant carbon preservation mechanism in this low-organic carbon, high-biomineral environment. The extent of preservation of organic compounds in these deposits appears to be dominated by their association with mineral phases. Some nonintracrystalline organic matter appears to be stable on 600-yr timescales. This organic matter may be stabilized by a variety of mechanisms including protection in intercrystalline spaces. Of the three classes of organic matter we studied, chloropigments are not occluded within carbonate biominerals and degrade rapidly at a similar rate to that found in terrigenous sediments. Lipids degrade in both intra and nonintracrystalline pools, although mineral-occluded lipids are less extensively altered. Neutral lipids are not as tightly bound to $CaCO_3$ as are fatty acids and are not preserved as extensively. Amino acids appear to be well protected from degradation within the mineral matrix, and their concentration remains constant with depth in the sediment. The composition of the nonintracrystalline amino acid pool changed dramatically with depth, presumably as a result of the degradation of organic matter from non-$CaCO_3$ sources. Changes in intracrystalline amino acid composition may have resulted from changes in source with depth, or from reprecipitation of calcium carbonate at depth. Finally, intracrystalline organic carbon and selected organic compounds are preferentially preserved relative to total OC due to physical protection by the biomineral. Only $\sim$15% of the sedimentary organic matter was characterizable as lipids, chloropigments, and amino acids, suggesting that unknown compounds or other compounds like carbohydrates and amino sugars may be abundant in both intracrystalline and nonintracrystalline organic matter.

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REFERENCES

Abelson P. H. (1955) Organic constituents of fossils. *Carnegie Inst. Wash. Yearb.* **54,** 107–109.

Aller R. C. (1982) Carbonate dissolution in nearshore terrigenous muds: the role of physical and biological reworking. *J. Geology* **90,** 79–95.

Aller R. C. (1994) Bioturbation and remineralization of sedimentary organic matter: effects of redox oscillation. *Chem. Geol.* **114,** 331–345.

Aller R. C. and Aller J. Y. (1998) The effect of biogenic irrigation intensity and solute exchange on diagenetic reaction rates in marine sediments. *J. Mar. Res.* **56,** 1–32.

Arnarson T. S. and Keil R. G. (2001) Organic-mineral interactions in marine sediments studied using density fractionation and X-ray photoelectron spectroscopy. *Org. Geochem.* **32,** 1401–1415.

Arnold J. D. and Pak C.-Y. C. (1962) Protein-protein interaction at the air-water interface. *J. Colloid Sci.* **37,** 2435–2447.

Bentley S. J. (1998) The Emplacement and Evolution of Sedimentary Fabric: Physical and Biological Influences in Three Contrasting Depositional Environments. Ph.D. Dissertation, Stony Brook University.

Bentley S. J. and Nittrouer C. A. (1997) Environmental influences on the formation of sedimentary fabric in a fine-grained carbonate-shelf environment: Dry Tortugas, Florida Keys. *Geo-Marine Lett.* **17,** 268–275.

Bianchi T. S., Findlay S., and Fontvieille D. (1991) Experimental degradation of plant materials in Hudson River sediments. I. Heterotrophic transformations of plant pigments. *Biogeochemistry* **12,** 171–187.

Bock M. J. and Mayer L. M. (2000) Mesodensity organo-clay associations in a near-shore sediment. *Mar. Geol.* **163,** 65–75.

Brunauer S., Emmett P. H., and Teller E. (1938) Adsorption of gases in multimolecular layers. *J. Am. Chem. Soc.* **60,** 309–319.

Burdige D. J. and Zimmerman R. C. (2002) Impact of sea grass density on carbonate dissolution in Bahamas sediments. *Limnol. Oceanogr.* **47,** 1751–1763.

Carballeira N. M., Sostre A., and Ballantine D. L. (1999) The fatty acid composition of tropical marine algae of the genus Halimeda (Chlorophyta). *Botanica Marina* **42,** 383–387.

Carter P. W. (1978) Adsorption of amino acid-containing organic matter by calcite and quartz. *Geochim. Cosmochim. Acta* **58,** 1239–1242.

Carter P. W. and Mitterer R. M. (1978) Amino acid composition of organic matter associated with carbonate and non-carbonate sediments. *Geochim. Cosmochim. Acta* **58,** 1231–1238.

Collins M. J., Muyzer G., Westbroek P., Curry G. B., Sandberg P. A., Xu S. J., Quinn R., and MacKinnon D. (1991) Preservation of fossil biopolymeric structures: Conclusive immunological evidence. *Geochim. Cosmochim. Acta* **55,** 2253–2257.

Collins M. J., Westbroek P., Muyzer G., and deLeeuw J. W. (1992) Experimental evidence for condensation reactions between sugars and proteins in carbonate skeletons. *Geochim. Cosmochim. Acta* **56,** 1539–1544.

Constantz B. and Weiner S. (1988) Acidic macromolecules associated with the mineral phase of Scleractinian coral skeletons. *J. Exp. Zool.* **248,** 253–258.

Cowie G. L. and Hedges J. I. (1992) Improved amino acid quantification in environmental samples: charge-matched recovery standards and reduced analysis time. *Mar. Chem.* **37,** 223–238.

Cowie G. L. and Hedges J. I. (1994) Biochemical indicators of diagenetic alteration in natural organic matter mixtures. *Nature* **369,** 304–307.

Cuif J. P., Dauphin Y., and Gautret P. (1999) Compositional diversity of soluble mineralizing matrices in some recent coral skeletons compared to fine-scale growth structures of fibers: discussion of consequences for biomineralization and diagenesis. *Int. J. Earth Sci.* **88,** 582–592.

D'Andrea A. F. and Lopez G. R. (1997) Benthic macrofauna in a shallow water carbonate sediment: major bioturbators at the Dry Tortugas. *Geo-Marine Lett.* **17,** 276–282.

Dauphin Y. (2001) Comparative studies of skeletal soluble matrices from some Scleractinian corals and Molluscs. *Int. J. Biol. Macromol.* **28,** 293–304.

Davis R. A. and O'Neill C. W. (1979) Morphodynamics of East Key, Dry Tortugas, Florida. In *Southeast Geological Society; Guide to Sedimentation for the Dry Tortugas*, Vol. Guidebook No. 21, pp. 7–13, Southeast Geological Society.

Degens E. T. and Mopper K. (1976) Factors controlling the distribution and early diagenesis of organic material in marine sediments. In *Chemical Oceanography* (eds. J. P. Riley and R. Chester), pp. 59–113. Academic Press.

Endo K., Walton D., Reyment R. A., and Curry G. B. (1995) Fossil intra-crystalline biomolecules of brachiopod shells: diagenesis and preserved geo-biological information. *Org. Geochem.* **13,** 661–673.

Furlong E. T. and Carpenter R. (1988) Pigment preservation and remineralization in oxic coastal marine sediments. *Geochim. Cosmochim. Acta* **52,** 78–99.

Furukawa Y., Lavoie D., and Stephens K. (1997) Effect of biogeochemical diagenesis on sediment fabric in shallow marine carbonate sediments near the Dry Tortugas, Florida. *Geo-Marine Lett.* **17,** 283–290.

Furukawa Y., Bentley S., Shiller A., Lavoie D., and Cappellen P. V. (2000) The role of biologically-enhanced pore water transport in early diagenesis: an example from carbonate sediments in the vicinity of North Key Harbor, Dry Tortugas National Park, Florida. *J. Mar. Res.* **58,** 493–522.

Gaffey S. J. and Bronnimann C. E. (1993) Effects of bleaching on organic and mineral phases of biogenic carbonates. *J. Sed. Petrol.* **63,** 752–754.

Gerino M., Aller R. C., Lee C., Cochran J. K., Aller J. Y., Green M. A., and Hirschberg D. (1998) Comparison of different tracers and methods used to quantify bioturbation during a spring bloom: 234-Thorium, luminophores and chlorophyll-*a*. *Est., Coast. Shelf Sci.* **46,** 531–547.

Hall P. O. J. and Aller R. C. (1992) Rapid small-volume, flow injection analysis for ΣCO_2 and NH_4^+ in marine and freshwater. *Limnol. Oceanogr.* **37,** 1113–1119.

Hedges J. I. and Keil R. G. (1995) Sedimentary organic matter preservation: an assessment and speculative synthesis. *Mar. Chem.* **49,** 81–115.

Hedges J. I., Eglinton G., Hatcher P. G., Kirchman D. L., Arnosti C., Derenne S., Evershed R. P., Kögel-Knabner I., deLeeuw J. W., Littke R., Michaelis W., and Rullkötter J. (2000) The molecularly-uncharacterized component of nonliving organic matter in natural environments. *Org. Geochem.* **31,** 945–958.

Hudson J. D. (1967) The elemental composition of the organic fraction, and the water content, of some recent and fossil mollusc shells. *Geochim. Cosmochim. Acta* **31,** 2361–2378.

Ingalls A. E., Aller R. C., Lee C., and Sun M. Y. (2000) The influence of deposit-feeding on chlorophyll-*a* degradation in coastal marine sediments. *J. Mar. Res.* **58,** 631–651.

Ingalls A. E., Lee C., and Druffel E. R. M. (2003) Preservation of organic matter in mound-forming coral skeletons. *Geochim. Cosmochim. Acta* **67,** 2827–2841.

Isa Y. and Okazaki M. (1987) Some observations on the Ca^{2+}-binding phospholipid from scleractinian coral skeletons. *Comp. Biochem. Physiol.* **87B,** 507–512.

Jackson T. A. and Bischoff J. L. (1971) The influence of amino acids on the kinetics of the recrystallization of aragonite and calcite. *J. Geol.* **79,** 493–497.

Jahnke R. A., Craven D. B., McCorkle D. C., and Reimers C. E. (1997) $CaCO_3$ dissolution in California continental margin sediments: the influence of organic matter remineralization. *Geochim. Cosmochim. Acta* **61,** 3587–3604.

King K. (1977) Amino acid survey of recent calcareous and siliceous deep-sea microfossils. *Micropaleontology* **23,** 180–193.

King K. and Hare P. E. (1972) Amino acid composition of the test as a taxonomic character for living and fossil planktonic foraminifera. *Micropaleontology* **18,** 285–293.

King L. L. (1993) Chlorophyll diagenesis in the water column and sediment of the Black Sea. Ph.D. Dissertation, Massachusetts Institute of Technology.

Leavitt P. R. and Carpenter S. R. (1990) Aphotic pigment degradation in the hypolimnion: implications for sedimentation studies and paleolimnology. *Limnol. Oceanogr.* **35,** 520–534.

Lee C., Wakeham S. G., and Hedges J. I. (2000) Composition and flux of particulate amino acids and chloropigments in Equatorial Pacific seawater and sediments. *Deep-Sea Res. I.* **47,** 1535–1568.

Levi Y., Albeck S., Brack A., Weiner S., and Addadi L. (1998) Control over aragonite crystal nucleation and growth: an *in vitro* study of biomineralization. *Chem. Eur. J.* **4,** 389–396.

Lindroth P. and Mopper K. (1979) High performance liquid chromatographic determination of subpicomolar amounts of amino acids by precolumn fluorescence derivatization with o-phthaldialdehyde. *Anal. Chem.* **51,** 1667–1674.

Lorenzen C. J. and Downs J. N. (1986) The specific absorption coefficients of chlorophyllide a and pheophorbide a in 90% acetone, and comments on the fluorometric determination of chlorophyll and pheopigments. *Limnol. Oceanogr.* **31,** 449–452.

Lowenstam H. A. and Weiner S. (1989) *On Biomineralization*. Oxford University Press.

Mallinson D., Locker S., Hafen M., Naar D., Hine A., Lavoie D., and Schock S. (1997) A high-resolution geological and geophysical investigation of the Dry Tortugas carbonate depositional environment. *Geo-Mar. Lett.* **17,** 237–245.

Mansour M. P., Volkman J. K., Jackson A. E., and Blackburn S. I. (1999) The fatty acid and sterol composition of five marine dinoflagellates. *J. Phycol.* **35,** 710–720.

Mantoura R. F. C. and Llewellyn C. A. (1983) The rapid determination of algal chlorophyll and carotenoid pigments and their breakdown products in natural waters by reverse-phase high-performance liquid chromatography. *Analytica Chimica Acta* **151,** 297–314.

Mayer L. M. (1994) Surface area control of organic carbon accumulation in continental shelf sediments. *Geochim. Cosmochim. Acta* **58,** 1271–1284.

Mayer L. M. (1999) Extent of coverage of mineral surfaces by organic matter in marine sediments. *Geochim. Cosmochim. Acta* **63,** 207–215.

Middelburg J. (1989) A simple rate model for organic matter decomposition in marine sediments. *Geochim. Cosmochim. Acta* **53,** 1577–1581.

Mitterer R. M. (1971) Comparative amino acid composition of calcified and non-calcified polychaete worm tubes. *Comp. Biochem. Physiol.* **38B,** 405–409.

Mitterer R. M. (1972) Biogeochemistry of aragonite mud and oolites. *Geochim. Cosmochim. Acta.* **36,** 1407–1422.

Mitterer R. M. (1978) Amino acid composition and metal binding capability of the skeletal protein of corals. *Bull. Mar. Sci.* **28,** 173–180.

Müller P. J. and Suess E. (1977) Interaction of organic compounds with calcium carbonate-III. Amino acid composition of sorbed layers. *Geochim. Cosmochim. Acta* **41,** 941–949.

Paterson G. W. (1974) Sterols in some green algae. *Comp. Biochem. Physiol. B. Biochem and Mol. Biol.* **47,** 453–457.

Ramseyer K., Miano T. M., D'Orazio V., Wildberger A., Wagner T., and Geister J. (1997) Nature and origin of organic matter in carbonates from speleothems, marine cements and coral skeletons. *Org. Geochem.* **26,** 361–378.

Ransom B., Kim D., Kastner M., and Wainwright S. (1998) Organic matter preservation on continental slopes: Importance of mineralogy and surface area. *Geochim. Cosmochim. Acta* **62,** 1329–1345.

Risk M. J. and Müller H. R. (1983) Pore waters in coral heads: Evidence for nutrient regeneration. *Limnol. Oceanogr.* **28,** 1004–1008.

Rude P. D. and Aller R. C. (1991) Fluorine mobility during early diagenesis of carbonate sediment: An indicator of mineral transformations. *Geochim. Cosmochim. Acta* **55,** 2491–2509.

Sansone F. J., Andrews C. C., and Okamoto M. Y. (1987) Adsorption of short-chain organic acids onto nearshore marine sediments. *Geochim. Cosmochim. Acta* **51,** 1889–1896.

Shuman F. R. and Lorenzen C. J. (1975) Quantitative degradation of chlorophyll by a marine herbivore. *Limnol. Oceanogr.* **20,** 580–586.

Stern B., Abbott G. D., Collins M. J., and Armstrong H. A. (1999) Development and comparison of different methods for the extraction of biomineral associated lipids. *Ancient Biomolecules* **2,** 321–334.

Suess E. (1970) Interaction of organic compounds with calcium carbonate-I. Association phenomena and geochemical implication. *Geochim. Cosmochim. Acta* **34,** 157–168.

Suess E. (1973) Interaction of organic compounds with calcium carbonate-II. Organo-carbonate association in recent sediments. *Geochim. Cosmochim. Acta* **37,** 2435–2447.

Sun M.-Y., Aller R. C., and Lee C. (1991) Early diagenesis of chlorophyll-*a* in Long Island Sound sediments: A measure of carbon flux and particle reworking. *J. Mar. Res.* **49,** 379–401.

Sun M.-Y., Lee C., and Aller R. C. (1993a) Laboratory studies of oxic and anoxic degradation of chlorophyll-*a* in Long Island Sound sediments. *Geochim. Cosmochim. Acta* **57,** 147–157.

Sun M.-Y., Lee C., and Aller R. C. (1993b) Anoxic and oxic degradation of ^{14}C-labeled chloropigments and a ^{14}C-labeled diatom in Long Island Sound sediments. *Limnol. Oceanogr.* **38,** 1438–1451.

Sun M.-Y., Aller R. C., and Lee C. (1994) Spatial and temporal distributions of sedimentary chloropigments as indicators of benthic processes in Long Island Sound. *J. Mar. Res.* **52,** 149–176.

Sun M.-Y., Wakeham S. G., and Lee C. (1997) Rates and mechanisms of fatty acid degradation in oxic and anoxic coastal marine sediments of Long Island Sound, New York, USA. *Geochim. Cosmochim. Acta* **61,** 341–355.

Swart P. K. (1981) The carbon isotope composition of organic material in coral skeletons and its effect on early diagenesis. *Proceedings 4th International Coral Reef Symposium.* **2,** 87–90.

Sykes G. A., Collins M. J., and Walton D. I. (1995) The significance of a geochemically isolated intracrystalline organic fraction within biominerals. *Org. Geochem.* **23,** 1059–1065.

Towe K. M. (1980) Preserved organic ultra-structure: an unreliable indicator for paleozoic amino acid biogeochemistry. In *Biogeochemistry of Amino Acids* (ed. P. E. Hare et al.), pp. 558, John Wiley & Sons.

Verardo D. J., Froelich P. N., and McIntyre A. (1990) Determination of organic carbon and nitrogen in marine sediments using the Carlo Erba NA-1500 Anaylzer. *Deep-Sea Res.* **37,** 157–165.

Veyera G. E., Brandes H. G., and Silva A. J. (2001) Geotechnical characterization of calcareous sediments from the Dry Tortugas Keys and Marquesas Keys CBBL SRP study sites, Lower Florida Keys. *Geo-Marine Lett.* **21,** 131–148.

Wainwright S. A. (1962) An anthozoan chitin. *Experientia.* **18,** 18–19.

Wakeham S. G. and Lee C. (1989) Organic geochemistry of particulate matter in the ocean: The role of particles in oceanic sedimentary cycles. *Org. Geochem.* **13,** 83–96.

Wakeham S. G. and Lee C. (1993) Production, transport and alteration of particulate organic matter in the marine water column. In *Organic Geochemistry* (eds. M. H. Engel and S. A. Macko), pp. 145–165. Plenum Press.

Wakeham S. G., Hedges J. I., Lee C., Peterson M. L., and Hernes P. J. (1997a) Composition and transport of lipid biomarkers through the water column and surficial sediments of the equatorial Pacific Ocean. *Deep-Sea Res. II.* **44,** 2131–2162.

Wakeham S. G., Lee C., Hedges J. I., Hernes P. J., and Peterson M. L. (1997b) Molecular indicators of diagenetic status in marine organic matter. *Geochim. Cosmochim. Acta.* **61,** 5363–5369.

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

Walter L. M., Bischof S. A., Patterson W. P., and Lyons T. W. (1993) Dissolution and recrystalization in modern shelf carbonates: evidence from pore water and solid phase chemistry. *Phil. Trans. R. Soc. Lond. A.* **344,** 27–36.

Walton D. (1998) Degradation of intracrystalline proteins and amino acids in fossil brachiopods. *Org. Geochem.* **28,** 389–410.

Weiner S. and Erez J. (1984) Organic matrix of the shell of the foraminifer, *Heterostegina depressa*. *J. Foram. Res.* **14,** 206–212.

Weiner S. and Lowenstam H. A. (1980) Well-preserved fossil mollusk shells: characterization of mild diagenetic processes. In *Biogeochemistry of Amino Acids* (ed. P. E. Hare et al.), pp. 95–441, John Wiley & Sons.

Withers N. W., Kokke W. C. M. C., Fenical W., and Djerassi C. (1982) Sterol patterns of cultured zooxanthellae isolated from marine invertebrates: synthesis of gorgosterol and 23-desmethylgorgosterol by aposymbiotic algae. *Proc. Nat. Acad. Sci. USA* **79,** 3764–3768.

Wright L. D., Friedrichs C. T., and Hepworth D. A. (1997) Effects of benthic biology on bottom boundary layer processes, Dry Tortugas Bank, Florida Keys. *Geo-Marine Lett.* **17,** 291–298.