Influence of Organic Matrix on the Post-Mortem Destruction of Molluscan Shells

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ABSTRACT

To examine the role of organic constituents in the destruction of calcium carbonate skeletons, we aged fresh shells of the bivalve *Nucula sulcata* (organic-rich mucous aragonites with low crystalline surface areas) and *Grossoidea edulis* (organic-poor porcellaneous aragonites, high crystalline surface areas) under sterile and non-sterile conditions for up to 11 months. Deterioration was tracked by SEM and weight-loss, and compared to damage produced by reagents of specific effect. The same qualitative sequence of damage was observed in all tests: for both species, but rates of deterioration were 2-5x higher in microsat...
information would be useful not only geochronologically but also paleobiologically, because intraskeletal orga
nics are common to all skellected groups and vary in content among higher taxa and life history. Organically mediated diagenetic alteration of carbo
nates occurs in a variety of temperate environments (references below) but has not been quantified and is generally agreement in discussions of carbonate cycling and fossil preservation. Intraskellectic organ
nics are relatively preserved, presumably in part because they are a minor shell component by weight (e.g., range of 0.01 to 5% across bivalve microstrucures [Mare and Akebono 1965] and because matrix concentration, particularly the insoluble frameworks that usually predominate, is still poorly known for some important groups (e.g., foraminifera, radiolarians, coccolithophores; Lorenzen and Weiner 1989). Organics are nonetheless an integral component of skeletal microstrucures and are intimately associated with the mineral phase, serving in life both as a template for biomineralization [Lorenzen and Weiner 1989] and as an elastic, strength-enhancing mortar (Curray 1990).

A variety of post-mortem roles, not mutually exclusive, has been suggested for organic matrix (Curray 1980) 1. The matrix may allow the complete decomposition, releases crystallites and accelerates physical disintegration (Alexanderson 1975, 1978; Lewy 1975, 1981; Emig 1980, Simon et al. 1990) 2. It may provide a coating that protects crystallites from ambient waters and thus inhibits dissolution (Kennedy and Hall 1967; Heinrich and Wefer 1986); 3. It may be an important chemical that affects bioturbation (Kastner 1986). Previous work has varied greatly in the types of carbonate grains studied and in the condition at the start of the experiment, in the aeration, microbial activity and salinity of the experimental waters and whether the saturation state is known, and in the sampling intervals and metrics for microstructural determination.

To explore the effects of organic matrix on the reactivity of biogenic carbonates, we tracked the deterioration of bivalve shells in artificial seawaters maintained at three qualitatively different but realistic saturation states (two gradual, 1 ppm increase in salinity at 10°C or a 1-ppm increase in salinity at 10°C). Each experiment was started with 25°C water (pH 7.8 to 8.2). To distinguish the effect of matrix from mineral reactivity and also the relative effectiveness of biotic and abiotic pro-

cesses in shell deterioration, each saturation state was run under both sterile (nonreact) and non-
natural conditions (oxygen present). All experiments were conducted at 10°C and 30°C, and the water was exchanged every 24 hours. The experiments were run for 6 months. The following conclusions were drawn from the results:

- Artificial seawaters were not as effective in promoting carbonate dissolution as natural seawaters.
- The presence of organic matrix significantly reduced carbonate dissolution rates.
- The effect of organic matrix on carbonate dissolution was more pronounced at lower temperatures.

The results of these experiments suggest that the presence of organic matrix in shell sediments can significantly decrease the rate of carbonate dissolution. This finding has implications for the interpretation of carbonate preservation in sedimentary rocks, as well as for the study of modern marine carbonate ecosystems.
In both species, the adductor muscle scars and pallial line are composed of organic-rich prismatic aragonite (Taylor et al. 1969), but these occupy only small areas of the shell interior. The exterior surface of shells was not examined because their condition typically varies widely among individuals in live populations, making it difficult to identify post-mortem deterioration unambiguously. Small specimens of Mytilus (avg. 18 mm) and of Ctenodiscus (avg. 23 mm) were collected from native habitats by the University Marine Laboratory, Millport, Scotland and air-shipped to Chicago. Live populations were held in cold (10°C) seawater aquaria until experimental tanks were ready. Vigorous animals were then carefully disarticulated and adhering tissues carefully removed by hand. Each shell (right or left valve) was numbered uniquely on its outer surface, weighed in ASW, and placed concave-up on the floor of a tank. The interior surface was not allowed to dry out at any time in this procedure, which took only a few minutes per specimen.

Three specimens of each species were sampled from each tank after the following intervals of time: 1, 2, 4, and 7 days; and 0.5, 1, 2, 3, 4, 6, and 11 months. Shells were detached and added to tanks in two batches. Shells to be sampled after 0.5 months were placed in tanks on day 1, and shells to be sampled after 1 to 7 days of treatment were added on day 21 (total N = 418). Weight of shell carbonate (in air, calculated from submerged weights) in each 8-litre reservoir was the start of the experiment: 28.36 g in the microbial undersaturated tank (MU), n = 30; 25.33 g in the sterile undersaturated tank (SU), n = 30; 52.17 g in the microbial saturated tank (MS), n = 48; 54.33 g in the sterile saturated tank (SS), n = 47; 45.98 g in the microbial supersaturated tank (MSS), n = 49; and 41.02 g in the sterile supersaturated tank (SSS), n = 48. Shell carbonate added for the short-term experiment was 24.55 g. SU = 20.19 g, MS = 28.72 g, SS = 20.69 g, MSS = 35.66 g, and SSS = 19.49 g (in 15 Ctenodiscus and 12 Mytilus shells in tank). Because shells were removed permanently when sampled and not replaced, solid to solution ratios decreased steeply from maximum values of ~10g carbonate/litre at the course of the experiment. Sampled shells were immediately weighed in ASW to determine weight loss, rinsed briefly in deionized water, and placed concave-down on laboratory tissue in an air-tight 10-litre box before being coated for Scanning Electron Microscopy (SEM). Interior surfaces of the whole shells were SEM-scanned along a transect perpendicular to the ventral margin, avoiding adductor muscle scars. An additional set of untraced shells was examined by SEM to establish the initial, "pristine" state of shell microstructures. Because of possible anacrobiosis and shell corrosion during the stress of air-shipping and holding tanks, this post-treatment condition is the most appropriate baseline for evaluating subsequent experimental deterioration.

Another set of fresh shells was used to establish the SEM signature of various reagents known to attack different parts of shell structure (Muir, 1984; Ca:Richarson 1991 pers. comm. for Pratease). To simulate the selective removal of organic matrix, shells were immersed for periods of either 1.5-2.5 hrs in a 8-12% solution of sodium hypochlorite or for 3-5 days in a 1mg/ml solution of the enzyme Pratease. To simulate selective attack on mineral crystals, fresh shells were immersed for periods of 1-3 days in 35% solutions of glutaraldehyde, which both decalcifies carbonate minerals and fixes proteins. To examine the effects of aging in atmosphere, simulating museum storage, an additional set of shells was left to dry uncovered on a laboratory bench for 11 months.

**Changes in Water Chemistry during the Experiment**

**Trends in pH.** All tanks fluctuated daily in pH (figure 1). Fluctuations were generally on the order of only a few hundredths of pH in the saturated and undersaturated tanks, which is, within the resolving power of the electrode. Fluctuations were larger and more frequent in the undersaturated tanks (~0.15 pH units, generally between pH 7.75 and pH 7.50) within a few hours after establishing undersaturated conditions by acid-titration, pH would rise as the ASW began to re-equilibrate toward saturation. The designation "undersaturated" thus indicates only that the ASW was at target pH for undersaturation (Dag = -0.5) for a few hours each day, followed by a rise to near saturation (Dag = -0.8) over the next 24 hrs. In each of the tanks, the largest excursions in pH were related to known perturbations, such as the temporary failure of a bubbler, the addition of shells for short-term experiments at the beginning of week 3, or the addition of fresh ASW or of deionized water to correct reservoir volume and salinity.

**Trends in Ca++.** Analysis of major ions after 3 months revealed an increase in concentrations, presumably due to evaporation of water. Thus, although pHs were relatively steady, saturation levels would have risen over this period in response to the increase in Ca++ (figure 1). The time course of evaporation is not known, and thus is plotted on figure 1 as a straight line. As a correction, tanks at 3 months were diluted to their original levels by factors of 1.6 to 1.52 in microbial tanks, and by 1.74 and 3.45 for sterile tanks. Evaporation was a greater problem in sterile tanks because these were kept under an exhaust hood. Dilutions required at subsequent one-month intervals were much smaller.

**Trends in Alkalinity.** There is also evidence that the pCO2 and total alkalinity of the ASW also increased over the 3 months, probably due to evaporative loss of water. Thus, although pHs were relatively steady, saturation levels would have risen over this period in response to the increase in Ca++ (figure 1). The time course of increasing alkalinity is not known.

**Water Saturation.** Supersaturated conditions appear to have prevailed in microbial and sterile suprasaturated tanks over the full 11 month period. ASW maintained a high pH without intervention, with a calculated DAg of 1.1 for the first week and 2 thereafter (figure 1). There was a slight drop in saturation from freshly mixed ASW during the first week. This may reflect precipitation of CaCO3 on newly introduced shells, which is common in reaction vessels (L.M. Walter pers. comm.), or may have been caused by decay of organic coatings on shells.

Undersaturated tanks received more acid than other tanks during the first 2 months of the experi...
Experimental Deterioration of Organic-Rich Nacreous Aragonites

Initial Condition. Interior surfaces of freshly dissected _Nucula_ shells had a distinct 200 μm wide pallial scar. The inner shell layer (inside the pallial band) was characterized by smooth, broadly overlapping shell laminae composed of a single layer of completely saturated 3–10 μm diameter tablets (sheet nacre). Isolated tablets occurred along the horizontally growing edges of laminae and were subcircular, diamond-shaped, or hexagonal in outline (figure 3a, 3b). In small areas on a few specimens, isolated tablets were irregular or elongated in outline and even perforate in small areas. This damage probably reflects metabolic stress associated with collection, shipping, or holding of live animals.

The middle shell layer (outside the pallial band) was characterized by tablets stacked 2–4 high into columns and elongated mesa. This stacked nacre had maximum relief toward the shell margin and rested on a smooth sublayer of completely fused aragonitic tablets. Near the pallial band, where tablets had not all joined into continuous laminae, tablets were smooth-edged and subcircular, diamond-shaped, or hexagonal in outline.

Damage Inside the Pallial Band. Sheet nacre deteriorated through a series of stages when examined at 2000× (figure 3c, 3d). The same sequence was observed in all tanks, but the rate at which it progressed and thus the cumulative damage to shells during the experimental period varied according to saturation state and microbial activity (figure 4).

Damage stages are assigned descriptive names and scaled arbitrarily from 0 to 4 in figure 4. The six tanks are designated: MU = microbial under-saturated; SS = sterile under-saturated; MS = microbial saturated; MSS = microbial super-saturated, and SSS = sterile super-saturated.

Pristine (0): No detectable change from condition at start of experiment.

Reticulated Shells (1): The first microstructural damage was the development of a reticulated (net-like) pattern on the surface of shell laminae. These lines were either dark shadows or brightly charged patterns between SEM and corresponded to organic-rich surfaces between aragonitic tablets, which remained pristine in outline and surface condition. Reticulated fabric was first seen in MU specimens after a few days (figure 4b) and dominated the area inside the pallial line by 2 weeks. It was not observed until the one-month sampling in MS, MSS, and SSU specimens, and not until 4 months in SS and SSS specimens (figure 4).

Canyoned Sheets (2) = Cuspathe Tablets (3): The reticulated pattern is incised into the surface, usually via a series of 50-80 μm-diameter pits that coalesce into an intersecting system of steep-walled canyons. Originally coherent shell laminae are transformed into horizons of discrete tablets. The edges of these tablets eventually become sharply cuspathe or perforate at a submicron-scale.

Canyons and edge-perforations were well developed by one month in the MU specimens (figure 4). Canyons were clear by two months in MS and MSS specimens, but had only begun to appear by that time in SSU specimens and did not appear in SS and SSS specimens even after 11 months (figure 4).

Jagged Tablets (4): An irregular, jagged shell surface...
Experimental Deterioration of Organic-Poor Porcellaneous Aragonites

Initial Condition. The pallial line appeared only as a slight change in slope on the interior surfaces of freshly dissected Cerastoderma shells. The entire interior surface did not reveal any structure at 200× with incident light. In experiments, the interior was coated by a thin (one crystallite thick) layer of irregular 1-2 μm granular crystallites (homogeneous microstructure of Taylor et al., 1969). Only larger, more compact cross-lamellar microstructures, composed of tightly-packed 0.5 μm laths dipping in opposing or radial directions respectively, were not observed until this superficial layer had been stripped. Interior surfaces showed no evidence of pitting or corrosion from metabolic stress.

Damage Inside the Pallial Line. Microstructural damage did not appear over the entire area at once, but started in scattered spots which then expanded outward (seen at 200×). Damage within patches proceeded through a series of stages (figure 6). The same sequence was observed in all tanks, but the rate and cumulative damage varied among tanks (figure 7). Damage was described in terms of the intensity of damage within patches seen at 2000× and the approximate area so affected (seen at 200×). Damage stages were assigned descriptive names and scaled arbitrarily from 0 to 4.

Pristine (0): No detectable change from condition at start of experiment.

Graveled Surface Coat (1). The first microstructural damage appeared as patches of fine-scale (sub-micron) roughening (200×). At 2000×, these patches were characterized by irregular crevices along the organic-rich sutures of 1-2 μm irregular crystallites, and by scattered holes comparable in size and shape to crystallites or small groups of crystallites (figure 6a). The shell layer that exhibited this style of damage appeared to be a single lamina only one crystallite thick. This damage appeared with a few days in all treatments except the SS and SSS tanks, where it was rare for the first 2 to 4 months (figure 7).

Laths Exposed (2): Removal of the surficial shell coat revealed 0.2-1.0 μm-long, lath-shaped crystals dipping at a low angle to the shell surface (cross-lamellar microstructure). Laths were oriented approximately parallel to each other, and stood out in pitted relief because of steep-sided canyons along suture lines (figure 6b). This stage was observed by 4 days in some patches on MU specimens, by 2 weeks in MS, MSS, and SU specimens, and was never seen in SS and SSS specimens (figure 7).

Radial Laminae Exposed (3): At 200×, the surface appeared pristinely smooth but a low-relief (less micron) microstructure developed with crests spaced ~20 μm apart. At 2000×, these balls consisted of radially dipping shell laminae that were each a few tenths of a micron thick and that imparted a surface pattern of arcuate swirls (complex cross-lamellar microstructure, figure 6c).

Crystallites within laminae were tightly packed and fused, without sutural crevices or canyons. This stage dominated MU specimens by 1 week, and drifted to dominant SU, SS, and SSS specimens by 1 month, and was never observed in SS and SSS specimens (figure 7).

Coarse Blocks (4): Where deterioration had advanced most deeply below the shell surface, a relatively coarse microstructure of 2-3 μm roughly rhombic blocks was exposed (figure 6d). This may be a form of complex cross-lamellar structure (cf. Taylor et al., 1969). A few blocky patches appeared within 2 weeks in MU specimens and dominated the surface of some specimens by 1 month, whereas this stage did not dominate MS and MSS specimens until 2-3 months and was never significant in SU, SS, and SSS specimens (figure 7).

The overall ranking of tanks for damage inside the pallial line was MU > [MS, MSS and SU] > [SS and SSS] (figure 7).

Damage Outside the Pallial Line. Microstructural damage was more difficult to detect outside the pallial line, and the stage with parallel laths (2) was not observed. Despite uncertainties (indicated by missing data in figure 7), deterioration proceeded fastest in MU, MS, and MSS tanks, much slower in the SU tank, and slowest in SS and SSS tanks where some shells remained pristine for 3 months.

The pallial line itself and the edges of internal ribs were roughened, exposing coarse blocky microstructure.

Other Damage. Cerastoderma shells in microhial tanks were bored in the same way as the Nucula shells (figure 5). However, borings were initially smaller (<5 μm), attained smallest maximum sizes (≈ 10 μm), were slower to appear (2 months), and remained sparse (maximum 0.8 per 100 μm × 100 μm area).

Comparison of Porcellaneous Microstructures. In general, cross-lamellar aragonite outside the pallial line deteriorated more slowly than complex cross-lamellar aragonite inside the pallial line, lagging by as much as one stage at each sampling interval (figure 7). The ranking of tanks was slightly different, with sterile tubes lagging behind all microhial tanks, and borings were less densely spaced than inside the pallial line.
produced some deep (10 μm) irregular pits. Such pitting was pervasive outside the pallial line, contrary to experimental shells where damage (including microbial boroholes) was greatest inside the pallial line. Glutaraldehyde had little effect on the pallial line itself, in contrast to experimental shells.

Experimental Weight Loss

Shells in undersaturated tanks were more likely to show weight loss than shells in saturated and supersaturated tanks, which were unchanged or gained in weight (Mann-Whitney U-test, 0.05 < p < 0.10 for Nucula and p < 0.025 for Cerastoderma; based on the most reliable samples: pooled MU and SU data at 1 month versus pooled MS, MSS, and SSS data at 2 months). In general, however, cumulative weight changes were small (±1% even at 4 months), variance was high, and numbers per sampling were necessarily small despite the large total number of shells in the experiment. Consequently, no other differences, such as between microbial and sterile tanks at a given Ω_m or between organic-rich and organic-poor shells within a tank, proved significant.

Discussion

Shared Patterns of Organic Influence. The SEM time-series data showed the same pattern of deterioration in all tanks, and comparison with simulated damage showed that deterioration was limited initially to decomposition of organic matrix. The retreat of matrix left crystallites in positive relief and permitted these to detach from the shell surface, both singly and in small groups. For all microstructures in all tanks, this loss of organic matrix was the rate-limiting step in shell deterioration. Only the rate of deterioration varied among tanks.

Dissolution must have occurred in undersaturated tanks, since water pH rose in response to acid-addition, but in situ crystallites generally remained pristine. Waters thus did not attack microstructure directly, and dissolution must have been focussed instead on particulate matter released from the shell surface. The only exception to this was scalloping and perforation of more tablets in the microbial undersaturated tank. This damage is a form of dissolution, but the fact that it was encountered only in microbial tanks and was limited to natal edges suggests that dissolution was linked to the process of matrix decomposition, probably via high CO_2 produced by microbial respiration of adjacent matrix. Pervasive pitting and

Simulation of Experimental Damage

Organic-Rich Nacreous Aragonites. Bleach and protease, which selectively remove organic matrix from shell, had little effect on the pallial band of Nucula, but otherwise replicated in form and scale the reticulated, canyoned, and cuspathe damage observed in experimental shells (figure 8c, d). Damage was greatest inside the pallial band, as also observed in experimental shells. Exposure to laboratory air for 11 months (dehydration and oxidation) also produced reticulated and canyoned damage similar to experimental shells (figure 8e). Decalcification by glutaraldehyde uniformly corroded nacre, leaving a granular texture. Even the mildest treatment produced pits across the entire upper surfaces of tablets (figure 8f), unlike experimental shells where damage was focussed exclusively on tablet edges, with upper surfaces of tablets remaining smooth. Longer treatment produced an irregular surface in which the original shape of the tablets was largely obliterated (figure 8g). This was an extreme form of the jagged tablets observed in experimental shells (e.g., figure 3d). Glutaraldehyde damage was most severe outside the pallial line, opposite to the pattern in experimental shells.

Organic-Poor Porcellaneous Aragonites. Protease damage to Cerastoderma was virtually indistinguishable in type and distribution to experimental damage. Damage was patchy at 300×. The smoothest areas revealed, at 2000×, either parallel laths separated by sutural crevices (stage 3) in experimental shells, as in figure 6b) or radial laminae (stage 3, as in figure 6c). The roughest patches were exposures of an underlying coarse-grained microstructure (stage 4, as in figure 6d). Crystallites stood in positive relief across the entire surface, with undamaged edges. Protease caused more damage inside than outside the pallial line and roughened the pallial line dramatically as in experimental shells. Glutaraldehyde uniformly roughened the entire surface inside the pallial line at 2000× and also
granulation typical of chemical [glutaraldehyde] attack was not observed during the course of the experiment, but relatively prolonged exposure (32 months) in the microbial undersaturated tank did produce some corrosion of nacre tablets in superficial shell laminae. This may reflect direct interaction between seawater and in situ crystallites, but it was limited to laminae in a relatively late stage of matrix loss.

The fact that rates of deterioration were \(a = 2x\) higher in microbial than in sterile tanks at any given saturation state, and were as high or higher in microbial saturated and supersaturated tanks than in sterile undersaturated tanks, underscores the controlling influence of organic matrix on the recrystallization of fresh shells. Organic coatings and matrix must be decomposed before crystallites become vulnerable to dissolution by ambient waters, and thus the initial role of organics is protectice. Upon decomposition of organics, whether by hydrolysis or by microbes, microstructures disintegrate by detachment of crystallites. In microbial, destruction is presumably furthered by respiration along crystalline sutures and by borers, which both undermine microstructure and increase its reactive surface area. During shell aging, therefore, organics apparently shift to making microstructures more vulnerable to physical disintegration and to bioerosion, and fuel dissolution by serving as a microbial substratum. Microbial respiration alone could not cause dissolution of an entire shell, given that even organic-rich microstructures contain only a few percent organics, but it might have a disproportionate effect given its proximity to crystallites.

This pattern is comparable to that reported for biogenic carbonates in natural environments. Alexanderson (1975) reported that "organic templates of skeletal carbonates disappear together with, or even slightly before, the mineral substance" in mollusk shells from the Skagerrak, thus weakening structurally complex grains and permitting physical disintegration of microstructures. He attributed organic loss to "leaching," and etching of in situ crystallites to undersaturation of Baltic waters. Levy (1975, 1981) attributed these same features to microbial attack and its attendant high CO2 conditions (see Gaspard 1989 and Simon and Pouliot, 1989). Heinrich and Wefer (1986) found that decomposition of diatom-rich surface coatings and cell walls and mechanical disintegration were more important than chemical dissolution in some taxa in undersaturated waters, based on specimens suspended for 52 days in the Drake Passage; that is, shells did not dissolve until they had been cleaned of organics. Roux et al. (1989) similarly found significant bioerosion and evidence of organic loss (inhaled crystallites) in aragonite pelagic after 3 yrs of exposure below the aragonite CCC, but no trace of aragonite dissolution.

Our experiments demonstrate that hydrolysis and leaching (Hudson 1987, Alexander 1975) are only of secondary importance to microbial decomposition in destroying organic matrix. Microbial deterioration proceeds 2 to 10x faster than abiotic processes in sterile aerated waters of comparable saturation, and only our microbial rates match the rapid rates of matrix loss documented in natural waters (e.g., Heinrich and Wefer, 1986, Jensen and Thomsen, 1987, Simon et al., 1990).

**Effect of Water Saturation:** Hypothetically, organic matrix should be vulnerable to microbial decomposition regardless of water saturation state, as suggested by Levy (1981). Our experiments support this: shells deteriorated via organic loss in all tanks. Saturated and supersaturated waters thus should not be regarded categorically as taphonomically neutral, given the potential for organic loss and consequent physical dissolution of crystallites. We have found examples of total organic loss in shells dredged from modern death assemblages (figure 9). These wet, organic-free shells had the flexible consistency of cardboard (and see Emig 1990 for brachiopods).

However, although saturation state does not determine the pathway of deterioration for fresh shells, our experiments indicate that it does influence the rate: microstructural deterioration rates were \(a = 2x\) faster in microbial undersaturated tanks than in other microbial treatments (deterioration was also higher in sterile undersaturated than in other sterile treatments). Undersaturated waters presumably are more effective in ridding shell surfaces of loosened or partially exposed crystallites, thereby more fully exposing matrix in underlying shell laminae to microbial attack (or hydrolysis). Undersaturated waters should also create less of a concentration gradient drawing matrix-sourced CO2 away from the shell surface.

Alexanderson (1979) reported that organic loss did not seem to be particularly important in tropical supersaturated waters, and many authors have noted that carbonate grains have shiny rather than dull surfaces in such settings. In these stable-water environments the effects of organic - perhaps masked by more aggressive algal microbor- (1-10 μm scale) with attendant micritization, or perhaps the sub-microbial voids created by matrix loss are quickly filled by mineral precipitates. The
role of organic matrix in carbonate grain destruction in these settings deserves re-examination.

**Differences in Vulnerability of Microstructures.**

Given experimental evidence for the changing role of organic matrix during shell aging, the net effect on shell preservation during time averaging is not deductively obvious. On the one hand, one might expect that organic-rich shells have relatively high preservation potential since matrix limits direct interactions between crystals and water (Kennedy and Hall 1967). On the other hand, organic-rich shells might have lower preservation potentials (Emig 1990). Simondini and Sposito (1989) also found that the more dependent the microstructure upon organic binding of crystals, the more vulnerable it should be to physical disintegration as organic are lost, and organic-rich microstructures might preferentially attract microbial decomposers and microborers.

In our experiments, deterioration in a given tank was usually more striking in organic-rich microstructures (Mucuna) than in organic-poor porcellaneous aragonites (Cerastoderma), but this is difficult to quantify. However, 1–10 μm scale microbial boring was

Figure 9. SEM of Recent mussel bivalve *Atrina costata* (inds) bored shell from pebble mud in Puget Sound, Washington. Numerous shells have lost their organic matrix, but tablets are otherwise in excellent condition and remain as apparent microstructural order. Macroscopically, these shells had slightly shelled surfaces, were somewhat flexible under pressure, and in some instances could be disarticulated into crystallites by turning them between the fingers. Brushholes are at the small end of the variance observed in experimental shells (figure 5) and are probably fungal in origin. Scale = 1 μm.

quantifiable. Organic-rich microstructures were colonized 4–5× faster and 4× more intensely than organic-poor types. Caspar (1989), Roux et al. (1986), and Simondini and Sposito (1989) also found positive relationships between rate of bioerosion and organic content, lending further support for Sposito’s (1985) suggestion that microbes exploit intraclastic organic matrix as an energy source. Such preferential destruction would be a contributing factor in lowering the preservation potential of organic-rich taxa.

Slight differences in the reactivity of microstructures found within the pallial line in each taxon (figures 4 and 7) may also reflect differences in matrix—e.g., its total weight %, the proportion of soluble and insoluble molecules, or the physical interconnections of sheaths—but this needs to be tested. It might also reflect the different functions of malleable tubes in these areas and thus the condition of the shell surface at the time of death. Inside the pallial line where the malleable tube is closely associated with acid-base metabolism, shell material is periodically corroded to buffer body fluids (Lutz and Rhoads 1977, Crenshaw 1980). This pre-mortem history and the absence of a surficial organic coating may cause the inner shell layer to be more reactive to post-mortem attack than the outside surface of the pallial line, where shell deposition is highest during life (Crenshaw 1980).

Between-taxon differences in weight loss (±36.6% change per sampling) were statistically insignificant (Mann-Whitney U test, p > 0.05 for pooled undersaturated waters). However, it is probably meaningful that the relatively organic-poor *Galeolaria* shells at most only matched the weighted loss of organic-rich *Nucula*, given the inner crystallites (0.5 μm vs. 5–10 μm in macro) and thus the greater potential surface area for mineral reaction. The fact that low surface area *Nucula* shells had weight-losses comparable to those of high-area *Galeolaria* is consistent with SEM evidence that organic matrix has not been as important as the chemical phase in determining reaction rates in fresh shells, and that the overall effect of organic matrix in microbially active environments is to increase its shell’s vulnerability to post-mortem disintegration.

This conclusion can be tested independently by comparing the composition of death assemblages with source communities (e.g., invertebrate time’s 1989 living and Pleistocene marine bivalves of California, only 48% of the 54 living species with predominantly nacreous shells occur in the fossil record, whereas 84% of the 185 living species with non-nacreous aragonitic shells are preserved as fossils (p < 0.001, G-test). Although some nacreous species also have small bodies and low population densities that would contribute to lower preservation potentials, as discussed by Valentine, nacreous species are not exclusively small and sparse and these characteristics are also common to many non-nacreous aragonitic taxa.

**Implications and Conclusions.**

**Dynamics of Early Diagenesis.**

The observation that dissolution does not proceed until organic residue is removed from mineral crystallites suggests that the dynamics of dissolution for fresh biogenic carbonates may differ significantly from the behavior of organic-free sedimentary grains, which show high initial dissolution rates in reaction vessels (Morse et al. 1980). Since biogenic carbonates in natural systems first enter the geochronological cycle with their organic matrix and coatings intact, the protective effect of organic has implications for patterns of shell preservation during early diagenesis. Specifically, the initial "grace period" of low mineral reactivity will generally coincide with early post-mortem seafloor exposure and shallow burial, when shells are likely to be associated with undersaturated waters. The slower the rate of microbial decomposition and the less desirable the shells for microborers, the longer the grace period and the more likely the shell will survive residence in this diagenic zone.

The low reactivity imposed by organics can be as brief as one or two months for the most vulnerable (organic-rich) microstructures in the most aggressive (aerobic microbial undersaturated) environments. This experimental result may provide only a minimum estimate of organic protection, since much as shells in other tanks showed a sharp drop in their rate of deterioration after the first 2 or 3 months (figures 4 and 7). Moreover, shells in natural settings can acquire protective post-mortem coatings (e.g., encrusting diatoms, Heinrich and Wetzel 1986, Echols 1993) which can outlast or replace the original matrix, thereby prolonging the period of limited dissolution. Protective organics may thus help to explain seemingly anomalous experimental results, such as the 2× slower dissolution of fresh than of bleached eococoids observed by Kurz (1980), and the 10× slower rates of dissolution measured in organic-free aragonitic sandstones than for aged material under laboratory conditions (Aller 1982, Archer et al. 1989) [Powell et al. 1990] found that some portion of a shell’s original matrix might persist for hundreds to a few thousands of years post-mortem. However, the exponential curve of organic loss was calibrated using a combination of dry-stored museum specimens and extrapolation from very short-term (1–12 days) experiments on fresh shells, and so its validity for marine assemblages is uncertain.

Another factor in the slower rates of dissolution observed for carbonates in natural systems, but not investigated here, may be the inorganic conditionning of crystalline surfaces. Organic-free biogenic aragonites in reaction vessels show very high initial rates of dissolution in undersaturated waters, matching thermodynamic values, but dissolution rates decrease rapidly over the first few weeks of reaction, presumably due to invasion of surface aragonite to a calcite or aragonite phase of greater chemical stability (Morse et al. 1980). Dissolution cannot resume until seawater becomes undersaturated with respect to this new surface phase. Given the similar time-scales over which organics are protective and mineral-conditioning occurs, it is possible that the two combine to lower the reactivity of fresh shell material during the first few critical months of the post-mortem period in natural settings as organics react and lose their protective capability, the exposed surfaces of crystals are shifting to more stable phases, thereby increasing the likelihood of shells forming time-averaged assemblages. In this scenario, crystallites released as particulate matter would have the highest reactivation potentials owing to greatest surface area, and thus would be the primary target of dissolution. Rapid permanent burial of shells to a supersaturated zone (Aller 1982) and episode burial during slow net sedimentation (Kidwell 1982, 1986, 1989, Davies et al. 1989) are commonly invoked preservation routes for shells and are probably operating in many settings, but even under these conditions shell accumulation would be further enhanced by lowered shell reactivities in the early post-mortem period and by the buffering effect of "sacrificial" crystallites on preservatives. Such self-buffeting by shell-rich sediments has been postulated as a preservational factor in both ancient (Kidwell 1986, 1989) and modern death assemblages (Koehler et al. 1992).

High rates of dissolution in modern sediments (e.g., potwater measurements of Aller 1982 for Long Island Sound silicilastic and of Walter and Burren 1990 for Florida Bay carbonates, calculated values for Pacific carbonate sediments adopted from Davies et al. 1989) thus are not incompatible with the formation of long-term death assemblages if, as in our experiments, dissolution is focused preferentially on particulate matter. Our experiments
Further indicate that particular carbonate will be preserved essentially by organic-rich skeletal types, and this is consistent with some field observations. For example, although they detected 0.1 to 50% weight loss this [17] on treated unaltered pets, Walter and Burton [1980] had difficulty discerning SEM evidence for dissolution on naturally occurring large shells, suggesting that dissolution had indeed preferentially removed fine aragonite, microparticulate, and calcite. Slightly calcified, well-exposed unaltered taxa might, however, show some evidence of dissolution. This would be consistent with the observation of Walter [1985] that, for older, organic-rich taxa, whose behavior is more closely regulated by mineralogy, grain size, and microstructural surface area.

Methodically, the experiments indicate that any pretreatment that might alter or remove organic matrix deserves rigorous evaluation as a potential source of experimental artifacts. This includes not only heating and bleaching (Gaffney et al. 1991), but the use of stains that have been stored or taken from modern dead assemblages rather than from live populations. Shells on and post below the seafloor may be hundreds of thousands of years old despite a macroscopically fresh appearance (review in Kidwell and Bosence 1991, Powell and Dunbar 1990, Plessa et al. 1994), and true fresh shells show significant loss in biodepositional strength both with drying (Westermarck and Ward 1980) and with exposure to supersaturated seawater (Labarbera and Merz 1992, Daley 1992), a phenomenon that is probably related to changes in organic matrix. Laboratory experiments on pretreated material, such as required for accurate mineral kinetic studies, should thus be extrapolated to natural systems with caution.

Environmental experiments. Hypothetically, organic-rich microstructures should be a greater preservational liability in some early diagenetic environments than in others. However, preservation is not a function of diagenesis alone, nor is diagenesis a behavior of organic matrix alone, and so field-tests in modern and ancient environments will be essential.

For example, although heat treated and supersaturated environments are not taphonomy neutral owing to the potential for matrix loss, complete diagenesis of shells requires physical reworking to desiccate loosened crystals. If unaltered, organic-rich taxa might still be recorded as sileden shells in matrix or, eventu-