THE EXCEPTIONAL PRESERVATION OF PLANT FOSSILS: A REVIEW OF TAPHONOMIC PATHWAYS AND BIASES IN THE FOSSIL RECORD

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ABSTRACT.—The exceptional preservation of plant fossils falls into two categories: whole plant preservation and anatomical detail. Whole plant preservation is controlled primarily by transport and event preservation (e.g., ash falls), whereas anatomical preservation can occur through one of several taphonomic pathways: compression-impression, silicification, coal-ball formation, pyritization, and charcoalification. This review focuses on these taphonomic pathways, highlighting important factors and controls on the exceptional preservation of plants. Special emphasis is given to data garnered from experimental and actualistic approaches.

INTRODUCTION

What is exceptional plant preservation?

Plants are fundamentally different from animals in several ways, and expectations for 'exceptional preservation' must change accordingly. Plants are modular organisms that readily disarticulate into various organs (leaves, stems, roots, and reproductive structures). Unlike animals, disarticulation occurs regularly over a plant's normal life cycle (e.g., deciduous trees shed leaves every autumn) as well as upon death (Spicer, 1989; Greenwood, 1991; Wing et al., 1992; Rowe and Speck, 1998; Gee and Gastaldo, 2005). The tissues of these organs are somewhat different from those of animals: the structural polysaccharides (cellulose, hemicellulose, and lignin) and waxy polymers comprising the cuticle (Briggs et al., 2000; Briggs, 2003; Fioretto et al., 2005; Wakeham and Canuel, 2006; Gupta et al., 2007a, b) have a much lower preservation potential than bones or shells, but are also much more likely to be preserved than animal soft parts. Most importantly, the way in which these plant parts find their way into the lithosphere is fundamentally different from the pathways followed by terrestrial or marine animals. Many marine invertebrates, like plants, disseminate propagules throughout the water column, but these are almost never preserved. In contrast, plant propagules (seeds, pollen) are exceptionally well preserved in great abundance and diversity throughout much of the Phanerozoic record. Similarly, although both terrestrial vertebrates and plant hard parts (stems, trunks) are preferentially preserved in fluvial deposits or debris flows, there is a strong ecological control on what types of plants grow or accumulate near water bodies (e.g., calamitaleans and sigillarian lycopsids during the Carboniferous and Permian periods; vines in the Cenozoic era), whereas these patterns are sometimes less clear for animal groups. Therefore, at the most basic level, the processes controlling plant fossilization are distinct from those affecting animals.

Exceptionally preserved plant fossils fall into two main categories. One type of exceptionally preserved plant fossil retains the entire and original arrangement of the various organs—from roots to reproductive structures (Scott and Rex, 1985). If organs are found separately, they are given distinct names, and only when two structures are found together can the complete plant be reconstructed, as was the case with *Archaeopteris* (Beck, 1960a, b). Fossils such as these are dependent on transport processes and unusual events such as ash falls (Ferguson, 2005). The second type of exceptional fossil preserves the internal structure and three-dimensional cellular detail. Although uncommon, such preservation can provide paleobotanists with unique taxonomic information (Smoot, 1984; Smoot and Taylor, 1986). This type of preservation is controlled by pre- and post-burial decay and diagenesis.

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Why study exceptionally preserved plant fossils?

The fossil record of land plants extends into the middle Ordovician. Numerous microfossils—spores, tubules, and cuticle fragments—are reported from Ordovician marine rocks around the world (Gensel 2008). Several authors (e.g., Gray et al., 1985; Wellman et al., 2003) suggested taxonomic placement of at least some of these microfossils within the bryophytes (hornworts, liverworts, and mosses), the sister groups to all other vascular plants (Nickrent et al., 2000; Nishiyama et al., 2004), based on the preserved anatomy, whereas vascular plant fossils do not appear until the late Silurian (Gensel, 2008).

The majority of plant fossils are preserved as either impressions (no organics remaining) or compressions (organics remain) (Collinson, 2011); these fossils are part of a continuum of more to less preserved organic material. Surface details, such as stomata, trichome bases, and epidermal cell arrangement may be preserved with or without organic remains, but the preservation of the ultrastructure of internal leaf anatomy varies widely. Woody organs, such as the axes and roots, are more often found preserved in three dimensions, but delicate tissues (e.g., cellulose-rich, lignin-poor phloem) are often not preserved due to more rapid decay.

Plant fossils from Lagerstätten can retain this internal anatomy and provide more morphological detail than the average compression-impression fossils. The early Devonian Rhynie Chert Lagerstätte, for example, contains a rich, in-situ assemblage where the anatomy of early plants and other organisms are silicified and preserve exceptional detail. This exceptional fossil deposit is one of several that have helped reveal major changes in plant evolution throughout the Phanerozoic (Table 1; Schopf, 1975; Knoll, 1985; Gensel, 2008). Additionally, the exceptional preservation of both the external morphology and internal anatomy of plants has allowed the study of the evolution of plant vascular systems (e.g., Wilson et al., 2009) and entire plant ecosystems (Scott and Rex, 1985). Without exceptionally preserved fossils and fossil assemblages, these insights into the past would be lost. Understanding how these fossils form is crucial to the interpretation of the functional and ecological information they hold. This paper will review the major taphonomic pathways leading to the exceptional preservation of plants, with a focus on experimental and actualistic studies of plant preservation.

TAPHONOMIC PATHWAYS

Three major concerns in the formation of plant fossils are: 1) how well anatomically important information is retained; 2) the taxonomic biases that may be introduced during the fossilization process; and 3) the degree to which paleoenvironmental data (e.g., isotopic information in cuticle waxes) are retained. The basic pathway for a plant organ, such as a leaf, to become a fossil is for it to be transported, buried, undergo some degree of decay, and survive long enough for the surrounding sediment to lithify (Rex and Chaloner, 1983; Ferguson, 2005), or for the tissues to be permineralized (e.g., Kenrick and Edwards, 1988). The highly resistant waxy cuticle is thought to favor this process (Collinson, 2011) by providing a robust external layer of protection to the more labile internal tissues of the leaf, but the degree of internal decay, as well as exposure to oxygen, will affect the final product (Yang and Huang, 2003). Different taphonomic modes occur on different timescales and under different environmental conditions, and may affect the formation of a fossil at different parts of the pathway to fossilization (Fig. 1). Additionally, tissues and organs may be preserved differently by different taphonomic pathways (Fig. 2).

Schopf (1975) presented a classic view on the four preservational modes that are important in fossil plant preservation: 1) duripartic (hard part) preservation, 2) organic compression/impression, 3) authigenic preservation, and 4) cellular permineralization. An additional mode, charcoalification, was recognized as an important mode of preservation, particularly of flowers, in the 1980s (e.g., Friis and Skarby, 1981). Paleontologists have long recognized that duripartic preservation is the most common, as evidenced by the extensive marine shelly fossil record. Authigenic mineralization occurs when the surrounding sediment is rapidly cemented, normally in the form of a concretion (Schopf, 1975). McCoy (2014) discusses the formation of concretions, so it is not considered here. Plant fossils are most often preserved as either impressions or compressions (Schopf, 1975; Greenwood, 1991), but often retain only gross morphological characters or epidermal anatomy through the preservation of the durable cuticle. Permineralized fossils can be the most useful to paleobotanists because internal anatomy is often

TABLE *1*.—Examples of plant Lagerstätten with different types of preservation through time. Clades: A = Angiosperms; Be = Bennettitales; Br = Bryophytes; Co = Conifers; Ex = Extinct seed plants; F = Ferns; Gn = Gnetales; Gk = Ginkgo; L = Lycophytes; Pt = Pteridophytes; R = Rhyniophytes; Sp = Sphenopsids; Un = Unknown affiliation; Zo = Zosterophylls. Preservation: Car = Carbonate coal balls; Com = compression; Con = concretion; IO = iron oxides; Py = pyritization; S = silicification.

Locality	Age	Clades	Preservation	Citations
Rhynie Chert	Devonian	Br, L, R, Un, Zo	S	Edwards, 1986; Lyon et al., 1991; Kerp et al., 2004; Channing et al., 2009
Brecon Beacons Quarry, Powys, Wales	Devonian	L, R, Zo	Py	Edwards, 1969; Kenrick and Edwards, 1988; Kenrick et al., 1991
Lancashire Coal Fields	Carboniferous	Co, L, P, Sp	S, Car	Galtier, 1997
American Coal Fields (e.g. Herrin, IL)	Carboniferous	Co, L, P, Sp	Car	Andrews, 1951
Mazon Creek	Carboniferous	L, Pt	Com, Con	Wittry, 2006
Clear Fork Group	Permian	Co, Pt, Sp,	IO	Chaney et al., 2009
Fremouw Formation	Triassic	Ex	Si	Taylor et al., 1989
Crato Formation	Cretaceous	A, Co, Ex, Gn	IO	Mohr and Friis,
North Almont	Paleocene	A, Co, Gk, Pt	S	Crane, 2013
London Clay	Eocene	A, Co, Pt	Py	Grimes et al., 2001
Messel	Eocene	A, Co, Pt, Un	Com	Schaal, 1992; Collinson et al., 2010
Musselshell Creek	Miocene	A, F, Gk, Co,	Com	Baghai and Jorstad, 1995
Clarkia	Miocene	A, F, Co,	Com	Baghai and Jorstad, 1995
Shanwang	Miocene	A, Co	Com	Yang and Yang, 2004

preserved. The three primary minerals involved in this type of preservation are silica (either as hydrous silica or microcrystalline quartz), calcite, and pyrite (Gastaldo, 1988).

Each mode of preservation requires certain environmental conditions, making it possible to infer more about the environmental setting than might normally be expected.

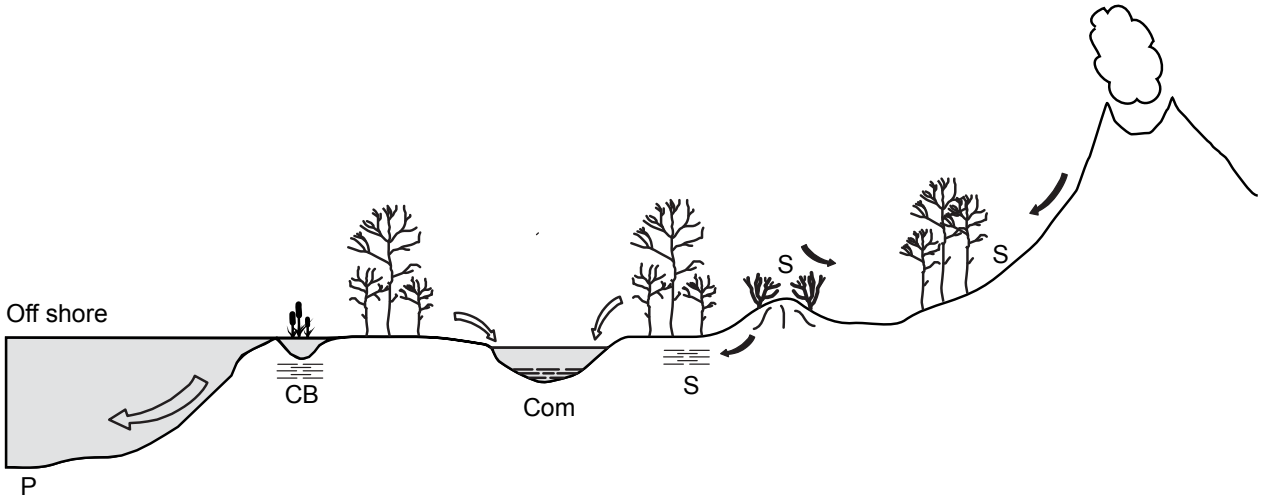

FIGURE *1*.—Cross-section through a hypothetical landscape showing different depositional environments and associated taphonomic pathways. White and gray arrows indicate transport of plant organs. Black arrows indicate transport of silica for silicification, which can occur through the flow of silica-rich ground water, in situ in hot spring environments, or through silica from volcanic ash. P = pyritization; CB = coal balls; Com = compression-impression; S = silicification.

Compression-Impression

The majority of plant fossils, primarily leaves, are preserved on a gradient from an impression with no organic preservation to partial or complete organic preservation (compression). These fossils form when a plant organ is buried in sediment and decays in situ to form a flattened version of the original (Rex and Chaloner, 1983). Impression fossils form when the organ is decayed away, leaving a void in the sediment, whereas compression fossils retain some of the plant tissue. These organics show a range of preservation depending on the original tissues, depositional environment, and burial history (Collinson, 2011). In rare cases, such as some leaves from the Miocene Clarkia and Succor Creek Lagerstätten (Niklas and Brown, 1981) and Jurassic lahar deposits in Sweden (Bomfleur et al., 2014), the original ultrastructure down to subcellular features (e.g., chloroplasts, chromosomes) is preserved. Other leaves from the same locality exist only as a cuticle envelope with the internal anatomy of the leaf entirely absent, making the preservation of such detail truly exceptional. In addition to anatomy, compression fossils provide valuable geochemical information, and have been used as paleoenvironmental indicators (e.g., Kuder and Kruge, 1998; Yang and Huang, 2003). The formation of compression-impression fossils and the biases behind their formation has been investigated both in relation to physical and geochemical processes.

Physical formation.—Understanding the biases introduced during the preservation of leaves as compression-impression fossils is critical in reconstructing past ecosystems. Fossil leaves record not only valuable taxonomic information, but also paleoclimate data related to past CO_2 levels (Beerling and Chaloner, 1993; Royer et al., 2001; Beerling and Royer, 2002; Doria et al., 2011). Changes to dimensions of the leaf may affect interpretation of past ecosystems by altering the density of the stomata. It had long been thought that during the formation of a leaf compression fossil, the primary axis of deformation was vertical, with little or no horizontal changes (Walton, 1936; Schopf, 1975). However, it has been shown that both during compaction and dehydration, horizontal changes to the linear dimensions of the leaf may be as great as 10% (Rex and Chaloner, 1983; Cleal and Shute, 2007). Therefore, stomatal density alone is not recommended as a paleoclimate proxy; rather, the stomatal index, which is the ratio of stomatal density to epidermal cell density, is preferred, as shrinkage or expansion of the cuticle does not affect this ratio (Cleal and Shute, 2007).

Axes of a plant are more subject to deformation than are other tissues. Fossil stems show a range of flattened to elliptical or circular cross-section, depending on the degree of compression (Chaloner and Collinson, 1975;

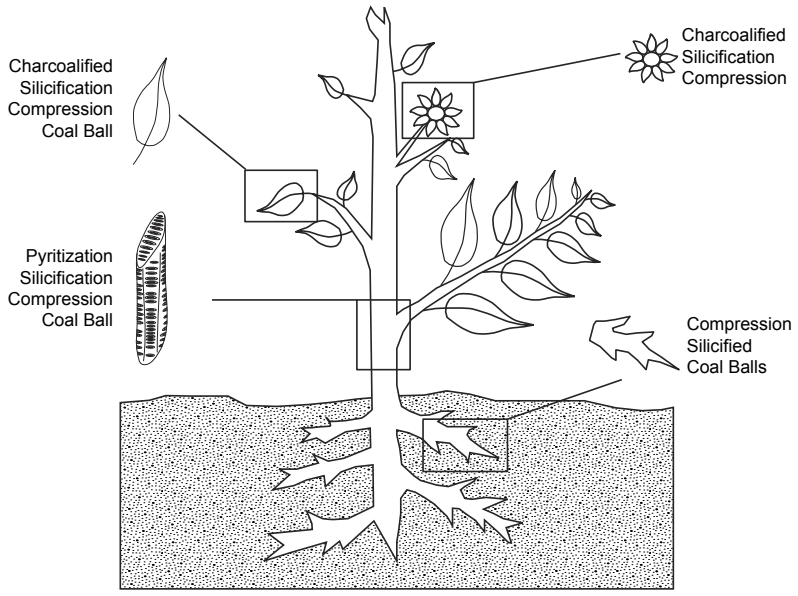

FIGURE *2*.—Examples of major plant organs (leaves, axes, roots, reproductive structures) and the taphonomic pathways that are most commonly associated with fossil examples.

Niklas, 1984). However, the dimensions of the compressed axis reflect the original diameter quite accurately (Niklas, 1978; Rex and Chaloner, 1983). On compressed axes, smaller-scale structures, such as stomatal pits, can retain their original dimensions (Spicer, 1977), emphasizing the importance of scale when examining changes during fossilization. The process of compression acts on the macromorphology of the organ, but the micromorphology is protected from deformation (Rex and Chaloner, 1983).

Sediment properties play a large role in the preservation of leaves as compression-impression fossils. The grain size of the surrounding sediment can control the degree of compaction that a plant experiences during fossilization. Coarse-grained sediments retain little water and undergo little compaction, with most of it occurring during early diagenesis (Rex and Chaloner, 1983). Finer-grained sediments, on the other hand, contain between 40–80% water, and experience significant dewatering during early diagenesis. In clay-rich sediments, particles align, losing water and enabling further compaction (Rex and Chaloner, 1983; Pittman and Larese, 1991; Giles et al., 1998). While the role of compaction in the formation of plant fossils has been researched (e.g., Rex and Chaloner, 1983), the role of rapid dewatering versus continued hydration has not yet been studied.

A common feature of many compression-impression fossils is the presence of a mineral coating, most commonly of iron oxides/oxyhydroxides. This phenomenon was first discussed by Spicer (1997), and was further investigated by Dunn et al. (1999). The formation of an iron-oxide coating happens within days to weeks of leaves settling in water. Bacteria, primarily from the surface of the leaf, colonize the anionic surface of the waxy cuticle and form biofilms. The extracellular polymeric secretions that form the biofilms are highly reactive, and quickly cause the precipitation of ferrihydrite (Dunn et al., 1997). This mineral coating is thought to enhance the preservation potential of the leaf in several ways. First, it acts as a sort of armor, preventing abrasion and damage due to transport and scavenging (Spicer, 1977, 1989). Second, the accumulation of iron can inhibit further bacterial activity, slowing down the decay of leaf tissues (Dunn et al., 1997). Finally, the rapid precipitation of minerals on the surface of the leaf may ensure the preservation of fine-scale topographic features that would normally be lost or obscured by decay or the collapse of internal tissues (Spicer, 1989; Dunn et al., 1997). In rare instances, fossils are preserved in iron oxides three-dimensionally (e.g., Permian Clear Fork Group: Chaney et al., 2009; Mio–Pliocene New Caledonia: Locatelli, 2013). In the case of the New Caledonian flora, this relates to the depositional environment: a shallow, oxic stream with high iron content due to weathering of ultramafic basement (Locatelli, 2013).

Chemical formation.—The chemical remains of plant fossils can provide valuable paleoenvironmental data through the preservation of hydrogen, carbon, and oxygen isotopes. The most widely used fossil biomolecules for paleoclimatic analysis are lipids (Briggs, 1999). Lipids are relatively robust to chemical diagenesis and can survive in the sediment for millions of years. Other useful macromolecules include the building blocks of most plants—the structural carbohydrates cellulose and lignin. The preservation of these molecules has been of interest for many years, and several authors have recently reviewed this topic (e.g., Collinson, 2011).

In plants, the primary source of lipids is the waxy epicuticle, which is composed of a variety of long-chain aliphatic compounds (e.g., hydrocarbons, alcohols, ketones, esters, and aldehydes), pentacyclic triterpenoids, and phytosterols (Logan et al., 1995). These biomolecules are recognized in modern lake sediments (Rieley et al., 1991; Huang et al., 2004) and lacustrine rocks (Logan et al., 1995; Yang and Huang, 2003), the latter in a slightly altered form due to diagenesis over millions of years (Gupta et al., 2007a, b).

In addition to providing lipids for geochemical analyses, the cuticle enhances the overall preservation potential of leaves due to its resistance to microbial decay (Kelleher et al., 2006), although fossil leaves may survive after the loss of cuticle (Collinson, 2011). It was long thought that the high preservation potential of the cuticle reflected the selective preservation of a decay-resistant molecule called cutan, a highly aliphatic and resistant biopolymer believed to be a hydrocarbon (Nip et al., 1986; Tegelaar et al., 1989, 1991). If the presence or absence of cutan was the primary control on the preservation of cuticle, and thus of leaves, the fossil record would be heavily biased toward the preservation of plants that contained cutan in their cuticle (Tegelaar et al., 1991). However, many studies have shown that cutan is found in only a limited group of plants, primarily the monocotyledons *Agave* (Agavaceae) and *Clivia* (Liliaceae) (Gupta et al., 2006 and references therein). Neither *Agave* nor *Clivia* are represented as fossils, while cutan-lacking plants such as *Gingko*, *Metasquoia*, and *Quercus* have extensive fossil records. Maturation experiments on the waxy cuticles of *Castanea* (Fagaceae), *Acer* (Aceraceae), *Pinus* (Pinaceae), *Quercus* (Fagaceae), and *Ginkgo* (Gingkoales) confirmed the absence of cutan or other aliphatic precursors in fresh cuticles, but showed that aliphatic compounds formed during maturation (Gupta et al., 2007a, b; Collinson, 2011). Other cuticular constituents, including cutin (a polyester), waxes, and internal plant lipids, undergo in-situ polymerization and form highly resistant geomacromolecules during fossilization.

Silicification

Silicified plant fossils are some of the most important for studying the evolution of vascular plants and other photosynthetic organisms (Greenwood, 1991; Knoll, 1985) due to their quality of preservation as well as their frequency in the fossil record (Stein, 1982). Silicified wood is particularly common, and is found from the Paleozoic to the Holocene. Internal anatomy, from details of cell wall structure to various stages of reproductive organ development, can be preserved at the subcellular level, giving unparalleled insight into the morphology and ultrastructure of fossil plants (e.g., Basinger and Rothwell, 1977; Kenrick and Crane, 1991; Dettmann et al., 2009) and other photosynthetic organisms (Tyler and Bargoorn, 1954; Knoll, 1985). The importance of silicified plant fossils in studying both the evolution of plants and the paleoecology of ancient environments demands that the controls on silicification be understood.

The source of silica can vary widely between depositional environments (Fig. 1). Volcanic ash and hydrothermal vent systems contain abundant silica, but in many fossil sequences, there is little evidence of volcanic or hydrothermal sources (Knoll, 1985). The marine realm is undersaturated with respect to silica. Diatoms, radiolarians, and sponge spicules have been cited as possible sources for silicification (Hesse, 1989), but the ultimate source of silica for the skeletons remains an open question. Plants are most commonly preserved in terrestrial settings, however, where silica is more widely available. The source of silica in terrestrial systems can be the dissolution of diatoms or detrital feldspar in immature sediments (Jefferson, 1987; Matysová et al., 2010). Even in systems lacking obvious sources of silica, the dissolved silica from siliciclastic rocks in groundwater may be enough to silicify plants, albeit on longer time scales (Knoll, 1985). In general, silica availability is not the limiting factor that controls silicification in terrestrial environments (Knoll, 1985; Hesse, 1989).

Under Leo and Barghoorn's model (1976),

some decomposition of the plant may enhance the process of silicification by creating an abundance of sites for hydrogen bonding. However, if too much decay of the organic matter occurs, the template on which silicification occurs is also lost. Therefore, silicification is somewhat time-dependent on the survival of organic matter. For those deposits in which internal anatomy of plants is exceptionally preserved, the rate of silicification would have been rapid, on the scale of days, weeks, or years, depending on the tissues and environment (Knoll, 1985; Channing and Edwards 2004; Ballhaus et al., 2012), in order to outpace the rate of decay.

Silicification of fossils begins with the initial deposition of silica, in the form of monomeric silicic acid H_4SiO_4, on and within cell walls of plants. Further silicification occurs through the polymerization of silicic acid and loss of water (Hesse 1989). Polymerization leads to the formation of opal-A, which then undergoes a maturation sequence to opal-CT, and finally to quartz given the right conditions and sufficient time (Buurman 1972; Leo and Barghoorn 1976; Hesse, 1989). The transformation from opal-A to opal-CT in fossil wood occurs at a rate comparable to silica transformations in biogenic siliceous oozes, which is on the order of millions of years (Stein 1982).

Experimental silicification.—Understanding the processes involved in silicification informs our interpretation of the fossil data. One of the primary questions paleobotanists have asked is what is the rate at which silicification occurs. The first attempt at experimental silicification of plants was to replicate silicified wood. Drum (1968), Leo and Barghoorn (1976), and Sigleo (1978) successfully silicified wood, showing that the permineralization of wood by silica is a void-filling permeation process rather than one of replacement. Dissolved silicon has an affinity for the exposed hydroxyl functional groups in these macromolecules, and rapidly forms hydrogen bonds (Knoll, 1985; Hesse, 1989). In Drum's experiments (1968), the internal anatomy of *Betula* wood cells was replicated by silica, albeit very thinly, after only 24 hours of submersion in a solution of sodium metasilicate. A more robust silicification capable of surviving fossilization takes longer, on the order of weeks to years (Channing and Edwards, 2004). Decay not only increases the number of bonding sites, but also allows silica-containing fluids to percolate through cracks (Knoll, 1985). Leo and Barghoorn (1976) suggested that further silica precipitation occurs through silicic acid polymerization (Knoll, 1985) following initial deposition of silica on organic surfaces through hydrogen bonding.

Drum's (1968) experiments were conducted under an alkaline system (pH=14), which is well outside common natural pH conditions (Ballhaus et al., 2012). Other experiments used silica-containing compounds that are not normally found in nature, such as ethyl silicates, silica compounds, silica sols, and silica gels, or they were conducted under vacuum. This compromises the use of the results to interpret natural silicification (Götze et al., 2008; Ballhaus et al., 2012). Most experimental silicification in laboratory settings has resulted in the deposition of amorphous silica, which is a precursor to opal, the form of silica that occurs in naturally silicified wood.

Ballhaus et al. (2012) aimed to silicify wood with a more natural silica source. Pieces of Douglas fir (*Pseudotsuga menziesii*) were placed in an autoclave and reacted with silica-enriched water, using crushed rhyolitic obsidian as the silica source. The driving factor behind silica deposition is the rapid pH change that occurs when silica-rich alkaline waters came in contact with the acidic interior of the wood (Ballhaus et al., 2012). This abrupt shift in pH conditions is thought to force the precipitation of silica as opal, and if this deposition occurs inside the plant tissue, it would cause permineralization. Additionally, the experiments accelerated the decomposition of the organic matter, which may have played an additional role in the silicification of the wood by creating more available binding sites.

Rhynie Chert experiments.—The most famous, and one of the most important silicified plant assemblages, is the early Devonian Rhynie Chert. Early land plants are preserved three-dimensionally, in-situ and erect, at the cellular and sub-cellular level, by silica, which is thought to have been deposited as hot-spring waters permeated the plants (Rice et al., 2002; Channing and Edwards, 2009; Ballhaus et al., 2012). The Rhynie Chert also contains some of the earliest insects, arachnids, and fungi, providing one of the earliest and most complete views into terrestrial ecosystems (Kidston and Lang, 1917, 1920a,b, 1921a,b; Trewin, 1996; Taylor and Taylor, 2000). In order to accurately interpret the rich paleobiological information held within the Rhynie Chert, a number of experiments have been

conducted to examine the taphonomic processes involved in the preservation of the plants.

One of the primary questions concerning the silicified plants within the Rhynie Chert is the rate of preservation. Experiments examining the rate of silicification at Yellowstone hot springs found evidence of silica deposition in stems submerged in hot hydrothermal fluids after only 30 days (Channing and Edwards, 2004), but deposition was not uniform in all tissues. Opal-A was observed after 30 days in some intracellular regions and on the internal surface of peripheral sclerenchyma bundles, shallow epidermal cells, and parenchymatous cells (Channing and Edwards, 2004). However, opal-A was deposited in the vascular bundle sheaths only after 330 days. This difference may reflect the relative decay rates of lignin and cellulose. The vascular bundle sheaths are more lignified, and thus decayed more slowly, opening up fewer available sites for hydrogen bonding.

A second area of interest regarding preservation in the Rhynie Chert is the bias of silicification in different hydrothermal environments. Using Yellowstone hot springs as a natural laboratory, Channing and Edwards (2009) examined subfossil specimens of *Eleocharis rostellata* (Cyperaceae) from a wetland downstream of a hydrothermal vent, and compared the subfossils with the results of their earlier experiments (Channing and Edwards, 2004). The 2004 experiments were conducted in water temperatures from 60–70°C, which excluded most plant-degrading fungi (Magan, 1997) and many heterotrophic bacteria (e.g., Blanchette et al., 1990). Indeed, microbes were all but absent in the experimental samples (Channing and Edwards 2009). In contrast, average temperatures of the wetland water were from 20–30°C, which falls in the optimum range for fungal activity (Magan, 1997). Plants examined from this environment were colonized by a consortia of microbes, including bacteria, fungi, protists, and diatoms (Channing and Edwards, 2009). Under this scenario, the wetland subfossils might be expected to exhibit a greater degree of decay and an overall poorer preservation. However, even the most delicate tissues were preserved in both hydrothermal sub-environments, and the most extreme form of degradation observed was cell collapse (Channing and Edwards, 2004, 2009).

Another difference in the preservation of the plants in the two sub-environments was the silica fabric texture. Plants submerged in hot hydrothermal fluid contained opal-A microspheres in a unimodal size class, whereas plants from the wetlands contained microspheres of many sizes (Channing and Edwards, 2009). This difference can be accounted for by the different physicochemical conditions in each environment. Plants in the vent waters were periodically subaerially exposed. During periods of flooding, the water was supersaturated with respect to silica (SI=0.11–0.12), and nucleation of silica microspheres was likely rapid. Conversely, in the ever-flooded wetlands, the water was at or just above the saturation level (SI=−0.09–0.08), and the nucleation of microspheres occurred continually, albeit slowly. However, Channing and Edwards (2009) found that the differences in silica fabric do not appear to detract from the quality of preservation in either sub-environment.

The preservation potential of *Eleocharis* did not differ in the different sub-environments in Yellowstone. These results are encouraging because they suggest that plants are preserved to the same degree in settings both distal and proximal to the hydrothermal vent area, thus eliminating biases that may result from sub-environments. However, biases still may exist that would skew the perception of these types of environments. One bias that Channing and Edwards (2009) noted was the type of plant used in the study. *Eleocharis* and many other members of the Cyperaceae, sedges that are often associated with wetlands, biomineralize parts of their tissues in silica during life, and this initial silica may act as a template for further silicification. Additionally, hydrothermal systems only capture a limited range of plant and animal diversity (Channing and Edwards, 2009), and thus care must be used when making larger assumptions about a regional ecosystem based on deposits of hydrothermal origin.

Coal Balls

A major source of Paleozoic paleobotanical information is concretions (coal balls), usually of carbonate but sometimes of silica, containing coalified plant remains (Scott and Rex, 1985). Most coal balls are Carboniferous in age, but they are also found in the Permian of China (e.g., Zhou et al., 2008). Coal balls are found as masses of variable size and shape that are distributed both horizontally and vertically within coal seams. Since their discovery in 1855, the paleoecological data garnered from coal balls has been invaluable in the reconstruction of the flora of one of the

major peat-forming periods in geologic history (Phillips and Peppers, 1984; Phillips et al., 1985).

The primary minerals in coal balls are calcite, dolomite, ferroan dolomite, and pyrite, with minor constituents including marcasite, gypsum, quartz, illite, kaolinite, and lepidocrocite (DeMaris, 2000). Coal-ball mineralogy is quite consistent in composition, but the proportions of different constituents vary, even in adjacent concretions (Stopes and Watson, 1909). The majority of coal balls are dominated by calcite (Stopes and Watson, 1909; DeMaris, 2000). Detrital minerals are rare, suggesting in-situ permineralization. Carbon isotope compositions range from −15 to −35‰ (DeMaris, 2000) in the purely plant-bearing concretions, and are slightly less ^{13}C-depleted (−8.9‰) in mixed plant- and marine-animal coal balls (Scott et al., 1996). These different carbon isotope compositions suggest varying amounts of fresh water input. Sr/Ca ratios, which can be used to determine carbonate provenance, range from 4.8 to 10.3 ($x\ 10^{-4}$), values that are congruent with freshwater values of 5.9–8.9 ($x\ 10^{-4}$) (Treese et al., 1981).

Coal ball formation.—Several models have been developed to explain coal-ball preservation. Early investigations of coal-ball formation were concerned primarily with the provenance of the plant material. Initial descriptions focused on the spherical nature of the coal balls, implying they were formed and transported a great distance before being deposited in the coal bed (Lomax, 1902). However, the uncompressed nature of much of the plant material and the exceptional preservation of even the most decay-prone tissues led to the development of taphonomic models to explain the uniqueness of coal-ball preservation.

Original hypotheses of the origin of coal balls stressed the importance of initial decay under anoxic and closed systems, based on the exceptional quality of the plant material and the presence of pyrite (e.g., Stopes and Watson, 1909). Following initial decay, a new source of water, likely marine, carrying carbonate and magnesium ions, flooded the forming peat. Stopes and Watson (1909) favored the importance of a marine source based on the presence of goniatites and marine pectinid bivalves. This influx caused the precipitation of carbonate minerals around decaying plant material, forming the concretion. However, isotopic data show that the cements were not formed from a purely marine source, and that mixing of marine and freshwaters must have occurred (Scott et al., 1996).

The occasional occurrence of marine animals in coal balls led Mamay and Yochelson (1962) to develop a model that would explain this observation. In their model, the peat body was spatially separated from the marine environment. During large storm events, sediments from the sea were ripped up and deposited within the peat, forming a nucleus for carbonate precipitation. This model is only applicable to mixed floral/faunal coal balls and cannot be applied to purely botanical concretions. Additionally, the mounting evidence of two carbonate origins—one marine, one freshwater—makes this model of limited value (Scott et al., 1996). Furthermore, there is evidence that much of the marine material preserved in coal balls is not actually mixed with original peat. Rather, the marine elements are fillings of burrows that entered the peat from the overlying marine environment after it transgressed the peat swamp, rendering the mixture of terrestrial and marine elements a taphonomic happenstance.

Anderson et al. (1980) proposed a pathway for coal-ball formation that related the coal balls to ombrotrophic peat (peats formed in water derived from rainfall rather than streams or groundwater). In this model, fresh meteoric waters may have infiltrated the forming peat in several episodes. Spicer (1989) expanded on this model, adding to it a layer of marine water at depth. As the peat formed, it began to sink and when it reached the marine-fresh water barrier, the pH changed from acid to alkali, allowing the precipitation of carbonate within the peat. Isotopic data, however, consistently support a freshwater origin of coal-ball formation (Scott et al., 1996). Additionally, no coal-ball-bearing coal has been considered ombrotrophic in origin (DiMichele and Phillips, 1994), so this model does not fully explain their formation. There are two major types of peat-forming bogs and swamps: 1) ombrogenous, which form above groundwater and are dependent on meteoric input; and 2) topogenous, which form within groundwater (Cecil et al., 1985). Comparisons of coal balls from American Pennsylvanian-age coals with characteristics of these two types of peats show that coal balls strongly reflect topogenous peat-forming environments, which contain high levels of sulfate, carbonate, and mineral matter (Phillips et al., 1985).

The most recent hypothesis of coal-ball formation places the peat-forming plants in fresh water as opposed to brackish environments

(DeMaris, 2000). The forming peat body was covered by non-marine muds during the initial phases of transgression. These muds initially originated from freshwater sources, generally large rivers that ran through the peat swamp. The siliciclastic sediment was backed up and forced inland by sea-level rise as the rivers turned into estuaries (Elrick and Nelson, 2010). Capped by these muds, pCO_2 increased within the peat body due to methanogenesis, resulting in very negative carbon isotope values and a low pH (DeMaris et al., 1983; DeMaris, 2000). Subsequent erosion removed the shale cap, releasing CO_2, raising pH, and reintroducing marine water into the peat. This change caused the chemical equilibrium to shift toward carbonate precipitation, which likely occurred very quickly (see DeMaris, 2000, for further discussion). Some coal balls contain growth rings (W. A. DiMichele, pers. comm., 2014), but the well-preserved anatomy within these coal balls suggest that these formed rapidly. Within a single coal ball, multiple sites of nucleation may have initiated precipitation, with the final coalescence forming the single, solid coal ball. Coal balls appear to have formed in those areas where gray muds were stripped away by the further action of marine transgression. It should be noted that in the coal beds studied by DeMaris (2000), coal balls occur exclusively beneath marine, generally black shale, roof rocks. Where gray shale was thick and remained intact, coal sulfur is generally lower than under marine roof rocks, and coal balls are not present.

Pyrite

Pyritized plant fossils are uncommon in the fossil record, but can retain spectacular anatomical information. The majority of pyritized plant fossils are axes of Devonian (e.g., Chaloner et al., 1978; Kenrick and Edwards, 1988) and Eocene age, particularly from the London Clay (Grimes et al., 2001, 2002; Brock et al., 2006), although partially pyritized fossils occur throughout the plant fossil record (Rickard et al., 2007). The discovery of the London Clay flora (Reid and Chandler, 1933) led to several methods of investigation of the fossils, as no previous methods allowed for examination of pyritic fossils (e.g., Beck, 1955). The preservation of cellular-level anatomy allows the classification of otherwise character-depauperate fossils. Most research on pyritized plant fossils has been focused on anatomical descriptions, but several models have been proposed to explain the process of pyritization. In the past thirty years, several advances have been made in understanding the process of plant pyritization. This section will focus on the insight gained from experiments on plant fossils. For a more general overview of pyritization, see Farrell (2014).

Pyrite in plant fossils.—One of the most intensively studied pyritized floras is from the London Clay (e.g. Grimes et al., 2001 2002; Rickard et al., 2007), and studies on the formation of pyrite have revealed much about the process and nature of pyritization. It should be noted that pyritized fossils are often coalified, such that pyrite is associated with an organic template (e.g., Grimes et al., 2002). Pyrite in the London Clay flora generally is found in one of four primary textures: framboidal, polycrystalline, subhedral to euhedral, or microcrystalline (Grimes et al., 2002). Generally, different pyrite textures occurred in particular cell types, with the exception of euhedral octahedral pyrite, which tends to be limited to parenchyma cells and occurs only in rare instances. However, different textures of pyrite are clearly associated with certain cell features. Amorphous microcrystalline pyrite is ubiquitous on the inner surface of the cell, within the lignified cell walls, and in the middle lamella (Grimes et al., 2002); however, microcrystalline pyrite was not found associated within cellulose cell walls, which are normally coalified. The presence of microcrystalline pyrite within lignified parenchymal cells and xylem vessels indicates that the lignified portions of the cell underwent decay before pyritization, as these features are normally impermeable (Grimes et al., 2002).

Most pyrite found in plant fossils occurs on the interior surface of cellulose cell walls forming internal casts of the cell and pits, with rare instances of pyrite found within walls (Grimes et al., 2002). Within a single cell, the pyrite textures are relatively uniform. Adjacent cells may exhibit different textures, however, indicating that separate chemical microenvironments formed during early diagenesis, reflecting changes in pH and Eh brought about by decay and mineralization (Grimes et al., 2002). The presence of pyrite, particularly of a microcrystalline texture, is essential to exceptional preservation: its presence on the internal surface of cells prevents collapse and leads to anatomical preservation. This initial formation of pyrite then prevents changes to morphology as other textures grow, often at different stages as the chemical microenvironment

changes through time.

Pyrite formation.—The primary control on the formation of pyrite in sediments, both in conjunction with fossils and as pure sedimentary pyrite, is the presence of oxygen. Pyrite only forms in anoxic conditions—oxygen must be excluded during early diagenesis. However, both in laboratory and actualistic studies of pyrite formation, the surrounding water and sediments may be oxygenated. Oxygen is removed from the sediment column during microbial respiration, and sediments can become anoxic in a matter of days (Grimes et al., 2001; Brock et al., 2006; Darroch et al., 2012). Iron is not known to be a limiting factor in the formation of pyrite because iron is available from many sources; however, the concentration of reactive iron is important. Iron bound in iron oxides reacts quickly with iron sulfides (fastest half-life is 2.8 hr), whereas iron from silicate rocks reacts much more slowly (half-life is 84,000 yr), and such a low reaction rate prevents soft-tissue preservation (Canfield, 1989; Canfield et al., 1992; Raiswell and Canfield, 1998). Sulfate is not thought to be limiting in normal marine settings (Kaplan et al., 1963), but fresh water contains two orders of magnitude less sulfate, and this is a major limiting factor on the formation of pyrite in such settings (Berner, 1984).

The series of reactions that iron and sulfur undergo in the process of forming pyrite is complex, and several different reaction pathways may exist (Brock et al., 2006). The formation of pyrite precursors, namely iron monosulfides (FeS), can occur through several important reactions, such as: 1) the reaction of detrital iron with hydrogen sulfide (Equation 1: Sørensen, 1982; Canfield, 1989a), 2) reduction of iron minerals by dissimilatory iron-reducing bacteria (Equation 2: e.g., Sørensen, 1982; Canfield, 1989b), 3) partial oxidation of iron sulfide minerals to produce ferrous iron (Equation 3: Aller, 1980; Giblin and Howarth, 1984), followed by 4) reaction with hydrogen sulfide (Equation 4: Brock et al., 2006); and 5) oxidation of iron (II) monosulfide by H_2S (Equation 5: Rickard and Luther, 1997).

Eq. 1) $2FeOOH + H_2S + 4H^+ \longrightarrow 2Fe_2^+ + S_0 + 4H_2O$

Eq. 2) $4FeOOH + CH_2O + 8H+ \longrightarrow CO_2 + 7H_2O$

Eq. 3) $2FeS_2 + 7O_2 + 2H_2O \longrightarrow 2Fe_2^+ + 4SO_4^{2-} + 4H^+$

Eq. 4) $Fe_2^+ + H_2S \longrightarrow FeS + 2H^+$

Eq. 5) $FeS + H_2S_{(aq)} \longrightarrow FeS_2 + H_{2(g)}$

Once iron monosulfides are available, they rapidly transform to pyrite during early diagenesis, but the mechanism is poorly understood (Brock et al., 2006).

For pyrite to form on the interior surface of a plant cell, iron and sulfur must be able to enter the cell. The cell-wall complex of plants is made of three fundamental components: the middle lamella, the cell wall, and the plasma membrane (Keegstra, 2010). The middle lamella is a pectin layer that coats the exterior of the cell wall, and its primary function is to join the cell walls of adjacent cells together, providing stability for the plant. The cell wall is composed of cellulose fibers and proteins, and is permeable to water and small dissolved particles. In specialized cells, such as tracheids, the cell wall is strengthened by lignin and other structural biopolymers that provide the extra support required to fulfill its function. The plasma membrane, which encases the cytoplasm, is a lipid bilayer with a hydrophobic interior that acts as a barrier to many polar molecules. Interactions between cells (i.e., ion transfer) occur through small pits in the middle lamella, and are mediated by carrier proteins in the cell wall and the plasma membrane. This complex provides a substantial barrier to exogenous substances entering the cell, including the pyrite precursors iron and sulfur (Rickard et al., 2007). After death and burial, these substances must enter the cell largely through diffusion-mediated processes. As decay progresses and these barriers are broken down through microbially mediated processes, the cell wall becomes more permeable to iron and sulfur species, allowing mineralization to progress (Grimes et al., 2002).

In addition to the transport of iron and sulfur into the cell, certain environmental parameters that change during the course of diagenesis affect the mode and tempo of pyritization, as evidenced by changes in pyrite texture within fossils (Grimes et al., 2002). The model for the chemical environment of pyritization was based on investigations of the preservation of the Eocene London Clay flora (Grimes et al., 2002). The

London Clay plants were deposited in anoxic sediments, then overlain by oxic waters carrying oxidized iron. This iron, and associated aqueous sulfate, were reduced to Fe(II) and S^{2-} during bacterial respiration, providing necessary elements for the formation of pyrite. Pyrite microcrystals and framboidal pyrite were the first textures to form on the interior surfaces of cell walls, within vessel elements, and in the middle lamella. After this initial mineralization occurred, the availability of Fe(II) decreased and the Eh became more reduced, resulting in a decreased rate of pyrite nucleation with respect to crystal growth. This change led to the formation of euhedral and polycrystalline pyrite textures that infilled the open spaces within the cell. However, it was the deposition of the microcrystalline cast that ensured anatomical preservation.

Experimental pyritization.—Much has been learned through experiments on the timing and environmental sensitivity of the pyritization pathway. Using the London Clay fossils as a model for plant pyritization because the flora contains anatomically preserved plants with close living relatives (*Platanus*), Grimes et al. (2002) and Brock et al. (2006) conducted a series of experiments using *Platanus* axes, and, in the case of Grimes et al. (2001), *Apium graveolens* (celery). The objective of these experiments was to 1) replicate pyrite textures within the London Clay flora, and 2) test different variables and their role in the rapid mineralization of plant floras. One major conclusion from these studies was that the exact environmental condition leading to pyrite formation is very subtle. Even in replicate experiments, pyrite did not form in every plant axis. Additionally, the experimentally formed pyrite was patchily distributed within a single sample, indicating that the conditions for pyrite precipitation are very specific.

In order to test one model of pyritization, Grimes et al. (2001) placed portions of *Apium graveolens* petiole in a chemical system with anoxic Fe^{2+} solution, aqueous S^{2-}, and H_2S to model the reaction between FeS and H_2S (Eq. 5). Portions of the celery petiole were soaked in the iron solution for one week before exposure to S^{2-}, then H_2S. The initial reaction product was amorphous ferrous monosulfide (FeS_{am}). After the celery samples were placed in a solution containing H_2S, pyrite formed within eight days as thin coatings on the inner walls of parenchyma cells, within cell walls, and in the middle lamella between cells. Pyrite was found within layers of cellulose fibrils in parenchyma cell walls, but not in the lignified portion of xylem cells, showing that the organic template influenced the nucleation of pyrite (Grimes et al., 2001). Additionally, pyrite was found only in void spaces between tissues rather than as a direct replacement of organic material. This is consistent with observations of Kenrick and Edwards (1988) on anatomically preserved Devonian plants.

Pyrite precipitation coincides with a decrease in the concentration of FeS_{am} (amorphous ferrous sulfide) and an increase in aqueous iron sulfide FeS_{aq}, supporting the hypothesis that this is an important component in the formation of pyrite (Rickard and Luther, 1997; Grimes et al., 2001; Rickard et al., 2007). The chemical experiments also highlighted the requirement for ion transport in pyrite formation. The experiments were conducted under natural iron concentrations (~0.1 mol/L). Assuming a 100% conversion rate, this would result in mineralization of only 0.25% of the original volume of the cell. The experiments resulted in a greater amount of pyrite precipitation, which requires the transport of iron into the cell, likely in the form of FeS_{aq}, diffusing through lignin-free areas of the cell wall (Grimes et al., 2001).

Grimes et al. (2001) and Brock et al. (2006) used stems of *Platanus* in a series of experiments to imitate the preservation of stems in the London Clay, focusing on the role of microbes rather than a purely chemical system. Their experiments included standard marine conditions, plus experiments that varied the concentrations of iron, sulfate, and organic matter; the reactivity of the iron; different plants and oxygen conditions; fungal decay; sterile conditions with H_2S and the absence of a bacterial inoculum. In their experiments, FeS_{am} and pyrite precipitated in only the standard marine decay systems. Additionally, within the successful experiments, pyrite was only found in systems where intense bacterial respiration resulted in rapid formation of FeS_{am} (Grimes et al., 2001; Brock et al., 2006).

The results of the various pyrite precipitation experiments support several observations from pyritized plant fossils. Pyrite precipitation in plants is dependent on many factors, and only occurs in specific microenvironments that often vary within a single specimen. This intense dependence on the environment results in the mineralization of only a small portion of the available material, which is consistent with the rarity of pyritized plant fossils in the fossil record

(Brock et al., 2006). When plants are successfully pyritized, however, they can retain spectacular anatomy, such as those from the early Devonian of Wales and the London Clay. The results of experiments suggest that a normal marine environment, combined with microenvironments that are created within cells due to decay and bacterial respiration, lead to pyrite formation.

One of the major biases in the fossil record of pyritized plant fossils is spatial and environmental heterogeneity. First, land plants are not normally found in marine sediments, and the primary control on this is related to transport either by long-distance floating and subsequent sinking, or instantaneous events, such as a debris flow that carries plants into bottom sediments. Second, the sulfate content in freshwaters in which plants are normally deposited is too low to generate the amount of pyrite needed for anatomical preservation. For this reason, impression fossils are associated with iron oxides (e.g., Dunn et al., 1997) and can even be permineralized and replaced with goethite (Locatelli, 2013), but are rarely associated with large amounts of pyrite. Some floras that are preserved in or associated with iron oxides, such as the Cretaceous Crato Formation flora, were originally preserved in pyrite that has weathered in-situ to iron oxides (Heimhofer et al., 2010). In the case of the Crato flora, the formation of pyrite is attributable to the constant influx of marine waters into the Araripe Basin, which provided the necessary amount of sulfate needed for pyritization

Charcoalification

Charcoalified fossils—or, more accurately, fossils preserved as fusain—have two main characteristics that make them an important paleobotanical resource: 1) anatomy is preserved in micron-scale pieces, which may allow taxonomic identification (Scott, 2001); and 2) charcoal is relatively inert, and thus is resistant to decay and easily preserved in the fossil record (Scott et al., 2000; Scott and Glasspool, 2007). Charcoalified fossils have proven essential in reconstructing ancient ecosystems, as they provide exquisite details of the plants themselves (e.g., Crepet et al., 2004; Scott, 2010), and enable the reconstruction of fire events through the Phanerozoic (e.g., Glasspool et al., 2004). Most charcoalified fossils are classified as mesofossils (millimeter scale), which has led many paleontologists and geologists to overlook them until recent decades (Scott, 2001). Charcoalified fossils are distinguished from coalified fossils by shape (charcoalified being more angular), silky luster, and the fine black dust that is produced by charcoal when rubbed (Scott, 2001).

Due to the chemically inert and physically robust nature of charcoal, charcoalified tissues have a high preservation potential. Larger pieces ($> 1cm^2$) are rare, as charcoal is brittle and prone to fracturing (Scott, 2001). However, even small pieces preserve exquisite internal anatomy and external morphology. Fusinized plant tissues are found in enormous quantities in coal balls and coal, and can be studied using petrographic thin sections (Phillips et al., 1985). Wood is the most common type of charcoalified fossil, but leaves and reproductive structures are also known (Alvin, 1974; Scott, 1989, 2000; Jones and Chaloner, 1991; Scott et al., 2001; Crepet et al., 2004). Charcoalified flowers have proven exceptionally useful in understanding angiosperm evolution. Charcoalified mesofossils are three-dimensional, with floral structure and organization preserved allowing for detailed study of floral evolution (Schönenberger, 2005; Friis et al., 2011). Flowers preserved as compressions, on the other hand, are difficult to study: details are obscured, particularly when cuticle is absent (Scott, 2001; Friis et al., 2011).

Formation of charcoal.—Fusain, 'the mother of charcoal' (Scott, 1989; Jones et al., 1991), has a high carbon content (60–90%; Scott, 1989, 2010). The formation of charcoal occurs during wildfire (Scott 2010). Fire requires oxygen, and burning of plant material with oxygen results in complete destruction (Scott, 1991). However, during most fires, some plant material becomes starved of oxygen while still being exposed to heat high enough for pyrolysis to occur, resulting in charcoal (Scott, 1991). During this process, cell walls become homogenized. Cellulose, which is the primary macromolecule of most woody cell walls (70%), is stable at temperatures up to 250°C (Pyne et al., 1996; Scott and Glasspool, 2007). At 325°C, cellulose begins to break down and form flammable gases (Scott and Glasspool, 2007). Lignin is more resistant to thermal degradation and will survive as a charred product in many instances (Pyne et al., 1996). For true charcoal to form, temperatures of at least 230°C appear to be needed to begin pyrolysis reactions; at lower temperatures, plants are charred and the middle lamella of the cell wall remains visible (Scott and Jones, 1991). Only at higher temperatures are cell walls homogenized.

The temperature of the fire and its vertical placement in the vegetation is important in the formation of charcoal. Single fires can create a range of temperatures, and certain types of fire are more likely to produce significant quantities of charcoal. Fires in the crown of the canopy reach temperatures of 700–980°C, and produce very little macroscopic charcoal (Pyne et al., 1996). Instead, microscopic charcoal and other combustion products are the primary product, and are wind-dispersed, often to great distances (Scott and Glasspool, 2007). Surface fires—fires that burn predominantly litter or shrubby vegetation—burn at temperatures around 300°C with elevated temperatures extending several centimeters down into the soil (Scott and Jones 1991). In this type of fire, large quantities of macroscopic charcoal form from both dead plant material in the litter and also living vegetation (Scott and Glasspool 2007).

Experimental formation.—Both laboratory experiments and investigations into modern fires have given insight into important parameters controlling the formation of charcoal. Jones et al. (1991) used a series of oven experiments on both angiosperm (*Betula*) and conifer (*Pinus* and *Picea*) wood. In their experiments, temperature, length of temperature exposure, sample size, and amount of available oxygen were varied to explore the importance of each in charcoal formation. Ultimately, restricted oxygen and temperature were found to be the two most important controls. Wood that sat on top of sand, maximizing oxygen content, was completely combusted at 220°C—below the temperatures present during wildfires above the surface. Wood that was buried under sand to restrict oxygen, however, turned to charcoal at temperatures between 250–920°C, with the best preservation occurring at 300°C (Jones et al., 1991). With increased temperature, reflectivity and clarity of cell walls also increased. These results indicate that tissues not in direct contact with the atmosphere, such as roots and trunk, are more likely to be preserved as charcoal (Jones et al., 1991).

The aftermath of modern wildfires provides excellent opportunities to study the formation of charcoal in natural settings. Charcoal represents a special form of preservation in that its formation is geologically instantaneous, as fires are discrete events, and therefore can be studied in nature under short timescales. Scott et al. (2000) investigated the charcoal formed during a surface fire (flames < 2 m in height) in southeast England that lasted for a few hours, with some litter and logs smoldering for up to 24 hours. The in-situ charcoal assemblage was exceptionally preserved, and much of the assemblage preserved fungal hyphae, showing that it was part of the litter before the fire (Scott et al., 2000). All types of plant organs—roots, wood, leaves, flowers, and fruits—were represented in the charcoal, and the taxonomic diversity of the charcoal assemblage accurately reflected the living vegetation known from the area. However, charcoal that was successfully transported to nearby lakes, i.e., the depositional setting, was primarily composed of wood of a single taxon (Scott et al., 2000). Scott et al. (2000) offered two explanations for this discrepancy: 1) charcoal formed from different taxa has different sinking rates, so that during water transport, certain species are carried further away from the source; and 2) organs such as leaves and flowers may be more fragile than charcoalified wood and are presumably destroyed during transport.

Despite exceptional preservation of anatomy and morphology, a major concern regarding the fidelity of taxonomic information in charcoalified fossils is the degree of shrinkage. Experimental charcoalification of reproductive structures (carpels, petals, and stamens) of seven angiosperm taxa confirmed the expectation that shrinkage occurs during the charcoalification process (Lupia, 1995). However, no consistent pattern of shrinkage was observed within or among taxa: shrinkage varied between 15–47%. Stamens and petals exhibited the greatest shrinkage (19.2–40.8% and 23.6–46.6%, respectively), whereas carpels showed the least amount of shrinkage (14.4–32.1%). Increased exposure time resulted in a greater amount of shrinkage. The results of this study have major implications for the reconstruction of floral morphology. The nonuniform shrinkage of various organs during charcoalification suggests that the dimensions of fossil flowers should not be interpreted as original. Additionally, because there is no discernible pattern, no scaling factor can be applied to fossils to correct for this shrinkage. However, because the relative size of organs (stamens < carpels < petals) was preserved in most experiments, fossil flowers that exhibit organs with structures whose dimensions differ by a factor of two or more probably reflect the true order (Lupia, 1995).

PRESERVATIONAL BIASES IN THE FOSSIL RECORD

Plant fossils are, by some definitions, exceptional, as plants are non-biomineralized organisms (Briggs 2003). However, exceptionally preserved plant fossils differ from exceptionally preserved animal fossils in that they do not affect our understanding of plant diversity to the same degree, with some important exceptions (e.g., the Rhynie Chert, coal-ball floras). Without exceptionally preserved soft-bodied animals (e.g., the Burgess Shale: Conway Morris, 1986), understanding of animal evolution and diversity would be severely impaired. The majority of plant fossils retain no anatomical preservation and yet still provide a good measure of the standing diversity at the time of deposition. The exceptionally preserved fossil plants—those that retain anatomy and morphology not normally preserved—have provided unique glimpses into certain aspects of plant evolution, such as early flower morphology (Friis et al., 2011) and vascular systems (Wilson et al., 2009), as well as the paleoecology of environments that were subject to major environmental perturbations, such as the Pennsylvanian wetlands during an age of glacial-interglacial cyclicity.

In each mode of preservation discussed above, certain biases become apparent. However, with the exception of compression floras, the major bias of each taphonomic pathway is the result of dependency on specific depositional environments rather than obviously taxonomic. For example, pyrite forms only when intense bacterial respiration is present in conjunction with sufficient quantities of iron and sulfate. As per observations from fossils and taphonomic experiments, the ideal environment for the preservation of plants in pyrite is a normal marine environment. This environmental dependency of each taphonomic pathway determines the proportion and frequency of different types of plant fossils in the fossil record. The Carboniferous was the most important peat-forming time in the Phanerozoic, and the majority of coal balls are found from Carboniferous and lower Permian peats (Scott and Rex, 1985). Similarly, plants are rarely transported into marine conditions, and the total number of pyritized plant fossils and localities reflects this rare event. Silicified plant fossils are not dependent on the amount of silica, but rather the duration for which the organic template survives.

Bacterial degradation is closely tied to the preservation of plants and animals. Fossilization results from the balance between decay and mineralization or organic stabilization, and microbes are important factors on each side of the equation. Microbial decay breaks down the original tissues, and if it proceeds unhindered, organics will not be preserved and the template for mineralization will be lost. Anoxic conditions may reduce the pace of decay by excluding microbial groups that require oxygen for their metabolism, but many other anaerobic microbes are capable of breaking down organic matter (Briggs 2003). The rate of microbial decay depends on the availability of oxidants in the depositional setting. Microbial activity, however, is not solely responsible for the loss of the original template. Bacterial degradation of organics can enhance or facilitate mineralization, thus driving fossilization. For example, the microbial degradation of the plant cell wall enhances silicification by creating more bonding sites for dissolved silica (Leo and Barghoorn, 1976; Knoll, 1985; Ballhaus et al., 2012). Pyritization requires several chemical reactions to occur, some of which are part of the metabolism of certain bacteria (Grimes et al., 2001). For a plant to be preserved, the mineralization process must be rapid enough to outpace decay. Exceptionally preserved fossils are found when the environmental conditions support rapid mineralization that far outpaces microbial degradation.

Compression fossils form the majority of the fossil plant record, and biases known to control both preservational quality as well as the fidelity with which the taxonomic diversity of the surrounding region is represented are well studied (e.g., Ferguson, 2005, and references therein). Once a leaf is buried, however, the process of fossilization is dependent on the rate of bacterial decay relative to the lithification of the surrounding sediment. Leaves in rapidly lithified sediment will be preserved as impression fossils and, if bacterial respiration does not remove all of the organic matter, as compression fossils. In extraordinary circumstances, such as those of the Miocene Clarkia Formation, internal anatomy and chemistry (e.g., chlorophyll) can be preserved for millions of years (Niklas and Brown, 1981). Organic matter is highly dependent on the hydration of the depositional environment as well: leaves in hydrated settings retain organic matter and cellular details to a greater degree than those

in more dehydrated sequences (Niklas and Brown, 1981).

The preservation of plant fossils, as with animal soft tissues, is dependent on a complex suite of biogeochemical conditions. To understand the taphonomic history of a fossil, many different factors must be considered. Anatomically preserved plant fossils have provided paleobotanists with a level of biological detail that is rare in the fossil record. Experimental taphonomic studies have provided a wealth of data that inform our understanding of many processes, but many factors that influence plant preservation remain poorly understood. For example, do certain lineages have a higher preservation potential (e.g., resistance to microbial degradation) than others? Why do coarse-grained sands often preserve plant fossils with fine-scale details, such as those from the Dakota Sandstone? The role of microbes in fossilization remains largely unexplored. As paleobotanists continue to increase our understanding of past climates and communities, it is vital that we further our understanding of the biases in the fossil record itself through both specimen-based actualistic and experimental approaches.

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REFERENCES

ALLER, R. C. 1980. Quantifying solute distributions in the bioturbated zone of marine sediments by defining an average microenvironment. Geochimica et Cosmochimica Acta, 44:1955–1965.

ALVIN, K. 1974. Leaf anatomy of *Weichselia* based on fusainized material. Palaeontology, 17:587–598.

ANDERSON, T. F., M. E. BROWNLEE, AND T. L. PHILLIPS. 1980. A stable isotope study on the origin of permineralized peat zones in the Herrin Coal. The Journal of Geology, 88:713–722.

ANDREWS, H. N. 1951. American coal-ball floras. The Botanical Review, 17:431–469.

BAGHAI, N. L., AND R. B. JORSTAD. 1995. Paleontology, paleoclimatology and paleoecology of the late middle Miocene Musselshell Creek flora, Clearwater County Idaho. A preliminary study of a new fossil flora. PALAIOS, 10:424–436.

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.

BASINGER, J. F., AND G. ROTHWELL. 1977. Anatomically preserved plants from the middle Eocene (Allenby Formation) of British Columbia. Canadian Journal of Botany, 55:1984–1990.

BECK, C. B. 1955. A technique for obtaining polished surfaces of sections of pyritized plant fossils. Bulletin of the Torrey Botanical Club, 82:286–291.

BECK, C. B. 1960A. Connection between *Archaeopteris* and *Callixylon*. Science, 131:1524–1525.

BECK, C. B. 1960B. The identity of *Archaeopteris* and *Callixylon*. Brittonia, 12:351–368.

BEERLING, D. J., AND W. G. CHALONER. 1993. The impact of atmospheric CO_2 and temperature changes on stomatal density: observation from *Quercus robur* lammas leaves. Annals of Botany, 71:231–235.

BEERLING, D., AND D. ROYER. 2002. Fossil plants as indicators of the Phanerozoic global carbon cycle. Annual Review of Earth and Planetary Sciences, 30:527–556.

BERNER, R. A. 1984. Sedimentary pyrite formation: an update. Geochimica et Cosmochimica Acta, 48:605–615.

BLANCHETTE, R. A., T. NILSSON, G. DANIEL, AND A. ABAD. 1990. Biological degradation of wood, p. 141–174. *In* R. M. Rowell and R. J. Borbour (eds.), Archaeological Wood: Properties, Chemistry and Preservation: Advances in Chemistry. American Chemical Society, Washington, D. C.

BOMFLEUR, B., S. MCLOUGHLIN, AND V. VAJDA. 2014. Fossilized nuclei and chromosomes reveal 180 million years of genomic stasis in royal ferns. Science, 343:1376–1377.

BRIGGS, D. E. G. 1999. Molecular taphonomy of animal and plant cuticles: selective preservation and diagenesis. Philosophical Transactions of the Royal Society of London B-Biological Sciences, 354:7–17.

BRIGGS, D. E. G. 2003. The role of decay and mineralization in the preservation of soft-bodied fossils. Annual Review of Earth and Planetary Sciences, 31:275.

BRIGGS, D. E. G., R. P. EVERSHED, AND M. J. LOCKHEART. 2000. The biomolecular paleontology of continental fossils, p. 169–193. *In*

D. H. Erwin and S. L. Wing (eds.), Deep Time: Paleobiology's Perspective. Paleobiology, 26 (supplement to no. 4).

BROCK, F., R. J. PARKES, AND D. E. G. BRIGGS. 2006. Experimental pyrite formation associated with decay of plant material. PALAIOS, 21:499–506.

BUURMAN, P. 1972. Mineralization of fossil wood. Scripta Geologica, 12:1–43.

CANFIELD, D. E. 1989. Reactive iron in marine sediments. Geochimica et Cosmochimica Acta, 53:619–632.

CANFIELD, D. E., R. RAISWELL, AND S. H. BOTTRELL. 1989. Sulfate reduction and oxic respiration in marine sediments: implications for organic carbon preservation in euxinic environments. Deep Sea Research Part A. Oceanographic Research Papers, 36:121–138.

CANFIELD, D. E., R. RAISWELL, AND S. H. BOTTRELL. 1992. The reactivity of sedimentary iron minerals toward sulfide. American Journal of Science, 292:659–683.

CECIL, C. B., R. W. STANTON, S. G. NEUZIL, F. T. DULONG, L. F. RUPPERT, AND B. S. PIERCE. 1985. Paleoclimate controls on late Paleozoic sedimentation and peat formation in the central Appalachian Basin (USA). International Journal of Coal Geology, 5:195–230.

CHALONER, W. G., AND M. E. COLLINSON. 1975. Application of SEM to a sigillarian impression fossil. Review of Palaeobotany and Palynology, 20:85–101.

CHALONER, W. G., A. HILL, AND E. C. W. ROGERSON. 1978. Early Devonian plant fossils from a southern England borehole. Palaeontology, 21:693–707.

CHANEY, D. S., S. H. MAMAY, W. DIMICHELE, AND H. KERP. 2009. *Auritifolia* gen. nov., probable seed plant foliage with comioid affinities from the early Permian of Texas, U.S.A. International Journal of Plant Sciences, 170:247–266.

CHANNING, A., AND D. EDWARDS. 2004. Experimental taphonomy: silicification of plants in Yellowstone hot-spring environments. Transactions of the Royal Society of Edinburgh: Earth Sciences, 94:503–521.

CHANNING, A., AND D. EDWARDS. 2009. Silicification of higher plants in geothermally influenced wetlands: Yellowstone as a Lower Devonian Rhynie analog. PALAIOS, 24:505–521.

CLEAL, C. J., AND C. H. SHUTE. 2007. The effect of drying on epidermal cell parameters preserved on plant cuticles. Acta Palaeobotanica Krakow, 47:315–326.

COLLINSON, M. E. 2011. Molecular taphonomy of plant organic skeletons, p. 223–247. *In* P. A. Allison and D. J. Bottjer (eds.), Taphonomy: Process and Bias through Time. Topics in Geobiology 32, Springer, New York.

CONWAY MORRIS, S. 1986. The community structure of the Middle Cambrian phyllopod bed (Burgess Shale). Palaeontology, 29:423–467.

CREPET, W. L., K. C. NIXON, AND M. A. GANDOLFO. 2004. Fossil evidence and phylogeny: the age of major angiosperm clades based on mesofossil and macrofossil evidence from Cretaceous deposits. American Journal of Botany, 91:1666–1682.

DARROCH, S. A. F., M. LAFLAMME, J. D. SCHIFFBAUER, AND D. E. G. BRIGGS. 2012. Experimental formation of a microbial death mask. PALAIOS, 27:293–303.

DEMARIS, P. J. 2000. Formation and distribution of coal balls in the Herrin Coal (Pennsylvanian), Franklin County, Illinois Basin, USA. Journal of the Geological Society, 157:221–228.

DEMARIS, P. J., R. BAUER, R. CAHILL, AND H. DAMBERGER. 1983. Geologic investigation of roof and floor strata: longwall demonstration, Old Ben Mine No. 24. Prediction of coal balls in the Herrin Coal. Final technical report: Part 2. [Mineralized peat balls]. Illinois State Geological Survey, Urbana, Illinois.

DETTMANN, M. E., H. T. CLIFFORD, AND M. PETERS. 2009. *Lovellea wintonensis* gen. et sp. nov.—Early Cretaceous (late Albian), anatomically preserved, angiospermous flowers and fruits from the Winton Formation, western Queensland, Australia. Cretaceous Research, 30:339–355.

DIMICHELE, W. A., AND T. L. PHILLIPS. 1994. Paleobotanical and paleoecological constraints on models of peat formation in the late Carboniferous of Euramerica. Palaeogeography, Palaeoclimatology, Palaeoecology, 106:39–90.

DORIA, G., D. L. ROYER, P. A. WOLFE, A. FOX, J. A. WESTGATE, AND D. J. BEERLING. 2011. Declining atmospheric CO_2 during the late Middle Eocene climate transition. American Journal of Science, 311:63–75.

DRUM, R. W. 1968. Silicification of *Betula* woody tissue in vitro. Science, 161:175–176.

DUNN, K. A., R. J. C. MCLEAN, G. R. UPCHURCH, AND R. L. FOLK. 1997. Enhancement of leaf fossilization potential by bacterial biofilms. Geology, 25:1119–1122.

ELRICK, S. D., AND W. NELSON. 2010. Facies relationships of the middle Pennsylvanian Springfield Coal and Dykersberg Shale: constraints on sedimentation, development of coal splits and climate change during transgression. Geological Society of America Abstracts with Programs, 42(2):51.

FARRELL, Ú. C. 2014. Pyritization of soft tissues in the fossil record: an overview, p. 35–57. *In* M. Laflamme, J. D. Schiffbauer, and S. A. F. Darroch (eds.), Reading and Writing of the Fossil Record: Preservational Pathways to Exceptional Fossilization. The Paleontological Society Papers

20. Yale Press, New Haven, Ct.

FERGUSON, D. K. 2005. Plant taphonomy: ruminations on the past, the present, and the future. PALAIOS, 20:418–428.

FIORETTO, A., C. DI NARDO, S. PAPA, AND A. FUGGI. 2005. Lignin and cellulose degradation and nitrogen dynamics during decomposition of three leaf litter species in a Mediterranean ecosystem. Soil Biology and Biochemistry, 37:1083–1091.

FRIIS, E. M., P. R. CRANE, AND K. R. PEDERSEN. 2011. Early Flowers and Angiosperm Evolution. Cambridge University Press.

FRIIS, E. M., AND A. SKARBY. 1981. Structurally preserved angiosperm flowers from the Upper Cretaceous of southern Sweden. Nature, 291:484–486.

GASTALDO, R. 1988. A conspectus of phytotaphonomy, p. 14–28. *In* W. A. DiMichele and S. L. Wing (eds.), Methods and Applications of Plant Paleoecology: Notes for a Short Course. Paleontological Society Special Publication 3, University of Tennessee, Knoxville.

GEE, C. T., AND R. A. GASTALDO. 2005. Sticks and mud, fruits and nuts, leaves and climate: plant taphonomy comes of age. PALAIOS, 20:415–417.

GENSEL, P. G. 2008. The earliest land plants. Annual Review of Ecology, Evolution, and Systematics, 39:459–477.

GIBLIN, A. E., AND R. W. HOWARTH. 1984. Porewater evidence for a dynamic sedimentary iron cycle in salt marshes. Limnology and Oceanography, 29:47–63.

GILES, M., S. INDRELID, AND D. JAMES. 1998. Compaction—the great unknown in basin modelling. Geological Society of London Special Publications, 141:15–43.

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

GRAY, J., W. G. CHALONER, AND T. S. WESTOLL. 1985. The microfossil record of early land plants: advances in understanding of early terrestrialization, 1970–1984 [and Discussion]. Philosophical Transactions of the Royal Society of London B-Biological Sciences, 309:167–195.

GREENWOOD, D. R. 1991. The taphonomy of plant macrofossils, p. 141–169. *In* S. K. Donovan (ed.), The Processes of Fossilization. Columbia University Press, New York.

GRIMES, S. T., F. BROCK, D. RICKARD, K. L. DAVIES, D. EDWARDS, D. E. G. BRIGGS, AND R. J. PARKES. 2001. Understanding fossilization: experimental pyritization of plants. Geology, 29:123–126.

GRIMES, S. T., K. L. DAVIES, I. B. BUTLER, F. BROCK, D. EDWARDS, D. RICKARD, D. E. G. BRIGGS, AND R. J. PARKES. 2002. Fossil plants from the Eocene London Clay: the use of pyrite textures to determine the mechanism of pyritization. Journal of the Geological Society, 159:493–501.

GUPTA, N. S., M. E. COLLINSON, D. E. G. BRIGGS, R. P. EVERSHED, AND R. D. PANCOST. 2006. Reinvestigation of the occurrence of cutan in plants: implications for the leaf fossil record. Paleobiology, 32:432–449.

GUPTA, N. S., R. MICHELS, D. E. G. BRIGGS, M. E. COLLINSON, R. P. EVERSHED, AND R. D. PANCOST. 2007a. Experimental evidence for the formation of geomacromolecules from plant leaf lipids. Organic Geochemistry, 38:28–36.

GUPTA, N. S., H. YANG, AND D. E. G. BRIGGS. 2007b. Molecular taphonomy of *Metasequoia*. Bulletin of the Peabody Museum of Natural History, 48:329–338.

HEIMHOFER, U., D. ARIZTEGUI, M. LENNIGER, S. P. HESSELBO, D. M. MARTILL, AND A. M. RIOS-NETTO. 2010. Deciphering the depositional environment of the laminated Crato fossil beds (Early Cretaceous, Araripe Basin, Northeastern Brazil). Sedimentology, 57:677–694.

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

HUANG, Y., B. SHUMAN, Y. WANG, AND T. WEBB. 2004. Hydrogen isotope ratios of individual lipids in lake sediments as novel tracers of climatic and environmental change: a surface sediment test. Journal of Paleolimnology, 31:363–375.

JEFFERSON, T. H. 1987. The preservation of conifer wood: examples from the Lower Cretaceous of Antarctica. Palaeontology, 30:233–249.

JONES, T. P., AND W. G. CHALONER. 1991. Fossil charcoal, its recognition and palaeoatmospheric significance. Palaeogeography, Palaeoclimatology, Palaeoecology, 97:39–50.

JONES, T. P., A. C. SCOTT, AND M. COPE. 1991. Reflectance measurements and the temperature of formation of modern charcoals and implications for studies of fusain. Bulletin de la Société Géologique de France, 162:193–200.

KAPLAN, I., K. EMERY, AND S. RITTENBEBG. 1963. The distribution and isotopic abundance of sulphur in recent marine sediments off southern California. Geochimica et Cosmochimica Acta, 27:297–331.

KEEGSTRA, K. 2010. Plant cell walls. Plant Physiology, 154:483–486.

KELLEHER, B. P., M. J. SIMPSON, AND A. J. SIMPSON. 2006. Assessing the fate and transformation of plant residues in the terrestrial environment using HR-MAS NMR spectroscopy. Geochimica et Cosmochimica Acta, 70:4080–4094.

KENRICK, P., AND P. R. CRANE. 1991. Water-conducting cells in early fossil land plants: implications for the early evolution of tracheophytes. Botanical Gazette, 152:335–356.

KENRICK, P., AND D. EDWARDS. 1988. The anatomy of Lower Devonian *Gosslingia breconensis* Heard

based on pyritized axes, with some comments on the permineralization process. Botanical Journal of the Linnean Society, 97:95–123.

KIDSTON, R., AND W. LANG. 1917. XXIV.—On Old Red Sandstone plants showing structure, from the Rhynie Chert Bed, Aberdeenshire Part I. Rhynia Gwynne-Vaughani, Kidston and Lang. Transactions of the Royal Society of Edinburgh, 51:761–784.

KIDSTON, R., AND W. LANG. 1920a. XXVI.—On Old Red Sandstone plants showing structure, from the Rhynie Chert Bed, Aberdeenshire. Part III. *Asteroxylon mackiei*, Kidston and Lang. Transactions of the Royal Society of Edinburgh, 52:643–680.

KIDSTON, R., AND W. LANG. 1920b, XXIV.—On Old Red Sandstone plants showing structure, from the Rhynie Chert Bed, Aberdeenshire. Part II. Additional Notes on *Rhynia* Gwynne-Vaughani, Kidston and Lang; with Descriptions of *Rhynia major*, n. sp., and *Hornea lignieri*, n. g., n. sp: Transactions of the Royal Society of Edinburgh, 52:603–627.

KIDSTON, R., AND W. LANG. 1921a. XXXII.—On Old Red Sandstone plants showing structure, from the Rhynie Chert Bed, Aberdeenshire. Part IV. Restorations of the vascular cryptogams, and discussion of their bearing on the general morphology of the Pteridophyta and the origin of the organisation of land-plants. Transactions of the Royal Society of Edinburgh, 52:831–854.

KIDSTON, R., AND W. LANG. 1921b. XXXIII.—On Old Red Sandstone plants showing structure, from the Rhynie Chert Bed, Aberdeenshire. Part V. The Thallophyta occurring in the peat-bed; the succession of the plants throughout a vertical section of the bed, and the conditions of accumulation and preservation of the deposit. Transactions of the Royal Society of Edinburgh, 52:855–902.

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.

KUDER, T., AND M. A. KRUGE. 1998. Preservation of biomolecules in sub-fossil plants from raised peat bogs—a potential paleoenvironmental proxy. Organic Geochemistry, 29:1355–1368.

LEO, R. F., AND E. S. BARGHOORN. 1976. Silicification of Wood. Harvard University Botanical Museum Leaflets, 25:1–47.

LOCATELLI, E. R. 2013. The exceptional preservation of leaves in iron-rich sediments from Oceania. Geological Society of America Abstracts with Programs, 45(7):455.

LOGAN, G. A., C. J. SMILEY, AND G. EGLINTON. 1995. Preservation of fossil leaf waxes in association with their source tissues, Clarkia, northern Idaho, USA. Geochimica et Cosmochimica Acta, 59:751–763.

LOMAX, J. 1902. On the occurrence of the nodular concretions (coal balls) in the Lower Coal Measures. Annals of Botany, 4:603–604.

LUPIA, R. 1995. Paleobotanical data from fossil charcoal: an actualistic study of seed plant reproductive structures. PALAIOS, 10:465–465.

MAGAN, N. 1997. Fungi in extreme environments, p. 99–114. *In* D. T. Wicklow and B. Söderström (eds.), The Mycota IV. Environmental and Microbial Relationships. Springer-Verlag, Berlin.

MAMAY, S. H., AND E. L. YOCHELSON. 1962. Occurrence and Significance of Marine Animal Remains in American Coal Balls. United States Geological Survey Professional Paper 354-I. U. S. Government Printing Office, Washington, DC.

MATYSOVÁ, P., R. RÖSSLER, J. GÖTZE, J. LEICHMANN, G. FORBES, E. L. TAYLOR, J. SAKALA, AND T. GRYGAR. 2010. Alluvial and volcanic pathways to silicified plant stems (upper Carboniferous–Triassic) and their taphonomic and palaeoenvironmental meaning. Palaeogeography, Palaeoclimatology, Palaeoecology, 292:127–143.

MCCOY, V. 2014. Concretions as agents of soft-tissue preservation: a review, p. 147–161. *In* M. Laflamme, J. D. Schiffbauer, and S. A. F. Darroch (eds.), Reading and Writing of the Fossil Record: Preservational Pathways to Exceptional Fossilization. The Paleontological Society Papers 20. Yale Press, New Haven, Ct.

NICKRENT, D. L., C. L. PARKINSON, J. D. PALMER, AND R. J. DUFF. 2000. Multigene phylogeny of land plants with special reference to bryophytes and the earliest land plants. Molecular Biology and Evolution, 17:1885–1895.

NIKLAS, K. J. 1978. Morphometric relationships and rates of evolution among Paleozoic vascular plants, p. 509–543. *In* M. K. Hecht, W. C. Steere, and B. Wallace (eds.), Evolutionary Biology: Volume 11. Springer, New York.

NIKLAS, K. J. 1984. Size-related changes in the primary xylem anatomy of some early tracheophytes. Paleobiology, 10:487–506.

NIKLAS, K. J., AND R. M. BROWN, JR. 1981. Ultrastructural and paleobiochemical correlations among fossil leaf tissues from the St. Maries River (Clarkia) area, northern Idaho, USA. American Journal of Botany, 68:332–341.

NIP, M., E. TEGELAAR, H. BRINKHUIS, J. DE LEEUW, P. SCHENCK, AND P. HOLLOWAY. 1986. Analysis of modern and fossil plant cuticles by Curie point Py-GC and Curie point Py-GC-MS: recognition of a new, highly aliphatic and resistant biopolymer. Organic Geochemistry, 10:769–778.

NISHIYAMA, T., P. G. WOLF, M. KUGITA, R. B. SINCLAIR, M. SUGITA, C. SUGIURA, T. WAKASUGI,

K. YAMADA, K. YOSHINAGA, AND K. YAMAGUCHI. 2004. Chloroplast phylogeny indicates that bryophytes are monophyletic. Molecular Biology and Evolution, 21:1813–1819.

PHILLIPS, T. L., AND R. A. PEPPERS. 1984. Changing patterns of Pennsylvanian coal-swamp vegetation and implications of climatic control on coal occurrence. International Journal of Coal Geology, 3:205–255.

PHILLIPS, T. L., R. A. PEPPERS, AND W. A. DIMICHELE. 1985. Stratigraphic and interregional changes in Pennsylvanian coal-swamp vegetation: environmental inferences. International Journal of Coal Geology, 5:43–109.

PITTMAN, E. D., AND R. E. LARESE. 1991. Compaction of lithic sands: experimental results and applications (1). AAPG Bulletin, 75:1279–1299.

PYNE, S. J., P. L. ANDREWS, AND R. D. LAVEN. 1996. Introduction to Wildland Fire, Edition 2. John Wiley and Sons, New York.

RAISWELL, R., AND D. E. CANFIELD. 1998. Sources of iron for pyrite formation in marine sediments. American Journal of Science, 298:219–245.

REID, E. M., AND M. E. J. CHANDLER. 1933. London Clay Flora. British Museum of Natural History, London.

REX, G., AND W. CHALONER. 1983. The experimental formation of plant compression fossils. Palaeontology, 26:231–252.

RICE, C., N. TREWIN, AND L. ANDERSON. 2002. Geological setting of the Early Devonian Rhynie cherts, Aberdeenshire, Scotland: an early terrestrial hot spring system. Journal of the Geological Society, 159:203–214.

RICKARD, D., S. GRIMES, I. BUTLER, A. OLDROYD, AND K. L. DAVIES. 2007. Botanical constraints on pyrite formation. Chemical Geology, 236:228–246.

RICKARD, D., AND G. W. LUTHER III. 1997. Kinetics of pyrite formation by the H_2S oxidation of iron (II) monosulfide in aqueous solutions between 25 and 125 °C: the mechanism. Geochimica et Cosmochimica Acta, 61:135–147.

RIELEY, G., R. J. COLLIER, D. M. JONES, G. EGLINTON, P. A. EAKIN, AND A. E. FALLICK. 1991. Sources of sedimentary lipids deduced from stable carbon-isotope analyses of individual compounds. Nature, 352:425–427.

ROWE, N. P., AND T. SPECK. 1998. Biomechanics of plant growth forms: the trouble with fossil plants. Review of Palaeobotany and Palynology, 102:43–62.

ROYER, D. L., S. L. WING, D. J. BEERLING, D. W. JOLLEY, P. L. KOCH, L. J. HICKEY, AND R. A. BERNER. 2001. Paleobotanical evidence for near present-day levels of atmospheric CO_2 during part of the Tertiary. Science, 292:2310–2313.

SCHÖNENBERGER, J. 2005. Rise from the ashes—the reconstruction of charcoal fossil flowers. Trends in Plant Science, 10:436–443.

SCHOPF, J. M. 1975. Modes of fossil preservation. Review of Palaeobotany and Palynology, 20:27–53.

SCOTT, A., AND G. REX. 1985. The formation and significance of Carboniferous coal balls. Philosophical Transactions of the Royal Society of London B-Biological Sciences, 311:123–137.

SCOTT, A. C. 1989. Observations on the nature and origin of fusain. International Journal of Coal Geology, 12:443–475.

SCOTT, A. C. 2001. Preservation by fire, p. 277–280. *In* D. E. G. Briggs and P. R. Crowther (eds.). Palaeobiology II. Blackwell Science, Oxford.

SCOTT, A. C. 2010. Charcoal recognition, taphonomy and uses in palaeoenvironmental analysis. Palaeogeography, Palaeoclimatology, Palaeoecology, 291:11–39.

SCOTT, A. C., J. A. CRIPPS, M. E. COLLINSON, AND G. J. NICHOLS. 2000. The taphonomy of charcoal following a recent heathland fire and some implications for the interpretation of fossil charcoal deposits. Palaeogeography, Palaeoclimatology, Palaeoecology, 164:1–31.

SCOTT, A. C., AND I. J. GLASSPOOL. 2007. Observations and experiments on the origin and formation of inertinite group macerals. International Journal of Coal Geology, 70:53–66.

SCOTT, A. C., D. P. MATTEY, AND R. HOWARD. 1996. New data on the formation of Carboniferous coal balls. Review of Palaeobotany and Palynology, 93:317–331.

SIGLEO, A. C. 1978. Organic geochemistry of silicified wood, Petrified Forest National Park, Arizona. Geochimica et Cosmochimica Acta, 42:1397–1405.

SMOOT, E. L. 1984. Phloem anatomy of the Carboniferous pteridosperm *Medullosa* and evolutionary trends in gymnosperm phloem. Botanical Gazette, 145:550–564.

SMOOT, E. L., AND T. N. TAYLOR. 1986. Structurally preserved fossil plants from Antarctica: II. A Permian moss from the Transantarctic Mountains. American Journal of Botany, 72:1683–1691.

SØRENSEN, J. 1982. Reduction of ferric iron in anaerobic marine sediment and interaction with reduction of nitrate and sulfate. Applied and Environmental Microbiology, 43:319–324.

SPICER, R. A. 1977. The pre-depositional formation of some leaf impressions. Palaeontology, 20:907–912.

SPICER, R. A. 1989. The Formation and Interpretation of Plant Fossil Assemblages. Academic Press, London.

STEIN, C. 1982. Silica recrystallization in petrified wood. Journal of Sedimentary Research, 52:1277–1282.

STOPES, M., AND D. WATSON. 1909. On the present distribution and origin of the calcareous concretions in coal seams, known as "coal balls." Royal Society of London Philosophical Transactions Series B, 200:167–218.

TAYLOR, T. N., AND E. L. TAYLOR. 2000. The Rhynie Chert ecosystem: a model for understanding fungal interactions, p. 31–47. *In* C. W. Bacon and J. F. White (eds.), Microbial Endophytes. Marcel Decker Inc., New York.

TEGELAAR, E. W., H. KERP, H. VISSCHER, P. A. SCHENCK, AND J. W. DE LEEUW. 1991. Bias of the paleobotanical record as a consequence of variations in the chemical composition of higher vascular plant cuticles. Paleobiology, 17:133–144.

TEGELAAR, E., R. MATTHEZING, J. JANSEN, B. HORSFIELD, AND J. DE LEEUW. 1989. Possible origin of n-alkanes in high-wax crude oils. Nature, 342:529–531.

TREESE, T. N., R. M. OWEN, AND B. H. WILKINSON. 1981. SrCa and MgCa ratios in polygenetic carbonate allochems from a Michigan marl lake. Geochimica et Cosmochimica Acta, 45:439–445.

TREWIN, N. H. 1996. The Rhynie cherts: an early Devonian ecosystem preserved by hydrothermal activity, p. 131–145. *In* G. R. Bock and J. Goode (eds.), Evolution of Hydrothermal Ecosystems on Earth (and Mars?). Ciba Foundation Symposium 202, Wiley, Chichester.

TYLER, S. A., AND E. S. BARGHOORN. 1954. Occurrence of structurally preserved plants in pre-Cambrian rocks of the Canadian Shield. Science, 119:606–608.

WAKEHAM, S. G., AND E. A. CANUEL. 2006. Degradation and preservation of organic matter in marine sediments, p. 295–321. *In* O. Hitzinger and J. K. Volkham (eds.), The Handbook of Environmental Chemistry, Vol. 2: Reactions and Processess, Part N: Marine Organic Matter: Biomarkers, Isotopes and DNA. Springer-Verlag, Berlin.

WALTON, J. 1936. On the factors which influence the external form of fossil plants, with descriptions of the foliage of some species of the Palaeozoic equisetalean genus *Annularia* Sternberg. Philosophical Transactions of the Royal Society of London Series B-Biological Sciences, 226:219–237.

WELLMAN, C. H., P. L. OSTERLOFF, AND U. MOHIUDDIN. 2003. Fragments of the earliest land plants. Nature, 425:282–285.

WILSON, J. P., A. H. KNOLL, N. M. HOLBROOK, AND C. R. MARSHALL. 2009. Modeling fluid flow in *Medullosa*, an anatomically unusual Carboniferous seed plant. Paleobiology, 34:472–493.

WING, S. L., W. A. DIMICHELE, T. PHILLIPS, R. TAGGART, B. TIFFNEY, AND S. MAZER. 1992. Ecological characterization of fossil plants, p. 139–180. *In* A. K. Behrensmeyer, J. D. Damuth, W. A. DiMichele, R. Potts, H.-D. Sues, and S. L. Wing (eds.), Terrestrial Ecosystems Through Time: Evolutionary Paleoecology of Terrestrial Plants and Animals. University of Chicago Press, Chicago.

YANG, H., AND Y. HUANG. 2003. Preservation of lipid hydrogen isotope ratios in Miocene lacustrine sediments and plant fossils at Clarkia, northern Idaho, USA. Organic Geochemistry, 34:413–423.

ZHOU, Y.-L., S.-J. WANG, J. HILTON, AND B.-L. TIAN. 2008. Anatomically preserved lepidodendralean plants from lower Permian coal balls of northern China: *Achlamydocarpon intermedium* sp. nov. Plant Systematics and Evolution, 273:71–85.