SEDIMENT EFFECTS ON THE PRESERVATION OF BURGESS SHALE–TYPE COMPRESSION FOSSILS

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ABSTRACT: Experimental burial of polychaete (Nereis) and crustacean (Crangon) carcasses in kaolinite, calcite, quartz, and montmorillonite demonstrates a marked effect of sediment mineralogy on the stabilization of nonbiomineralized integuments, the first step in producing carbonaceous compression fossils and Burgess Shale–type (BST) preservation. The greatest positive effect was with Nereis buried in kaolinite, and the greatest negative effect was with Nereis buried in montmorillonite, a morphological trend paralleled by levels of preserved protein. Similar but more attenuated effects were observed with Crangon. The complex interplay of original histology and sediment mineralogy controls system pH, oxygen content, and major ion concentrations, all of which are likely to feed back on the preservation potential of particular substrates in particular environments. The particular susceptibility of Nereis to both diagenetically enhanced preservation and diagenetically enhanced decomposition most likely derives from the relative lability of its collagenous cuticle vs. the inherently more recalcitrant cuticle of Crangon. We propose a mechanism of secondary, sediment-induced taphonomic tanning to account for instances of enhanced preservation. In light of the marked effects of sediment mineralogy on fossilization, the Cambrian to Early Ordovician taphonomic window for BST preservation is potentially related to a coincident interval of glauconite-prone seas.

INTRODUCTION

Carbonaceous compression fossils are a major source of paleobiological data, in particular as it relates to capturing the early Paleozoic record of “exceptional” Burgess Shale–type (BST) macrofossils (Butterfield 1990, 1995; Gaines et al. 2008; Page et al. 2008; Orr et al. 2009) and their microscopic counterparts (Butterfield and Harvey 2012). Even so, the circumstances and processes leading to the preservation of such fossils—and thereby their paleobiological implications—have yet to be fully resolved. The Phanerzoic record of BST-type preservation, for example, appears to be limited to an early (but not earliest) Cambrian to Early Ordovician taphonomic window (Butterfield 1995; Van Roy et al. 2010), obscuring its contribution to both the Cambrian and Ordovician radiations. Localized dysoxia–anoxia is certainly a prerequisite for preserving nonbiomineralizing fossils, but this falls well short of a full explanatory account. Even in the absence of oxygen, simple hydrolysis, autolysis, and the activities of anaerobic microbes continue to degrade carbonaceous substrates, rapidly obliterating original morphology.

Sedimentary matrix is fundamental to the fossilization process, not only as basic packing material but also based on its potential to alter the chemistry of early diagenesis. Despite reports of accelerated carcass decay associated with some sediments (e.g., Plotnick 1986; Allison 1988; Briggs and Kear 1993), most models for BST preservation invoke mineral-specific diagenesis as an essential factor, either by suppressing normal enzyme–microbial-based decay processes (e.g., Butterfield 1990, 1995; Gaines et al. 2005, 2012) or secondarily by enhancing the recalcitrance of relatively labile substrates (e.g., Orr et al. 1998; Petrovich 2001). Surprisingly, there has been little attempt to test these various models, though Martin et al. (2004) have shown that sedimentary particles will adhere to lobster eggs in the presence of bacteria, and Naimark et al. (2013) have documented substantially enhanced preservation of Artemia when they are buried in kaolinite. In this study we adapt the seminal, sediment-free decay experiments of Briggs and Kear (1993, 1994a) to investigate the effect of sediment mineralogy on the decay and early diagenesis of two “model” nonbiomineralizing marine invertebrates: Nereis virens (polychaete annelids with collagenous cuticle, sclerotized collagenous jaws, and sclerotized chitinous chaetae) and Crangon crangon (crustacean arthropods with variably sclerotized chitinous cuticle).

MATERIALS AND METHODS

In order to test the effects of sediment mineralogy on preservation potential, we buried freshly killed Nereis and Crangon in four different seawater-saturated sediments: kaolinite, quartz, calcite, and Ca-montmorillonite. After 4 months the carcasses were exhumed for qualitative morphological assessment and semiquantitative chemical analysis (structural protein, chitin, water-soluble protein, carbohydrate, and phospholipid).

All of the sediments used in the experiments were mineralogically pure and texturally homogeneous, though the particle size (measured using a Micromeritics SediGraph, model 5100) differed among the four materials: (1) kaolinite, a 1:1 layer clay, supplied by ECC International (St. Austell, UK); particle size 0.5 to 10 μm; (2) marble-derived calcite, supplied by English China Clay International (St. Austell, UK); milled particle size 0.5 to 10 μm; (3) quartz, supplied by Hanson PLC (Maidenhead, UK); milled particle size 10 to 30 μm; and (4) Ca-montmorillonite, a 2:1 layer clay, supplied by Rockwood Additives Ltd. (Widnes, UK); particle size <0.5 μm.

All of the experiments were conducted using artificial seawater (ASW) prepared from Instant Ocean® sea salts and deionized water (mixed to a salinity of 1.022–1.024 and with a pH of 8.4). The ASW was inoculated with bacteria by introducing a population of 11 live mussels (Mytilus edulis) to the aerated reservoir 2 weeks prior to use.

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All of the experimental subjects were alive and in good condition at the start of the experiments. Crangon specimens (body length 50–70 mm, supplied by Millport Marine Station, western Scotland) were killed by subaerial exposure ca. 2 hours prior to burial. For Nereis (body length 125–250 mm, supplied by Seabait Ltd., Northumberland, UK), one series of specimens was killed by immersion in freshwater (with a potential for associated osmotic cell rupture) and a second by exposing their heads to a stream of hot water (see Briggs and Kear [1993]).

For each of the taxon–sediment combinations, three to four freshly killed specimens were buried horizontally within 4 cm of ASW-saturated sediment and flooded with an overlying layer of ASW (Supplementary Material, Fig. S1); individual plastic containers were closed with rubber-sealed lids for the duration of the experiments, substantially restricting oxygen availability. A sediment-free control for each taxon was also run. Where possible, the pH, oxygen concentration, and major ion concentrations of both the ASW and sediment were measured at the beginning and end of the experiments (Cranwell CR-95 digital pH meter, Jenway model 970 digital DO meter, Varian Vista Axial Inductively Coupled Plasma–Optical Emission Spectrophotometer).

After 4 months (17 weeks) the containers were opened (Supplementary Material, Figs. S2, S3), the overlying ASW was siphoned off, and the sediments were dried by continuous airflow in a laboratory fume cupboard. The carcasses were then exposed by scraping away the overlying sediments. Following qualitative assessment of the remains (Supplementary Material, Table S1), the carbonaceous residues were carefully collected and cleaned of adhering sediment via a sequence of rinsing (on a 63-μm sieve with distilled water), ultrasonication (30 seconds in distilled water), and rotary tumbling (24 hours in distilled water + Calgon defloculant). This procedure also served as a general measure of cuticle integrity. Where morphologically intact structures remained at the end of this process (i.e., Nereis in kaolinite), these were further prepared for scanning electron microscopy (SEM) and histological sectioning.

The cleaned organic residues were dried, powdered, and chemically analyzed for (1) non–water-soluble protein, (2) chitin, (3) water-soluble protein, (4) carbohydrate, and (5) phospholipid, using the various hydrolysis and colorimetric techniques employed by Briggs and Kear (1993). As a result of the obscuring effects of the sediment it was not possible to document absolute amounts, so these data have been recorded as concentrations of both the ASW and sediment were measured at the beginning and end of the experiments (Cranwell CR-95 digital pH meter, Jenway model 970 digital DO meter, Varian Vista Axial Inductively Coupled Plasma–Optical Emission Spectrophotometer).

RESULTS

Sediment mineralogy had a pronounced effect on the preservation of primary anatomical features in both Nereis and Crangon, but with marked taxonomic differences. In Nereis (Figs. 1, 2), both the sediment-free control and the montmorillonite treatment yielded only chaetae and jaws (Stage 5; Supplementary Material, Table S1), whereas the calcite-hosted and quartz-hosted specimens also preserved thin collagenous remains of the original integument (Stages 4 and 4/3, respectively). By far the most substantial effect, however, was with the kaolinite-hosted worms, where flattened but otherwise complete integuments were recovered, including well-preserved segmentation, parapodia, palps, tentacular cirri, and, in one instance, the gut (Stage 2). These kaolinite-hosted remains were sufficiently robust to allow the extraction of entire worm cuticles, and for dissected portions to withstand both extended tumbling and preparation for stained sections and SEM (Figs. 1A–2). In carbonate- and montmorillonite-hosted Nereis there was a conspicuous development of carcass-associated carbonate mineralization which was not observed in kaolinite or quartz. Montmorillonite-hosted specimens typically failed to collapse in concert with the decay of soft tissues, resulting in a three-dimensional void.

For Crangon (Fig. 3), none of the sediment types substantially enhanced anatomical preservation relative to the ASW control, although it is notable that the control itself preserved a significant degree of articulated cuticle (Stage 3, Supplementary Material, Table S1). As with Nereis, it was the kaolinite system that preserved the greatest level of anatomical detail (Stage 3), whereas calcite and quartz appear to have accelerated decay (Stage 4). In montmorillonite, Crangon typically occurred as thin cuticular films adhering to uncollapsed sedimentary matrix, along with significant accumulations of a pinkish-white mineral within the body cavity—probably calcium phosphate (cf. Briggs and Kear 1994a). Although equivalent to Stage 3 or better in some respects (e.g., the robustly preserved tail fan), the overall quality of Crangon preservation in montmorillonite was substantially lower than its counterparts in kaolinite, calcite, and ASW. Crangon in quartz also resulted in a three-dimensional void, but this was not accompanied by the pronounced mineralization associated with montmorillonite. None of the Crangon treatments yielded coherent cuticle following the cleaning/tumbling procedure.

The distinctive morphological expression of the variously treated carcasses was reflected in their residual chemical composition (Fig. 4). In both taxa, for example, it was the kaolinite system that preserved the highest percentage of protein—though once again there was no measurable difference between Crangon in kaolinite and its ASW control. Indeed, the protein:chitin:carbohydrate ratios of Crangon were not substantially altered in any of the sediment treatments, apart from modest increases in the chitin content (at the expense of protein) in quartz, montmorillonite, and calcite.

By contrast, sediment mineralogy had a profound effect on the chemical composition of the Nereis residues (Fig. 4). In kaolinite the percentage of preserved protein was twice that of the ASW control (including a significant occurrence of otherwise-unpreserved water-soluble protein) whereas in quartz and montmorillonite it was less than half. The balance was met almost exclusively by chitin, with kaolinite-hosted...
specimens represented by ~12% chitin, compared to ~75% for those in quartz and montmorillonite. The Nereis-quartz and Crangon-kaolinite experiments also preserved a small amount of phospholipid.

The differing treatments also had idiosyncratic effects on whole-system chemistry (Tables 1, 2). Most conspicuously, the addition of kaolinite induced a significant drop in pH relative to all other treatments, though only in Nereis was this maintained to the end of the 4-month experiment. As expected, the oxygen content of the sediments and overlying ASW declined in all of the decay experiments; however, the residual oxygen levels were substantially lower in quartz and montmorillonite than in kaolinite or carbonate. Oxygen drawdown in kaolinite- and carbonate-hosted Crangon was less than half of that in corresponding treatments of Nereis (possibly a function of differing carcass:sediment ratios, which were not quantitatively monitored), but within the Nereis experiments the least drawdown occurred in kaolinite.

In terms of major ion chemistry (of the overlying ASW), there was little systematic change in the concentrations of Cl, Na, Mg, or K over the course of the experiments, apart from marked loss of Mg in the two carbonate treatments (Table 2). By contrast, Ca concentrations declined significantly in sediment-free and carbonate-hosted Nereis, while increasing for the equivalent conditions with Crangon—and increasing regardless of carcass identity in kaolinite. Sulfur concentrations declined substantially in the carbonate and quartz treatments of both taxa but rose in the two kaolinite experiments. Results for montmorillonite were not available because of its complete absorption of the overlying ASW during the course of the experiments (see Supplementary Material, Fig. S3).

Despite the localized species effects, the different sediments exhibited broadly characteristic responses to carcass degradation. In quartz, for example, both Nereis and Crangon produced a permeating black exudate that gradually dissipated over the course of the experiment (Supplementary Material, Figs. S2–S4), whereas localized “black stains” developed in the vicinity of montmorillonite-hosted carcasses (more conspicuously in Nereis than in Crangon; Supplementary Material, Fig. S3). In calcite, all of the associated sediments turned pale gray within the first few weeks (more conspicuously in Nereis than in Crangon), but eventually returned to their original white color (by week 13 for Nereis and by week 17 for Crangon). Neither of the kaolinite treatments exhibited any color changes, though both developed thick floating fungal colonies by the end of the experiment (Supplementary Material, Fig. S3). Nonfungal biofilms formed in both of the quartz treatments and the ASW controls...
more conspicuously in Nereis than in Crangon); there was no obvious microbial growth in the montmorillonite or calcite treatments (Supplementary Material, Fig. S3).

**DISCUSSION**

The incorporation of sediment into laboratory decay experiments sheds fundamental new light onto taphonomic pathways, if only because all fossils form within some sort of sedimentary matrix. At the same time, however, this actualistic approach adds significant new levels of diagenetic and logistic complexity, not least of which involves the challenge of recovering quantitative data from sediment-bound residues while also monitoring the qualitative effects of sediment on carcass morphology (cf. Plotnick 1986; Allison 1988; Martin et al. 2004; Darroch et al. 2012). The compounding diagenetic feedbacks between carcasses and sedimentary matrix also make it difficult to resolve underlying mechanisms, though our experimental results introduce some intriguing possibilities.

**FIG. 2.—Exhumed Crangon remains after 17 weeks in A) kaolinite, B) calcite, C) quartz, and D) montmorillonite. A’–D’ are the corresponding isolated remains following a screen rinse, ultrasonic bath, and 24 hours of aqueous tumbling. Scale bar in A equals 5 mm for A–D and 8 mm for A’–D’.
Sediment Effects on the Preservation of Carbonaceous Fossils

These experiments demonstrate that sediment mineralogy can have profound effects—both positive and negative—on the morphological preservation of interred carcasses. Such taphonomic realignment is hardly surprising given the well-documented influence of mineralogy on the preservation of sedimentary organic carbon in general (Theng 1979; Ransom et al. 1998; Lützow et al. 2006; Ziervogel et al. 2007; Wu et al. 2012) and, indeed, the preferential occurrence of carbonaceous compression fossils and microfossils in siliciclastic (vs. carbonate-rich) mudstones. Curiously, however, it was the kaolinite system that induced the most pronounced positive effects on carcass preservation, despite the modest physicochemical properties of this 1:1 layer clay. By contrast, montmorillonite—an expanding 2:1 layer clay with exceptionally high surface area, cation exchange capacity, and potential to suppress enzymatic activity (Theng 1979; Butterfield 1990, 1995)—conspicuously accelerated decay.

In addition to sediment mineralogy, it is clear that the chemistry and histology of the interred carcasses also influence taphonomic trajectories. In the present experiments, for example, the most pronounced effects of sediment on preservation potential (both positive and negative) were associated with relatively labile collagen-based polychaete cuticle, whereas the more recalcitrant chitin-based arthropod cuticle exhibited only modest differences relative to the sediment-free control. Such behavior is broadly analogous to the enhanced susceptibility of exceptionally labile (i.e., chemically reactive) tissues to early diagenetic mineralization (Butterfield 2002, 2003). Insofar as Nereis cuticle in kaolinite ended up more robustly preserved than Crangon cuticle under any of the experimental conditions, its recalcitrance was clearly acquired secondarily, a product of early diagenetic interaction with its sedimentary matrix.

Sediment-induced changes in morphological preservation potential also correlate with the chemistry of fossil residues, though not necessarily in a straightforward fashion. For Nereis in kaolinite and montmorillonite, the quality of cuticle preservation varied directly with the percentage of preserved protein, suggesting a novel possibility for the formation of carbonaceous compression fossils: rather than structural polysaccharides such as chitin and cellulose, the key ingredients might well be proteinaceous. Even so, Nereis cuticle was also relatively well preserved in quartz, which exhibited the lowest overall levels of protein and the highest levels of chitin.

Taphonomic Pathways

At a minimum, the extended preservation of carbonaceous substrates requires the suppression of aerobic heterotrophs, typically through the removal or exclusion of free oxygen. The marked drawdown of oxygen in all of the experiments (Table 1) can be ascribed to the early aerobic decay of the carcasses and is presumably a primer for subsequent carbonaceous preservation. Even so, the substantially lower levels of oxygen in the montmorillonite and quartz treatments demonstrate that morphological preservation is not solely a function of limited oxygen. Indeed, the degree of oxygen drawdown—along with the production of significant black exudates (Supplementary Material, Figs. S2–S4)—may simply reflect the extent of initial carcass decay. For Nereis in kaolinite and Crangon in both kaolinite and calcite, the relatively high concentrations of residual oxygen (at or above the 18% level at which decomposition begins to be oxygen-limited; see Briggs and Kear [1993]) point to preservational mechanisms other than anoxia—possibly even a requirement for molecular oxygen (see below).

The lack of correspondence between grain size and morphological preservation suggests that sediment permeability was not a primary factor in the preservation of carbonaceous films. Whereas the demonstrably permeable quartz and calcite systems (evinced by uniform changes in sediment color) yielded significant organic residues, the much finer-grained, relatively impermeable montmorillonite treatments (with localized black stains; Supplementary Material, Fig. S3) exhibited the poorest...
overall quality of preserved cuticle. These closed conditions, however, corresponded conspicuously with mineral precipitation, especially within the body cavity of *Crangon* (Fig. 2D), suggesting that sediment sealing may be essential for fossilization via early diagenetic mineralization (cf. Briggs and Kear 1994a; Gaines et al. 2012).

Given the marked effect of sediment mineralogy on carbonaceous preservation, there is a case to be made for differential adsorption of degradative enzymes on mineral surfaces (Butterfield 1990, 1995). As originally formulated, this enzyme suppression model focused on the high specific surface areas and high cation exchange capacity of expanding clays such as montmorillonite. These properties clearly failed to enhance preservation in the current experiments, in which the greatest (positive) response was associated with the relatively low surface area and cation exchange capacity of kaolinite. It is possible, however, that enzyme adsorption on montmorillonite accounts for at least some of the observed pattern, acting not so much to suppress the activity of degradative exoenzymes as to stabilize them, thereby extending their effective lifespans (Ziervogel et al. 2007). Such preservational effects conceivably account for the accelerated decay of sediment-associated carcasses documented by Plotnick (1986); Allison (1988); and Briggs and Kear (1993).

The particular mechanisms by which sediments enhance the preservation of labile organic compounds remain poorly understood, but substrate protection/stabilization—as opposed to enzyme suppression—appears to be the primary control in both soils (Lützow et al. 2006; Mikutta et al. 2006) and marine sediments (Ransom et al. 1998; Satterberg et al. 2003; Arnarson and Keil 2005; Ziervogel et al. 2007). Sediment mineralogy is recognized as a key factor in such stabilization, but so too is the chemical structure of the substrate, pH, the isoelectric points of the sediment and substrate, availability of floc-inducing multivalent cations, and organic loading. Aluminum and iron oxides have a particularly high capacity for preserving organic carbon, as do allophane-rich volcanic soils. At least some kaolinitic soils have greater capacity for stabilizing organic matter than do montmorillonite soils, possibly as a result of enhanced ligand adsorption on the broken edge surfaces of kaolinite at low pH (Bruun et al. 2010).

One of the problems in adapting models of organic preservation from soil science and organic geochemistry to paleontology is that they do not obviously address the issue of morphological preservation; i.e., stabilization of carbonaceous substrates at a sufficiently early stage to capture anatomical form. Especially for macroscopic compression fossils, the processes responsible for preserving morphological organic carbon are unlikely to be the same as those acting on total organic carbon (TOC). In the present experiments, for example, there is no particular reason to assume that the montmorillonite treatments preserved less TOC than did kaolinite—only that macromolecular structures were more readily broken down into smaller migration-prone compounds (with a corresponding loss of morphology but enhanced likelihood of mineral adsorption and amorphous recondensation [Lützow et al. 2006; Wu et al. 2012]). The lack

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**FIG. 4.**—Chemical composition of *Nereis* and *Crangon* remains after 4 months of burial in differing sediment mineralogies and the control. ASW = artificial seawater; Kao = kaolinite; Calc = calcite; Qtz = quartz; and Mont = montmorillonite.

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**TABLE 1.**—*pH* and oxygen concentration of the sediment and overlying artificial seawater (ASW) at the end of the taphonomic experiments (initial values in parentheses). Note the low *pH* values associated with kaolinite (*) and *Nereis* (**) . No final values are available for montmorillonite as a result of its complete absorption of the ASW.

|                | pH–Sediment | pH–ASW | O₂%–Sediment | O₂%–ASW |
|----------------|-------------|--------|--------------|---------|
| N-ASW          | NA          | 8.6    | NA           | 41 (75) |
| N-Kao          | 4.77** (4.71*) | 5.1** (4.8) | 17 (47) | 28 (75) |
| N-Calc         | 7.31 (7.48) | 7.2 (8.4) | 10 (53) | 28 (75) |
| N-Qtz          | 7.80 (7.06) | 7.8 (8.4) | 4 (39) | 10 (75) |
| N-Mont         | 6.24 (8.92) | NA (8.4) | 8 (65) | NA (75) |
| C-ASW          | NA          | 6.7 (8.4) | NA           | 48 (75) |
| C-Kao          | 7.34 (3.78*) | 7.2 (8.4) | 29 (48) | 22 (75) |
| C-Calc         | 7.31 (7.48) | 7.3 (8.4) | 30 (53) | 54 (75) |
| C-Qtz          | 8.17 (6.95) | 8.3 (8.4) | 11 (36) | 53 (75) |
| C-Mont         | 6.22 (8.44) | NA (8.4) | 7 (42) | NA (75) |

N = *Nereis*; C = *Crangon*; Kao = kaolinite; Calc = calcite; Qtz = quartz; Mont = montmorillonite; NA = not available.
of color change in the kaolinite systems suggests that significantly less structural material was degraded and dispersed at the outset.

The circumstances leading to the exceptional preservation of *Nereis* in kaolinite (Figs. 1, 2) clearly interfered with normal decay processes at a very early stage, but the phenomenon cannot be explained simply in terms of reduced rates or temporary suspension. Despite the morphological fidelity, the exhumed remains are constitutionally and chemically distinct from the original carcasses; only cuticular structures remain, and these exhibit none of their original susceptibility to decomposition in water (Fig. 1A). Partial decay will, of course, change the chemistry of any substrate, and Gupta et al. (2009) have demonstrated that lipids can contribute to the polymerization of decaying tissues within weeks of death. Such alteration, however, rarely leads to the morphological preservation of carbonaceous substrates, at least in the absence of an external fixing agent.

**Taphonomic Tanning—A Hypothesis**

One of the most common means of enhancing the recalcitrance of organic substrates is through tanning, a process involving the secondary cross-linking of structural biomolecules. Tanning occurs biologically, where it determines the primary recalcitrance of particular substrates such as polychaete chaetae, arthropod cuticle, and hard keratin in vertebrates, but it can also be induced abiotically via external tanning agents. In the leather industry, collagen-based hides are tanned using mineral salts (e.g., chromium sulfate, aluminum sulfate) or polyphenolic vegetable tannins, though there is a range of alternative tanning agents, including multivalent Fe, Zr, Ti, and Si, polyphosphates, and various aluminosilicate minerals (Kanagy and Kronstadt 1943; Covington 1997; Hueffer et al. 2010); in at least one patented process, the agent is derived from kaolinite (Plapper et al. 1981). Under particular circumstances, postmortem tanning can also take place naturally. In the case of recent tanned cadavers, for example, the exceptional preservation of external morphology appears to be related to salty, marine-influenced groundwater and conspicuously sticky soil (Ruwanpura and Warushahennadi 2009). By contrast, the tanning agent responsible for the selective preservation of skin and keratin in medieval peat bogs has been identified as a carbonyl-rich polysaccharide (sphagnan), facilitated by a suppression of exoenzymes at moderately low pH (Painter 1991).

Reduced pH also appears to have been a significant factor in the postmortem stabilization of *Nereis* cuticle in kaolinite (Table 1), likely induced by the high proportion of reactive crystal edges and low cation exchange capacity of the clay component (Tombácz and Szekeres 2006), but also by the effects of incorporated organic acids and CO₂ (e.g., Hutcheon et al. 1993). It is possible that the preservation effects were due entirely to such pickling, though this fails to explain the histological selectivity, focused exclusively on structural cuticle (cf. Painter 1991). Moreover, the 4.7 to 5.1 pH of the *Nereis*-kaolinite system is well above levels that interfere with anaerobic fermentation or bacterial sulfate reduction (Painter 1991; Fauville et al. 2004). The preferential and exceptional preservation of collagenous cuticle in kaolinite suggests a significant level of secondary, diagenetically induced tanning (alongside the biologically tanned chaetae and jaws).

In industrial tanning, an initial pickling phase is necessary to reduce the rate of collagen cross-linking and to enhance the penetration of tanning agent, while background ionic concentrations (salts) limit osmotic swelling and deformation; controlling the balance between substrate reactivity, penetrability, and (morphological) integrity is key to the tanner’s art (Covington 1997). The same situation is likely to hold for taphonomic tanning, in which the interplay of degrading carcasses and sedimentary matrix determines the progress of secondary cross-linking and, ultimately, the quality of a potential carbonaceous compression fossil. In the case of the *Nereis*-kaolinite experiment, we suggest that the enhanced preservation was controlled by the presence of a sediment-derived (presumably Al-based) tanning agent combined with a particularly favorable compliment of ion concentrations and pH trajectory (cf. Naimark et al. 2013). The proclivity of organic material to concentrate environmental Al under acidic conditions (Mulholland et al. 1987) may have been a significant factor in this process.

Kaolinite-based tanning clearly cannot account for all instances of enhanced preservation, since *Nereis* carcasses in both quartz and carbonate also survived substantially better than does the sediment-free control. Nor is tanning necessarily the only contributing process: given the relatively elevated S and O₂ concentrations associated with the kaolinite experiments (Tables 1, 2), it is possible that disulfide bonding (via the oxidation of sulfhydryl groups) might also have contributed to the stabilization of morphology-defining proteins (cf. Visschers and de Jongh 2005). If so, then localized availability of free oxygen might be a critical factor in fossil preservation, just as it is for the (primary) cross-linking of hard keratins (Greenberg and Fudge 2013).

**Implications for BST Preservation**

Burgess Shale-type preservation is a loosely defined taphonomic mode characterized by the exceptional preservation of carbonaceous compression fossils in marine shales (Butterfield 1995; Gaines et al. 2008). Much of the BST fossil record derives from biologically tanned structures such as arthropod cuticle and polychaete chaetae, which tend to be sharply, if not always robustly, preserved. Not surprisingly, the situation with biologically untanned integument is much more variable. Polychaete

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**Table 2.** Major ion concentration (in ppm) of the overlying artificial seawater (ASW) at the beginning and end of the taphonomic experiments. Note the contrasting effects of carcass type on Ca (in ASW [*] and calcite [**]) and the generally elevated S in kaolinite [***]. No final values are available for montmorillonite as a result of its complete absorption of the ASW.

|                | Cl  | Na  | Mg  | K   | Ca  | S   |
|----------------|-----|-----|-----|-----|-----|-----|
| Initial ASW    | 14,137 | 8769 | 1053 | 329 | 296 | 242 |
| N-ASW          | 14,949 | 8020 | 927  | 362 | 51* | 234 |
| N-Kao          | 13,066 | 8294 | 977  | 384 | 394 | 291***|
| N-Calc         | 15,758 | 8425 | 484  | 410 | 76**| 98  |
| N-Qtz          | 14,275 | 7821 | 353  | 153 | NA  | NA  |
| N-Mont         | NA   | NA  | NA   | NA  | NA  | NA  |
| C-ASW          | 11,924 | 8313 | 999  | 335 | 415*| 234 |
| C-Kao          | 12,765 | 8437 | 341  | 548 | 98  | 290***|
| C-Calc         | 12,767 | 8636 | 355  | 1113**| 150|
| C-Qtz          | 15,106 | 8112 | 349  | 176 | NA  | NA  |
| C-Mont         | NA   | NA  | NA   | NA  | NA  | NA  |

N = *Nereis*; C = *Crangon*; Kao = kaolinite; Calc = calcite; Qtz = quartz; Mont = montmorillonite; NA = not available.
cuticle in the Burgess Shale, for example, sometimes exhibits exquisite levels of anatomical detail but is usually less precisely preserved (Conway Morris 1979), typically appearing more like _Nereis_ in quartz (Fig. 1C) than like _Nereis_ in kaolinite (Fig. 1A); in many Burgess Shale specimens segmentation is only recognizable through the preservation of segmentally disposed chaetae. Such variability points to complex diagenetically and phylogenetically sensitive taphonomic pathways, consistent with a diagenetic tanning mechanism.

The potential for secondarily tanned structures to taphonomically outperform inherently more recalcitrant structures is demonstrated in BST biotas by the common preservation of carbonaceous gut structures (Wilson 2006); indeed, it is the exceptionally thin (i.e., more tenuously preserved) nature of most arthropod cuticle (Orr et al. 2009) that reveals this internal anatomy. By contrast, secondarily tanned structures tend to be much more uniformly expressed and can be exceptionally thick and/or reflective, as in the case of _Eldonia_ guts (Butterfield 1996). A similar, highly reflective style of carbonaceous preservation occurs in the stem-group chordate _Pikaia_ (Butterfield 1990, 2003; Briggs and Kears 1994b; Conway Morris and Caron 2012), which might also be ascribed to the taphonomic tanning of a collagen-based integument.

The recognition of secondary, diagenetically induced shifts in preservation potential also has important implications for interpreting the histological and phylogenetic affiliations of problematic BST fossils (Butterfield 2003). By selectively enhancing the preservation potential of more labile substrates, early diagenetic tanning—like early diagenetic mineralization—undermines assumptions of tapho-anatomical ordering based on sediment-free degradation experiments (e.g., Allison 1988; Briggs and Kears 1993, 1994a; Sansom et al. 2010). At the other end of the scale, sediment mineralogy has the potential to accelerate the degradation of inherently more recalcitrant substrates; e.g., _Crangon_ in montmorillonite, but also notable in soils, where lignin commonly degrades more rapidly than sediment-stabilized polysaccharides and proteins (Lützow et al. 2006; Mikutta et al. 2006; Schmidt et al. 2011). Unfortunately, the complex interplay of original histology and early diagenesis precludes most broad-scale generalizations.

Despite the idiosyncratic nature of exceptional preservation, the distinctive expression of BST biotas and corresponding small carbonaceous fossils through the Cambrian and Early Ordovician suggests a broadly comparable diagenetic context (Butterfield 1995, 2003; Van Roy et al. 2010; Butterfield and Harvey 2012). In light of the present experiments, secular changes in the average clay mineralogy and ocean chemistry are likely to have been significant factors in the opening and closing of this taphonomic window. Intriguingly, oceanic pH is estimated to have been at its Phanerozoic minimum during the early Paleozoic (Arvidson et al. 2013), coincident with the interval of enhanced BST preservation. Elevated kaolinite input may well have played a role but is difficult to demonstrate in particular BST settings because of instances due to secondary alteration of original clay minerals (cf. Powell 2003; Forchielli et al. 2013).

At a broader scale, there is a conspicuous correlation between BST preservation and a Cambro–Ordovician spike in the occurrence of anomalously shallow-water glauconite (see Brasier 1980; Chafetz and Petrovitch 2001). As a product of early diagenesis, glauconite does not represent the original mineralogy of incoming aluminosilicates and may not itself be the cause of early Paleozoic shifts in preservation potential. Many Cretaceous greensands, for example, appear to be derived from volcanic sources (Jeans et al. 1982), and it is clear that glauconite forms from a wide range of precursor minerals, including kaolinite (Mennier and El Albani 2007). Evidence of intense, large-scale continental weathering through the Cambro–Ordovician interval (Avigad et al. 2005; Peters and Gaines 2012) implies significant inputs of Al-rich clays to the global oceans at this time, potentially contributing to both the spike in both shallow-water glauconite and BST preservation.

**CONCLUSION**

Entry into the body fossil record requires that carcasses, or components of carcasses, survive their individual taphonomic thresholds. For _Nereis_-type polychaete cuticle this means disrupting the normal course of decomposition within the first 2 to 4 weeks, and for _Crangon_-type arthropod cuticle, it means disrupting the course within 25+ weeks (Allison 1988; Briggs and Kears 1993, 1994a). Our experimental results indicate that this can be readily achieved with burial in sediments of particular mineralogies—provided the accompanying histologies and pore-water chemistries are all suitably aligned. The sensitivity of such systems to local circumstance suggests that exceptional BST preservation is likely to be the exception, even where conditions are generally favorable (such as in the low-pH, glauconite-prone oceans of the early Paleozoic)—hence, the vast volumes of unoxidized marine mudstones lacking any hint of BST fossils. Conversely, the identification of first-order effects of sediment mineralogy on the preservation potential of carbonaceous substrates offers an explanatory mechanism for fossilization, even under seemingly suboptimal conditions, such as the surprisingly common occurrence of well-defined leaf compression–impression fossils in coarse-grained sandstones (see Krishtofovich [1944]).

The other critical factor is the carcasses themselves. Some tissues are inherently more recalcitrant than others, but their potential for fossilization depends on the interplay of particular organic substrates and their early diagenetic conditions. Despite the conventional focus on biologically tanned chitinous cuticle, exceptional BST preservation may owe more to the secondary tanability of more labile substrates, particularly proteins. Given the marked sensitivity of this phenomenon to local circumstance, perhaps the most remarkable aspect of BST preservation is its capacity to capture such a range of histological and phylogenetic diversity in localized Lagerstätten.

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