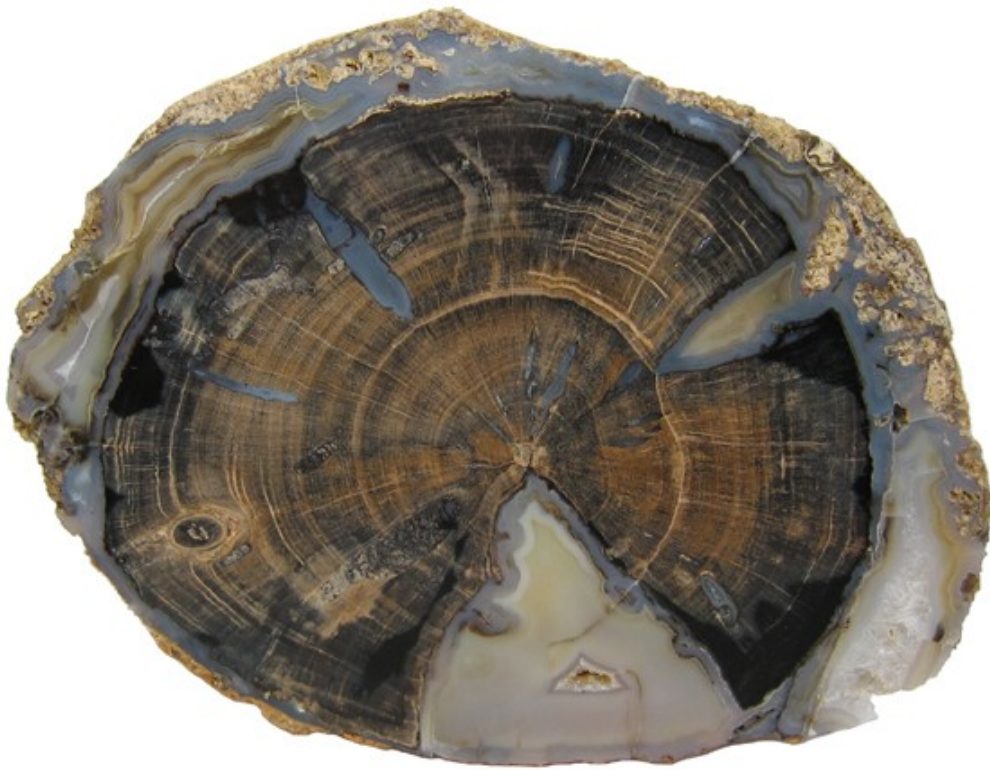


Petrified Wood:
The Silicification of Wood by Permineralization
Mike Viney



Organisms entombed in sediment, such as volcanic ash, which becomes saturated with water, may petrify or permineralize under the right pH and temperature conditions. Traditionally, petrification or petrification refers to animal or plant tissue that has turned to stone. Petrified wood and dinosaur bone are familiar examples; however, these fossils actually form through permineralization and often contain original organic material. In this article we will use petrification and permineralization synonymously.

Permineralized fossils form when solutions rich in minerals permeate porous tissue, such as bone or wood. Minerals precipitate out of solution and fill the pores and empty spaces. In the case of wood, petrification occurs when cellulose, hemicellulose, and lignin within the cell walls of the woody tissue act as a framework to preserve cell structure. Silicates, iron oxides, metal sulfides, native elements, carbonates, and sulfates can be involved in permineralization. Silicified wood is the most common and provides the most detailed preservation of cell structure.

The specimen above is a cross-section of a limb permineralized with silica. Volcanic material often serves as a source of silica for wood and bone. Pyroclastic flows and lahars can bury forests that later become permineralized. Many permineralized specimens retain patterns of cell structure. Both cell structure and insect damage, in the form of galleries, have been preserved in the above specimen.

Silicified Fossil Wood Composition

When one holds a specimen of silicified wood it certainly appears to be made entirely of mineral matter with no original cellular material remaining. However, when examined under magnification many specimens reveal microscopic cellular structure leaving one to wonder if some of the original organic matter is still present. It is informative to make some basic comparisons between fresh wood and fossil wood.

Cellulose, hemicellulose and lignin account for over 95% of the dry weight of wood (Leo & Barghoorn, 1976, p. 2). The average density of 43 species of extant softwoods and 96 species of extant hardwoods examined by Hoadley is 0.53 g/cm^3 (Hoadley, 1990, pp. 49-51). The average density of the softwoods alone was 0.43 g/cm^3 , while for the hardwoods it was 0.57 g/cm^3 . Silicified wood generally contains more than 90%, by weight, of silica (Leo & Barghoorn, 1976, pp. 8-9; Sigleo, 1978, p. 1401; Mustoe, 2008, p. 132). Woods mineralized with opal have densities of 2.04 g/cm^3 or less. Woods permineralized with quartz have densities of 2.34 g/cm^3 or greater (Mustoe, 2008, p. 132).

How much of the original wood is present? The first well documented attempt to answer this question was carried out by St. John (1927). St. John examined 25 prepared sections of various silicified wood specimens for cell structure under a light microscope. The sections were treated with a solution of one third hydrofluoric acid and two thirds alcohol to remove silica and then reexamined under the microscope. Some specimens retained most or some of the structure indicating the presence of organic matter. Other specimens lost all of their structure with no trace of organic matter (pp. 733-739). Mustoe (2008 and

written personal communication, 2011) employed a more quantitative method to determine the presence of organic matter utilizing heat to destroy residual organic matter and measuring loss in mass. Mustoe concluded that most of the plant tissue is destroyed during silicification. Sigleo (1978) isolated lignin derivatives from 200 Ma *Araucarioxylon arizonicum* specimens demonstrating that small traces of relic organic matter can persist after many millions of years. Overall, evidence suggests that very little of the original organic matter remains in silicified wood. What are the conditions and processes that lead to the formation of siliceous petrifications?

Geochemical Conditions for Silicification

Silicified wood forms in principally two geologic environments. Trees transported by streams and rivers can become buried in the fine-grained fluvial sediments of deltas and floodplains or volcanic ash can bury trees while still upright (Mustoe, 2003, p. 34). Fresh wood entombed in soft mud beneath water carrying large amounts of sediment may set up conditions necessary for fossilization. Rapid burial in volcanic ash is the initial stage for many fossil woods preserved with silica (Leo & Barghoorn, 1976, p. 5). Volcanic ash acts as an abundant source of silica for groundwater. The presence of water is important for several reasons: it reduces oxygen thereby inhibiting tissue deterioration from aerobic fungi, acts as an agent for the alteration of ash, maintains wood shape for maximum permeability, and creates a medium for the transport and deposition of silica. The conditions of temperature and pressure during fossil wood formation are equivalent to those found in sedimentary environments of shallow depth. The pH of the sediment-laden water is probably neutral to slightly acidic (Leo & Barghoorn, 1976, p. 27). These conditions help to create an environment in which wood can act as a template for silica deposition.

The Process of Wood Silicification

Buurman (1972, pp. 1-43) examined fossil wood specimens preserved with a variety of minerals using X-ray diffraction, optical and scanning electron microscopy. We will summarize his findings relating to silicification. In one group of silicified woods Buurman found evidence suggesting that wood preservation is best when disordered tridymite (opal-CT) replaces cell walls or when this opal is subsequently transformed to chalcedony through recrystallization. In both instances, Buurman suggests the fossil wood has formed by replacement rather than filling. A second group of silicified woods preserved with chalcedony and quartz retained some woody tissue. Buurman suggested that these specimens had formed through permineralization (filling). Buurman concluded that replacement and permineralization are distinct processes.

In a more detailed study, Scurfield and Segnit (1984, pp. 165-167) examined 75 fossil wood specimens from Australia using X-ray diffraction, differential thermal analysis, electron probe techniques, optical and scanning electron microscopy. Their study found that replacement of the cell walls of tracheids and vessels occurred in addition to permineralization. They conclude that petrification of wood occurs in five stages, summarized as follows:

1. Wood is permeated by silica solution or colloid.
2. The pores of cell walls are penetrated.
3. Progressive dissolution of cell walls occurs as a mineral framework builds to maintain wood structure.
4. Silica deposits in voids, intercellular spaces, and finally cell lumina.
5. Lithification occurs, as water is lost. Silica may transform from one form to another by pseudomorphic replacement and/or repeated solution and recrystallization.

Scurfield and Segnit found evidence, in the specimens they studied, for transformation from opal-CT to chalcedony and chalcedony to quartz. Evidence for the conversion of opal-A to opal-CT was not strong. They also hypothesized that the rate of cell wall breakdown may determine whether opal-CT or chalcedony is the initial replicating substance.

When wood is permeated by silica solution, hydrogen bonding links silicic acid to the cellulose making up the inner cell walls. As water is lost silicic acid is polymerized into opal. Layers of silica are deposited with the wood acting as a template. Initially, silica is fixed to the inner cell walls and infill pits connecting adjacent cells.

Cell walls may be replaced with silica as permineralization continues. Amorphous silica is highly hygroscopic (attracts water) and highly permeable to fluid flow (Leo & Barghoorn, 1976, p. 20). The ability of silica to penetrate cell walls is supported by its occurrence in plants such as *Equisetum* and many hardwoods. It has also been shown that waterlogged spruce wood contains micropores large enough for the entry of silica solution (Scurfield & Segnit, 1984, p. 164). To replicate cell structure with high fidelity a balance between wood degradation and mineral deposition must be achieved. As silicification proceeds to more advanced stages cellulose degrades leaving more room for the emplacement of silica between cells and within cell wall layers. Lignin is the most decay resistant compound in wood and continues to act as a template for structural detail. In fact, fossil woods show an increase in the ratio of lignin to holocellulose (cellulose & hemicellulose) when compared with contemporary counterparts. Specimens aged Eocene or older are devoid of holocellulose (Leo & Barghoorn, p. 5). Thus, lignin is the last organic matter to be replaced.

As the process continues silica deposits in intercellular spaces and voids created by wood degradation. Finally, silica deposition forms layers towards the inside of cells that eventually fill the lumina or cell space. Silica that initially fixes to the wood structure is amorphous. This amorphous silica is unstable and slowly crystallizes to more stable forms. The transition to more stable forms of silica involves continued polymerization and water loss. Higher ordered forms of opal are created through this process and eventually lead to the thermodynamically more stable silica quartz (Stein, 1982, p. 1277).

The progressive transformation of opal-A to opal-CT to chalcedony and finally quartz is an important aspect of the accepted model for wood silicification. Recent work by

Mustoe (2008) reveals that the silica transformation aspect of this model is inconsistent with the mineralogy of fossil wood in the Florissant Formation (pp. 127-140). Mustoe examined 15 specimens representing six silicified stumps. The samples were analyzed using X-ray diffraction, X-ray fluorescence, scanning electron microscopy/energy-dispersive X-ray spectrometry (SEM/EDX), and optical microscopy. Basic physical properties including density, color, and loss on ignition were also determined.

Some of the specimens were permineralized with only opal-CT, others were a combination of opal-CT and chalcedony, and still others were quartz. In specimens permineralized with both opal-CT and chalcedony the two silica phases appeared to coexist as primary minerals. Thus, evidence for the transformation of opal-CT to chalcedony was missing. Evidence gathered by this study suggests that the Florissant specimens were directly mineralized with chalcedony. The precipitation of opal, chalcedony, and quartz are influenced by concentrations of dissolved silica. Opal is precipitated with high concentrations of dissolved silica while chalcedony is precipitated with low concentrations and quartz still lower. Mustoe speculates that these geochemical characteristics may explain the patterns of mineralization found at Florissant.

Mustoe concluded that petrification at Florissant occurred in several stages. First, amorphous silica precipitated on cell wall surfaces. Second, opal-CT and chalcedony filled cell lumina. Finally, chalcedony filled fractures that crosscut permineralized tissues in some specimens. Spaces between adjacent tracheids were often unmineralized, making the fossil wood permeable to water and susceptible to cleaving radially, tangentially and transversely from freeze-thaw weathering. This finding has important implications to the preservation of specimens at Florissant Fossil Beds National Monument. Mustoe's findings are important because they suggest that petrification may occur through multiple processes or pathways.

Karowe and Jefferson (1987) investigated the initial stages of silicification by examining trees buried by Mount St. Helens lahars or mudflows dated at 1980, 1885, A.D. 1450-1550 and 36,000 years B.P. Wood samples were examined using scanning electron microscopy and energy dispersive X-ray analyses. Wood buried in 1980 showed no significant mineral deposition. Wood buried in 1880 and A.D. 1450-1550 exhibited traces of silica on cell walls as well as cell wall decay. Wood buried 36,000 years B.P. showed silica impregnation of cell walls. Decay in these older specimens affected the secondary wall and removed the middle lamella (pp. 198-200). Karowe and Jefferson concluded that the increase in silica deposition as well as decay associated with the age of these trees supported the model of silicification proposed by Leo and Barghoorn in 1976.

Time and Silicified Wood

Fossil plant deposits including petrified forests from around the world allow paleontologists to trace the evolutionary history of vascular plants from 420 Ma ago (Silurian) to the present (Kerp, 2002, p. 23). Petrified forests throughout the world capture the public's imagination (Ransom, 1955; Dernbach, 1996; Dernbach and Tidwell, 2002; Daniels and Dayvault, 2006). Many want to know how long it takes to form

natural petrified wood. Some Pleistocene deposits contain peat and wood fragments that can be carbon dated. Ice Age gravels deposited 12,000 years ago contain fresh looking wood pieces. Wood dated at 15 million years weathering out of the Wilkes Formation in Washington can be carved with a pocketknife and ignited with a match (Mustoe, 2001, p. 18). It is clear that wood can be preserved for long periods of time under the right conditions.

It is equally clear that wood can be quickly mineralized under the right conditions. Timbers in copper mines from Cyprus and Arizona have been found that contain copper (Daniels & Dayvault, 2006, p. 173). Wood buried in ash produced from the 1886 eruption of Mt. Tarawera in New Zealand is mineralized with silica. Silicified wood from Wyoming contained enough organic material to be carbon dated at less than 3,000 B.P. X-ray diffraction reveals that these recently silicified woods are impregnated with amorphous opal (Leo & Barghoorn, 1976, p. 15; Stein, 1982, p. 1279). These recent petrifications are not what collectors think of as high quality petrified wood.

The initial emplacement of silica as a film may occur rapidly. Artificial silicification of wood in the lab and studies of natural silicified wood demonstrate that the physical state of silica in newly formed petrifications is amorphous (Leo & Barghoorn, 1976, p. 28). Conversion of this silica to increasingly stable forms of opal-A (amorphous), to opal-CT (cristobaite & tridymite), to chalcedony (cryptocrystalline quartz), and finally to microgranular quartz requires millions of years (Leo & Barghoorn, 1976, p. 29; Stein, 1982, p. 1281; Kuczumow, Venkemans, Schalm, Dorrine, Chul-Un, Janssens, & Van Grieken, 1999, p. 436). Under normal conditions conversion of opal to quartz requires tens of millions of years; however, under geothermal conditions the same process may occur in 50,000 years or less (Mustoe, 2003, p. 34).

X-ray diffraction patterns for different aged silicified specimens examined by Stein support the well established transformational sequence of opal-A to opal-CT, to quartz. A Yellowstone Wyoming sample carbon dated at 2,430 years was composed of opal-A. A Pliocene-aged sample from the Sante Fe Formation of New Mexico was composed of opal-CT. A Miocene-aged sample from the Bozeman Lake Beds was composed of opal-CT and some quartz. A Late Eocene sample from Florissant, Colorado was composed of quartz. However, Mustoe (2008) has shown that some Florissant wood is permineralized with opal-CT and chalcedony as well. Still, chalcedony and microgranular quartz are the most common forms of silica found in fossil woods that are Eocene or older. X-ray diffraction studies, specific gravity measurements and indices of refraction all support an increase in silica ordering with increase in age (Stein, 1982, pp. 1277-1280).

Instant Petrified Wood?

Fascination with natural permineralized specimens has spurred interest in creating methods for artificial petrification. Artificial petrification reflects both scientific and commercial interests. Leo and Barghoorn (1976) document early attempts at creating artificial silicified woods in the 1500's by Basil Valentine and Johannes Kentmann.

Experimental replication of these early recipes has not been successful (p. 10). More recent attempts have produced some positive results.

Ryan W. Drum from the University of Massachusetts, Amherst describes his attempt at the laboratory silification of twigs in a 1968 article that appeared in the journal *Science*. Twigs were soaked in solutions of sodium metasilicate, washed, and then treated with chromic acid to remove organic remains. Entire twigs did not remain intact; however, single cells and small aggregates of cells were replicated in silica. Drum described these replicas as very fragile and included electron micrographs of his results. Drum goes on to say that his in vitro silification process might provide a method to study cellular spaces in 3-D, intercellular connections, and the morphology of woody cells.

Leo and Barghoorn (1976) improved upon Drum's experiments. Their procedure included boiling wood to degas and waterlog specimens. The wood was alternately soaked in solutions of water and ethyl silicate at neutral pH and 70 degrees Celsius. Ethyl silicate decomposes to monomolecular silicic acid, which is thought to be the silicifying agent in natural processes. Nitric acid and potassium chlorate were used to remove organic matter. The silica lithomorphs that remained replicated cell structure and were more substantial than those produced from Drum's procedure. The silica lithomorphs were fragile and composed of amorphous silica. These silica lithomorphs resemble the first stages of permineralization observed in recently silicified specimens (p. 12-15). These experiments would suggest that the organic cell structure of wood acts as a template for initial silica deposition.

The process of natural permineralization has also inspired the pursuit of artificial wood composites. These wood composites use fresh wood as a framework for creating either a wood composite or a ceramic. An October 1992 *Popular Science* news article read 'Instant petrified wood?' In reality researchers at the Advanced Ceramic Materials Lab at the University of Washington in Seattle were making wood ceramic composites. Wood is soaked in solutions of silica and aluminum and then oven-cured to create the composites. The solution penetrates the wood to a depth of up to 0.2 inches. The wood is abrasive, but can be worked with carbide tools. The authors speculate that these composites could be made with the same rock-hardness of petrified wood. The composite is wood impregnated with silica and aluminum up to a depth of 0.2 inches.

Yongsoon Shin and colleagues at the Pacific Northwest National Laboratory (PNNL) developed a method for creating a silica-based ceramic that mimics wood structure. The process uses surfactants and silicate solutions to mineralize wood that has been soaked in an acid solution. After the silicate solution penetrates cell wall structures it is heated to high temperatures in air to oxidize the silicate and remove organic residue. This method creates a ceramic, which faithfully reproduces cellular structures in great detail as confirmed by SEM images (Shin, Liu, Chang, Nie, & Exarhos 2001, p. 728). Shin et al (2001) points out that, "Another important phenomenon related to the current study is natural petrification, which takes place over a very long period of time. In some cases the cellular tissue is completely replaced by silicate and other minerals. Our study not only

points to a more rapid approach to transforming organic tissues into ceramic materials, it may also shed some light on how natural petrification takes place (p. 731).”

An article on ChemicalProcessing.com entitled ‘Petrified wood yields super ceramics’ describes a process developed at PNNL for using wood to form the ceramics silicon carbide (SiC) and titanium carbide (TiC). The process involves soaking the wood in acid, infusing it with titanium or carbon, and baking it in an argon-filled furnace at 1,400 degrees Celsius. This process is the same as Shin’s 2001 study except for heating in an argon atmosphere instead of air. The 2001 and 2005 experiments used small blocks of pine and poplar wood. Both the macro and microstructure of the wood is preserved in this ceramic. The material has the strength of steel, and can resist temperatures of up to 1,400 degrees Celsius. PNNL scientist Yongsoon Shin is quoted as saying that one-gram of this material flattened has enough porosity to cover an entire football field. SEM and TEM images were used to study the microscopic structure of these ceramics (Shin, Wang, & Exarhos 2005, pp. 73-76). The SiC ceramics could be used for making filters, catalysts, cutting tools, abrasives, and coatings. The purpose of Shin’s research is to develop methods for using natural biological materials as templates to construct inorganic materials.

Hamilton Hicks was issued US patent 4612050 on September 16, 1986 for a mineralized sodium silicate solution used to create wood with the “non-burning characteristics of petrified wood” (Patent Storm). In one experiment a horse stall was set on fire with combustible materials. The treated wood showed signs of charring, but did not burn. The patent indicates that the treated wood is non-toxic and has an inherently bad taste. This bad taste prevents horses from “chewing or nibbling the wood to shreds”. The inventor speculates, “petrification” of the treated wood is achieved when minerals in his solution “replace the cells” and the solution hardens the wood. It would be interesting to compare the amount of wood still present as well as the nature and extent of silicification in this product with that found in naturally silicified wood.

Products referred to as “instant petrified wood” may provide insights into the initial stages of permineralization. However, many of the materials and procedures used to make these products are not found in nature. Products made from the initial emplacement of silica, represented by both artificial and recent natural petrifications do not resemble what a collector regards as high quality petrified wood. Multiple lines of evidence suggest that natural fossil wood permineralized with opal-CT, chalcedony and microgranular quartz requires millions of years to form.

Conclusion

Evidence for pathways that lead to the formation of silicified wood comes from studies of fossil wood, laboratory simulations of petrification, production of organic composites, and examination of trees buried recently by volcanic deposits. The formation of silicified wood includes permineralization, replacement and recrystallization. A summary of an accepted model for natural silicification is as follows.

When wood is permeated by silica solution, hydrogen bonding links silicic acid to the cellulose making up the inner cell walls. As water is lost silicic acid is polymerized into opal. Silica that initially fixes to the wood structure is amorphous and recrystallizes to a more stable form. Layers of silica are deposited with the wood acting as a template. Initially, silica is fixed to the inner cell walls and infill pits connecting adjacent cells. Cell walls may be replaced with silica as permineralization continues. To replicate cell structure with high fidelity a balance between the chemical and biological decomposition of wood and the precipitation of silica must be achieved. As silicification proceeds to more advanced stages cellulose degrades leaving more room for the emplacement of silica between cells and within cell wall layers. Note that this replacement is not molecule by molecule. Lignin is the most decay resistant compound in wood and continues to act as a template for structural detail. Later, cell interiors (lumina) along with cracks and fractures are permineralized with silica. The general model of silicification described above includes a transformation of silica to increasingly more stable forms from opal-A to opal-CT to chalcedony and finally to quartz. Evidence for the recrystallization of silica is lacking in some specimens suggesting there is more than one pathway for the formation of silicified wood.

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Schinoxylon sp.
Green River Formation
Cenozoic; Paleogene; Eocene
Blue Forest, Wyoming
12 cm x 10 cm