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FOSSIL WOOD FROM BIG BEND NATIONAL PARK, **BREWSTER COUNTY, TEXAS: PART II — MECHANISM OF** SILICIFICATION OF WOOD AND OTHER PERTINENT FACTORS

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Abstract

A theoretical mechanism for the silicification of wood is presented. Possible rapid burial and silicification are discussed within the framework of a young earth model. Laboratory means to implant silica in wood are reviewed. Autochthonous and allochthonous deposition of woody material in various locations is explored. Key Words: Silicification, Silicic Acid, Fossil Wood, Autochthonous Deposition, Allochthonous Deposition.

Introduction

The formations in which the fossil wood specimens were found in Big Bend National Park were discussed in Part I (Williams and Howe, 1993). The importance of bentonite deposits in relation to the silicification of wood also was presented. Applications were suggested within a tentative catastrophic model. This part discusses: how wood is petrified, how rapidly it silicifies, and the process by which the material is carried to its burial site. In mentioning time estimates, I am quoting the opinions of the various workers involved. I do not subscribe to the standard geologic timetable.

Petrification of Wood

For readers who do not wish to wade through the technical aspects of the petrification of wood, a brief but accurate discussion of the process can be found in Barghoorn (1987).

One of the most remarkable mechanisms by which the remains of extinct organisms are preserved in the fossil record is the process of petrifaction. In petrifactions (though chiefly in the case of plants rather than animals) the original shape and topography of the tissues, and occasionally even minute cytological details, are retained relatively undeformed (p. 250).

Through the years there has been controversy as to whether the organic matter of wood is replaced molecule-by-molecule with mineral matter (replacement) or whether the mineral infiltrates the cellular structure and is deposited from solution (infiltration). The latter process is thought to be more likely and the details of that model will be elucidated.

Common agents involved in petrification are silica (SiO_2) and calcium carbonate $(CaCO_3)$, in the form of calcite). Occasionally phosphate minerals, pyrite and hematite are involved in petrification. Where silica is the major agent in petrification, the process is called

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silicification and generally, "the most perfect preservation of original structure is found in siliceous petrifactions" (Barghoorn, 1987, p. 250).

Silicification of Wood and Other Organic Matter

Silica is found in many living plants—for a specific example, see Howe, et al., 1987. Scurfield et al. (1974a, p. 211) claim that a previous study "... lists 440 species distributed over 144 genera and 32 families as forming wood in which silica occurs ..." Thus one could reach the conclusion that some plants either have an affinity for silica, readily absorb it or utilize the compound in their structure. Scurfield et al. (1974a) examined 32 species of woody perennials employing scanning electron microscopy to determine the location and form of silica in the plants. They assumed that SiO₂ entered plants as monosilicic acid (H₄SiO₄).* The form in which silica is transported in trees was not detected. However they claimed that it is deposited in wood in an amorphous form (a colloid such as a gel). Later the silica gel, deposited on the inner surfaces of the plant cells, continually dries and hardens as water is lost.

In a classic study on 24 specimens of silicified wood and one of calcified wood, Ruth St. John (1927, pp. 729-739) reached the following conclusions concerning how the process of petrification may occur:

- 1. Infiltration of mineral matter into the cell cavities and intercellular spaces, with the vegetable tissue preserved.
- 2. Complete replacement of the plant tissue, but this may be due to the spaces being filled first, and later the tissue being replaced.
- 3. Complete replacement of portions of the mass and filling only of cavities in the other parts (p. 739).

How wood petrifies in the presence of mineral matter is not completely understood but as stated earlier, the mechanism of infiltration appears to be the presently accepted one. However in 1944, Kryshtofovich wrote that:

True petrifications are plant remains where the original carbonic plant matter is intimately replaced more or less posthumously by mineral matter and by a penetration of silica or carbonates into the interstitial tissue (p. 62).

Schopf (1971, p. 523) in an investigation on silicified Antarctic peat made the following observations:

Comments on the nature of siliceous permineralized plant materials also may be of interest because so many geologists have been taught that petrified wood, well represented in the peat of this deposit, is a result of siliceous "replacement" True mineralogic replacement of plant tissue in a pseudomorphic sense is possible, but, when the plant structures are preserved with marvelous fidelity, one may be confident that permineralization rather than replacement is responsible. Pseudomorphic replacement probably is incapable of more than crude replication of microscopic tissue structure. In permineralized tissue the cell lumens, intercellular spaces, and the cell-wall structure itself are penetrated ("permeated") by microcrystalline mineral matter, often without visible disturbance of either the tissue or the interpenetrating microscopic crystal patterns.

He postulated three stages of silicification in the preservation of the peat (p. 541). First, a chalcedonic mineralization which preserves the tissue structure; second, another chalcedonic step which lithifies the deposit; and third, clear quartz is deposited in the remaining fissures and cavities of the peat. This latter operation is evident in some of the specimens we collected except that most of the silica was milky in color (Figure 1).

Buurman, et al. (1973) in an investigation of plant material recently silicified in acid sulphate soils (pH 3-4),* concluded that thin coatings of silica were present on former cell walls of the plants. "Structures formed this way are in fact replicas, and replica-like fossilizations of what was perhaps epidermis tissue . . ." (p. 121).

After an extensive study of petrified woods from Australia, Scurfield, et al., (1974b, pp. 389-396) offered the following model for silicification.

1. The process takes place under acid conditions suggested by the "frequent association of iron oxide and silica" (p. 395) in silicified woods.

2. Polyphenols in plants may encourage the deposition of SiO_2 , (i.e., silica accumulates in lignified cell walls). SiO_2 may attach itself to lignin in pores of water soaked wood.

3. As the wood decays or is attacked by microoganisms, SiO_2 may further deposit in the recently generated empty spaces.

An exchange between the authors and a reviewer is revealing (p. 396).

Reviewer V: Does this study indicate that because of their chemical similarity, the carbon molecules are replaced one at a time by silica during the petrifaction process; or is the silica just precipitated on the cell wall as a coating?

Authors: No, atoms and molecules are not the same thing. We cannot conceive of silicon (not



Figure 1. Pieces of silicified wood that have disintegrated from a recently exposed log in the Dawson Creek region of Big Bend National Park. Light areas are fairly pure (~97%) silica that probably filled cavities within the log. Photograph by Glen Wolfrom. *Possibly wood is silicified rapidly in an acidic environment.

 $^{^{*}}H_{4}SiO_{4}$ is referred to as orthosilicic acid in Nebergall, Schmidt and Holtzclaw (1976, p. 733).

silica) atoms replacing carbon atoms. The structures of cell wall polymers are entirely different from those of silica.

Schopf (1975, pp. 27-53), in an article on the modes of fossil preservation, gave a history of the theories of petrification. He briefly developed the molecule-bymolecule replacement concept, then called the scheme "hypothetical and essentially fictitious" (p. 31). He argued that the smaller inorganic molecules assume a different geometry from the larger organic molecules they are supposed to replace. Then he stated:

Many silicified fossils are essentially pseudomorphs in which external detailed appearance is faithfully preserved, but *not* by molecule-by-molecule replacement . . .

Cellular permineralization is the most faithful to life of any mode of fossil preservation that is known (p. 31).

He reiterated that the mechanism of permineralization is not completely understood.

Probably the most respected work on the mechanism for the silicification of wood was performed by Leo and Barghoorn (1976, pp. 1-47). They formulated a fairly complete model for the process. Of interest to Flood geologists is the emphasis of water action as needed for silicification.

The role of water in petrifaction is of paramount importance. Water is a necessary agent for ash alteration and mineral diagenesis. Saturation of the sediment serves to exclude oxygen, thereby inhibiting deterioration of tissue structure, through the maintenance of reducing conditions. Waterlogging dispels entrapped air, and maintains the wood in a swollen and plastic state, thereby maintaining maximum permeability (p. 27).

Leo and Barghoorn (1976, pp. 16-22) postulated a physical model for the silicification process. In the early stages, silica deposits upon readily accessible cell surfaces such as "the perimeter of the lumen and on the lining of the pit chamber" (p. 17) and builds outward to fill empty spaces. Apparently some SiO₂ goes into the cell walls and deposits within the organic material. They felt that wood acts "as an active template for silica deposition during petrifaction" (p. 19). As the process continues the organic template deteriorates, leaving more space for further SiO₂ deposition. Obviously they considered that petrification occurs in a sequence of steps. The natural processes of wood removal and silica deposition should not be considered perfect. The distribution of SiO₂ through a petrified wood can vary. As can be observed in field work, specimens from any "area containing petrified wood" vary as to structural retention and some specimens may not show any wood structure preserved.

Leo and Barghoorn summarized the discussion as follows:

Petrifaction is fundamentally a process of infiltration and impregnation, wherein wood substance serves as an active template for silica deposition (p. 21). In considering the chemistry of the silicification operation, these authors suggested that molecular silicic acid likely was involved. The initial chemical bonding might be hydrogen bonding (pp. 22-23) between the wood tissue molecules and molecules of silicic acid. As the acid concentrations in the wood increase, its molecules could polymerize "forming siloxane bonds" (p. 23) along with the removal of water. As the polymer extends, it forms a film over the surface of cells. After studying silicified wood from the Petrified Forest National Park, Sigleo (1978) said that her study indicated "that silicification is an impregnation (void-filling), not an organic replacement process" (p. 1404).

ing), not an organic replacement process" (p. 1404). Knoll, in an investigation of the silicification of photosynthetic organisms in carbonates and peats (1985, pp. 111-122), considered the model proposed by Leo and Barghoorn satisfactorily explained his observations and added that,

... a limited degree of decomposition (of organic material) may actually increase chances for long term preservation by providing abundant sites for hydrogen bond formation as well as microcracks and holes through which ground water can percolate (p. 115).

He emphasized the need for high concentrations of sedimentary organic matter to encourage silicification. From the standpoint of Flood geology, the water of the Flood should have been "loaded" with a variety of organic materials.

Jefferson (1987, p. 242), in his work on fossil conifer wood, employed the silicification model of Leo and Barghoorn. He proposed that: "The process . . . for the Alexander Island fossil woods involves permineralization of the cell wall structures rather than replication ..." (pp. 240, 242). He suggested that "early decay" of the wood promoted hydrogen bond formation of silicic acid with hydroxyl groups in the molecules of the cell wall. He visualized silicification as occurring in two major stages; (1) formation of a silica film over cell wall structures, (2) a later and slower "cavity-fill process, in which silica filled the cell lumen . . ." (p. 242). Also Jefferson considered that Murata's view (1940) on the production of free silica by the devitrification of volcanic tuff (see Williams and Howe, 1993, pp. 47, 50) and later formation of silicic acid was applicable to the silicification of the Alexander Island wood. Chapman and Smellie (1992, p. 165) indicated that the fossil wood samples they studied from Livingston Island, Antarctica were silicified within ash-flow tuffs supporting Murata's suggestion. Also the initial preservation of the wood (silicification of cell walls) was similar to that as postulated by Jefferson (1987). See Chapman and Smellie (p. 170).

Rapid Burial Necessary

Rapid burial is necessary to preserve the wood before decay and deterioration destroys much of its structure. Leo and Barghoorn (1976, p. 4) stated that in order to preserve any fossil wood, it must be isolated from an oxygen supply. Referring to Murata's article (1940), they noted that, "The initial stage for many of the fossil woods that are preserved as silicified woods appears to be rapid burial in volcanic ash . . ." (p. 5). Also see Dorf, 1964, p. 111; Jefferson, 1982, p. 705. Ransom (1955, p. 15) claimed that: If a tree is submerged in water it becomes waterlogged, and like a deadhead in a present day lake, it sinks to the bottom. Here, deprived of oxygen, decay of the tissues may be retarded indefinitely.

For instance Leo and Barghoorn (1976, pp. 4-5) noted that:

Water-logged wood "mined" from stagnant lake bottoms after a hundred or more years of submergence was found to be perfectly sound . . . Wooden stakes driven into anaerobic muds over 4,500 years ago, when recovered and examined, were found to be histologically intact and recognizable as to botanical taxa . . .

However these latter samples had a greatly reduced holocellulose content yet all of the lignin content was retained but "chemically modified" . . . (p. 5). Thus lignin resists degeneration as compared to holocellulose under anaerobic conditions. Allison (1988) stated that, "Anoxia retards decay but does not halt it" (p. 341). As a comparison he explained that generally ". . . chitin will persist in sediment longer than muscle . . . cellulose will persist for even longer . . . and lignified cellulose for even longer still . . . " (p. 341).

Consider the conditions mentioned above from the standpoint of a Flood model, (remembering that catastrophic conditions are suggested i. e., the removal of the woody material to a place where it can become waterlogged [flooding] then later covered with volcanic ash or silica-rich sediment). Obviously abundant water necessary to waterlog trees is available in a universal Flood. Also the power to transport large quantities of logs, etc. is available. In post-Flood times as the waters receded from the land, waterlogged trees could have been stranded on shore and covered with volcanic ash when considerable volcanic activity occurred. Also assuming a high rainfall climate after the Flood (Oard, 1990) as well as the presence of many post-Flood lakes (particularly in the western U. S.), severe local flooding possibly occurred. Logs could have been washed into areas to be covered by ash or silica-rich sediments.

Continuing rain and local flooding could have provided the water necessary to devitrify volcanic ash or chemically alter silica-rich sediments thereby releasing orthosilicic acid for later petrification of any buried, waterlogged wood. This tentative model deals with postulated conditions during the Flood and hypothetical conditions viewed as after-effects of the Flood.

Rapid Silicification of Wood and Other Organic Matter

Interestingly, it has been determined that the silicification of wood is a rapid process. Murata (1940, p. 590) reported from another study ". . . that wood immersed in the siliceous hot springs of Yellowstone Park becomes partly impregnated with silica in a few months." Buurman, et al. (1973) noted that plant remains were silicified in acid sulfate soils ". . . within the last centuries" (p. 123). Again a quote from Scurfield et al. (1974b) concerning an exchange between the authors and a reviewer is illuminating.

Reviewer IV: On the basis of the rate of chemical exchange, can you estimate the time required to produce "petrified wood"?

Authors: We suspect tens, perhaps hundreds, rather than thousands of years in view of the reported finding of a nail embedded in a specimen of petrified wood (p. 396).

Sigleo (1978, p. 1404) quoted other sources and claimed that ". . . silica nucleation and deposition can occur directly and rapidly on exposed cellulose surfaces." Note the following comments by Leo and Barghoorn (1976, p. 4):

Fossilization, with preservation of histological detail, apparent or real, is restricted to a limited number of geological situations with suitable biogeochemical histories. The environmental parameters of such situations are essentially those which arrest or curtail microbial activity, particularly that of lignin-digesting fungi. Among the more important of these parameters are (a) moisture, (b) temperature, (c) aeration, (d) pH, and (e) sedimentary setting. Time appears to be of consequence only in reference to the duration of operation of one or more of the aforementioned factors when functioning adversely in effect.

Later in discussing the chemistry of silicified wood "... from the Upper Devonian to the past century in age" (p. 8) the authors note: "There is no consistent time (geological age) correlation with either the amount of wood or its state of preservation" (pp. 8, 9). In the last section of the paper, Leo and Barghoorn (1976, p. 29) say "In terms of geologic time, the emplacement of silica in wood, as a molecular film, probably occurs rapidly." Then they felt that from this state to formation of an opaline state "probably requires a much longer time" (p. 29). Finally they postulated:

The ultimate fate of all silica is transformation to low quartz. Under conditions normally present at or near the surface of the earth, this conversion may require millions of years . . . In the presence of organic matter, however, crystallization to quartz may be appreciably accelerated . . . (p. 29).

Supporting the concept of rapid petrification of wood, many investigators have "artificially" caused silicification of wood in the laboratory. Some of these studies will be reviewed. Drum (1968a, pp. 175-176; 1968b, pp. 784-785) was able to silicify portions of woody tissue within 24 hours by soaking the plant material in a solution of sodium metasilicate. Oehler and Schopf (1971, pp. 1229-1231) developed a technique to silicify blue-green algae. They employed a solution of colloidal silica and later exposed the "fossil" gel to slightly elevated temperatures and high pressures to crystallize the SiO₂. A temperature of 150°C and pressures of 2000-3000 bars for two to four weeks produced the best results. They claimed their laboratory technique was ". . . analogous to processes involved in the deposition of natural bedded cherts" (p. 1231). The artificial silicification process of Leo and Barghoorn (1976) employed solutions of ethyl silicate in water with the wood being submerged for time intervals from a few days to a year or more.

It appears that the silicification process does not require vast intervals of time to accomplish the permineralization (petrification) of wood. Thus the operation could conceivably function within the restrictions of a young earth model.

Transportation to Burial Site or In-Place Burial?

There has been considerable discussion in the scientific literature as to how plant material was deposited at its burial site before petrification, i. e., buried at place of growth (autochthonous) or transported by water (allochthonous). It appears that the vast majority of cases support allochthonous origins but there are reported instances of autochthonous origins.

Penhallow (1907, pp. 93-113) in investigating specimens of fossil wood from east Texas stated:

They all gave evidence of water transportation at a time preceding silicification, which I assume to have taken place subsequently to deposition in the locality where found. The evidence of such transportation appeared in the very advanced condition of decay presented by many of the specimens, and more particularly in the rounded and waterworn surfaces and ends, an abrasion which was accomplished prior to silicification (p. 93).

He proposed two possibilities, either (1) deposition of the wood by southward flowing rivers or (2) abrasion in lakes or lagoons from wave and wind action if the wood were of local origin. As you can see he equivocated somewhat and managed to leave room for either allochthonous or autochthonous origins.

Moore (1958, pp. 401-402) claimed that fossil woods in the Petrified Forest National Park were carried many miles to their present location. Leo and Barghoorn (1976, p. 7) believed in an allochthonous origin for this fossil material and Dorf (1964, p. 107) agreed with this conclusion. Ransom (1955, p. 12) stated that most petrified forests, particularly the petrified forests of Arizona, show evidence of being washed into place. Jefferson (1982) gave evidence in his paper on the fossil forests of Alexander Island, Antarctica that supports the concept of in-place burial at this location.

Probably the most famous example cited as evidence of trees buried in place is the petrified forests of Yellowstone Park. Earling Dorf (1964), in his wellknown work on these forests, said:

On a steep bluff overlooking the Lamar River a few miles above its confluence with the Yellowstone River . . . no fewer than 27 distinct layers of petrified trees have been exposed by erosion (p. 107).

A beautiful drawing of the cliff is given on page 110 of the 27 layers of volcanic sediment with entombed logs. Interestingly some logs are shown in horizontal positions, others in differing angles to the horizontal as well as vertically positioned stumps. This has led investigators to offer interpretations other than in-place burial. Fritz (1980a, p. 312) mentioned that:

Besides vertical stumps \ldots , logs that are parallel and diagonal to the bedding also occur in abundance \ldots . In all sections, with the exception of several small intervals in the Specimen Ridge section, fossilized horizontal logs are most abundant and make up 60% to 100% of the total.

Fritz postulated that volcanic flows from stratovolcanos saturated with water moving downward into the narrow valley (through which the Lamar River flows) "... uprooted trees growing in high-elevations, cooltemperate habitats... During transport, roots and branches were broken off" (p. 312). Geological evidence was offered to support this view. Thus the author considered that the petrified forests of Yellowstone had an allochthonous origin. Later Fritz (1980b, pp. 586-588) used field evidence of mud flows from the 1980 Mount St. Helens eruption to show how the same type of action could have produced vertical fossil stumps at Yellowstone in the past. He devoted a chapter in his well-written *Roadside Geology of the Yellowstone Country* (1985, pp. 9-26) to his interpretation of how the trees were entombed in the Lamar River and Sepulcher formations.

Yuretich (1984, pp. 159-162) accepted the mudflow concept of Fritz but claimed that ". . . there is no evidence that the upright stumps have undergone transport" (p. 159). Likely there will be continual sparring in the geological literature over autochthonous vs. allochthonous deposition of erect tree stumps as well as other features in the geologic record. Many geologists who prefer uniformitarian concepts may realize the connection between allochthonous deposition and the Noachian Deluge (i.e., Gastaldo, 1989, p. 1).

Harold Coffin (1976, pp. 539-543) has done considerable work on the Yellowstone petrified forests. In his excellent book Origin By Design, he devoted an entire chapter (1983, pp. 134-151) to the subject. He offered evidence that favors the transportation hypothesis against in situ burial. These evidences are categorized as abrupt root terminations, overlapping levels of the tree layers, orientation of vertical and petrified trees, ecological diversity of fossil trees, bands of organic matter in various "soil" levels, arrangement of the organic matter in the levels, evidence of water sorting, type of organic matter in "soil" layers, geochemistry of layers, nature of the sediments in which the trees are contained and a discussion of the vertical flotation of trees. Interested readers should consult this treatise. Also since the petrified forests are preserved in a National Park, they offer research opportunities for creationists interested in this topic.

Steve Austin (1986, p. 4), in his work on the Mount St. Helens explosion of 1980, discussed finding upright deposited logs in Spirit Lake. As he noted (p. 4):

The landslide-generated waves on Spirit Lake stripped the forests from the slopes adjacent to the lake and created an enormous log mat.... Careful observation of the floating log mat indicates that many trees float in upright position with a root ball submerging the root end of the trunk while the opposite end floats out of the water... These trees, if buried in sediment, would appear to have been a forest which grew in place over hundreds of years...

Also Austin related the results of sidescan sonar and scuba diving work in surveying the lake bottom (p. 4):

Hundreds of upright, fully submerged logs were located . . . Extrapolating from the small area of lake floor surveyed to the entire lake bottom, we estimate more than 15,000 upright stumps existed on the floor of the lake in August 1985. The average height of an upright deposited stump is 20 feet. Sonar records and scuba investigation verified that many of the upright deposited trees have root masses radiating away from the bases of the trunks.

Concerning the fossil woods from our study of the Dawson Creek area of Big Bend National Park, all observed material appears to have been washed into place from a distant source. No specimens that exemplify in-place burial were found. More discussion of this allochthonous origin will be presented in subsequent parts of this report. For a possible situation where examples of both autochthonous or allochthonous tree stumps could have been present if transported and standing stumps would have been buried by silica-rich material and later silicified, see Williams, 1993, particularly Figures 3b, 4a and 4b.

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Quote

... every system of thought has its own concept of ultimacy, and, in all, the locale of ultimacy is also the source of determination, for ultimacy requires it. In Biblical theology, all things are created, predestinated, and governed by the sovereign God. Predestination is an inescapable concept; it is simply a declaration that somewhere an ultimate law, force, cause, power, or direction governs all things. If this be denied to God, predestination then accrues to some other agency. The results are various: doctrines of Karma, fate, dialectical materialism, naturalistic determinism, and so on. If one form of the doctrine is denied, it is implicitly in favor of another form. In the modern form, it usually means total planning by the sovereign state. Whereas a theistic transcendental predestination is internal and non-coercive the immediate determinism of the state is external and coercive. It means that the state competes with man for control of the same ground.

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