SILICIFICATION

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ABSTRACT.—Silicification is the replacement of original skeletal material accomplished through the concurrent dissolution of calcium carbonate and precipitation of silica. The processes is aided by the nucleation of silica to organic matter which surrounds the mineral crystallites within the shell. Factors that control silicification are those that influence the dissolution/precipitation process: shell mineralogy, shell ultrastructure (and, therefore, surface area), the amount and location of organic matter, and the character of the enclosing matrix. Silicification, like all types of fossilization, can produce taphonomic biases: it is far more common in Paleozoic than younger deposits, is more likely to occur in organisms with low-magnesium calcite shells, in carbonate sediments, and in environments with elevated dissolved silica.

INTRODUCTION

Silica—dissolved, and as amorphous or microquartz (opal, chalcendony, and microcrystalline quartz phases), and crystalline megaquartz—is a common component in sediments, and is found in solution and as nodules, cements, and clastic material. Fossilization involving silica occurs by three methods: permineralization, entombment, and replacement. Permineralization is the precipitation of silica within the natural cavities of porous materials, such as wood and bone, from silica-enriched percolating fluids. Silica entombment mainly occurs in hydrothermal settings by precipitation of silica on the external surfaces of organic objects. Silica can precipitate in molds created by dissolution, but replacement, or silicification *sensu strictu*, is the concurrent dissolution of original skeleton material and precipitation of silica: this is the primary focus of this paper. Silica replacement affects shells at the exclusion of the matrix, indicating an organismal genesis of the process. It was suggested in Newell et al. (1953, p. 173), one of the first discussions of skeletal silica replacement in the literature, that shells were "for some unknown reason, centers of acidification, while the surrounding matrix remained at a higher pH level."

Silicified fossils are ideal for taxonomic studies because they can be extracted without damage using acids (hydrochloric or acetic). However, care must be taken with diversity and paleoecological studies because silicification, except in rare occurrences, introduces a taphonomic bias. Silicification is biased by the organism itself (composition, texture, and organic content of the shell) and by local depositional controls (matrix and pore-water geochemistry). There is a temporal pattern of silicification—it is more common in Paleozoic rocks than younger rocks—but it is also strongly linked to local factors (i.e., high dissolved silica levels associated with volcanic deposits). Linking that pattern to environmental factors is problematic, but the decline in post-Paleozoic silicification can be linked to a shift in the proportion of calcitic to aragonitic marine organisms.

Exceptional preservation with silica replacement is concurrent with degradation of organic matter, which creates the active sites necessary for silica nucleation and provides the framework to preserve the ultrastructure of skeletal material. The presence and location of organic matter and the solubility of the mineral phase—factors that are controlled taxonomically—would have the greatest impact on the propensity for and fidelity of replacement, assuming a sufficient source of dissolved silica is present. Recent experimental permineralization of wood (Akahane et al., 2004; Ballhaus et al., 2012) gives tremendous insight to the process and geochemical controls that can be applied to the study of silicification in skeletal material.

Silicified fossils are fairly common and are found worldwide in rocks of all ages.

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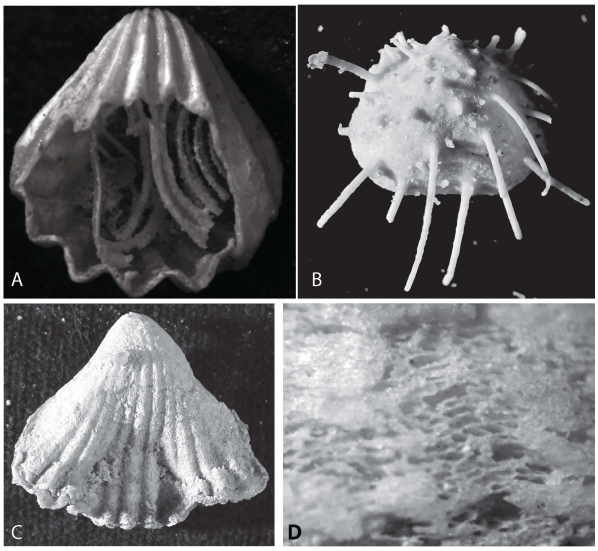

FIGURE *1*.—Examples of silicification from the Permian of West Texas. A) *Hustedia* sp. (YPM. 175528), showing silicified spiralium. B) Juvenile *Echinaurus* sp. (YPM.205721). C, D) *Stenocisma* sp. (YPM.205615); (C) exhibiting partial silicification; (D) magnification of the umbonal region showing polygonal structures interpreted to be silicified organic sheaths surrounding the (dissolved) crystallite. All specimens from the Yale Paleontology Museum, Division of Invertebrate Paleontology.

Silicification controls are more critical on a local scale than a regional or temporal scale.

Perhaps the most well-known of all silicified fossils (Figure 1) are those of the Permian basins of West Texas (especially the Midland and Delaware basins), studied extensively by Newell, Cooper, and Grant in the Guadalupe Mountains, Glass Mountains, and adjacent ranges (Newell et al., 1953; Cooper and Grant, 1972). The silicification process was discussed in Newell et al. (1953) and Cooper and Grant (1972). Newell et al. (1953) described the variation in silicification, stating that most of the silicification is 'spongy and fragile' (partial) and 'hollow' (non-pervasive) (parentheses use terminology of Butts and Briggs, 2011; a scheme for descriptive characterization of silicification can be found therein). Many exhibit beekite rings, concentric rings of silica that likely form in times of limited or fluctuating silica supply. Specimens appear to be perfectly preserved to the naked eye, but when examined in petrographic thin sections and under SEM, the silicification in the Glass Mountains material is of relatively low fidelity. Except in rare occurrences when silicification is partial, shells of brachiopods and bivalves lack ultrastructural detail due to the neomorphism of silica to megacrystalline quartz.

Many of the well-known silicified faunas were deposited in tectonically active basins associated with ash-producing volcanism, an association that has been discussed peripherally in papers on silicified faunas and chert. In New York, the upper Silurian to Devonian Acadian foreland basins (Ver Straeten, 2009) have silicified fossils in rocks containing tephras of clay-rich K-bentonites (Ver Straeten, 2009). The Antler orogeny and associated volcanism correlates to silicified faunas in the Carboniferous of Idaho, Montana, and Wyoming (Schmitt and Boyd, 1981; Daley and Boyd, 1996; Butts, 2007). In Gotland, Sweden, Silurian silicification has been ascribed to volcanism (tuffs, lava, rhyolites) in the Caledonian geosyncline (Laufield and Jeppsson, 1976). Laufield and Jeppsson (1976) discussed the publication history of occurrences of altered volcanic ash layers in association with silicified beds. K-bentonites are also prevalent in the Permian basins of West Texas (Nicklen, 2003) where silicified faunas are common.

Silicification has the ability to provide a high-fidelity snapshot of life on Earth when it is pervasive. For example, beds in the Silurian of Gotland, with complete infiltration of matrix and taxa with chert, record diversity with exceptional clarity (Laufield and Jeppsson, 1976). Records of bias are scattered throughout the literature in notes on preservation in taxonomic treatments of faunas, but are often anecdotal, rather than statistical. The accounts can be parsed into two main categories: taxonomically and lithologically induced bias. Sometimes, both factors play a role in susceptibility to silicification (Newell et al., 1953; Butts, 2007). Examining the bias recorded in the fossil record allows for interpretation of how the controls may have operated.

EXTRACTION AND PREPARATION

Extraction of silicified faunas is a simple process that requires few resources and one cubic foot of rock may provide thousands of exceptionally preserved fossils. Large blocks of rock can be etched and fossils freed of matrix using hydrochloric acid (15% or lower) or acetic acid, using safety precautions for strong acids. First, one face of the rock that is to be used as a base is painted with latex paint, which is acid-resistant and allows the block to acidize from the sides and top only to prevent crushing of specimens as

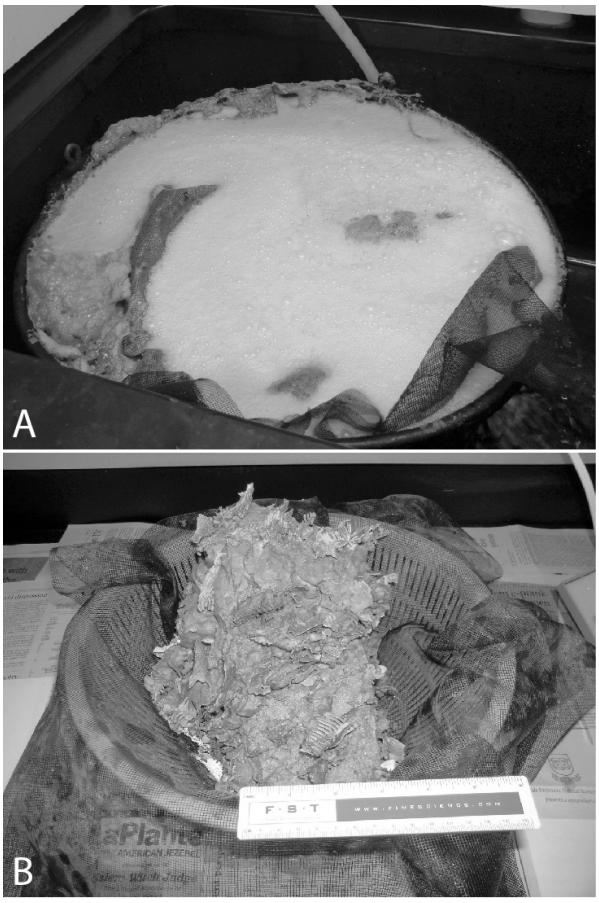

FIGURE 2.—Processing of silicified fossils using hydrochloric acid. A) Immersion of rock into acid bath. B) Fossil residue on screen in colander after acid etching is complete.

matrix is removed. The rock is placed painted-side down on a nylon window screen and inserted in a bucket with drainage holes (or into a sieve or colander), then immersed in an acid bath (Fig. 2A). Occasionally, a rock requires very gentle shaking if the rock contains fine-grained siliciclastic material or dolomitized matrix. After the rock is digested, the acid bath is replaced with gently flowing water and rinsed for several hours. The bucket, sieve, or colander is extracted (Fig. 2B), and the screen is very gently lifted and spread out on a table by two people holding the corners. Live-insect forceps are used to pick specimens. More elaborate contraptions for acid etching and storage of individual specimens are described in Cooper and Grant (1972).

In thin section, silicified skeletal material is best observed under crossed nicols with insertion of the first-order red (gypsum) plate (Scholle and Ulmer-Scholle, 2003). As the stage is rotated, carbonate changes between first-order white and purple, while quartz (generally as cryptocrystalline chalcedony that has replaced the skeletal fabric) alternates between first-order red, yellow, and blue (Daley, 1987).

SILICIFICATION CONTROLS AND BIASES

A simplified process for silicification involves the concurrent dissolution of calcium carbonate and precipitation of silica. These processes are controlled intrinsically and extrinsically by taxonomic and lithologic conditions that affect the rate of organism decay and dissolution of skeletal material, and the precipitation of silica (see Butts and Briggs, 2011). Early diagenetic chert deposits of the Proterozoic were dictated by sediment permeability, silica availability, and concentration of organic matter (Knoll, 1985) and these criteria are the main sedimentary controls on silicification through the Phanerozoic. A taphonomic bias can be introduced in the process, but the dearth of studies devoted to silica replacement (as opposed to brief mentions in taxonomy, sedimentology, or paleoecology papers) allows for conjectural interpretation of how the controls lead to biases.

Taxonomic controls and biases

Organismal control of silicification is evident in the simple fact that silicified fossils can be found in otherwise unaltered rocks. Silicification can vary by taxon, presenting a significant bias in interpretation of fossils. Marine organisms have a range of skeletal mineralogies, bound together by varying amounts of organic matrix, in a range of ultrastructural configurations that create the skeletal component of the organism. These three factors (mineralogy, distribution of organic matter, and ultrastructure) are the taxonomic controls on the dissolution of calcium carbonate and precipitation in silica.

Shell mineralogy.—The rate and conditions for dissolution of carbonate are well known (Walter, 1983, 1985; Walter and Morse, 1984, 1985). There are three common biogenic carbonate phases: high-magnesium calcite (HMC >8.5 mol% $MgCO_3$), low-magnesium calcite (LMC <4 mol% $MgCO_3$), and aragonite (Chave, 1954a). Skeletal mineralogy is taxonomically controlled, and organisms may be constructed of more than one type of mineral. There are additional variations in the ion content based on latitude (Chave, 1954a), position within the shell (Buening and Carlson, 1992), and the ambient sea water (Stanley and Hardie, 1998). Dissolution is

affected by the stability of the calcite phase, the saturation state of the pore water solution, and the reactive surface area of the shell (review in Morse, 1983; Walter, 1985). Solubility is influenced by variations in seawater Mg/Ca, and the relative solubility of these phases has varied through time (Ries, 2010; references therein). HMC is more stable than LMC, which is more stable than aragonite in seawater with a Recent Mg/Ca ratio (Chave et al. 1962; Berner, 1975), although in some studies, HMC and aragonite dissolution rates are equivalent (Berner et al., 1976; Walter and Morse, 1985). The crystallography of aragonite, a calcite polymorph, is influenced by the minor presence of large cations, notably Mg (Folk, 1974). It is stable at higher pressures and lower temperatures than calcite, but is less stable at atmospheric conditions, and neomorphoses to more stable calcite (Klein et al., 1993), making it increasingly less common in rocks of increasing age (Land, 1967). However, original aragonite is known in shells as old as Devonian, and aragonite preservation is ubiquitous in some Paleozoic units (e.g., the Upper Carboniferous Breathitt Formation of Kentucky; Brand, 1983). Due to the high solubility of aragonite, dissolution of shell material frequently occurs prior to burial, a point that will be discussed later in terms of secular variation in ocean geochemistry and dissolution of carbonate bioclasts.

Shell ultrastructure.—Biomineralization is mediated by the organic matrix which, by controlling parameters such as saturation, ionic strength, pH, surface energies, and character and quantity of active sites, results in the precipitation of a mineralized skeleton or shell of an organism (Crenshaw, 1990). Skeletal biomineralization and ultrastructure varies taxonomically, and is thoroughly characterized in Carter (1990) for both invertebrates and vertebrates. Brachiopods have a primary layer or granular calcite in a matrix of glucosaminoglycans, an organo-crystalline secondary layer, and less commonly, a tertiary prismatic layer (Williams, 1997). In some organisms, ultrastructure is taxonomically uniform. For example, the two most abundant classes, Rhynchonellata and Strophomenata, have fibrous and cross-bladed laminar ultrastructures (Fig. 3) in the secondary layer, respectively. Mollusks have at least nine different ultrastructures (i.e., nacreous, foliated, prismatic; Fig. 3) that vary taxonomically, but all have one or more ultrastructure of multilayered organic material and crystalline aragonite and/or calcite (Carter, 1990).

Shell ultrastructure dictates surface area available for dissolution of skeletal material. Early experiments in controls on dissolution were conducted with carbonate material free of organic matter, but recent studies have also used complete skeletal material or bioclasts with the organic component intact, which show that increased surface area of the crystallites results in an increased dissolution rate of skeletal material (Chave 1954b; Henrich and Wefer, 1986; Glover and Kidwell, 1993; Harper, 2000).

Location and abundance of organic matter.—Abundance and location of organic matter in extinct organisms is not always obtainable, but it influences the geochemical microenvironment in ways that influence silicification. There are significant variations in mineralogy, microstructure, and the location and content of organic matter between different taxa (e.g., brachiopods and mollusks) and within taxonomic groups (e.g., brachiopod orders) and between shell layers in a single taxon, especially with multiple ultrastructures (Fig. 3). Skeletal organic matter varies by organism, and occurs in very minute amounts within the crystallites (intracrystalline) and surrounding the crystallites (intercrystalline) (Crenshaw, 1982).

Organic matrix is secreted by the organism along the growing edge of the shell. The composition of the matrix serves as a nucleating agent and controls for the calcium carbonate polymorph by regulating the shape and orientation of the crystals. Since organic matter and biomineralization of marine organisms is a study in and of itself, two morphologically similar and commonly fossilized organisms are compared: brachiopods and bivalves. 'Articulate' brachiopods (including rhynchonellates and strophomenates, as discussed in the ultrastructure section) have less than 5% of total weight (periostracum, soft-tissue, and shell) in organic matter (Jope, 1965), but may have 40–50% of their organic material contained within the shell (Curry and Ansell, 1986; Curry et al., 1989). Features of brachiopod shells, such as spines and punctae, contain additional organic material (Williams, 1997), and one modern punctate brachiopod (*Liothyrella uva*) has up to 75% of the organic material in the shell (Peck et al., 1987). Linguliform brachiopods have very high organic shell content (Cusack, 2001). Bivalve mollusks have 15–30% of total weight as organic matter

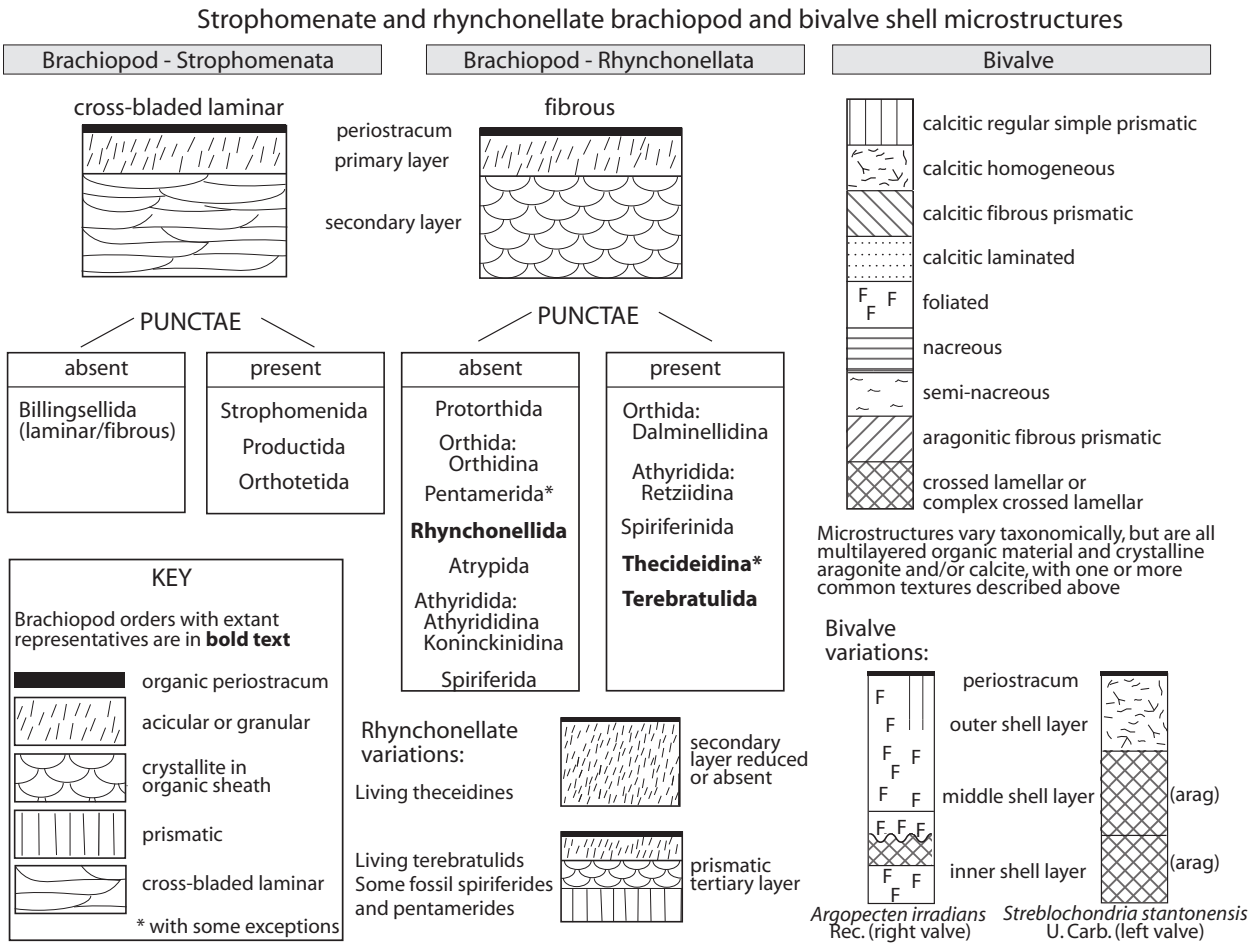

FIGURE *3*.—Shell structures of the two most abundant classes of brachiopods, Rhynchonellata and Strophemata, and generalized molluscan ultrastructure. Compiled from Carlson and Leighton (2001) and Carter (1990).

(periostracum, soft-tissue, and shell) (Peck et al., 1987; Peck, 1993). Mollusk shells are 95% to 99% $CaCO_3$ and 1% to 5% organic matrix, which is a mix of proteins, glycoproteins, proteoglycans, chitin, polysaccharides (Marin and Luquet, 2004), and 16 known molluscan shell proteins (Keith et al., 1993; Hattan et al., 2001).

Organic matter can either accelerate or decelerate the process of decay (Emig, 1990; Glover and Kidwell, 1993; Tomasovych and Rothfus, 2005) and it is nearly insoluble in dilute acid solutions (Hudson, 1967). Differential dissolution of organic-poor and organic-rich aragonitic molluscan shell material was observed by Glover and Kidwell (1993) in sterile and non-sterile controlled seawater composition environments. In the initial stages of degradation, the presence of intercrystalline matter (terminology note: Glover and Kidwell, 1993 refer to material surrounding the crystallite as 'intracrystalline,' but in the definitions above, it would be considered intercrystalline, as defined in Crenshaw, 1982) can serve as a scabbard protecting the crystallite from dissolution (noted by slow dissolution in sterile environments). However, at a certain point, the decay of organic material initiates conditions that actually accelerate crystallite dissolution (Glover and Kidwell, 1993) both by lowering the pH and by mechanical degradation as the crystallites become unbound from the ultrastructure. Rapid alteration of organic matter within the secondary shell layer of terebratulid brachiopods caused weakening and fragmentation of the shell structure and reduction of the shell to microfibers within six to seven months. In marine settings, punctate (terebratulid) brachiopods have a higher rate of shell degradation than impunctate (rhynchonellid) brachiopods due to a greater abundance of skeletal organic matter (Tomasovych and Rothfus, 2005). Well-preserved nacreous microstructures found in Cretaceous ammonoids are considered to

result from protection by organic matter (Clark, 1999).

Silicification is often discussed tangentially in a systematic treatment of a faunal assemblage. Synthesis of these discussions gives insight into susceptibility and the taxonomic hierarchy of silicification. There is overlap of causes, and some contradiction, but silicification is biased by the original shell mineralogy, microstructure (e.g., surface area of crystallites), and organic matter location and abundance. It is often difficult to tell mold-filling silicification from replacement, so only articles in which the textural replacement is indicated (or interpreted from other information) are referenced.

A literature study of 291 papers with occurrences of silicified faunas found brachiopods and mollusks have the highest tendency to silicify, followed by corals, arthropods, and echinoderms (Schubert et al, 1997). In Permian rocks of West Texas, Newell et al. (1953) observed taxonomic susceptibility to silicification, listed from the most to least susceptible: 1) bryozoans, tabulate corals, and punctate brachiopods; 2) impunctate brachiopods and mollusks; 3) echinoderms (as crust on an ossicle, not replacement); 4) foraminifera; and 5) calcareous sponges and dasyclads. When impunctate brachiopods are silicified, then punctate brachiopods (which have decreased susceptibility relative to impunctate brachiopod), are silicified as well. If all taxa are silicified, then the matrix can also be silicified (Newell et al., 1953). Erwin and Kidder (2000) reported the following hierarchy: echinoid spines, brachiopods, and scaphopods; bellerophonts; and straparolids and pleurotomarid gastropods (in a gastropod-dominated fauna), with smaller specimens having more complete silicification.

In fossils from the Carboniferous of Idaho, there is excellent silica replacement in brachiopods, rare corals, and a single vertebra, but pelmatozoans, bryozoans, inarticulate brachiopods, rare bivalves and gastropods, algal mats, and trilobites were not silicified (Butts, 2003). In the Silurian of Gotland, silicification is most prevalent in LMC taxa (brachiopods and bivalves), followed by corals, ostracods, gastropods, crinoids, bivalves, trilobites, sponge spicules, and *Tentaculites* (Laufield and Jeppsson, 1976). As with the Permian material studied by Newell et al. (1953), silicification operated hierarchically, and in the most drastic cases, affected even the matrix.

The link between selectivity of silicification and microstructure (the perimeter of each crystallite is silicified) was established by Daley and Boyd (1996) and Sun and Balinski (2008). Both papers included SEM pictures showing fine-scale textural replacement preserving ultrastructure in Mississippian brachiopods. However, these authors attributed the microstructural control to thickness of the shell and infiltration of fluids preferentially along the shell layers. Location and preservation of organic matrix in shell and matrix and the permeability of the matrix are listed as possible contributors, but not discussed (Daley, 1987; Daley and Boyd, 1996; Sun and Balinski, 2008).

Differential silicification of brachiopods is commonly noted as well. Brown et al. (1969) found that in partially silicified fossils from the Cretaceous chalks of England, rhynchonellids silicified preferentially (more completely) than terebratulids. Spirifers are known to preferentially silicify (Loope and Watkins, 1989; Tucker and Wright, 1990). Taxonomic bias was attributed to ultrastructural controls in the Mississippian Lodgepole Limestone in Wyoming. In Lodgepole Limestone brachiopods, fibrous (rhynchonellate) ultrastructure was more susceptible to silicification than laminar (strophomenate) ultrastructure and prismatic ultrastructure (a tertiary layer in spiriferides and athyridides; Daley and Boyd, 1996). Holdaway and Clayton (1982) attributed selective silicification directly to the size of crystallites, emphasizing a taxonomic control.

In some cases, differential silicification can be observed in a single taxon. The Permian Park City Formation (Wyoming) contains mixed aragonite/calcite bivalves, where calcite is silicified, but aragonite is not: presumably, dissolution preceded silicification (Schmitt and Boyd, 1981). The same pattern is seen in pseudomonotids from West Texas (Newell and Boyd, 1970). Silicification of outer lamellar layers in brachiopods and exclusion of inner prismatic layers has been noted by several authors (Daley and Boyd, 1996; Butts, 2007), and is likely due to the outer silicified layers precluding interaction with porewaters rather than being a strictly taxonomic control. Aragonitic faunas, with high relative solubility, often dissolve prior to silicification of other organisms (Holdaway and Clayton, 1982; Cherns and Wright, 2000; Wright et al., 2003).

Many have argued about the influential role of organic matter in the silicification of marine organisms (Holdaway and Clayton, 1982; Knoll,

1985; Klein and Walter, 1995; Erwin and Kidder, 2000). One of the first papers to propose the influence of organic matter in the replacement of fossils with silica was by Holdaway and Clayton (1982), who found structures resembling the configuration of organic material in brachiopods from the Upper Cretaceous of the UK. In these brachiopods, silicification preserved the microstructural fabric and appeared to be both encasing the crystallite and replacing the crystallite (Holdaway and Clayton, 1982). The association is well established in microbial and plant silicification (Barghoorn and Tyler, 1965; Leo and Barghoorn, 1976; Francis et al., 1978a; b; Walters et al., 1977; Knoll, 1985; Akahane et al., 2004), and silicified plants illustrate the affinity of silica to organic matter even at the micrometer scale (Boyce et al., 2001).

Despite these commonalities in the hierarchy, silicification does not always work on a similar hierarchy, or the details of possible controls are not well established in the literature. In the Silurian of Utah, silicification was most common in trilobites; brachiopods, bryozoans, and ostracods were partially silicified; and gastropods and cephalopods were not replaced. In correlative rocks in central Nevada, trilobites were not replaced, but brachiopods and gastropods were silicified, with the disparity being attributed to depositional environment of the basin (Hintze, 1953). In the Mesozoic of Slovakia, Mišík (1995) found bivalves silicified more readily over brachiopods, echinoderms, corals, and other taxa. From these occurrences, it can be determined that the pattern of silicification is biased by original mineralogy, with calcitic organisms (i.e., brachiopods) being more susceptible to silicification than aragonitic faunas, and LMC favoring silicification over HMC, probably due to relative rates of dissolution for those carbonate phases (i.e., aragonitic faunas dissolve at a rate that surpasses the rate of silica precipitation). Presence of organic matter plays a role based on evidence that punctate brachiopods, with a greater proportion of organic matter in their shells, silicify more readily than impunctate brachiopods. Note that punctate representatives are found in both of the two most abundant clades of brachiopods, Strophomenata and Rhynchonellata, which are characterized by different skeletal ultrastructures of the same mineralogy. However, these interpretations are not a substitute for a statistical analysis of silicified taxa.

Lithological controls and biases

Silicification occurs in deposits ranging from supratidal to basinal (Knoll, 1985). The geochemical environment of the sediments, including matrix composition, permeability and porosity, and organic matter content, has a direct effect on the dissolution of carbonate and precipitation of silica. As with the taxonomic controls, the propensity for silicification with variations in these conditions is poorly studied. The composition of the sediment—carbonate versus siliciclastic—mediates chemical reactions by controlling solubility of bioclasts and interaction with clays. Solubility and precipitation of silica are reduced in the presence of fine-grained siliciclastics. Organic matter is incorporated into the matrix and serves a source for silica nucleation. Organic matter (Hinman, 1990) and certain ions derived from carbonate and clay minerals (Lancelot, 1973; Hinman, 1998) also influence the rate of silica phase changes. Diagenetically, opal-A to opal-CT conversion is optimal in carbonates and retarded in clays sediments (Kastner et al., 1977).

Matrix composition of the sediment influences susceptibility and fidelity of silicification. Silicification is enhanced and of higher fidelity in open-marine, siliciclastic-poor sediments (Erwin and Kidder, 2000; Butts, 2007). Silicification was more common and of higher fidelity in open-marine environments of the Permian basins of southwestern United States (Arizona, New Mexico, and West Texas)—a link attributed to greater silica availability and more rapid burial (Erwin and Kidder, 2000). Newell et al. (1953) also noted that silicification is more common in open-marine (basinal) carbonate settings, and also noted that silicification is associated with depositional structures (toe of talus slope). In the Carboniferous Antler Foreland Basin, silicification is more common in carbonates than in fine-grained siliciclastics (Butts, 2007). In the Devonian Helderberg Group of New York, there is a positive correlation between lithology and silicification. Heterolithic carbonate and siliciclastic (silt- and clay-stone) outcrops have uniform faunas from shallow-marine environments (probably lagoonal), but silicification is more common in carbonate than in fine-grained siliciclastics (Butts, 2004; pers. obs.). Incomplete or poor silicification can occur, particularly in mollusks, in shallow-water calcareous fine-grained siliciclastic-rich sediments (Newell et al., 1953; Kidder and Erwin,

2001; Butts, 2007).

Stratigraphic position (related genetic factors of deposition, such as increasing or decreasing water depth, emergence, etc.) and sedimentological controls can also play a role (see Butts and Briggs, 2011). For example, lithological compartmentalization occurring in icehouse climates (Read, 1998) may create porosity barriers that locally are favorable to silicification on flanks of reefs (Newell et al., 1953) or Waulsortian mounds (Meyers, 1977).The influence of cements can preclude silicification by decreasing the permeability of the matrix. Crinoid ossicles, which are HMC and therefore could be expected to silicify readily, often have early syntaxial cements when found in crinoid mounds and banks, and can resist silicification due to the large crystal size of the cement. Silicified brachiopods in crinoid grainstone suggest that while syntaxial cements prevented the replacement of echinoderm bioclasts with silica, they did not prevent the silicification of brachiopod bioclasts contained within the grainstone matrix (Butts, 2007).

Silicified fossils and matrix from the Silurian of Gotland conform to bedding and directly underlie bentonite deposits, indicating an obvious connection between the silica source and the occurrence of silicification (Laufeld and Jeppsson, 1976). Silicification in the Upper Proterozoic of Greenland is more prevalent in sediments high in organic matter than in organic-poor sediments (Knoll, 1985), a correspondence first noted in Siever (1962). In some areas, such as sponge bioherms, all taxa have a greater likelihood of silicification (Cooper and Grant, 1972). Silicification is more common and higher fidelity in carbonate sediments versus fine-grained siliciclastics, likely due to the reactivity of clays and the increased solubility of calcite bioclasts in an undersaturated environment.

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Knauth's (1979) classic model of silicification proposed that the mixing of meteoric and marine ground waters promotes a geochemical shift, which then promotes silica precipitation. In many examples of silicification, however, there is no link to terrestrial emergence. Maliva and Siever (1988) discussed force of crystallization as the primary driver of the replacement of calcite with silica, and felt the organic matter within a shell was insufficient to promote dissolution of the shell. However, the role of organic matter is significant in both the dissolution of carbonate and precipitation of silica, as demonstrated in experiments and fossil analysis.

Degradation of organic matter by microbial activity within the skeletal material lowers the pH, increases CO_2, and promotes dissolution of calcium carbonate (Jacka, 1974; Schmitt and Boyd, 1981; Holdaway and Clayton; 1982; Cherns and Wright, 2000). Organic matter nucleates silica, a process that has been demonstrated in the lab (Amores and Warren, 2007) and in natural settings, such as sinters (Guidry and Chafetz, 2003; Konhauser et al., 2004 [although they argue microbes do not contribute to the process, they acknowledge the passive role of microbial organic matter in nucleating silica precipitation]; Lynne et al., 2007) and desert varnishes (mineralized coatings on rock surfaces; Perry, 2003). In laboratory studies, silicification of microbes (Amores and Warren, 2007) and skeletal material (Paraguassu, 1976; Butts et al., 2011) occurred in silica-saturated conditions in acidic, low-temperature conditions. This indicates that a taxonomic bias may be introduced by the presence and distribution of organic matter in skeletal material. In experiments using ground rhyolitic obsidian as a silica source in aqueous solution at at 100°C, plant tissues attracted silica complexes from solution that subsequently precipitated onto organic matter (Ballhaus et al., 2012). Knoll (1985) also suggested that a modest amount of degradation of organic matter would enhance silicification by increasing the reactivity (number of sites available for hydrogen bonding) and introduction of structural gaps (i.e., microcracks or holes) for silica infiltration. The generalized processes and controls for silicification are shown in Figure 4.

Silica is adsorbed to organic matter and undergoes further polymerization to more stable silica phases by hydrogen bonding to hydroxyl groups (Iler, 1979); the rate is slower at lower pH (Hinman, 1987). Organic matter has weak acidic functional groups that form surface complexes with relatively basic surface hydroxyls. Relatively acidic surface hydroxyls form weaker complexes, and under natural (freshwater) conditions, may not be covered with organic material (Davis, 1982). Silicic acid can form a variety of complexes with ions and organic molecules including mucopolysaccharides and hydroxyl amino acid-enriched glycoproteins. Organic

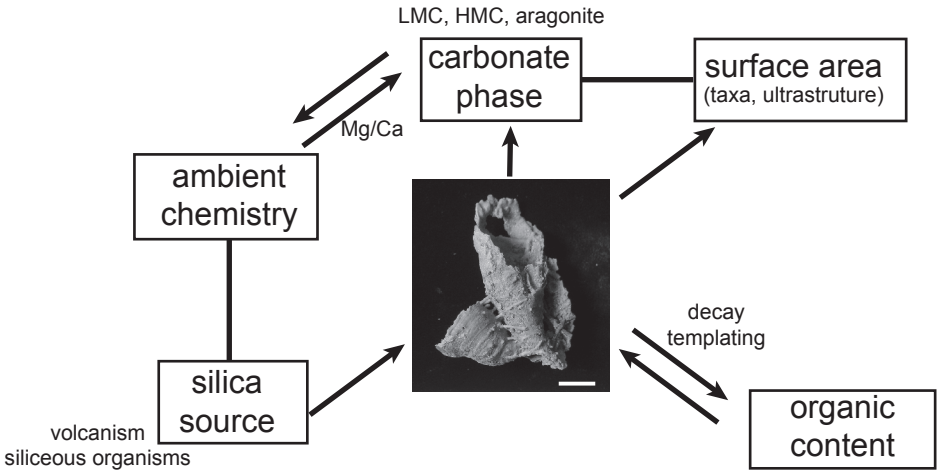

FIGURE *4*.—Process and controls of silicification. Arrows directed away from the silicified richthofenid represent processes or controls that affect dissolution of carbonate, arrows directed away affect the precipitation of silica, and coupled controls are bonded.

substances can contribute to the polymerizing, cross linking, and hardening (by elimination of water) of silicic acid, and can incorporate metals as well (Perry, 2003). Polymerization occurs between pH 3–10, but the optimal rate is at pH 7–9 (Iler, 1979).

Based on this process, silicification technically could happen at any point in the pre-lithification diagenetic history of an organism, even high-fidelity silicification that retains the character of shell ultrastructure. Intercrystalline organic matter is taphonomically robust, and has been found in fossils as old as the Pennsylvanian. The organic matter retains the texture of the crystallites (polygonal in prismatic ultrastructures, tabular in nacreous), viewable by performing critical point-drying on the specimens after etching. Protection by organic matrix, and from conditions that also precluded degradation or dissolution of the crystallites themselves (with low permeability rock matrix), is attributed to the protection of aragonite in shells from the Cretaceous (Clark, 1999).

The conditions conducive to silicification are not exactly consistent with general marine geochemical conditions either in carbonate or siliciclastic environments, so the establishment of microenvironments is likely essential to this process. Schmitt and Boyd (1981) felt that an early diagenetic micritic envelope was enough to create an acidic microenvironment. The structural framework of the shell ultrastructure and the resistance of skeletal organic matter to decay could also provide isolation of geochemical conditions. Nascent experimental silicification experiments of Butts et al. (2011) at Yale University showed that silica infiltrates the intercrystalline organic matter within the shell, even as carbonate persists, which could indicate isolated microenvironments. A shift in geochemical conditions, such as rapid increase in acidity, could also trigger silica precipitation. Basinal fluctuations in temperature or pH could promote wide-scale silica precipitation.

Silicified fossils grow increasing susceptible to loss of fidelity as silica neomorphism occurs. After precipitation, silica goes through a series of diagenetic transformations: opal-A (amorphous) > opal A' (secondary) > opal CT > opal CT (reordered phase) > cryptocrystalline quartz or chalcedony > microcrystalline quartz (Iler, 1979; Williams and Crerar 1985; Hesse 1989). The increasingly coarse nature of the silica may obliterate preserved ultrastructure, which may be the case for the Permian Basin faunas.

EXPERIMENTAL SILICIFICATION

The earliest accounts of experimental silicification are examples of petrifaction of wood for experimental and utilitarian purposes that are referred to in Leo and Barghoorn (1976). One example from the 1500s states, "When one brews beer, alderwood is simmered in the pot until the hops are done. Afterwards, one buries the wood for three years in fresh sand or gravel in a cellar, after which it turns hard, making the best whet- or flintstone." (from Meyer's 1791 account, translated in Leo and Barghoorn, 1967, p. 10). In that case, barley grains contain a significant

supply of amorphous silica as phytoliths (abundant in Poaceae), which go into solution and precipitate in the cavities of the wood, and dehydration completes the petrifaction. An excellent historical overview is provided in Leo and Barghoorn (1976). Contrary to conventional wisdom of the slow nature of fossilization, the process of silicification is proving to be a rapid process in both laboratory and natural experimental procedures (Leo and Barghoorn, 1976; Karawoe and Jefferson, 1987; Akahane et al., 2004; Ballhaus et al., 2012). This section discusses experimental silicification, both in the laboratory and in natural settings, which have helped to elucidate the processes and controls on silicification.

Experiments with microbes and petrified wood

Research on experimental fossilization with silica is most robust with respect to permineralization (Leo and Barghoorn, 1976) and entombment (of microbes) (Barghoorn and Tyler, 1965; Walters et al., 1977; Francis et al., 1978a, b). Permineralization of wood was achieved in a laboratory setting at near-neutral pH conditions by soaking wood in water to remove gas, then immersing it in ethyl silicate solutions for months at 70°C with intermittent vacuum impregnation Without vacuum impregnation, permineralization was incomplete, and the structure crumbled when the organic matter was removed. The siliceous lithomorphs were constructed of highly disordered α-cristobalite, similar to Recent fossilized wood specimens in volcanic ash from the 1886 eruption of Mt. Tarawera, New Zealand (Leo and Barghoorn, 1976). Leo and Barghoorn (1976) proposed that silicification occurred as monomeric (or possibly low molecular weight polymeric) silicic acid infiltrated void spaces in the wood structure and cell walls, which, by hydrogen bonding between soluble silica and polysaccharides in contact with organic matrix, preserved the histological characters of the wood.

Based on the experiments by Leo and Barghoorn (1976), Francis et al. (1978a, b) undertook experimental silicification of algae and microbes (entombment) using tetraethyl orthosilicate (TES) at 55–60°C for weeks to months in an attempt to correlate with silicified structures in Precambrian cherts. Silicification correlated with organic content. It did not occur on freshwater microbes that lacked an organic sheath, and was greatest in organisms that had a robust extracellular sheaths. Silicification was influenced by temperature (55°C was optimal) and water content (neither wet nor dry materials silicified because ethyl silicate is immiscible in water). These experiments concluded that silicification can create a high-fidelity reproduction of an organism, although internal structures may not preserve and shrinkage can alter the final product, and that silica precipitation was favored by the complexing of silica by organic matter (Francis et al., 1978a).

Field examples indicate a geologically rapid rate of permineralization. Wood fragments placed in silica-saturated hot springs (70°C, pH=3, 323.3–378 mg/l monomeric silica) were silicified 40% (by weight) after just seven years of immersion. The authors concluded that silicified wood can form in silica-rich hot waters associated with volcanic or pyroclastic rocks in the span of tens to hundreds of years (Akahane et al. 2004). Leo and Barghoorn (1976) found permineralized specimens of wood retrieved from a hot spring that had formed in the last 13 years.

Industrially, wood permineralization experiments using various carriers for silica have aimed to produce a more durable wood product. Tetraethoxysilane (TEOS) was determined to be the most effective vehicle for penetration of silica and preservation of wood structures. TEOS hydrolyzes during the transition from gel to sol and forms monosilicic acid, which then polymerizes to opal-A (chemical reactions in Götze et al., 2008). Other solutions, such as silica sols and sodium metasilicate, were less effective or damaged the wood (sodium metasilicate is highly alkaline).

One laboratory experiment utilized a silica source that would be found in nature—ground rhyolitic obsidian— which, at 100°C, went into solution to produce clay minerals, ionic K^+ and Na^+, and silicic acid. Addition of NaOH was necessary to promote dissociation of neutral silicic acid species. At pH of 9.5 and below, the obsidian solution contained around 6.24 mmol/L SiO_2. Despite the initial spiking with NaOH, the addition of wood caused acidification, decreased silica solubility, and precipitation of silica, with the introduced pH gradient being a primary control on the process (Ballhaus et al., 2012).

Experiments with replacement

Despite the abundance of studies on the experimental permineralization of wood, little experimental work has been performed on shelly material to emulate replacement. The first

published experiment to replace skeletal material of an organism was performed in the 1970s by Paraguassu (1976). Paraguassu suspended live-collected mollusk shells from threads in a solution of sodium metasilicate and adjusted the pH to promote dissolution of skeletal material (2g/liter SiO_2, pH=2 was ideal for a 0.5g shell). Silica flocculated on the exterior of the shell within three weeks. After three weeks, the shells were removed from the solution and were found to be flexible. After eight months, shells were removed and dehydrated in ambient air conditions. The shells contracted slightly due to loss of water, and were found to be 75% silica in composition; the remainder was organic matter and unmobilized microelements. He performed additional experiments removing Ca^{2+} from solution, which can decrease the solubility of silica (Paraguassu, 1976).

Experimental silicification by Butts et al., (2011) linked the process of silicification to the adsorption of silica to intercrystalline organic matter of modern bivalves. *Mytilus* were live-collected, stripped of flesh, and placed in a solution of sodium metasilicate. Sodium metasilicate is a strong base, so an initial addition of HCl was necessary. Afterward, the experiment was kept at constant low pH (1, 2, and 4) in replicate sets. *Mytilus* contains two skeletal ultrastrutures, prismatic and nacreous (both aragonitic in composition), with two proteins that are common only in their respective shell layer. These two proteins are thought to be the controls on the construction of the shell ultrastructure (Weiner, 1983). The adsorption of silica to organic matter was observed in a span of tens of days. In these experiments, the silica extended beyond dissolution of the crystallite to within the ultrastructure where carbonate material was still intact as seen under electron microprobe. There was no significant difference between silicification in the two layers, so it was assumed that the particulars of the shell organic matrix composition, and perhaps among all taxa, are of minor importance (Butts et al., 2011).

TEMPORAL BIASES IN SILICIFICATION

A temporal bias in silicification has been connected to secular variations in sea water geochemistry, abundance of siliceous and calcium carbonate animals, abundance of chert deposits, sea-level changes, and rock volume, but patterns of silicification are still poorly constrained.

Ocean geochemistry and global climate

Ocean geochemistry has fluctuated with respect to Mg/Ca over the course of geologic time, driven mostly tectonically by the production of ocean crust at spreading centers (Stanley and Hardie, 1998, 1999) and ρCO_2 (Zhuravlev and Wood, 2009), as demonstrated by sampling evaporate deposits (Hardie, 1996), abiogenic carbonates (Sandberg, 1986), and the Mg/Ca ratio of organisms that secreted their tests in equilibrium with the Mg/Ca of seawater (Stanley and Hardie, 1998). Silicification necessarily is preceded by the dissolution of skeletal material, and differential dissolution rates of carbonate phases are based on local and global geochemistry. Because of the importance of carbonate solubility to silicification, the effect is seen in the abundance and selectivity of silicified faunas through time. The link between relative solubility and silicification is not direct, but rather a contributing factor because it influences the relative dissolution of organisms at a given time, a key part of the silicification process. In global greenhouse climates, deposition is characterized by thick sequences of carbonate lithologies with small spatial variations in depositional environments laterally and vertically (Read, 1998). Since silicification is favored in carbonate lithologies, silicification may be overrepresented in greenhouse climates due to the higher relative proportion of carbonate rocks. In terms of global ocean geochemistry, calcite-saturated greenhouse seas would favor dissolution of aragonite (see Palmer et al., 1988). As suggested by Kidder and Erwin (2001), greenhouse and icehouse conditions also influence biogenic silica burial. In icehouse climates, increased siliciclastic deposition may reduce the abundance of silicified faunas, bearing in mind that no connection has been drawn between coarse- and medium-grained siliciclastic sediment and a silicification bias; a negative bias is attributed only to fine-grained (silt- and clay-sized) siliciclastic sediments. The high-amplitude, high-frequency sea-level changes in icehouse climates repeatedly expose sediment to meteoric diagenesis, which would result in either rapid dissolution preceding silicification (see Palmer et al., 1988) or conversely, geochemical conditions favoring silicification (see Knauth, 1979). Seas saturated with aragonite favor the dissolution of both HMC and LMC taxa, with preference to LMC.

In the absence of a strong greenhouse/ icehouse signal (Kidder and Erwin, 2001) or with

carbonate rock volume (Schubert et al., 1997), patterns seen from surveys of silicified faunas may relate to sampling of exceptionally preserved, compartmentalized, silicified faunas that override the general signal of silicification preference during greenhouse times. Also contributing to the lack of a pattern is the superposition of the marine diversity curve over geologic time onto the global ocean climate curve, specifically the abundance and diversity of potentially silicified organisms of specific mineralogy (HMC, LMC, or aragonite), and the abundance and diversity of silicified faunas as a silica source.

The relative solubility of marine organisms of a given mineralogy is susceptible to shifts in ocean Mg/Ca, making it the greatest variable in skeletal dissolution, and therefore, tendency to silicify. It can also result in large-scale dissolution as seen in Upper Ordovician and Jurassic marine deposits. These calcitic greenhouse seas promote dissolution of aragonitic faunas (Palmer et al., 1988). In one example from the Silurian of Gotland, early diagenetic silicification preceded aragonite dissolution, and resulted in loss of molluscan diversity in silicified versus non-silicified deposits (70% versus 3%; Cherns and Wright, 2000). In the Jurassic of South Wales, there is a 65% decrease in the diversity of bivalve genera where dissolution of aragonite preceded silicification (Wright et al., 2003). Seas saturated with aragonite favor the dissolution of HMC and LMC taxa, with preference to LMC.

The dissolution of skeletal matter may be significantly altered by shifting geochemical conditions that can produce large-scale dissolution events (Henrich, 1985; Palmer et al., 1988; Cherns and Wright, 2000; Wright et al., 2003; James et al., 2005). Aragonitic faunas become increasing dominant through the Phanerozoic because of declining pCO_2 leading to decreasing total alkalinity and dissolved inorganic carbon and increasing pH, assisted by mass-extinction events that enhanced the survival of aragonitic faunas (Zhuravlev and Wood, 2009).

Dissolved silica supply in the oceans

The limiting factor in silicification is silica availability. Silica in the oceans is input by rivers, hydrothermal systems, and from weathering of sediments. Uptake is mediated by the production of siliceous tests by marine organisms (Goering et al., 1973). Crystalline silica is not considered a silica source because it is much less soluble than amorphous silica (Iler, 1979; Fleming and Crerar, 1982; Ballhaus, 2012). Monomeric silicic acid is the most common dissolved silica source in marine and fresh waters (Tréguer et al., 1995). Silicic acid (H_2SiO_4) is a weak acid and has four hydroxyl groups per molecule, making it highly reactive (Iler, 1979; Leo and Barghoorn, 1976). It is the raw material for the tests of siliceous organisms, including radiolaria, diatoms, and silicoflagellates (algae), and so is an important transfer in silica cycling (Goering et al., 1973). The primary source of removal of silica at present is diatoms (Tréguer et al., 1995), but Paleozoic removal was by radiolaria and sponges (Siever, 1992; Kidder and Erwin, 2001). Dissolved silica is a minor constituent in natural waters with an average concentration of 120 μg/l in natural waters (Milliman and Boyle, 1975). Siever (1957) offered the following assessment of dissolved silica in natural systems: rivers have from a few to 35 ppt silica, some lakes and rivers are higher (up to 75 ppm), alkaline lakes can be 300 ppm, ground waters are 50–60 ppm (but can be higher in areas of meteoric mixing), oceans have less than one up to 12 ppm, ocean sediments can have up to 68 ppm, and hydrothermal deposits up to 400 ppm. Silicic acid occurs abiologically through the breakdown of siliceous microorgansims (Calvert, 1974; Tréguer et al., 1995) and through terrestrial and submarine weathering (Tréguer et al., 1995), notably devitrification of volcanic ash and clay mineral diagenesis (Siever, 1957; Leo and Barghoorn, 1976), so local concentrations can be much higher (Calvert, 1974) in the vicinity of these factors.

Silicified flora and fauna are commonly associated volcanic ashes, including deposits of the Permian Basin of Texas (e.g., bentonites, Nicklen and Bell, 2007; Nestell et al., 2012), Gotland (Laufeld and Jeppsson, 1976), and New York (Bald Hills volcanics with K-bentonite ash layers, Dennison and Textoris, 1979; Smith and Way, 1988; Butts, 2004), petrified woods (Scurfield and Segnit, 1984; Senkayi et al., 1985), and Recent hot-spring deposits (Leo and Barghoorn, 1976; Akahane et al., 2004). Permineralization of wood is associated with volcanic ashes, afforded by both the ample supply of silica and by creating anoxic conditions which preclude the degradation of lignin, the primary component of wood (Leo and Barghoorn, 1976).

Proterozoic silicification

Silica concentrations are low today due to the

efficacy of organisms in removing silica from ocean water, and there is little fossil evidence for silica-secreting organisms prior to the Phanerozoic (Siever, 1992). The silica cycle in the Precambrian has typically been interpreted as abiologically mediated by weathering, tectonism, and hydrothermal activity (Maliva et al., 2005), and lacking a strong biological output, interpreted by the lack of fossil record of siliceous organisms at this time (Siever, 1992); however, this interpretation was recently challenged by Sperling et al. (2010).

Silica-replaced remains of microbes have been found in cherts of the 2000 My Gunflint Iron Formation (Barghoorn and Tyler, 1965). Paleoproterozoic iron formations, including some containing microbial remains, were deposited by widespread primary silica precipitation directly from silica-supersaturated seawater (Maliva et al., 2005). Proterozoic examples of silicification are limited to cherts containing microfossils that are considered early diagenetic peritidal deposits (Maliva et al., 2005; references therein). Abundant organic matter in peritidal environments may have served as a nucleation site for silica precipitation (Maliva et al., 2005). Reactions with organic matter to precipitate silica would have been common in Proterozoic sediments, and organic compounds can be extracted from Proterozoic sediments (Summons and Walter, 1990). Experiments suggest some bacteria promote silicification (Birnbaum and Wireman, 1984, 1985), as do the products of organic degradation (Siever, 1992). Organic matter, abundant in Proterozoic carbonate sediments (Knoll, 1985), would degrade, creating complex compounds capable of polymerizing silica (Siever, 1992).

Phanerozoic silicification

The evolution of silica biomineralizing organisms over the course of the Phanerozoic introduced a major biological influence into the silica cycle (Maliva et al., 1989). Secular trends in silicification should be tied to the relative abundance of organisms of the different carbonate phases, their relative solubility based on the Mg/Ca ratio of the ocean at the time, and the abundance of siliceous organisms (as a source of silica).

Maliva et al. (2005) attributed the temporal and spatial distribution of chert to the evolutionary history of siliceous organisms, particularly sponges, radiolaria, and diatoms. Two shifts were found in the facies distribution of chert in the Paleozoic: Cambro–Ordovician (increasingly peritidal to subtidal chert related to the radiation of sponges and radiolarians in the Ordovician), and Late Cretaceous to Paleogene (chert deposition moves to deep shelf and ocean basin environments, corresponding to the radiation of radiolarians) (Maliva et al., 2005). An upper Carboniferous peak in silicification coincides with a rebound in shelfal cherts (Maliva et al. 2005). Kidder and Erwin (2001) found that drops in abundance in chert and silicified fossils and bedded cherts coincided with four of the five mass-extinction events at the end of the Ordovician, late Devonian, end-Permian and the Cretaceous–Paleogene. Increases were linked to radiations in the Ordovician and Siluro–Devonian (Kidder and Erwin, 2001).

A literature review by Schubert et al. (1997) looked specifically at silicified faunas based on photographic documentation and observances in manuscripts, and found that they are more common in Paleozoic (21% of publications) sediments than post-Paleozoic sediments (4% of publications). In decreasing order, compared to unsilicified occurrences and normalized for duration of time period, silicification was most prevalent during the Silurian, Ordovician, Carboniferous, and Triassic (Shubert et al., 1997). This was correlated to a post-Paleozoic shift from calcitic to aragonitic faunas (Wilkinson, 1979; Railsback and Anderson, 1987), decrease in sponge spicule abundance, and possibly to a shift from nearshore to offshore cherts related to the radiation of diatoms in the Cretaceous (Schubert et al., 1997). However, they found the decline in silicified fossils in the Triassic predates the rise of diatoms, indicating they do not appear to be driving the silica cycle (Shubert et al., 1997). Ultimately, local patterns, such as silica-rich environments associated with volcanism and hydrothermal activity or geochemical shifts, may make broad patterns difficult to establish.

CONCLUSIONS

Permineralization, entombment, and replacement with silica occur by similar processes because silica adsorbs to either the organic matter next to a void space in wood, the organic sheath of a microbe, or the organic matter that permeates the interior of a marine organism's shell. Silicification is the concurrent dissolution of carbonate skeletal material and precipitation of silica, aided by the

nucleation of silica by organic matter. As such, the process is mediated by the original mineralogy, ultrastructure, and location and abundance of organic matter within the shell (taxonomic controls), and geochemical environmental at deposition and during the early diagenetic history of the fossil (lithological controls).

Dissolved siliceous skeletal material has long been considered the source for silica in replacement, but considering the frequent co-occurrence of volcanic ash sediments and silicified faunas, a non-biogenic source is evident as well. Modern examples of silicification occur in sinters, geothermal waters enriched in silica, and with very a different set of geochemical constraints than those of normal marine carbonate environments, the depositional environments in which most silicified fossils are found, but the creation of geochemical microenvironments, such as a shell enclosed within a micritic envelope, or crystallites within an organic sheath, may allow for such conditions to exist. Fine-scale textural evidence of silica-replaced flora and fauna and laboratory experiments suggest that silicification of any type can be geologically instantaneous. The demonstrated proclivity for organic matter to nucleate silica, and the persistence of organic matter in skeletal material, suggests that the pre-lithification window for silicification could be sizable. Temporal patterns of silicification show that silicification was more prominent in the Paleozoic, and has decreased over time, a pattern ascribed to the evolution of more aragonitic faunas through the Phanerozoic.

Understanding the process of silicification, and particularly the association with organic matter, may be useful for recognizing chert and silicified deposits as petroleum source rocks because it points to the location of organic matter. More importantly, understanding the processes and controls on silicification of fossils allows an understanding of a taphonomic filter that biases the interpretation of the record of biodiversity through time. The exact nature of this bias is not clearly ascertained with our present knowledge of silicification patterns and the process and controls on silicification. Broad patterns of silicification could certainly be driven by global ocean geochemistry and climate, and by the control of the history of life and variation of organisms by mineralogy, and presence and abundance of silica. The most notable effect is the transition from Paleozoic calcite-dominated taxa to post-Paleozoic aragonitic faunas and the origin, diversification, and extinction of major siliceous biota, such as sponges and radiolarians. On a smaller scale, silicification is clearly biased towards preservation of lower solubility LMC organisms, as aragonite and, to a lesser degree, HMC faunas, fall victim to dissolution prior to silicification unless in exceptional situations.

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REFERENCES

AKAHANE, H., T. FURUNO, H. MIYAJIMA, T. YOSHIKAWA, AND S. YAMAMOTO. 2004. Rapid wood silicification in hot spring water: an explanation of silicification of wood during the Earth's history. Sedimentary Geology, 169:219–228.

AMORES, D. R. AND L. A. WARREN. 2007. Identifying when microbes biosilicify: The interconnected requirements of acidic pH, colloidal SiO_2 and exposed microbial surface. Chemical Geology, 240:298–312.

BALLHAUS, C., C. T. GEE, C. BOCKRATH, K. GREEF, T. MANSFELDT, AND D. RHEDE. 2012. The silicification of trees in volcanic ash—an experimental study. Geochimica et Cosmochimica Acta, 84:62–74.

BARGHOORN, E. S. AND S. A. TYLER. 1965. Microorganisms from the Gunflint Chert—These structurally preserved Precambrian fossils from Ontario are the most ancient organisms known. Science, 147:563–575.

BERNER, R. A. 1975. The role of magnesium in the crystal growth of calcite and aragonite from sea water, Geochimica et Cosmochimica Acta, 39:489–504.

BERNER, R. A., E. K. BERNER, AND R. S. KEIR. 1976. Aragonite dissolution on the Bermuda Pedestal: Its depth and geochemical significance. Earth and Planetary Science Letters, 30:169–178.

BIRNBAUM, S. J., AND J. W. WIREMAN. 1984. Bacterial

sulfate reduction and pH: implications for early diagenesis. Chemical Geology, 43:143–149.

BIRNBAUM, S. J., AND J. W. WIREMAN. 1985. Sulfate-reducing bacteria and silica solubility: a possible mechanism for evaporite diagenesis and silica precipitation in banded iron formations. Canadian Journal of Earth Sciences, 22:1904–1909.

BOYCE, C. K., R. M. HAZEN, AND A. H. KNOLL. 2001. Nondestructive, *in situ*, cellular-scale mapping of elemental abundances including organic carbon in permineralized fossils. Proceedings of the National Academy of Sciences of the United States of America, 98:5970–5974.

BRAND, U. 1983. Mineralogy and chemistry of the Lower Pennsylvanian Kenrick Fauna, eastern Kentucky, U. S. A., 3. Diagenetic and paleoenvironmental analysis. Chemical Geology, 40:167–181.

BROWN, G., J. A. CATT, S. E. HOLLYER, AND C. D. OLLIER. 1969. Partial silicification of chalk fossils from the Chilterns. Geological Magazine, 106:583–586.

BUENING, N., AND S. J. CARLSON. 1992. Geochemical investigation of growth in selected Recent articulate brachiopods. Lethaia, 25:331–345.

BUTTS, S. H. 2003. Taxonomy, taphonomy, and paleoecology of the Arco Hills Formation (Chesterian), east-central Idaho. Unpublished Ph.D. dissertation, University of Idaho, Moscow, 215 p.

BUTTS, S. H. 2004. Silica diagenesis in the Lower Devonian Helderberg Group of New York. Geological Society of America Abstracts with Programs, 36(5):383–384.

BUTTS, S. H. 2007. Silicified Carboniferous (Chesterian) Brachiopoda of the Arco Hills Formation, Idaho. Journal of Paleontology, 81:48–63.

BUTTS, S. H., AND D. E. G. BRIGGS. 2011. Silicification through time, p. 411–434. *In* P. Allison and D. J. Bottjer (eds.), Taphonomy: Process and Bias Through Time. Topics in Geobiology 32. Springer.

BUTTS, S. H., R. A. KRAUSE, JR., AND D. E. G. BRIGGS. 2011. Experimental silicification of bivalves: understanding taphonomic bias. Geological Society of America Abstracts with Programs, 43(5):504.

CALVERT, S. E. 1974. Deposition and diagenesis of silica in marine sediments, p. 273–299. *In* K. J. Hsu and H. C. Jenkyns (eds.), Pelagic Sediments: On Land and Under The Sea. Special Publication of the International Association of Sedimentologists 1. Blackwell Publishing Ltd., Oxford, UK.

CARLSON, S. J., AND L. R. LEIGHTON. 2001. The phylogeny and classification of Rhynchonelliformea, p. 27–51. *In* S. J. Carlson and M. R. Sandy (eds.), Brachiopods Ancient and Modern: a Tribute to G. Arthur Cooper. Paleontological Society Papers 7, Columbus, Ohio.

CARTER, J. G. (ED.) 1990. Skeletal Biomineralization: Patterns, Processes and Evolutionary Trends. Short Courses in Geology 5, American Geophysical Union, Washington, D. C.

CHAVE, K. E. 1954A. Aspects of the biogeochemistry of magnesium 2. Calcareous sediments and rocks. The Journal of Geology, 62:587–599.

CHAVE, K. E. 1954B. Aspects of the biogeochemistry of magnesium 1. Calcareous marine organisms. Journal of Geology, 62:266–283.

CHAVE, K. E., K. S. DEFFEYES, P. K. WEYL, R. M. GARRELS, AND M. E. THOMPSON. 1962. Observations on the solubility of skeletal carbonates in aqueous solutions. Science, 137:33–34.

CHERNS, L., AND V. P. WRIGHT. 2000. Missing molluscs and evidence of large-scale, early skeletal aragonite dissolution in a Silurian sea. Geology, 28:791–794.

CLARK, I. I., AND R. GEORGE. 1999. Organic matrix taphonomy in some molluscan shell microstructures. Palaeogeography, Palaeoclimatology, Palaeoecology, 149:305–312.

COOPER, G. A., AND R. E. GRANT. 1972. Permian Brachiopods of West Texas, I. Smithsonian Contributions to Paleobiology 14. Smithsonian Institute Press, Washington, D. C.

CRENSHAW, M. A. 1982. Mechanisms of normal biological mineralization of calcium carbonates, p. 243–257. *In* G. H. Nancollas (ed.), Biological Mineralization and Demineralization. Springer, Berlin.

CRENSHAW, M. A. 1990. Biomineralization mechanisms, p. 1–9. *In* J. G. Carter (ed.), Skeletal Biomineralization: Patterns, Processes and Evolutionary Trends. Short Courses in Geology 5, American Geophysical Union, Washington, D. C.

CURRY, G. B., AND A. D. ANSELL. 1986. Tissue mass in living brachiopods. Biostratigraphie du Paléozoique, 4:231–241.

CURRY, G. B, L. S. PECK, A. D. ANSELL, AND M. JAMES. 1989. Physiological constraints in fossil and recent brachiopods. Transactions of the Royal Society of Edinburgh, Earth Sciences, 80:255–262.

CUSACK, M. 2001. Biomineralization in brachiopod shells, p. 105–116. *In* S. J. Carlson and M. R. Sandy (eds.), Brachiopods Ancient and Modern: a Tribute to G. Arthur Cooper. Paleontological Society Papers 7, Columbus, Ohio.

DALEY, R. L. 1987. Patterns and controls of skeletal silicification in a Mississippian fauna, northwestern Wyoming. Unpublished Masters thesis, University of Wyoming, 140 p.

DALEY, R. L., AND D. W. BOYD. 1996. The role of skeletal microstructure during selective silicification of brachiopods. Journal of Sedimentary Research, 66:155–162.

DAVIS, J. A. 1982. Adsorption of natural dissolved organic matter at the oxide/water interface. Geochimica et Cosmochimica Acta, 46:2381–2393.

DENNISON, J. M., AND D. A. TEXTORIS. 1970. Devonian Tioga Tuff in northeastern United States. Bulletin Volcanologique, 34:289–294.

EMIG, C. C. 1990. Examples of post-mortality alteration in Recent brachiopod shells and (paleo) ecological consequences. Marine Biology, 104:233–238.

ERWIN, D. H., AND D. L. KIDDER. 2000. Depositional controls on selective silicification of Permian fossils, southwestern United States, p. 407–415. *In* B. R. Wardlaw, R. E. Grant, and D. M. Rohr (eds.), Guadalupian Symposium. Smithsonian Contributions to Earth Science 32. Smithsonian Institution Press, Washington, D. C.

FLEMING, B. A. AND D. A. CRERAR. 1982. Silicic acid ionization and calculation of silica solubility at elevated temperature and pH application to geothermal fluid processing and reinjection. Geothermics, 11:15–29.

FOLK, R. L. 1974. The natural history of crystalline calcium carbonate: effect of magnesium content and salinity. Journal of Sedimentary Research, 44:40–53.

FRANCIS, S., L. MARGULIS, AND E. S. BARGHOORN. 1978a. On the experimental silicification of microorganisms II. On the time of appearance of eukaryotic organisms in the fossil record. Precambrian Research, 6:65–100.

FRANCIS, S., E. S. BARGHOORN, AND L. MARGULIS. 1978b. On the experimental silicification of microorganisms III, Implications of the preservation of the green prokaryotic alga *Prochloron* and other coccoids for interpretation of the microbial fossil record. Precambrian Research, 7:377–383.

GLOVER, C. P., AND S. M. KIDWELL. 1993. Influence of organic matrix on the postmortem destruction of molluscan shells. Journal of Geology, 101:729–747.

GOERING, J. J., D. M. NELSON, AND J. A. CARTER. 1973. Silicic acid uptake by natural populations of marine phytoplankton. Deep-Sea Research, 20:777–789.

GÖTZE, J., R. MÖCKEL, N. LANGHOF, M. HENGST, AND M. KLINGER. 2008. Silicification of wood in the laboratory. Ceramics Silikáty, 52:268–277.

GUIDRY, S. A., AND H. S. CHAFETZ. 2003. Anatomy of siliceous hot springs: examples from Yellowstone National Park, Wyoming, USA. Sedimentary Geology, 157:71–106.

HARPER, E. M. 2000. Are calcitic layers an effective adaptation against shell dissolution in the Bivalvia? Journal of Zoology, 251:179–186.

HATTAN, S. J., T. M. LAUE, AND N. D. CHASTEEN. 2001. Purification and characterization of a novel calcium-binding protein from the extrapallial fluid of the mollusc, *Mytilus edulis*. Journal of Biological Chemistry, 276: 4461–4468.

HENRICH, R. 1985. A calcite dissolution pulse in the Norwegian-Greenland Sea during the last deglaciation. Geologische Rundschau, 75:805–827.

HENRICH, R., AND G. WEFER. 1986. Dissolution of biogenic carbonates; effects of skeletal structure. Marine Geology, 71:341–362.

HESSE, R. 1989. Silica diagenesis; origin of inorganic and replacement cherts. Earth Science Reviews, 26:253–284.

HINMAN, N. W. 1987. Organic and inorganic chemical controls on the rates of silica diagenesis; a comparison of a natural system with experimental results. Unpublished Ph.D. dissertation, University of California, San Diego. 402 p.

HINMAN, N. W. 1990. Chemical factors influencing the rates and sequences of silica phase transitions: Effects of organic constituents. Geochimica et Cosmochimica Acta, 54:1563–1574.

HINMAN, N. W. 1998. Sequences of silica phase transitions: effects of Na, Mg, K, Al, and Fe ions. Marine Geology, 147:13–24.

HINTZE, L. F. 1953. Silicification of Ordovician fossils in Utah and Nevada. Geological Society of America Bulletin, 64:1508–1508.

HOLDAWAY, H. K., AND C. J. CLAYTON. 1982. Preservation of shell microstructure in silicified brachiopods from the Upper Cretaceous Wilmington Sands of Devon. Geological Magazine, 119:371–382.

ILER, R. K. 1979. The Chemistry of Silica: Solubility, Polymerization, Colloid and Surface Properties, and Biochemistry. Wiley, New York.

JACKA, A. D. 1974. Replacement of fossils by length-slow chalcedony and associated dolomitization. Journal of Sedimentary Petrology, 44:421–427.

KASTNER, M., J. B. KEENE, AND J. M. GIESKES. 1977. Diagenesis of siliceous oozes; I, Chemical controls on the rate of opal-A to opal-CT transformation; an experimental study. Geochimica et Cosmochimica Acta, 41:1041–1059.

KEITH, J., S. STOCKWELL, D. BALL, K. REMILLARD, D. KAPLAN, T. THANNHAUSER, AND R. SHERWOOD. 1993. Comparative-analysis of macromolecules in mollusk shells. Comparative Biochemistry and Physiology B-Biochemistry & Molecular Biology, 105:487–496.

KIDDER, D. L., AND D. H. ERWIN. 2001. Secular distribution of biogenic silica through the Phanerozoic: Comparison of silica-replaced fossils

and bedded cherts at the series level. Journal of Geology, 109:509–522.

KLEIN, C., C. S. HURLBUT, AND J. D. DANA. 1993. Manual of Mineralogy (21st Edition). Wiley, New York.

KLEIN, R. T., AND L. M. WALTER. 1995. Interactions between dissolved silica and carbonate minerals: An experimental study at 25–50°C. Chemical Geology, 125:29–43.

KNAUTH, L. P. 1979. A model for the origin of chert in limestone. Geology, 7:274–277.

KNOLL, A. H. 1985. Exceptional preservation of photosynthetic organisms in silicified carbonates and silicified peats. Philosophical Transactions of the Royal Society of London B-Biological Sciences, 311:111–122.

KONHAUSER, K. O., B. JONES, V. R. PHOENIX, G. FERRIS, AND R. W. RENAULT. 2004. The microbial role in hot spring silicification. AMBIO: A Journal of the Human Environment, 33:552–558.

LANCELOT, Y. 1973. Chert and silica diagenesis in sediments from the central Pacific. Initial Reports of the Deep Sea Drilling Project, 17:377–405.

LAND, L. S. 1967. Diagenesis of skeletal carbonates. Journal of Sedimentary Petrology, 37:914–920.

LAUFELD, S., AND L. JEPPSSON. 1976. Silicification and bentonites in the Silurian of Gotland. Geologiska Föreningens i Stockholm Föhandlingar, 98:31–44.

LEO, R. F., AND E. S. BARGHOORN. 1976. Silicification of Wood. Botanical Museum Leaflets 25. Harvard University, Cambridge, MA.

LOOPE, D. B., AND D. K. WATKINS. 1989. Pennsylvanian fossils replaced by red chert: early oxidation of pyritic precursors. Journal of Sedimentary Petrology, 59:375–386.

LYNNE, B. Y., K. A. CAMPBELL, B. J. JAMES, P. R. BROWNE, AND J. MOORE. 2007. Tracking crystallinity in siliceous hot-spring deposits. American Journal of Science, 307:612–641.

MALIVA, R. G., A. H. KNOLL, AND R. SIEVER. 1989. Secular change in chert distribution: A reflection of evolving biological participation in the silica cycle. PALAIOS, 4:519–532.

MALIVA, R. G., A. H. KNOLL, AND B. M. SIMONSON. 2005. Secular change in the Precambrian silica cycle; insights from chert petrology. Geological Society of America Bulletin, 117:835–845.

MALIVA, R. G. AND R. SIEVER. 1988. Mechanisms and controls of silicification of fossils in limestones. Journal of Geology, 96:387–398.

MARIN, F., AND G. LUQUET. 2004. Molluscan shell proteins. Comptes Rendus Palevol, 3:469–492.

MEYER, F. A. A. 1791. Briefe über einige mineralogische Gegenstände an Herrn Peter Camper, Göttingen.

MEYERS, W. J. 1977. Chertification in the Mississippian Lake Valley Formation, Sacramento Mountains, New Mexico. Sedimentology, 24:75–105.

MILLIMAN, J. D., AND E. BOYLE. 1975. Biological uptake of dissolved silica in the Amazon River estuary. Science, 189:995–997.

MIŠÍK, M. 1995. Selective silicification of calcitic fossils and bioclasts in the West-Carpathian limestones. Geologica Carpathica, 46:151–159.

MORSE, J. W. 1983. The kinetics of calcium carbonate dissolution and precipitation. Reviews in Mineralogy and Geochemistry, 11:227–264.

NESTELL, M. K., G. P. NESTELL, B. R. WARDLAW, G. L. BELL, AND A. O. IVANOV. 2012. Biostratigraphy of a complete Pinery Section (Bell Canyon Formation, Guadalupian, Middle Permian), Guadalupe Mountains, West Texas. Geological Society of America Abstracts with Programs, 44(1):4.

NEWELL, N. D., AND D. W. BOYD. 1970. Oyster-like Permian Bivalvia. Bulletin of the American Museum of Natural History, 143:217–282.

NEWELL, N. D., J. K. RIGBY, A. G. FISCHER, A. J. WHITEMAN, J. E. HICKOX, AND J. S. BRADLEY. 1953. The Permian Reef Complex of the Guadalupe Mountains Region, Texas and New Mexico; A Study in Paleoecology. W. H. Freeman, San Francisco.

NICKLEN, B. L., AND G. L. BELL. 2007. Ancient ash beds in the type area of the Middle Permian, Guadalupe Mountains National Park, West Texas, USA. Geological Society of America Abstracts with Programs, 39(6):148.

PALMER, T. J., J. D. HUDSON, AND M. A. WILSON. 1988. Palaecological evidence for early aragonite dissolution in ancient calcites seas. Nature, 335:809–810.

PARAGUASSO, A. B. 1976. Experimental replacement of silica. Revista Brasiliera de Geociências, 6:89–94.

PECK, L. S. 1993. The tissues of articulate brachiopods and their value to predators. Philosophical Transactions of the Royal Society of London, 339:17–32.

PECK, L. S., A. CLARKE, AND L. J. HOLMES. 1987. Size, shape, and the distribution of organic matter in the Recent Antarctic brachiopod *Liothyrella uva*. Lethaia, 20:33–40.

PERRY, R. S. 2003. Preservation of bioorgainc molecules in amorphous silica in nature. Geological Society of America Abstracts with Programs, 35(6):457

RAILSBACK, L. B., AND T. F. ANDERSON. 1987. Control of Triassic seawater chemistry and temperature on the evolution of post-Paleozoic aragonite-secreting faunas. Geology, 15:1002–1005.

READ, J. F. 1998. Phanerozoic carbonate ramps from greenhouse, transitional and ice-house worlds:

clues from field and modelling studies. Geological Society of London Special Publications 149:107–135.

RIES, J. B. 2010. Geological and experimental evidence for secular variation in seawater Mg/Ca (calcite-aragonite seas) and its effects on marine biological calcification. Biogeosciences, 7:2795–2849.

SCHMITT, J. G., AND D. W. BOYD. 1981. Patterns of silicification in Permian pelecypods and brachiopods from Wyoming. Journal of Sedimentary Research, 51:1297–1308.

SCHOLLE, P. A., AND D. S. ULMER-SCHOLLE. 2003. A Color Guide to the Petrography of Carbonate Rocks: Grains, Textures, Porosity, Diagenesis. American Association of Petroleum Geologists Memoir 77, Tulsa, Oklahoma.

SCHUBERT, J. K., D. L. KIDDER, AND D. H. ERWIN. 1997. Silica-replaced fossils through the Phanerozoic. Geology, 25:1031–1034.

SCURFIELD, G., AND E. R. SEGNIT. 1984. Petrifaction of wood by silica minerals. Sedimentary Geology, 39:149–167.

SENKAYI, A. L., J. B. DIXON, L. R. HOSSNER, B. P. K. YERIMA, AND L. P. WILDING. 1985. Replacement of quartz by opaline silica during weathering of petrified wood. Clays and Clay Minerals, 33:525–531.

SIEVER, R. 1957. The silica budget in the sedimentary cycle. American Mineralogist, 42:821–841.

SIEVER, R. 1962. Silica solubility, 0–200°C and the diagenesis of siliceous sediments. The Journal of Geology, 70:127–150.

SIEVER, R. 1992. The silica cycle in the Precambrian. Geochimica et Cosmochimica Acta, 56:3265–3272.

SIEVER, R., AND N. WOODFORD. 1973. Sorption of silica by clay minerals. Geochimica et Cosmochimica Acta, 37:1851–1880.

SMITH, R. C., II, AND J. H. WAY. 1988. The Bald Hill bentonite beds; a Lower Devonian pyroclastic-bearing unit in the northern Appalachians. Northeastern Geology, 10:216–230.

SPERLING, E. A., J. M. ROBINSON, D. PISANI, AND K. J. PETERSON. 2010. Where's the glass? Biomarkers, molecular clocks, and microRNAs suggest a 200−Myr missing Precambrian fossil record of siliceous sponge spicules. Geobiology, 8:24–36.

STANLEY, S. M., AND L. A. HARDIE. 1998. Secular oscillations in the carbonate mineralogy of reef-building and sediment-producing organisms driven by tectonically forced shifts in seawater chemistry. Palaeogeography, Palaeoclimatology, Palaeoecology, 144:3–19.

STANLEY, S. M., AND L. A. HARDIE. 1999. Hypercalcification: paleontology links plate tectonics and geochemistry to sedimentology. GSA Today, 9:1–7.

SUMMONS, R. E. AND M. R. WALTER. 1990. Molecular fossils and microfossils of prokaryotes and protists from Proterozoic sediments. American Journal of Science, 290:212–244.

SUN, Y., AND A. BALINSKI. 2008. Silicified Mississippian brachiopods from Muhua, southern China: Lingulids, craniids, strophomenids, productids, orthotetids, and orthids. Acta Palaeontologica Polonica, 53:485–524.

TOMASOVYCH, A., AND T. A. ROTHFUS. 2005. Differential taphonomy of modern brachiopods (San Juan Islands, Washington State): effect of intrinsic factors on damage and community-level abundance. Lethaia, 38:271–292.

TRÉGUER, P., D. M. NELSON, A. J. VAN BENNKOM, D. J. DEMASTER, A. LEYNAERT, AND B. QUÉGUINER. 1995. The silica balance in the world ocean: A reestimate. Science, 268:375–379.

TUCKER, M. E., AND V. P. WRIGHT. 1990. Carbonate Sedimentology. Blackwell Science Ltd., Oxford.

VER STRAETEN, C. A. 2009. The classic Devonian of the Catskill Front: a foreland basin record of Acadian Orogenesis, p. 7-1–7-26. *In* F. Vollmer (ed.), 81st Annual Meeting Guidebook, New York State Geological Association, New York

WALTER, L. M. 1983. The dissolution kinetics of shallow water carbonate grain types; effects of mineralogy, microstructure, and solution chemistry. Unpublished Ph.D. dissertation, University of Miami, 347 p.

WALTER, L. M. 1985. Relative reactivity of skeletal components during dissolution, p. 3–16. *In* N. Schneidermann and P. M. Harris (eds.), Carbonate Cements. SEPM Special Publication 36. SEPM, Tulsa, Oklahoma.

WALTER, L. M., AND J. W. MORSE. 1984. Reactive surface area of skeletal carbonates during dissolution; effect of grain size. Journal of Sedimentary Petrology, 54:1081–1090.

WALTER, L. M., AND J. W. MORSE. 1985. The dissolution kinetics of shallow marine carbonates in seawater: A laboratory study. Geochimica et Cosmochimica Acta, 49:1503–1513.

WEINER, S. 1983. Mollusk shell formation: isolation of two organic matrix proteins associated with calcite deposition in the bivalve *Mytilus californianus*. Biochemistry, 22:4139–4145.

WILKINSON, B. H. 1979. Biomineralization, paleoceanography, and the evolution of calcareous marine organisms. Geology, 7:524–527.

WILLIAMS, A. 1997, Shell Structure, p. 267–320. *In* R. L. Kaesler (ed.), Treatise on Invertebrate Paleontology, Part H (revised), Brachiopoda, Vol. 1. Geological Society of America and University of Kansas Press, Boulder, CO, and Lawrence, KS.

WILLIAMS, L. A., AND D. A. CRERAR. 1985. Silica diagenesis II. General Mechanisms. Journal of Sedimentary Petrology, 55:312–321.

WRIGHT, V. P., L. CHERNS, AND P. HODGES. 2003. Missing molluscs: Field testing taphonomic loss in the Mesozoic through early large-scale aragonite dissolution. Geology, 31:211–214.

ZHURAVLEV, A. Y., AND R. A. WOOD. 2009. Controls on carbonate skeletal mineralogy: Global CO_2 evolution and mass extinctions. Geology, 37:1123–1126.