

Article

Multi-Stage Silicification of Pliocene Wood: Re-Examination of an 1895 Discovery from Idaho, USA

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Academic Editor: James Schmitt

Received: 3 March 2016; Accepted: 30 March 2016; Published: 26 April 2016

Abstract: The 1895 discovery of a petrified tree near Clover Creek in south-central Idaho, USA, attracted worldwide attention and resulted in the naming of a new species of ancient oak, *Quercinium pliocaenicum* Schuster. For more than a century, the discovery has largely been forgotten, even though specimens reside in reputable museums. Reinvestigation of the locality in 2014/2015 resulted in newly-collected specimens and a wealth of new data. Optical microscopy confirms the cellular anatomy used for the original taxonomic study. X-ray diffraction, scanning electron microscopy, energy-dispersive electron spectroscopy, Raman spectroscopy and cathodoluminescence microscopy reveal details of the mineralization, showing the presence of opal-CT as the primary component, with chalcedony as a lesser constituent. This mineralogy suggests petrification occurred in at least two stages, beginning with opalization of cellular tissue, leaving open vessels that became filled with chalcedony during a later mineralization episode. Clover Creek oak represents relict flora growing in a wetter climate before the uplift of the Cascade Range created a rain shadow that caused profound desertification of the inland Pacific Northwest.

Keywords: chalcedony; Glens Ferry Formation; Snake River Plain; Idaho; opal-CT; opalized wood; paleobotany; petrified wood; *Quercinium pliocaenicum*

1. Introduction

This report describes the rediscovery of a historic North American fossil wood locality, its geologic setting and a detailed re-examination of newly-collected specimens using a variety of petrographic and geochemical methods.

In 1895, land surveyors working 11 km northwest of Bliss, Idaho, discovered intact branches of a fossil tree protruding a meter above the ground surface [1]. When excavated down to the 8-m level, the trunk's diameter was nearly 2 m. The fossil tree was believed to be standing where it grew, and no other fossil wood was found in the vicinity. Approximately two tons (1800 kg) of the opalized wood

were shipped to Philadelphia mineral dealer A.E. Foote by 1897 [1]. All Foote labels corresponding to the Clover Creek material bear the number 212 [2] as a reference to opal's order in the sixth edition of *Dana's System of Mineralogy*. The Twentieth Report of the United States Geological Survey of 1898 [3] included Foote's description of the Clover Creek fossil find and highlights the amazing preservation of the cellular tissue and apparent woody structure and color. The report indicated that the largest intact branch sections measured 12 inches (30 cm) in diameter.

Clover Creek specimens found their way into museums in the United States, Canada and Europe, commonly displayed in systematic mineral collections as an example of opalization (Figure 1). Clover Creek samples are likewise described in the mineralogical literature as examples of wood preserved by opal [4–6]. Even philatelists are confronted with a picture of a Smithsonian Clover Creek sample on two first-day covers of the 1974 stamp issue of the U.S. postal office celebrating U.S. mineral heritage; another serious reason to clearly establish the provenance of Clover Creek opalized wood.

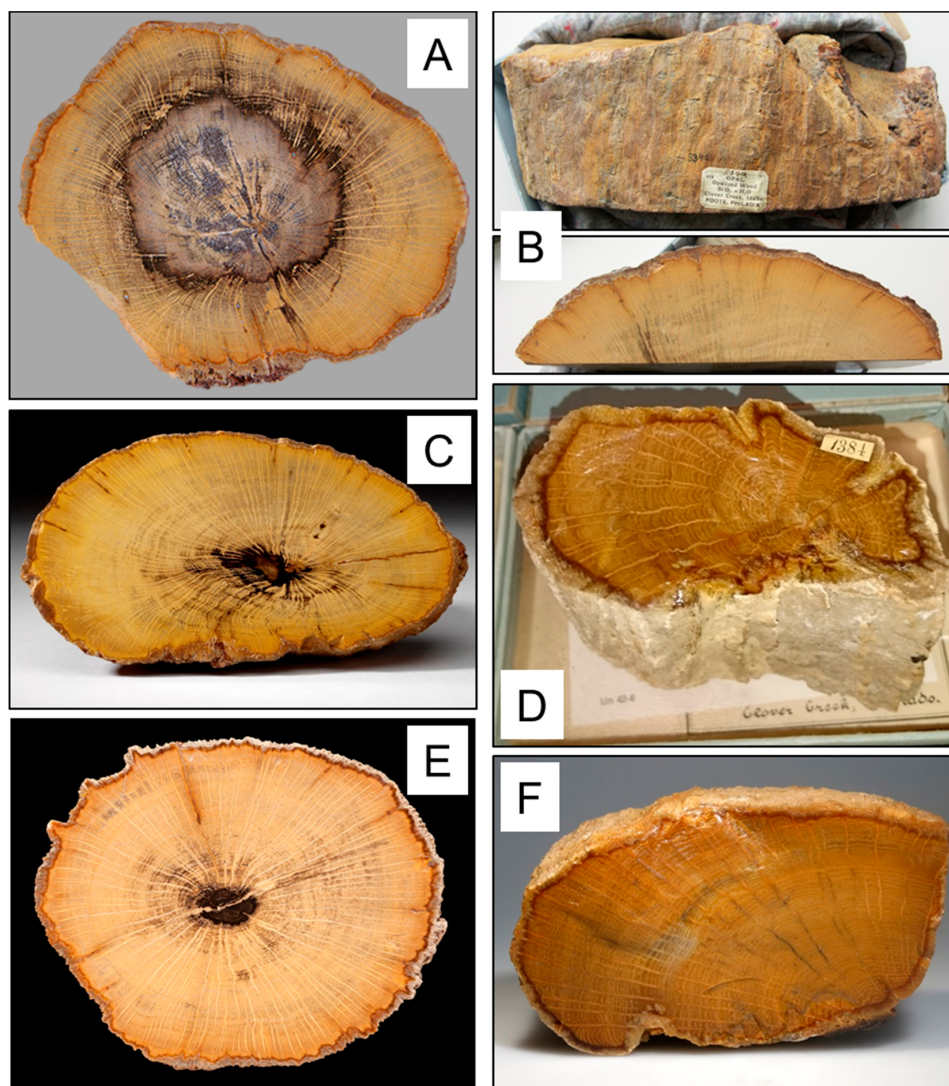


Figure 1. Opalized wood from C+bblover Creek, Idaho. (A) Specimen at School of Mines, Golden, Colorado; (B) Naturhistorisches Museum der Burgergemeinde Bern, Switzerland; (C) Royal Ontario Museum Toronto, Canada; (D) Statens Naturhistoriske Museum Kobenhavn, Denmark; (E) Natural History Museum (British Museum) London, U.K.; (F) Senckenberg Naturhistorische Sammlungen Dresden, Germany (for more information, refer to the Supplementary Material).

Prior to our investigations, scientific study of the Clover Creek fossil wood was limited to a single report in 1908 [7]. The author Julius Schuster received Clover Creek samples from Johann Traugott Sterzel, a German teacher, paleobotanist and first director of the Natural History Collections of Chemnitz, Germany, who obtained them from the German mineral dealer Dr. Friedrich. Krantz. Sterzel assigned the specimens to *Quercinium* and asked Schuster for a detailed examination of thin sections prepared by the company Voigt and Hochgesang, Goettingen (Figure 2), today part of the Sterzel collection at Museum für Naturkunde Chemnitz, Germany. Schuster established a new species name, *Q. pliocaenicum* [7]. Subsequently, the German mineral dealer Krantz offered Clover Creek specimens for sale in 1908 [8], adding the new scientific name in 1909 [9].

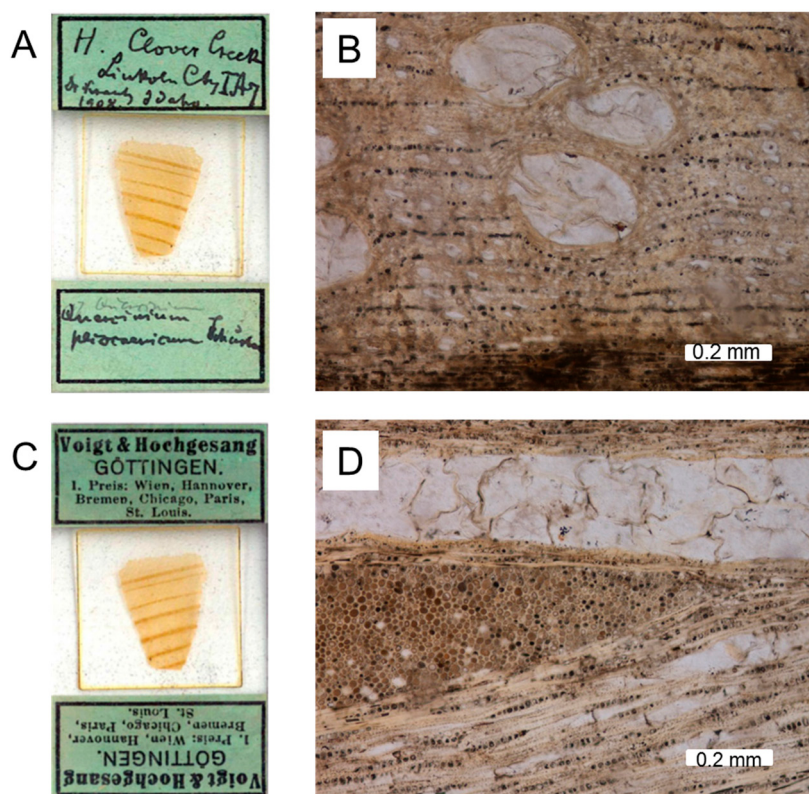


Figure 2. (A,) back side of an original thin section (transverse plane) examined by Schuster [7]; (B) recently taken OM micrograph showing transverse plane; (C) front side of original thin section; (D) recent OM micrograph showing an original thin section in the tangential longitudinal plane.

Quercinium was established as a morpho-genus by Unger [10] to describe petrified wood having a cellular anatomy characteristic of the modern oak family (*Fagaceae*). In later years, fossilized oak-like wood has been described as *Quercoxylon* [11–14], but *Quercinium* continues to be used [14,15]. We have not attempted to emend the taxonomy of *Q. pliocaenicum*, but instead focus on geologic and mineralogical aspects.

Clover Creek opalized wood has been referenced in several compendia [16–18], but an exact location or story behind the discovery is not given. Modern paleobotany books do not mention the Clover Creek find, even though many specimens are displayed in major museums. Originally, the locality was reported as being in Lincoln County, Idaho, but present county boundaries now place the site in Gooding County (Figure 3, [19]). The 2014 rediscovery of the site is described by Viney *et al.* [20]. The GPS coordinates are 42°59′46.70″N, 115°00′28.66″W, elevation 1009 m (3300 feet).

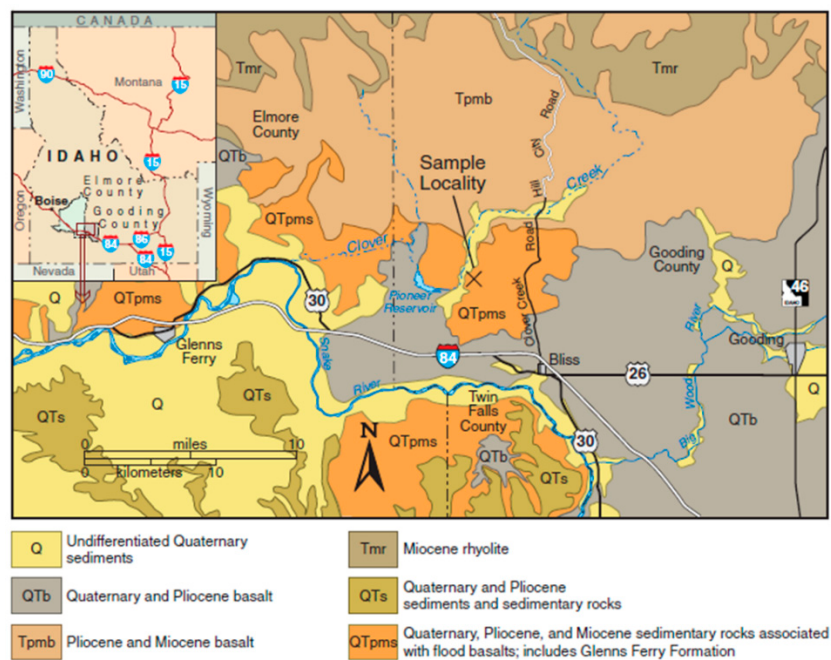


Figure 3. Locality map of the fossil site in Idaho, modified from Lewis *et al.* [19] (courtesy of William W. Besse).

The purpose of our study is to provide a comprehensive re-evaluation of this locality, using contemporary knowledge of the geologic setting, and to analyze newly-discovered specimens by contemporary analytical methods not available in 1908. This research is based on examination of the original 1908 thin sections and new thin sections prepared from specimens we collected in 2014. In addition, we extend the taxonomic work of Schuster [7] by providing analyses of the composition and microstructure of Clover Creek *Q. pliocaenicum*.

2. Geology of the Area

The opalized remnants of oak wood are found in flat-lying sandstone and siltstone of the Glens Ferry Formation, at an elevation 1009 m, on the east side of Clover Creek. The light-gray and light-brown siltstone and sandstone of the fossil site are in the upper member of the Glens Ferry Formation, stratigraphically above the Clover Creek basalt flow and below the Shoestring Road basalt. The strata are of Pliocene age and lie above the rhyolitic Fossil Gulch ash, with dates of about 3.3 Ma [21,22] (Figure 4).

The Pliocene Glens Ferry Formation of the Idaho Group contains sediment deposited in Lake Idaho, an inland lake that occupied the Snake River Plain from about 6.5 to 1.5 million years ago. The initial spillover of Lake Idaho was about four million years ago, but the age is not tightly constrained [23]. At the Clover Creek fossil site, about 60 m of sediment are exposed below the Shoestring Road Basalt, which forms the upland land surface (Figure 5, stratigraphic column). Exposure is intermittent. The sediment contains poorly- to well-sorted, subangular, medium to granule-sized volcanic lithic sandstone, interbedded with white to gray siltstone that bears small rhizoliths. The volcanic lithic grains are mainly rhyolite and pumice, with subordinate basalt. The sandstone also contains feldspar, quartz and biotite, attesting to the derivation from granitic rocks of the Cretaceous Idaho batholith to the north.

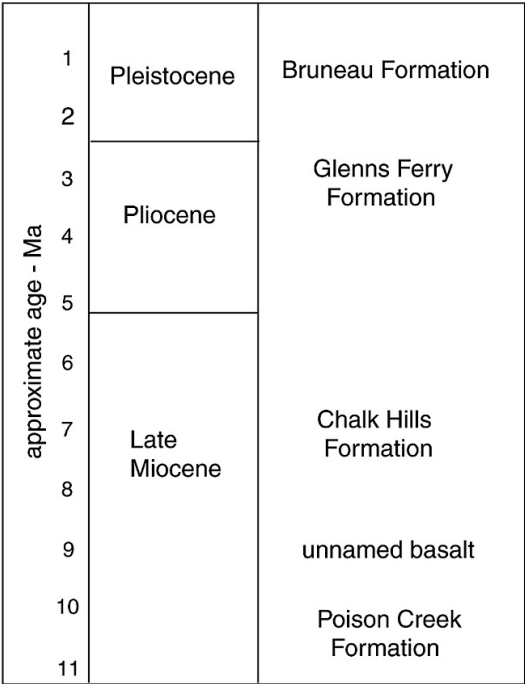


Figure 4. Stratigraphy of the western Snake River Plain, Idaho.

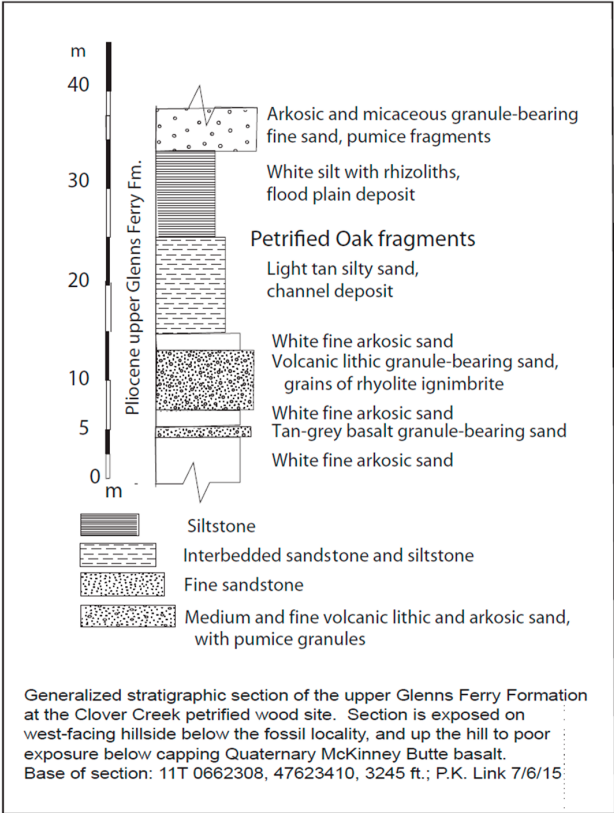


Figure 5. Generalized stratigraphic section of the upper Glenns Ferry Formation at the Clover Creek petrified wood site. Base of the section is in UTM coordinates.

Though exposure is poor, we estimate that about half of the strata are sand and half are siltstone. The sandstone represents fluvial channels, and the siltstone represents the adjacent flood plain. The most abundant fossil wood fragments are in a siltstone interval, suggesting the tree grew in the flood plain. Fragments of well-cemented coarse sandstone are also found with the wood fragments, suggesting that the sand acted as a permeable zone for silica-bearing fluids.

Detrital-zircons from central Idaho suggest that the Glenns Ferry Formation represents the paleo-Wood River, rather than the paleo-Snake River [24]. The Glenns Ferry Formation contains extraordinary vertebrate fossils at Hagerman Fossil Beds National Monument, 20 km to the southeast [25].

3. Materials and Methods

Specimens were cut to reveal transverse, tangential and radial planes of subsequently polished thin-sections. Optical Microscopy (OM) was performed using a Nikon SMZ1500 stereomicroscope (Tokio, Japan), a Nikon Eclipse ME600 petrographic microscope equipped with a Nikon DS-5M-L1 digital camera and a Zeiss Photomicroscope II equipped with a Spot Infinity digital camera. Specimens, thin sections and digital photomicrographs are archived at the Geology Department, Western Washington University, USA, at Museum für Naturkunde Chemnitz and Professur Werkstoff- und Oberflächentechnik, Technische Universität Chemnitz, Germany.

Bulk powdered samples were analyzed by means of an X-ray diffractometer (Bruker AXS D8, Berlin, Germany) using Ni-filtered Cu K α radiation.

Scanning Electron Microscopy (SEM) was done using a VEGA (Tescan, Brno, Czech Republic) for secondary electron (SE) images, a NEON40EsB (Zeiss, Jena, Germany) combined with an GEMINI (EDAX, Mahwah, Mahwah, NJ, USA) energy-dispersive X-ray detector for backscatter electron (BSE) images and elemental analysis and an Nova NanoSEM (FEI, Hillsboro, Hillsboro, OR, USA) equipped with a cathodoluminescence (CL) detector (GATAN monoCL, Pleasanton, CA, USA). CL spectroscopy and CL imaging (CL-OM) were done on carbon-coated, polished thin sections in the SEM operated at 20 kV and a “hot cathode” CL microscope HC1-LM (lumic, Dortmund, Germany) operated at a 14-kV accelerating voltage and a current of 0.2 mA (current density of about 10 $\mu\text{A}/\text{mm}^2$). Luminescence images were captured “on-line” during CL operations using a Peltier cooled digital video camera (OLYMPUS DP72, Tokio, Japan). CL spectra in the wavelength range 380 nm to 1000 nm were recorded with an Acton Research SP-2356 digital triple-grating spectrograph with a Princeton Spec-10 CCD detector that was attached to the CL microscope by a silica-glass fiber guide. CL spectra were measured under standardized conditions (wavelength calibration by an Hg halogen lamp, spot width 30 μm , measuring time 2 s). Raman spectroscopic measurements were performed with a 785-nm laser for excitation in a confocal Raman microscope (Renishaw inVia Reflex, Wotton-under-Edge, Gloucestershire, UK).

4. Results

4.1. Microscopy

Analytical methods for studying silicification have greatly advanced since the work of Schuster [7]. However, his keen powers of observation are evident in the description of the anatomical characteristics with which he established the new species. Petrographic thin sections made from a sample collected in 2014 compare closely to photomicrographs of Schuster’s original thin sections (Figures 6 and 7), confirming that the recently-collected material matches the original 1895 discovery.

Schuster [7] focused his work on taxonomy, based on the well-preserved cellular detail. However, he also provided a description of petrographic features, observing that polished wood cross-sections were light yellow, with brownish discoloration along the outer margins. Schuster believed that brownish zones are probably caused by the presence of hydrated ferric oxide. In radial sections, the opal was reported to have a blue color.

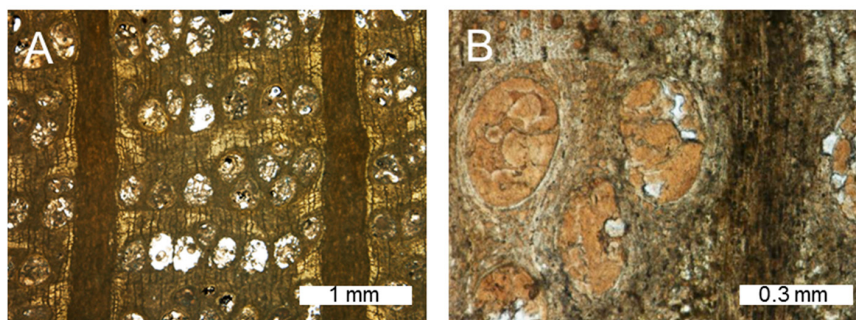


Figure 6. Petrographic thin sections of the 2014 specimen, transverse plane. (A,B) show anatomical detail matching Schuster's Table III, Figures 1 and 2 respectively [7].

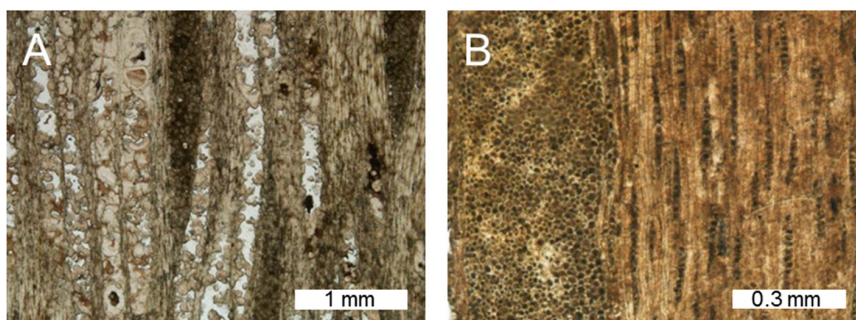


Figure 7. Petrographic thin sections of the 2014 specimen, tangential longitudinal plane. (A,B) show anatomical detail matching Schuster's Table IV, Figures 1 and 2 respectively [7].

Schuster's comments on mineralogy are brief, but he made an important observation: the silicification primarily consists of common opal, isotropic under polarized light, but most of the vessels are filled with chalcedony. Schuster [7] believed that the "more or less spherulitic chalcedony" originated from devitrification of the original opal. As discussed later, a more likely explanation is that the chalcedony filling the vessels represents a second stage of silica deposition, not a transformation of opal to chalcedony. The coexistence of opal and chalcedony is evident in thin sections prepared from the 2014 material (Figure 8).

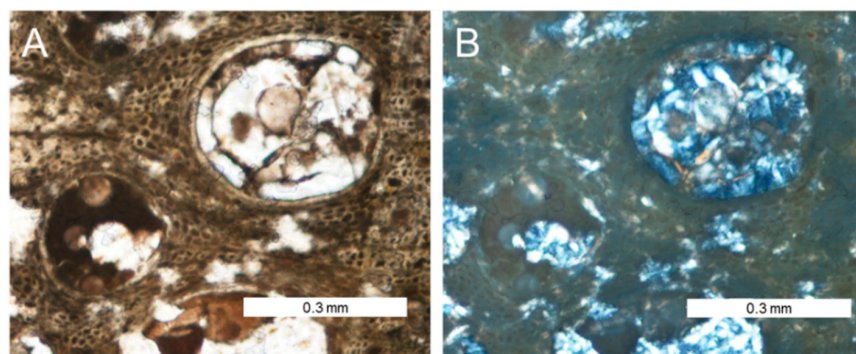


Figure 8. Petrographic thin sections of the transverse plane. (A) Vessels surrounded by cellular tissue in plain light illumination and (B) in cross-polarized light illumination.

Most of the cellular tissue is mineralized with opal-CT. Opalization of tracheids commonly includes mineralization of spaces between adjacent cells, accounting for the vitreous luster of hand specimens. The transparency of the silicified tissue makes transmitted light microscopy an effective

method for revealing the detailed anatomical preservation. Cellular tissue has been mineralized with opal-CT, but vessels remained open during this phase of silicification. Later, chalcedony was precipitated by silica-bearing fluids permeating these vessels. Frequently, vessels were not completely filled with silica. Chalcedony surfaces that face these openings typically have a botryoidal texture. Polarized light microscopy allows for a clear distinction between opal-CT, chalcedony and open spaces. Opal-CT appears dark in cross-polarized light illumination; open spaces appear bright; and chalcedony exhibits birefringence (Figure 8B).

Opalized regions typically appear rather featureless in SEM views because the mineralization of intercellular spaces obscures cellular topography. In regions where intracellular spaces are not completely mineralized, the morphology of individual adjacent cells is visible. In areas of incomplete silicification, the morphologies of individual tracheids and mineral textures are evident (Figure 9). Tracheids are mineralized with tabular microcrystals that are a common form of opal-CT (Figure 9B,C). Mineralization of vessels is very different from that of the surrounding wood. Vessels remain partially unmineralized. Silica in the vessels is commonly present in the form of chalcedony (Figure 10). SE SEM images clearly show the cellular tissue mineralized with opal-CT to form a vitreous groundmass, in contrast to adjacent vessels that have been partially filled with chalcedony. In both transverse and radial views (Figure 10B,C), the semi-hemispherical shape of individual chalcedony masses facing the hollow interior of vessels can be observed.

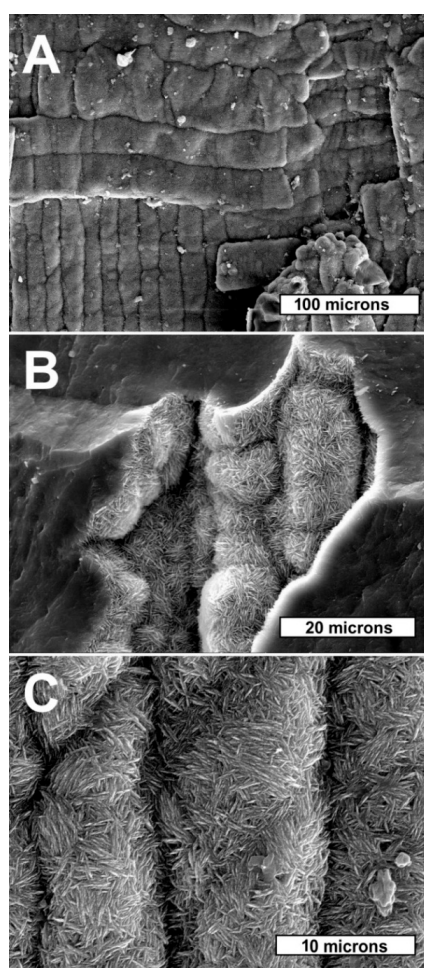


Figure 9. SEM SE images showing the external morphologies of petrified cells. (A) Radial view of tracheids and ray cells; (B) silicification of intracellular spaces results in relatively smooth vitreous fracture surfaces, with areas of incomplete silicification revealing the morphologies of individual tracheids; (C) individual cell walls mineralized with tabular opal-CT microcrystals.

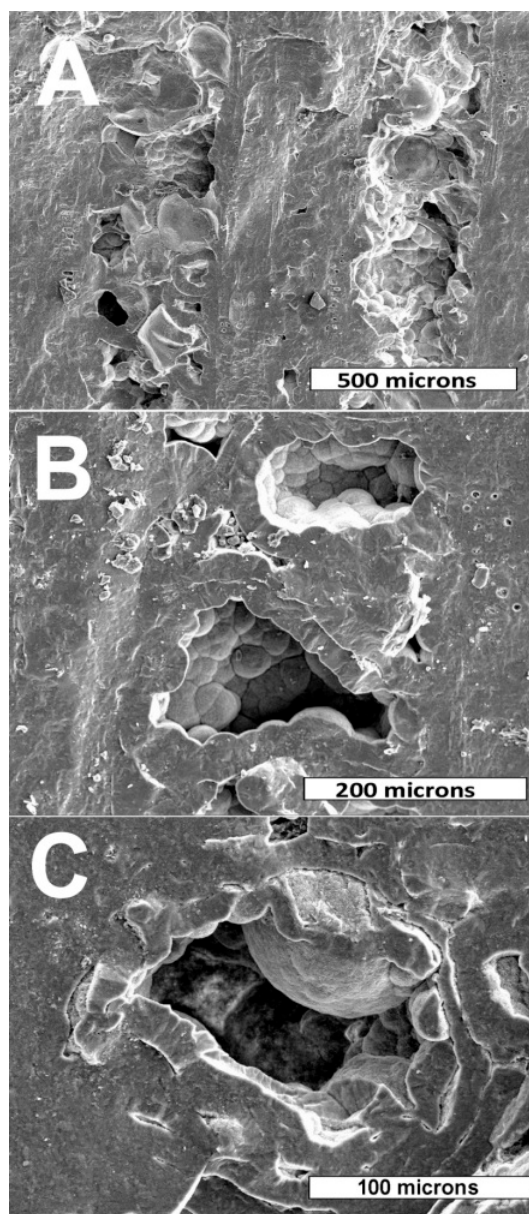


Figure 10. SEM SE images showing vessels partially filled with chalcedony. (A) Tangential view of two vessels surrounded by vitreous opal; (B) tangential view, fibrous chalcedony forming walls in the vessel and semi-spherical masses (botryoidal texture); (C) transverse view of a chalcedony-mineralized vessel.

The coloration of the fossil wood may be at least in part the result of trace amounts of iron. In some regions, silicified cells contain iron-rich microcrystals (Figure 11, Table 1). Atomic percentages calculated from EDS spectra indicate the presence of several iron minerals. Crystal shapes most commonly appear to be variations of the trigonal system, suggesting hematite as a possible parent mineral. Other symmetries are present, however, including orthorhombic forms that could have originated as marcasite. The presence of diverse iron minerals is perhaps the result of alteration related to multiple episodes of mineralization. The internal architecture of these crystals suggests complex paragenesis.

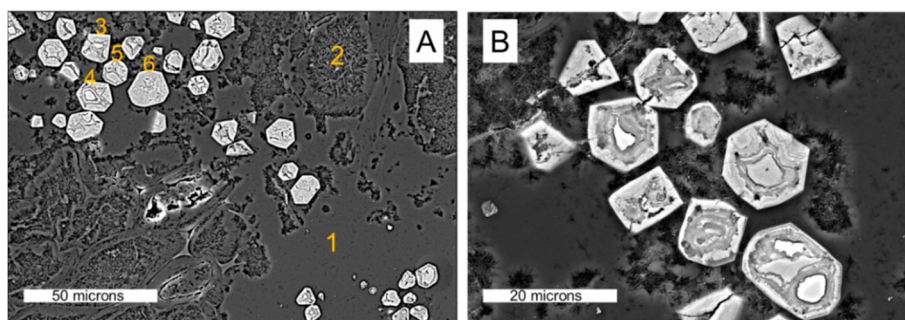


Figure 11. Elemental analyses of opalized wood. (A) Positions of the analyses (1–6) shown in Table 1; (B) detailed SEM BSE image of iron-rich microcrystals.

Table 1. Elemental analysis by EDS of Clover Creek opalized wood, the part with iron-rich microcrystals.

Location	Element Percent				Inferred Mineralogy
	Si	O	Fe	S	
1	32	68	-	-	opal
2	30	70	-	-	opal, chalcedony?
3	1	23	29	47	marcasite?
4	1	17	50	32	marcasite?
5	3	65	32	-	hematite?
6	4	54	32	1	hematite?

4.2. Diffraction and Spectroscopy

X-ray diffraction, Raman spectroscopy and cathodoluminescence microscopy were used to better understand the mineralogy. The X-ray diffraction pattern from a bulk powdered sample (Figure 12) shows the presence of two forms of silica, consistent with the evidence from optical and scanning electron microscopy. Opal-CT peaks are very evident. Modeling this mineral phase as interstratified layers of cristobalite and tridymite [26] results in a cristobalite/tridymite ratio around 0.54 and crystallite sizes around 25 nm. Quartz peaks apparently indicate chalcedony present as vessel filling; no other forms of quartz were observed by microscopy. The size of those crystals is between 60 and 80 nm, which is consistent with the expectation of fibrous chalcedony.

Raman spectroscopy provides molecular information by inelastic scattering of photons and complements the crystallographic information achieved by elastic scattering of X-rays. Structure-building units, which are composed of a few silicon-oxygen tetrahedra, can be identified by means of vibrational, rotational and other low-frequency modes in the silica system. Different parts of the Clover Creek sample selected by OM indicate different silica polymorphs (Figure 13). Spectra gained from tracheids and medullary rays of the Clover Creek sample (Figure 13, Spectra c to h) exhibit peaks at 220 cm^{-1} , 310 cm^{-1} , 365 cm^{-1} and 415 cm^{-1} with varying intensities. These peaks are attributed to Si–O–Si bending vibrations, suggesting that the structure is close to an opal-CT type consisting of a matrix of intergrown tridymite- and cristobalite-type nano-domains according to [27]. Additionally, a higher portion of tridymite-like structural units can be inferred, which is in accordance with our XRD measurements.

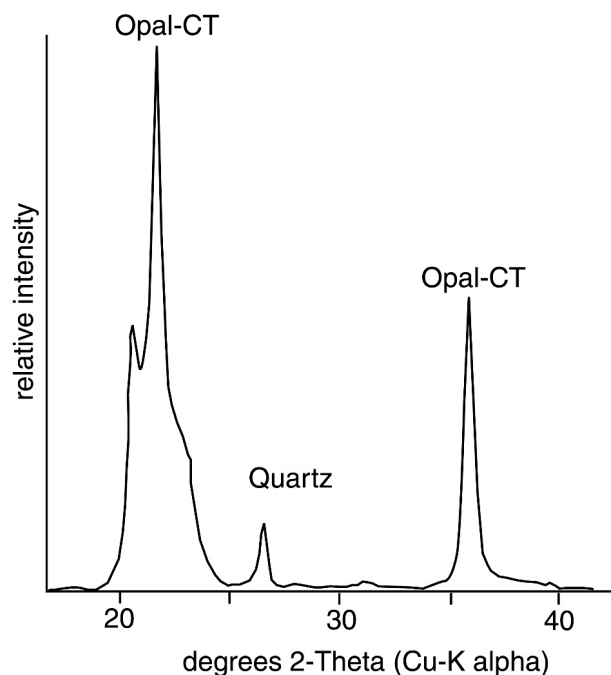


Figure 12. X-ray diffraction pattern for bulk powdered Clover Creek fossil wood.

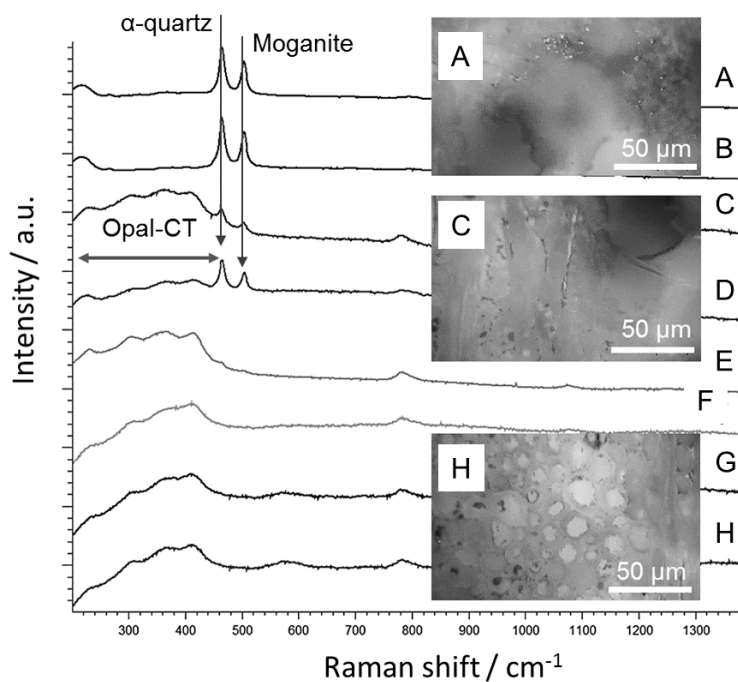


Figure 13. Raman spectra observed at different parts of the xylem. (A,B) Early wood vessels; (C–E) medullary rays; and (F–H) tracheids. Photomicrographs are OM images of a polished specimen.

Raman shifts at 464 cm^{-1} and 502 cm^{-1} are evident at early wood vessels (Figure 13, Spectra A,B). The peak at 464 cm^{-1} is attributed to α -quartz and the peak at 502 cm^{-1} to moganite. First described in 1984, but not formally recognized as a valid mineral species until 2007, moganite is a monoclinic SiO_2 polymorph that commonly occurs as a constituent in chalcedony and other varieties of microcrystalline quartz [28]. The moganite content of chalcedony has been reported to range from 26% to 82%, [29], but because moganite identification is usually based on Raman spectroscopy, the possible presence of

this mineral in silicified wood has historically been overlooked. Götze *et al.* [30] provided a calibration curve for determining the moganite content in nano-crystalline α -quartz (chalcedony). Accordingly, the measured peaks were fitted by Lorentzian distributions for calculating the peak integral ratio. The result (0.5 to 0.7) indicates moganite content between 70 and 78%. Moganite occurs in chalcedony as nano-range lamellae down to single Brazil law twin planes detectable by Raman spectroscopy, but too small for the long-range order-dependent XRD. The spatially-resolved distribution of moganite in a chalcedony-preserved early wood vessel is shown by an intensity map of the moganite-related Raman peak (Figure 14).

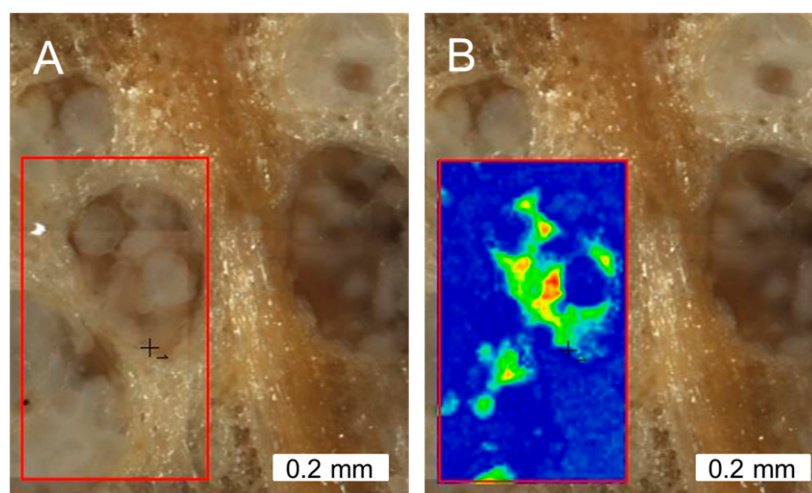


Figure 14. Moganite in a chalcedony-preserved early wood vessel. (A) OM image with field of view; (B) OM image with overlay of the Raman map generated from the 502-cm^{-1} peak intensity showing high (red) and low (blue) moganite content.

CL spectroscopy in combination with microscopy provides information about the distribution of impurities and structural defects. This information can indicate mineralization sequences or hydrothermal mineralization and alteration of silica polymorphs. Four CL peaks were detected, with intensities that varied with respect to sample position and the CL analytical method. CL peaks at $\sim 380\text{ nm}$, 450 nm and 650 nm were detected by electron beam excitation with the SEM. Peaks at $\sim 550\text{ nm}$ and 650 nm were detected using the optical microscope hot cathode CL system [30,31]. In the latter system, UV radiation cannot be detected because of the absorption effects of the glass optics.

A silicified early wood vessel in the transverse section is shown by SEM BSE imaging, panchromatic SEM-CL imaging and corresponding CL spectra (Figure 15). The peaks at 450 nm , attributed to an oxygen-deficiency center [32], and 650 nm , attributed to a non-bridging oxygen hole center [30], are common in quartz and opal from igneous, volcanic and metamorphic processes. The chalcedony, which filled the early wood vessel, is the source of an additional peak at $\sim 380\text{ nm}$, which is typical for cryptocrystalline quartz with a hydrothermal origin [33].

The observation of CL peaks was accomplished using an optical CL microscope with a defocused electron beam. OM-CL images (Figure 16) show early wood vessels in the tangential longitudinal section by polarized light microscopy and OM-CL. The polarized light micrograph confirms that the silicified wood consists of a relative dense opal and larger vessels partially lined with chalcedony. The OM-CL images reveal bluish luminescence in the opal matrix and blue-violet luminescence in the vessels. OM-CL spectra are similar for Opal-CT and Chalcedony. The OM-CL spectrum shows only a slight shoulder of the UV band because of the system's detection limits. Cathodoluminescence changed in intensity with increasing radiation dose, this change being more evident in opal as compared to chalcedony (Figure 17). The bluish CL of opal turns to slight yellowish due to the activation of more defects. The CL spectrum of chalcedony is characterized by an increase of the 650 nm band and a

decrease of the UV band around 380 nm (not visible in the OM-CL spectra). This is typical behavior for quartz crystallized from low temperature aqueous solutions (e.g., hydrothermal fluids) [33] and indicates a multi-stage process of silicification for the Clover Creek samples.

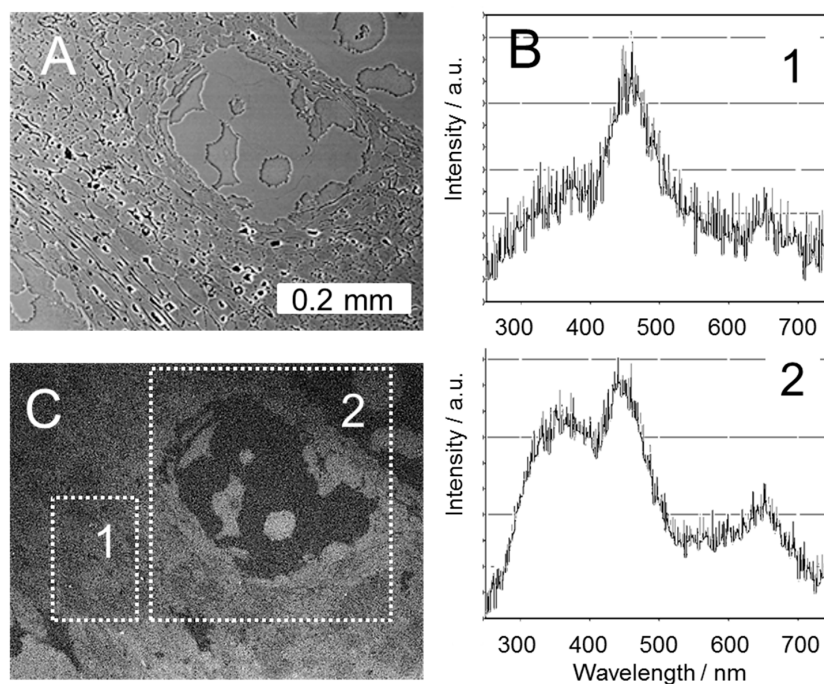


Figure 15. SEM-CL emerging from opalized tissue surrounding an early wood vessel (transverse plane). (A) SEM BSE image; (B) CL spectra for regions 1 and 2 marked in (C) panchromatic SEM-CL image.

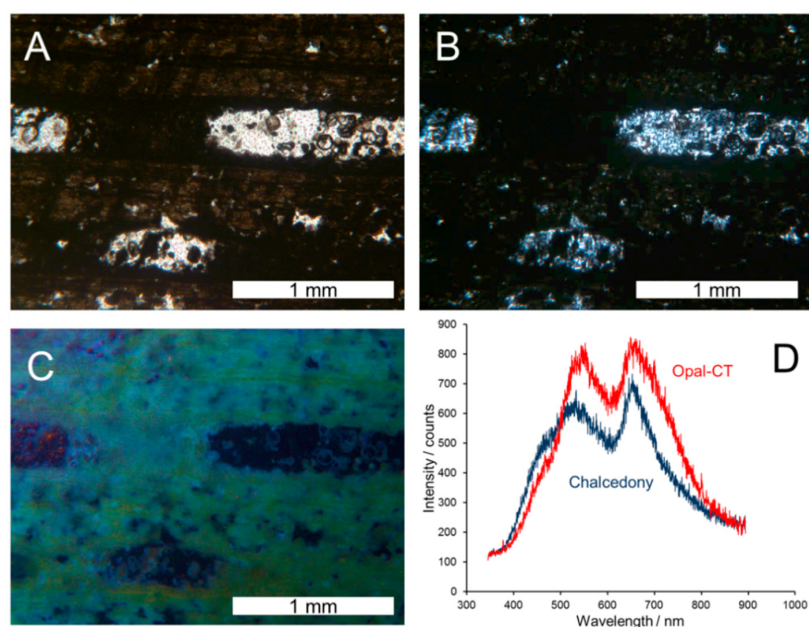


Figure 16. Photomicrographs of chalcedony-mineralized early wood vessels surrounded by opalized tissue (tangential plane). (A) Transmitted light OM image; (B) Cross-polarized light OM image; (C) panchromatic OM-CL image; (D) CL spectra taken from opal/chalcedony rich regions.

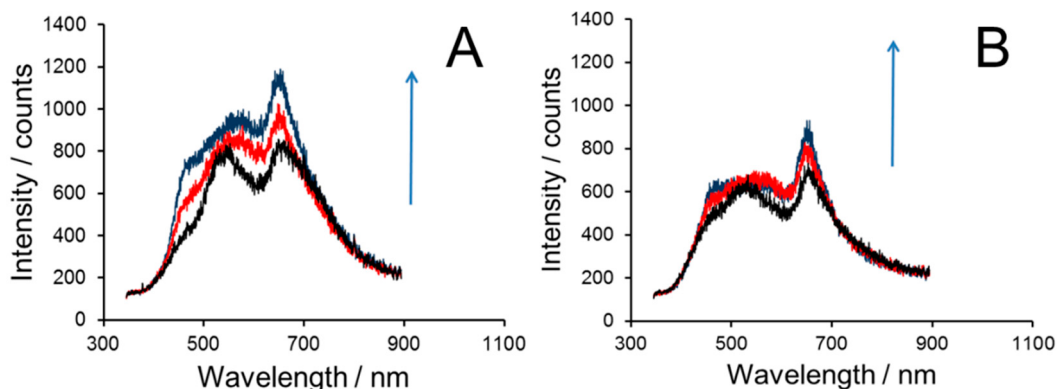


Figure 17. CL spectra taken at the initial state (black), after 60 s (red) and 180 s (blue). (A) Opaline matrix; (B) vessel region with chalcedony.

5. Discussion

5.1. Taxonomy

The proposed taxonomy for fossil oak wood has not received universal agreement. The first description of fossil oak was by Göppert [34] who introduced *Klödenia quercoides* as a name for wood from northern Germany and Silesia. This taxonomy became confused because *Klödenia* was later accepted as a name for an ostracod genus [35]. Unger [10] proposed *Quercinium* as the genus to be used for fossil oak wood exhibiting the cellular anatomy characteristic of the modern oak family (*Fagaceae*). This taxonomy received scant attention until Felix [36,37] published descriptions of known species and added four new ones.

As noted, Schuster [7] named the Clover Creek wood *Q. pliocaenicum*, and Boeshore and Jump [38] described *Q. album* from the Miocene Payette Formation of southwestern Idaho. Boeshore and Jump [38] include a table in their paper that listed all *Quercinium* species recognized in the literature at the time (1938); interestingly, Schuster's *Q. pliocaenicum* was not included. Other investigators have used other taxonomic strategies. Penhallow [39] described Holocene oak wood from Illinois as *Quercus*, a practice that has enjoyed continued use, e.g., [40]. Hofman [11] suggested *Quercoxylon* as a form genus name for fossil oak wood, but did not name a type species. Kräusel [12] designated *Q. retzianum* as a type species for this new genus.

It is not our intent to resolve these taxonomic complexities. We have retained the original *Quercinium pliocaenicum* nomenclature because of historical precedence and because this fossil genus has been applied to most other North American occurrences of fossil oak wood (e.g., [15,41,42]). For a more detailed discussion of these taxonomic issues, see Iamandei *et al.* [14].

5.2. Paleoclimate and Paleoenvironment

At the time of the 1895 discovery and the subsequent published study [7], knowledge of the regional geology was rather scanty. Prior to the advent of radiometric dating, fossils offered a way to estimate ages of sedimentary strata and, by inference, the ages of associated igneous rocks. In recent decades, the geology of the Snake River Plain has received considerable attention, and our knowledge of the ages of rock units has been greatly refined thanks to precise radiometric ages determined for the many volcanic interbeds [21,43–45]. Snake River Plain sediments range from late Miocene to early Pleistocene. *Quercus* leaves are preserved in the late Miocene to early Pliocene Poison Creek and Chalk Hills Formations; Cherry Creek fossil oak wood is probably from the late Pliocene Glens Ferry Formation.

While Schuster did not offer any thoughts on the paleoclimate associated with *Q. pliocaenicum*, he did use the presence of narrow growth rings to infer that the tree was deciduous and growing in poor conditions. Today, the Snake River Plain sediments provide one of the best-documented records

of Neogene paleoclimate in the western USA. Paleoclimatic inferences have been derived from fossil mammals [46], fish [47,48] and pollen [49,50], as well as isotopic investigations [51]. The paleoflora document the presence of diverse deciduous trees in the central Idaho region during the late Miocene. The Pliocene Glens Ferry flora records a significant climate change, with the appearance of *Artemisia* (sagebrush), *Sarcobatus* (saltbush) and abundant Poaceae (grasses). Pollen from aquatic plants indicates the presence of ponds and lakes. Tree pollen includes *Pinus* (pine) as the most common conifer, but diverse hardwood pollen includes *Quercus*. Mustoe and Leopold [50] believed that this floral evolution is the result of the late Miocene or early Pliocene rise of the Cascade Range, resulting in a rain shadow. Glens Ferry sediments appear to have been deposited in a region of gentle topography, with grasslands, areas of temperate forest and scattered wetlands. The overlying early Pliocene Bruneau Formation shows a marked increase in the abundance of *Artemisia* and *Sarcobatus* and a decline in Poaceae and aquatics, indicating increasing aridity. Mustoe and Leopold [50] used Jaccard similarity coefficients to estimate paleoclimatic conditions for Neogene paleoflora of Washington, Oregon and Idaho. These data suggest that the floral composition of the Glens Ferry Formation flora resembled modern vegetation from Lewiston, Idaho, ~600 km to the northwest. The Glens Ferry paleoflora is estimated to have had a mean annual temperature (MAT) of ~12 °C and annual precipitation of 300 to 325 mm. This compares to the modern climate at nearby Hagerman, Idaho, with MAT of 10 °C and annual precipitation of ~250 mm. Pollen studies for Glens Ferry Formation and Idaho Group strata between 12 and 4 Ma suggest a savannah-like setting, with an annual precipitation of up to ~500 mm [22,49,52].

The ancient oak tree whose remains were preserved at Clover Creek presumably flourished at a time when the climate was somewhat warmer and wetter than at present. One of the most significant climatic differences is seasonality; estimated July precipitation was ~17 mm during Glens Ferry time, compared to ~5 mm in the modern era. This increased seasonality was an important factor in the appearance of sagebrush steppe flora and explains the decline in habitat for oaks and other broadleaf hardwoods in the central Idaho region.

5.3. Silicification Pathway

One of the most significant aspects of the Clover Creek fossil wood is the evidence it provides for the silicification processes. Schuster [7] observed that the wood cells were mineralized with common opal, but that vessels contain chalcedony. Schuster believed that the “more or less spherulitic chalcedony” originated from devitrification of the original opal. During that era, processes of wood silicification were poorly understood, and although Schuster did comment on transformation processes, he did not propose possible mineralization processes.

Pathways for the formation of petrified wood have been discussed as early as 1665 when Robert Hooke used his newly-invented microscope to inspect the cellular structure of petrified wood for the first time [53]. In 1976, Leo and Barghoorn [54] established a key concept for wood silicification that includes two basic assumptions. First, wood acts as a template for silica, even as it slowly degrades and is replaced. Second, silica sol is the silicifying agent that forms hydrogen bonds with hydroxyl groups exposed on cell walls. This concept has been incorporated into every silicification model that has since been proposed. Dietrich *et al.* provide a review of studies on artificial and natural silicification [55]. More recently, Mustoe [56] studied the evidence of multiple silicification pathways of Neogene fossil woods. Mustoe’s model includes early mineralization of cell walls followed by a later silica deposition in lumina, vessels and rot pockets from groundwater that permeated open spaces. He also described the process of open-space filling as analogous to the genesis of geodes and veins, where multiple episodes of hydrothermal precipitation produce opal, chalcedony and quartz as deposits within a single cavity.

Clover Creek fossil wood is a good example of polyphasic and polyminerale petrification. Although most of the cellular tissue has been mineralized with opal, the extent of mineralization is not homogeneous. In many regions of the specimens, cell walls, lumen and intracellular spaces are

completely mineralized to produce a solid mass of opal. X-ray diffraction and Raman spectroscopic data reveal this material to consist of opal-CT. SEM images show the platy crystalline structure of this opal, but there is no visible evidence of opal lepispheres, the common architecture of opal-A. Instead, opal-CT appears to have formed as a primary mineral. During this initial phase of silica deposition, vessels remained open.

At a later stage of mineralization, many of the vessels became partially filled with chalcedony. The geode-like architecture suggests that the chalcedony was precipitated from hydrothermal fluids during a later episode, unrelated to the initial silicification phases that mineralized both tracheids and ray parenchyma with opal-CT. The observation that vessels are only partially filled with chalcedony is evidence that a silica-bearing hydrothermal fluid was able to permeate the wood even after the tracheids enclosing the vessels were thoroughly opalized. This characteristic suggests that the conductive components of the xylem (tracheids, vessels and fibers) were an important conduit for the entry of silica sol during early stages of petrification. This interpretation is consistent with the experimental evidence [54] that suggests that the earliest phase of silica deposition involves precipitation on cell wall surfaces because of the affinity between cellulose and hemicellulose with silicic acid (silica sol). Because some intracellular spaces and some vessels remain open, Clover Creek fossil wood remains potentially susceptible to additional future episodes of mineralization. The initial mineralization of cell walls followed by a later episode of silica deposition in vessels from hydrothermal fluids that permeated these open spaces is consistent with similar observations [56]. The coloration of the fossil is in part the result of hydrated iron oxide. Some silicified cells additionally contain trigonal and orthorhombic pseudomorphs. The internal architecture of these crystals suggests complex paragenesis and may provide additional evidence in support of multiple episodes of mineralization.

6. Conclusions

Clover Creek opalized wood is displayed as a mineral variant instead of a fossil in major museums in the U.S., Canada and Europe, even though the mineral dealer Foote [2] described the specimen as “the most perfect and beautiful petrification in existence”. Interestingly, only a single scientific work in German describing the anatomy and providing the scientific name of *Quercinium pliocaenicum* for this historic find existed up until this publication. Schuster’s paper [7] has recently been translated to English (see the Supplementary Material). Historical research uncovering the provenance of museum specimens, rediscovery of Schuster’s original thin section slides, along with rediscovery of the original site and the collection of new specimens allowed for a thorough scientific investigation of the geologic setting and wood mineralization. Clover Creek museum specimens can now be understood in the context of modern analyses of the geologic setting and mineralization.

The mineralization of Clover Creek opalized wood adds to a growing body of evidence suggesting a multistage pathway for wood silicification. X-ray diffraction indicates that the wood is mineralized with opal-CT and chalcedony. OM and SEM reveal that most of the cellular tissue is mineralized with tabular opal-CT microcrystals with no evidence of opal lepisphere precursors, whereas inner vessel walls are lined with botryoidal chalcedony. Raman spectroscopy provides evidence for the intergrowth of chalcedony and moganite. The observation that opal-CT has replaced most of the tissue, with vessels partially filled by chalcedony, each silica polymorph originating as a primary mineral, was substantiated by CL. This is interpreted as evidence for a multiple stage mineralization process. EDS spectra reveal the presence of authigenic iron-rich microcrystals having both trigonal and orthorhombic shapes. The low abundance of these crystals suggest they are not a major cause of the wood’s lustrous brown coloration, which is more likely caused by submicroscopic particles. However, the internal architecture of these crystals suggests complex paragenesis, perhaps representing further evidence for multiple episodes of mineralization.

The current study verifies that the fossil tree was recovered from the upper Glens Ferry Formation along Clover Creek in Idaho. The geologic setting in which the tree was deposited and fossilized reveals that it grew in a flood plain along a fluvial channel. The tree grew at a time when the climate

was warmer and wetter; however, the influence of the Cascade rain shadow slowly produced a dryer climate that over time would be less conducive to growing oaks, such as *Q. pliocaenicum*.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2076-3263/6/2/21/s1>: pdf file 1: Translation Schuster *Q. pliocaenicum*, pdf file 2: Supplement XRD", pdf file 3: Clover Creek Museum specimens.

Acknowledgments: The authors would like to thank the following people for answering requests and providing photographs: Katherine Dunnell, Royal Ontario Museum, Canada; Peta Hayes and Mike Rumsey Natural History Museum London, U.K.; Bruce Geller, Beth Simmons, and Sam Allen, Colorado School of Mines Geology Museum, USA.; Klaus Thalheim, Senckenberg Naturhistorische Sammlungen Dresden/Museum für Mineralogie und Geologie, Germany; Achim Reisdorf, Geologisch-Paläontologisches Institut der Universität Basel and Thomas Burri, Naturhistorisches Museum der Burgergemeinde Bern, Switzerland; Zina Fihl, Statens Naturhistoriske Museum Kobenhavn, Denmark; Ursula Müller-Krantz, Dr. F. Krantz Rheinisches Mineralien-Kontor GmbH and Co. KG, Germany. We thank William W. Besse, Associate Cartographer for *Rocks and Minerals* magazine, Philadelphia, USA, for use of his Clover Creek map.

Thomas Mehner, Professur Werkstoff- und Oberflächentechnik, TU Chemnitz, performed the XRD analyses. Daniel Wett, Professur Verbundwerkstoffe, TU Chemnitz, and Massimiliano Rocchia, Thermo Fisher Scientific, Milano, Italy, provided Raman data. Steffen Schulze, Professur Analytik an Festkörperoberflächen, TU Chemnitz, achieved the SEM-CL data. We are much obliged to Alex Brandl, Colorado State University Colorado, USA, for his assistance in translating the paper of Schuster into English (see the Supplementary Material).

Author Contributions: Mike Viney revived the history of the samples. Mike Viney and Paul Link rediscovered the fossil site and investigated the stratigraphy. George Mustoe performed Optical Microscopy (OM) and Scanning Electron Microscopy (SEM) studies. Ronny Rößler provided OM on ancient and newly-prepared thin sections. Jens Götze performed CL measurements. Dagmar Dietrich performed energy dispersive spectroscopy (EDS) analysis. Thomas Lampke contributed analytical tools and supervised Dagmar Dietrich, who was responsible for collecting, analyzing and interpreting the analytic results. Mike Viney, George Mustoe, Paul Link and Dagmar Dietrich wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

The following abbreviations are used in this manuscript:

XRD	X-Ray Diffraction
SEM	Scanning Electron Microscopy
EDS	Energy Dispersive Spectroscopy
T	Transverse
TL	Tangential Longitudinal
RL	Radial Longitudinal
OM	Optical Microscopy
SE	Secondary Electron
BSE	backscattered electron
CL	cathodoluminescence

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