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Mineralogy and geochemistry of late Eocene silicified wood from Florissant Fossil Beds National Monument, Colorado

George E. Mustoe*
Geology Department, Western Washington University, Bellingham, Washington 98225, USA

ABSTRACT

Silicified stumps preserved within a late Eocene lahar deposit have diverse mineralogy, ranging from opal-CT to chalcedony. In specimens that contain both silica polymorphs, the minerals appear to have originated independently, rather than from diagenetic transformation of an opaline parent material. This petrifaction process is unlike the progressive transformation of opal-A→opal-CT→chalcedony that has long been accepted as a general model for wood silicification. At the Florissant fossil forest, petrifaction occurred in several stages, beginning with precipitation of amorphous silica on cell wall surfaces. Cell lumina later became filled with opal-CT and chalcedony. A final phase of silica deposition is evidenced by chalcedony-filled fractures that crosscut permineralized tissues in some specimens. Spaces between adjacent tracheids commonly remain unmineralized, causing the silicified wood to remain permeable to water, and to readily cleave radially and tangentially. To a lesser degree, the fossilized wood is subject to transverse fracturing. This combination of structural characteristics causes Florissant fossil stumps to be susceptible to damage from freeze-thaw weathering.

Keywords: chalcedony, opal-A, opal-CT, petrified wood, silicification.

INTRODUCTION

The late Eocene Florissant Formation provides a notable example of an ancient depositional environment that preserved an assemblage of fossilized stumps and logs. Located within a single 5-m-thick volcaniclastic debris flow, these silicified trunks range in diameter from 0.5 to 4 m, with heights of 1–4 m. Although petrified forests are known throughout the world (Dernbach, 1996; Daniels and Dayvault, 2006), decades of careful paleontologic research combined with the well-defined stratigraphic and geologic characteristics of the deposit make the Florissant fossil forest an invaluable site for studying the petrifaction processes. The 70-m-thick Florissant Formation is composed of tuffaceous lacustrine, fluvial, and lahar sediments that were deposited in a paleovalley on the high-elevation, low- to moderate-relief erosion surface of central Colorado, during the late Eocene (Gregory and Chase, 1994; Evanoff et al., 2001). A detailed stratigraphic column was published by Evanoff et al. (2001) and reproduced with minor alterations by Gregory-Wodzicki (2001) and Meyer (2003). Single crystal laser-fusion ^{40}Ar/^{39}Ar analyses of sanidine crystals from pumice near the top of the formation yielded a mean age of 34.07 ± 0.10 Ma (Evanoff et al., 2001).

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*mustoeg@cc.wwu.edu

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Compressed remains of plants, insects, and fish in thinly bedded lacustrine shales of the Florissant Formation have received considerable attention from researchers (see bibliography in Meyer, 2003). Although the fossil forest began attracting tourists in the 1860s, many decades passed before the silicified stumps were studied by paleontologists. Andrews (1936) described *Sequoia*-like wood that he named *Sequoioxylon pearsalii*, now known to be the most common taxon in the fossil forest. Evanoff (cited in Gregory-Wodzicki, 2001) mapped 31 fossil stumps, of which 91% were vertical, leading him to conclude that the fossils represent a single forest that was buried in situ. Gregory-Wodzicki (2001) speculated that the trees died because the mudflow prevented oxygen from reaching their roots. Portions of the trunks exposed above the level of the mudflow were susceptible to rapid decay. Wheeler (2001) described five dicot wood types, and Gregory-Wodzicki (2001) investigated ring width and variability in 28 *Sequoioxylon* stumps to cross-date the trees and to evaluate paleoclimatic conditions.

My investigations focused on the mineralogic and geochemical characteristics of an assemblage of specimens chosen by National Park Service personnel as being representative of various types of fossil wood preserved at Florissant Fossil Beds National Monument. These samples include material from some of the best-known specimens exposed near the visitor center. Analytical data obtained from these fossils are important for several reasons. Determining the mineralogy, chemical composition, and microscopic characteristics of Florissant fossil wood is an important step for increasing our understanding of how wood becomes petrified. In particular, the discovery that some of the silicified wood specimens contain both opal-CT and chalcedony provides new insights into the petrifaction process, hinting that silicification may proceed along more than one geochemical pathway. In addition, understanding the mineralogic composition and physical properties of silicified wood is essential for developing effective strategies for protecting the fossil stumps from weathering, a major conservation challenge facing the personnel responsible for conserving this magnificent fossil forest.

WOOD SILICIFICATION: AN OVERVIEW

Petrified wood is abundant in the fossil record, and a multitude of researchers have described taxonomic and paleoenvironmental aspects of fossil forests. In contrast, the subject of how wood becomes petrified has received much less attention. Indeed, the most comprehensive studies date back more than two decades (e.g., Murata, 1940; Buurman, 1972; Mitchell and Tufts, 1973; Leo and Barghoorn, 1976; Stein, 1982; Scurfield and Segnit, 1984). Although new data continue to be added, the basic hypotheses regarding the petrifaction process have largely remained unchanged. As discussed later in this report, new evidence from Florissant fossils challenges some of these long-held ideas.

Two mechanisms have been proposed to explain how wood becomes petrified. *Replacement* describes precipitation of minerals in spaces formerly occupied by organic matter (Correns, 1950). *Permineralization* results when cell material remains at least partially intact and open spaces become filled with minerals. In support of the latter hypothesis, Schopf (1971) noted that the success of the acetate peel method is clear evidence that intact cellular tissues are sometimes preserved. However, St. John (1927) noted that when 25 petrified wood specimens from a variety of localities were treated with hydrofluoric acid, some samples contained no visible traces of plant tissue, whereas other specimens preserved detailed cell structures—evidence that wood petrifaction may result from replacement, permineralization, or a combination of the two processes.

The most-studied aspect of wood petrifaction has been the initial infiltration of dissolved silica into plant cells. Schopf (1971) suggested that silica is precipitated from groundwater as a replacement for water molecules in the cell walls, a process that entombs organic matter. The most widely accepted hypotheses is that of Leo and Barghoorn (1976), who postulated that silicification occurs because the original organic materials have an affinity for dissolved silicic acid molecules, causing petrifaction to begin with the accumulation of amorphous silica as a film on cell walls. Porous silica preserves the cell morphology, while allowing organic matter to degrade slowly. This organic templating process has been confirmed in subsequent studies (e.g., Karowe and Jefferson, 1987; Wang et al., 2001). In a general sense, the process can be thought of as "replacement," because as minerals are precipitated, organic components are simultaneously lost through microbial or chemical attack. However, on a cellular level the templating process does not involve a molecule-by-molecule replacement of organic polymers by silica. The end result is petrified wood that may preserve much microscopic detail, but which typically contains only a small fraction of the original organic matter.

Organic templating may begin the process, but complete petrifaction requires a series of events. Scurfield (1979) and Scurfield and Segnit (1984) described a five-step sequence: (1) silica-bearing groundwater penetrates via splits and checks; (2) silica-laden water enters individual cells via reticulated micropores, which gradually enlarge as organic components of the cell wall break down, increasing permeability; (3) petrifaction results only if the deposition of silica occurs at a rate that exceeds decay, preserving the dimensional stability of the wood; (4) deposition of silica in cell lumina and intercellular voids may occur as a separate episode of late-stage mineralization; (5) lithification is accompanied by loss of water from hydrous silica. Transformation of one form of silica to another may occur.

Scurfield and Segnit (1984) recognized four forms of silica that may be present in petrified wood: (1) highly disordered, nearly amorphous hydrous SiO_2 (opal-A); (2) a disordered interlayering of tridymite and cristobalite (opal-CT); (3) chalcedony (microcrystalline quartz); and (4) quartz, characterized by individual crystals large enough to be easily visible under a light microscope.

Mineralogic transformation of silica during wood petrifaction has become a widely accepted hypothesis, even though the supporting evidence is largely indirect. Petrified wood composed of opal-A is rare (perhaps because it rapidly transforms to opal-CT), and X-ray diffraction patterns typically show that opalized woods contain opal-CT as the major constituent (Mitchell and Tufts, 1973). The alleged transformation of opal-CT to chalcedony has been based in part on the abundance of opalized wood in Cenozoic deposits, in contrast to the predominance of wood mineralized with chalcedony and microgranular quartz in Mesozoic deposits (Felix, 1897; Stein, 1982).

Indirect evidence of mineral transformation comes from siliceous sediments and hot spring sinters. The diagenetic change of opal-A→opal-CT→chert in siliceous biogenic deposits is well documented in both marine and nonmarine environments (Davis, 1918; Ernst and Calvert, 1969; Mizutani, 1970, 1977; Murata and Nakata, 1974; Kastner et al., 1977; Iijama and Tada, 1981; Williams and Crerar, 1985; Williams et al., 1985), and in siliceous hot spring sinters (White et al., 1964, 1992; Herdianita et al., 2000; Smith et al., 2001; Guidry and Chafetz, 2003).

Mineralogic transformation may be an important process, but it may not be the only mechanism responsible for silicification of wood. Buurman (1972) believed that the presence of lignified organic remains in chalcedonized wood was evidence of direct precipitation of quartz. Observations of agates and silica geodes show that opal-CT and chalcedony can be directly precipitated as alternating layers within a single specimen (Augustithis, 1982). Experimental evidence of silica precipitation under simulated hydrothermal conditions has yielded conflicting results. Flörke et al. (1990) found that cristobalite could form directly without requiring an amorphous opaline precursor. White and Corwin (1961) reported that chalcedony did not precipitate from synthetic hydrothermal solutions, but chalcedony was observed to have crystallized directly from experimental solutions (Oehler, 1976).

Polymineralic silica assemblages have been reported in petrified wood from Antarctica (Jefferson and McDonald, 1981) and New Zealand (Sutherland, 1994), but in both instances the silica mineral paragenesis was not resolved. The Florissant petrified forest provides a particularly good opportunity for studying the silicification process. Fossils are preserved in a single stratum deposited during a rapid geologic event, but the mineralogy of the silicified wood is surprisingly diverse, ranging from pure opal to pure quartz, with some stumps consisting of a mixture of the two minerals.

ANALYTICAL METHODS

Data were obtained from specimens selected from six silicified stumps (Figs. 1 and 2) by National Park Service personnel. Samples comprised one example of *Chadronoxylon* (a dicot) and 14 specimens of *Sequoioxylon* that span a range of colors and textures. Locality data are shown in Figure 1; sample numbers refer to the National Park Service Inventory and Monitoring of paleontological sites. Data for each sample consisted of density and loss on ignition values, major element composition, mineral identification, and microstructure as revealed by optical and scanning electron microscopy. Analytical methods were chosen on the basis of several factors. Developing new analytical methods or instrumentation was not a goal of this research, and data were obtained using well-established protocols for laboratory instruments that are commonly available to geologists. This strategy will, I hope, encourage other investigators who wish to attempt to replicate this study, or to apply these analytical techniques to their own research. In addition to determining basic physical properties such as density, color, and loss on ignition, silicified wood samples were analyzed using a combination of X-ray diffraction, X-ray fluorescence, scanning electron microscopy/energy-dispersive X-ray spectrometry (SEM/EDX), and optical microscopy.

The density of each specimen was calculated using a Sartorius Model 2000 electronic analytical balance equipped with a Model 6069 hydrostatic weighing device. Loss on ignition (LOI) values were obtained by heating powdered samples at 900 ºC. For silicified wood, this weight loss is the result of loss of structural water and combustion of organic carbon. For quartz-permineralized wood, the amount of structural water is low, and LOI values provide an indication of the amount of relict organic carbon. For fossil woods permineralized with opal, weight loss primarily represents loss of structural water from hydrous silica. Colors of powdered samples were described using the Munsell Soil Color Chart (McBeth Division of Kollmorgen Instrument Corporation, New Windsor, New York, 1994). Major element compositions were determined with a Rigaku Model 3070 X-ray fluorescence spectrometer from glass discs prepared by fusing 3.5 g of powdered petrified wood and 7 g of lithium tetraborate at 1000 ºC, using analytical protocols developed by Johnson et al. (1999). Scanning electron photomicrographs were made using a Tescan Vega SEM equipped with an EDAX nondispersive X-ray spectrometer. Samples were attached to aluminum stubs with epoxy adhesive and sputter-coated with palladium. Optical photomicrographs were made with a Spot Infinity digital camera, using a Wild model 420 stereo microscope for bulk specimens and a Zeiss Photomicroscope for thin sections. X-ray diffraction patterns were obtained from packed powders using a General Electric XRD-5 diffractometer operated at a 2θ scan rate of 2º/min using Cu $K\alpha$ radiation. Index of crystallinity values for quartz-mineralized specimens were determined using the method of Murata and Norman (1976), using diffraction patterns obtained from a Rigaku Geigerflex diffractometer operated at a step increment of 0.02º and a dwell time of 10 s.

RESULTS

Mineralogy and Geochemistry

Major element compositions of Florissant fossil wood (Table 1) indicate that silica is the dominant constituent of all samples. Siliceous volcanic rocks are a likely source of dissolved silica for wood petrifaction (Murata, 1940), and the local abun-

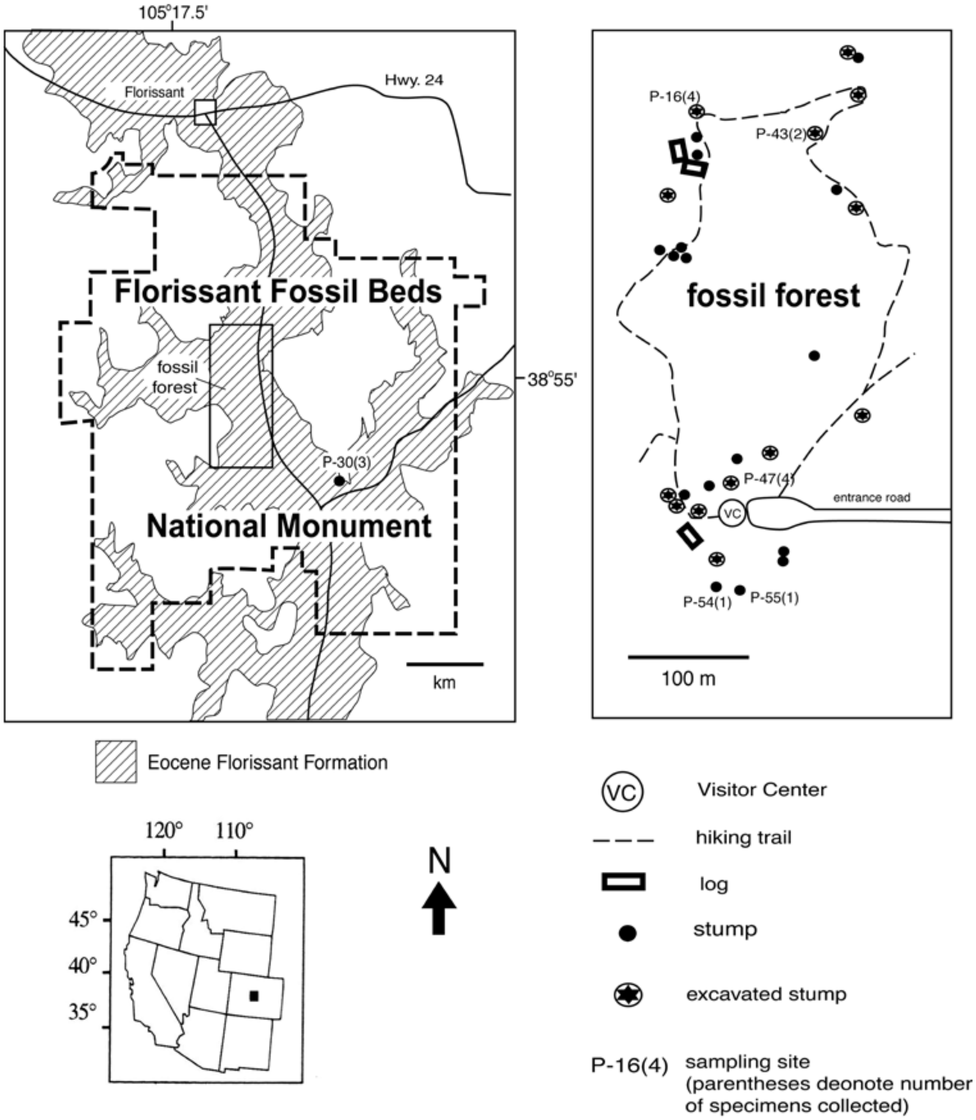

Figure 1. Location map, modified from Evanoff et al. (2001) and Gregory-Wodzicki (2001). Petrified stumps are labeled using Florissant Fossil Beds National Monument inventory numbers.

dance of ash and pumice in the Florissant Formation was an important geologic factor during preservation of the fossil forest. The abundance of diatoms in lacustrine strata are evidence of dissolved silica in surface waters during deposition of the Florissant strata (Harding and Chant, 2000; O'Brien et al., 2002, this volume). Diagenetic alteration of the host rocks would have released a diverse variety of elements, but only silica was precipitated in large quantities within the buried trees, an observation consistent with the Leo and Barghoorn (1976) hypothesis that organic constituents of cell walls have a strong affinity for silicic acid molecules.

The mineralogy of silicified trees within a single lahar deposit is surprisingly diverse. X-ray diffraction patterns reveal that *Sequoioxylon* stumps P-43 and *Chadronoxylon* stump P-30 are composed of nearly pure opal-CT. Specimens from *Sequoioxylon* stumps P-54 and P-55 consist of pure quartz, whereas *Sequoioxylon* stump P-47 contains appreciable amounts of both opal-CT and quartz. Stump P-16 is of particular interest. With an estimated mass of 60 metric tons and a basal diameter of 5.9 m (3.7 m at breast height), "Big Stump" (Fig. 2A) is one of the largest fossils at Florissant Fossil Beds National Monument (Meyer, 2003). Five samples collected from different color zones have mineral compositions that include pure opal-CT, a mixture of opal-CT and quartz, and pure quartz (Fig. 3**)**.

Murata and Norman (1976) used X-ray diffraction to quantify the degree of crystallinity of quartz samples, using the resolution of the 1.3820Å (67.74° 2θ) X-ray peak to calculate a crystallinity index (C.I.) for individual specimens. Index numbers are obtained by determining the peak height above background level for the 67.8º 2-theta (1.38Å d-spacing) diffraction peak measured for a powdered quartz crystal (Fig. 4). The pure quartz is arbitrarily considered to have a C.I. index of 10.0, and indi-

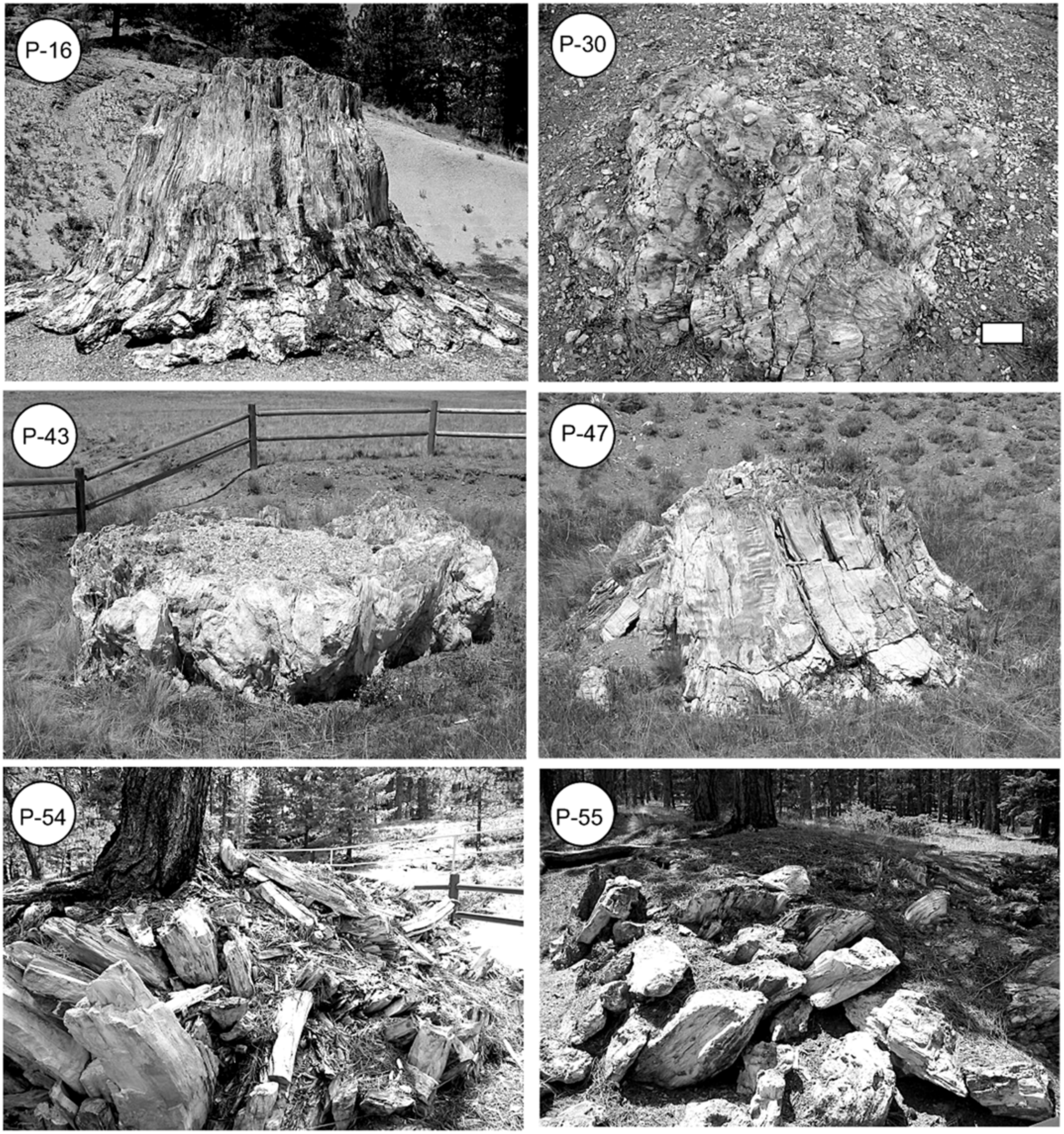

Figure 2. Samples used in this study were collected from six silicified stumps, labeled here with Florissant Fossil Beds National Monument inventory numbers. Specimen P-30 is *Chadronoxylon,* a dicot. Scale bar = 10 cm. All other specimens are *Sequoioxylon*. Photos by Melissa Barton.

TABLE 1. MAJOR ELEMENT COMPOSITION OF FLORISSANT SILICIFIED WOOD

Sample:	P-16a	P-16b	P-16c	P-16d	P-30	P-43	P-47	P-54	P-55
Mineralogy:	Opal and trace quartz	Quartz	Opal-CT	Opal-CT	Opal-CT	Opal-CT	Quartz and opal-CT	Quartz	Quartz
Oxide wt%									
SiO_2	86.61	97.49	94.66	95.81	88.71	93.39	96.08	96.60	97.07
Al_2O_3	0.00	0.00	0.00	0.00	0.40	0.10	0.09	0.06	0.14
TiO_2	0.09	0.02	0.04	0.04	0.03	0.02	0.02	0.01	0.01
Fe_2O_3*	0.10	0.45	0.43	0.56	2.12	0.33	0.09	0.00	0.09
MgO	0.02	0.03	0.10	0.00	0.07	0.00	0.00	0.03	0.04
MnO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CaO	0.13	0.10	0.35	0.06	0.27	0.18	0.16	0.27	0.13
K_2O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Na_2O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
P_2O_5	0.04	0.07	0.05	0.00	0.84	0.10	0.04	0.04	0.08
LOI at 900°C	13.41	2.71	3.96	3.58	5.65	4.34	2.57	2.62	1.52
Total	100.40	100.89	99.59	100.05	98.09	98.46	99.05	99.63	99.08
Density g/cm^3	2.03	2.32	1.84	2.13	1.82	2.04	2.38	2.47	2.34
Munsell color	7.5YR3/3 dark brown	10YR6/3 pale brown	10YR6/3 pale brown	7.5YR5/2 brown	10YR4/3 brown	7.5YR7/2 pinkish gray	10YR8/1 white	10YR8/1 white	67.5YR8/2 pinkish white

Note: LOI—loss on ignition.

*Total iron calculated as Fe_2O_3.

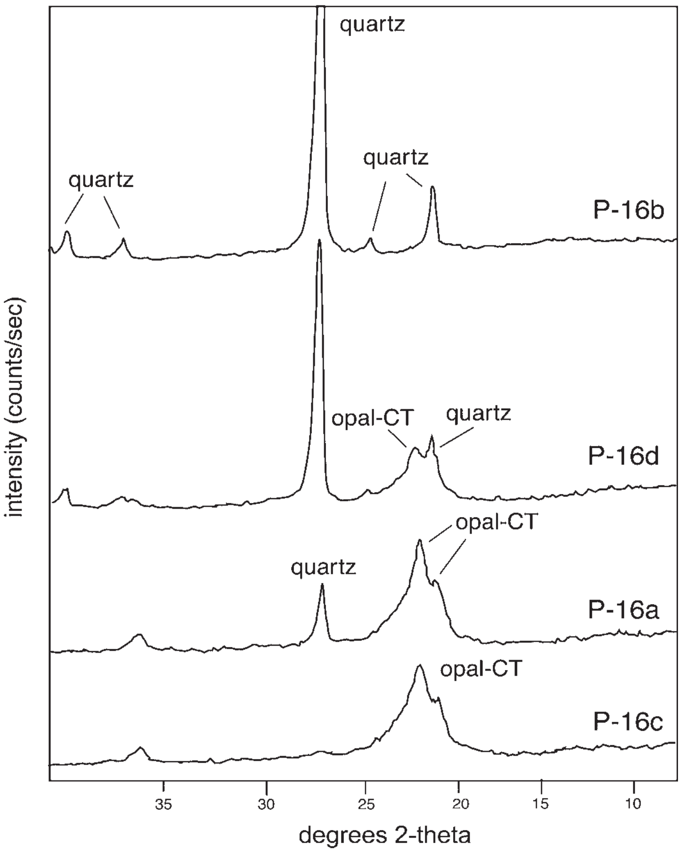

Figure 3. X-ray diffraction patterns of four samples from *Sequoioxylon* stump P-16. Patterns are offset along the y-axis for clarity.

ces for silicified wood samples are calculated as ratios of their peak heights to this calibration standard. Florissant samples that yielded pure quartz X-ray diffraction patterns have C.I. values of <1.0, evidence that quartz is present as chalcedony, consistent with microscopic evidence from thin sections. From a geochemical point of view, one measure of the uniqueness of the Florissant fossil wood is that crystallinity indices are the lowest values that I have measured from quartz-mineralized wood from 29 localities worldwide (C.I. numbers from these localities range from 1.3 to 9.0).

Mineralogic characteristics are related to density and LOI values (Table 1). Woods mineralized with opal have densities of 2.04 g/cm^3 or less, in contrast to densities of 2.34 g/cm^3 or greater for quartz-mineralized wood. For opalized samples, relatively high LOI values (3.96–13.41 wt %) are primarily caused by loss of water from opal and to a lesser extent from combustion of relict organic matter. Quartz-mineralized woods yielded LOI values of 2.34–2.47 wt %, probably mostly representing organic matter.

In unweathered specimens, opalized woods vary from dark brown to gray in color. Brown colors are caused by relict organic matter, as evidenced by bleaching that occurs during natural weathering and in the laboratory when powdered samples are

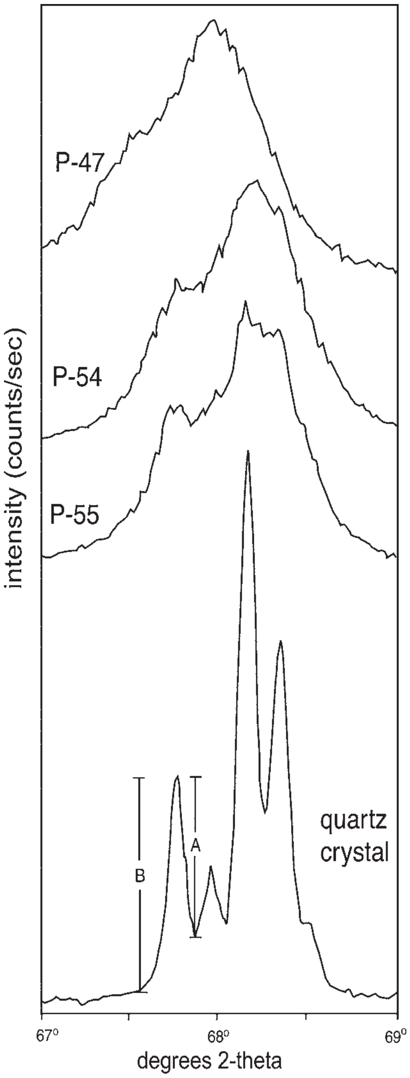

Figure 4. Crystallinity index values for Florissant specimens that contained only quartz were calculated relative to the A/B ratio measured for the 67.8° 2-theta X-ray diffraction peak for a pure powdered quartz crystal. See "Analytical Methods" for details.

heated at 450 °C. Samples that contain quartz as the major constituent are typically tan or cream colored in hand specimen and white when powdered. These results indicate that as a quick field test, mineral composition of Florissant fossil wood can be estimated simply by looking at color.

Iron-rich minerals play a minor role in determining color, producing variegated reddish-brown areas on some fossil stumps. Iron oxide contents range from <0.1 wt% for quartz wood to 0.33–2.12 wt% for opalized specimens. SEM/EDAX analysis suggests that this iron was originally present as disseminated grains of iron pyrite that oxidized to limonite during weathering. The variation in iron content was not studied in detail, and several factors may be involved. A higher iron concentration was observed for the *Chadronoxylon* (dicot) wood as compared to *Sequoioxylon* specimens, but the significance of this observation is not clear. Iron is typically an element that is transported into plant tissues during fossilization, rather than accumulating during the life of the tree. Perhaps *Chadronoxylon* wood was more permeable to iron-bearing groundwater than wood of *Sequoioxylon*. An alternative possibility is the fact that the *Chadronoxylon* stump is located in a different part of the fossil bed than the other specimens (Fig. 1), and the differences in iron content may simply reflect local variations in the dissolved element content of groundwater.

Microscopy

SEM images primarily show topography, and relict anatomical features are most likely to be observed when cell lumina and intercellular spaces remain unmineralized, so that cell wall surfaces are exposed when specimens are fractured (Mustoe, 2004). Topographic features of cell surfaces are preserved with great fidelity in both opalized and chalcedony-mineralized specimens (Fig. 5).

With optical microscopy, the visibility of relict cell architecture in silicified wood is largely determined by the transparency of silica minerals and the presence of opaque or colored inclusions that delineate relict tissue structure (Figs. 6 and 7). Preservation of relict organic matter causes cell structures to be readily visible in most Florissant petrified wood specimens (Fig. 7). Carbonaceous material causes the brownish color characteristic of fossilized cell walls, in contrast to the colorless silica that fills cell lumina and intercellular spaces. SEM/EDAX spectra show a distinct carbon X-ray peak (Fig. 7E); silica is a major constituent of relict cell walls, consistent with the organic templating hypothesis (Leo and Barghoorn, 1976). The quality of anatomical preservation is variable, and cells in some specimens have been deformed or destroyed by biogenic decomposition, but in many specimens the preservation of anatomical detail is excellent (Figs. 6 and 7).

A variety of instrumental methods have been used to map the distribution of elements in permineralized fossils. Analytical techniques include conventional X-ray microprobe (Dietrich et al., 2000), synchrotron-based X-ray microprobe (Kuczumow et al., 2001), electron microprobe (Boyce et al., 2001), and SEM/EDX (Kuczumow et al., 2001; Scott and Collinson, 2003). For some samples, elemental distributions can be correlated with microscopic anatomical features (e.g., cell walls). Elemental mapping has proved to be most successful when fossils contain several mineral phases, such as fossil woods that are permineralized with a combination of silica and calcium carbonate (Scott and Collinson, 2003; Siurek et al., 2004), and carbonaceous fossils preserved as inclusions in chert (Boyce et al., 2001). Studies in our laboratory indicate that elemental mapping is less useful for petrified wood that contains silica as the only major inorganic constituent. SEM/EDX maps of Florissant fossil wood specimens are relatively featureless. Silicon and oxygen tend to be ubiquitous in these silicified fossils. EDX analyses commonly detect

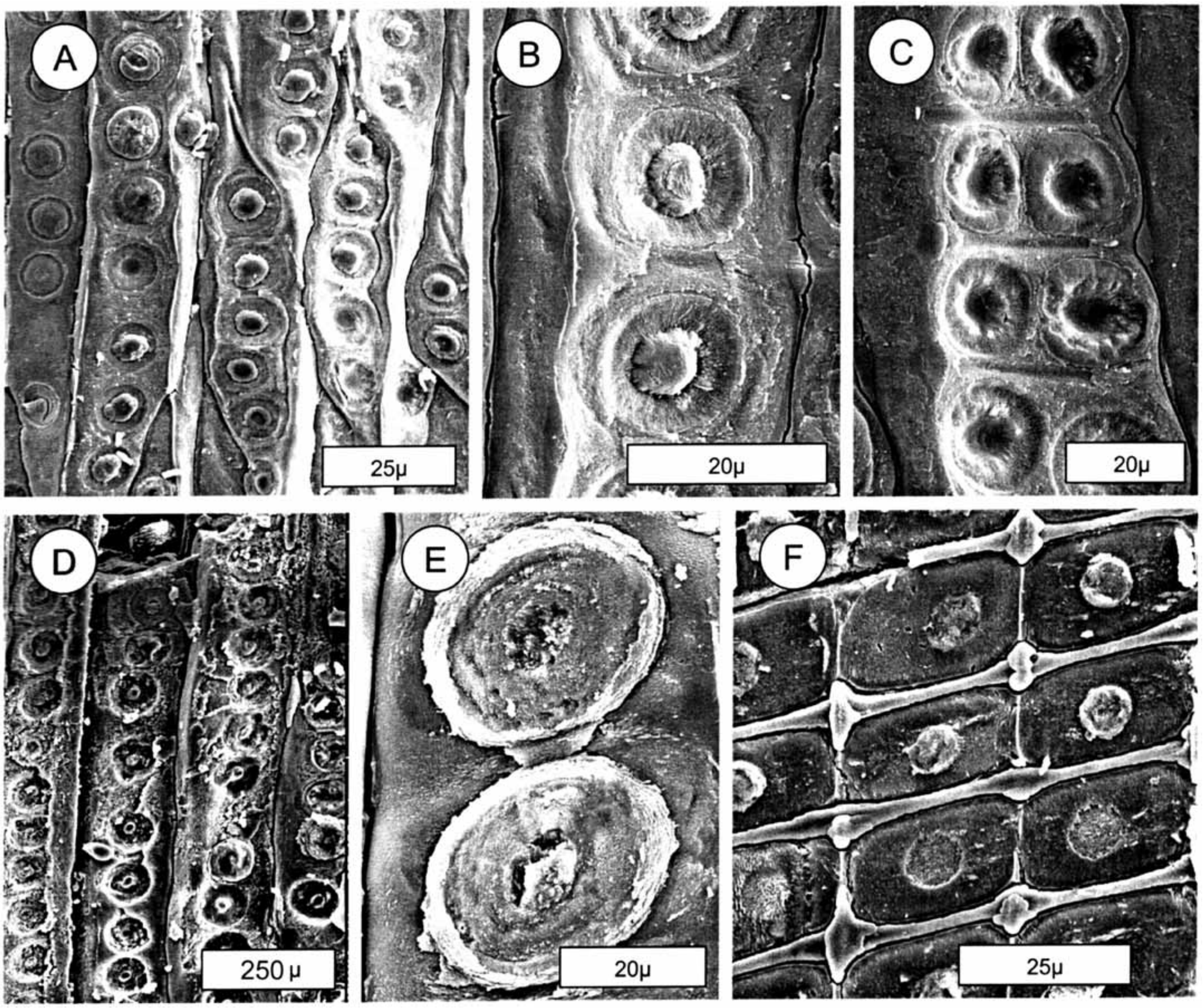

Figure 5. SEM radial views of Florissant fossil *Sequoioxylon* wood showing tracheids with bordered pits. (A–C) Opalized specimen P-16c. (D, E) Chalcedonized specimen P-55a. (F) Parenchyma cells with cross-field pits, specimen P-55a.

the presence of carbon, and when the scan area of the electron beam is minimized, the EDX spectra usually show that carbon is enriched in relict cell walls relative to silica-filled lumina. However, cell walls were not visible in X-ray maps of polished silicified wood samples. The failure of X-ray mapping to reveal variations in carbon content results from a combination of factors. The EDX detector uses a supercooled silicon wafer to detect X-rays emitted when atoms in the specimen are energized by the incident electron beam. These X-rays are processed one photon at a time, a very demanding challenge for the electronic detecting system. The very-low-energy (0.277 KeV) X-rays emitted by carbon atoms are particularly difficult to detect and quantify, lying very close to the light element detection limit of the EDX analyzer. Analysis is further complicated by the fact that carbon has a very low fluorescence yield, causing EDX spectra to have poorer detection limits for this element compared to elements having higher atomic numbers. Figure 8 provides an illustration of these problems, depicting X-ray maps of carbon, oxygen,

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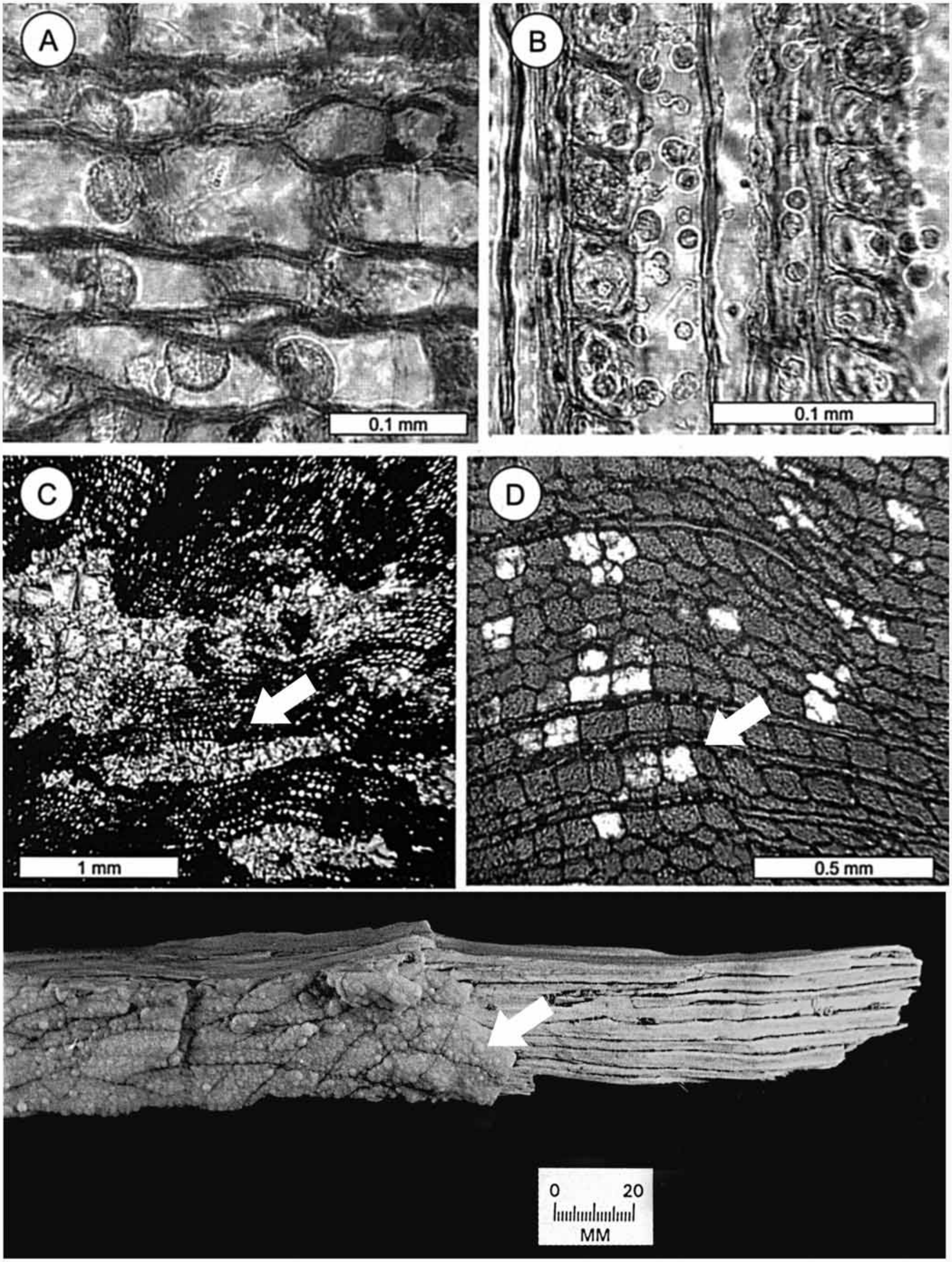
Figure 6. Transmitted-light thin-section photomicrographs of *Sequoioxylon* specimens that contain both opal-CT and chalcedony. (A, B) Transverse and radial views of sample P-16a show lepispheres of opal-CT attached to cell walls, surrounded by clear chalcedony. (C) Transverse view of P-16d reveals chalcedony filling fractures. (D) In specimen P-16c cell lumina are filled with opal-CT, but in one area of this transverse section a few of the tracheids are mineralized with chalcedony. (E) Botryoidal chalcedony crusts are present in fractures in opalized wood from stump P-47.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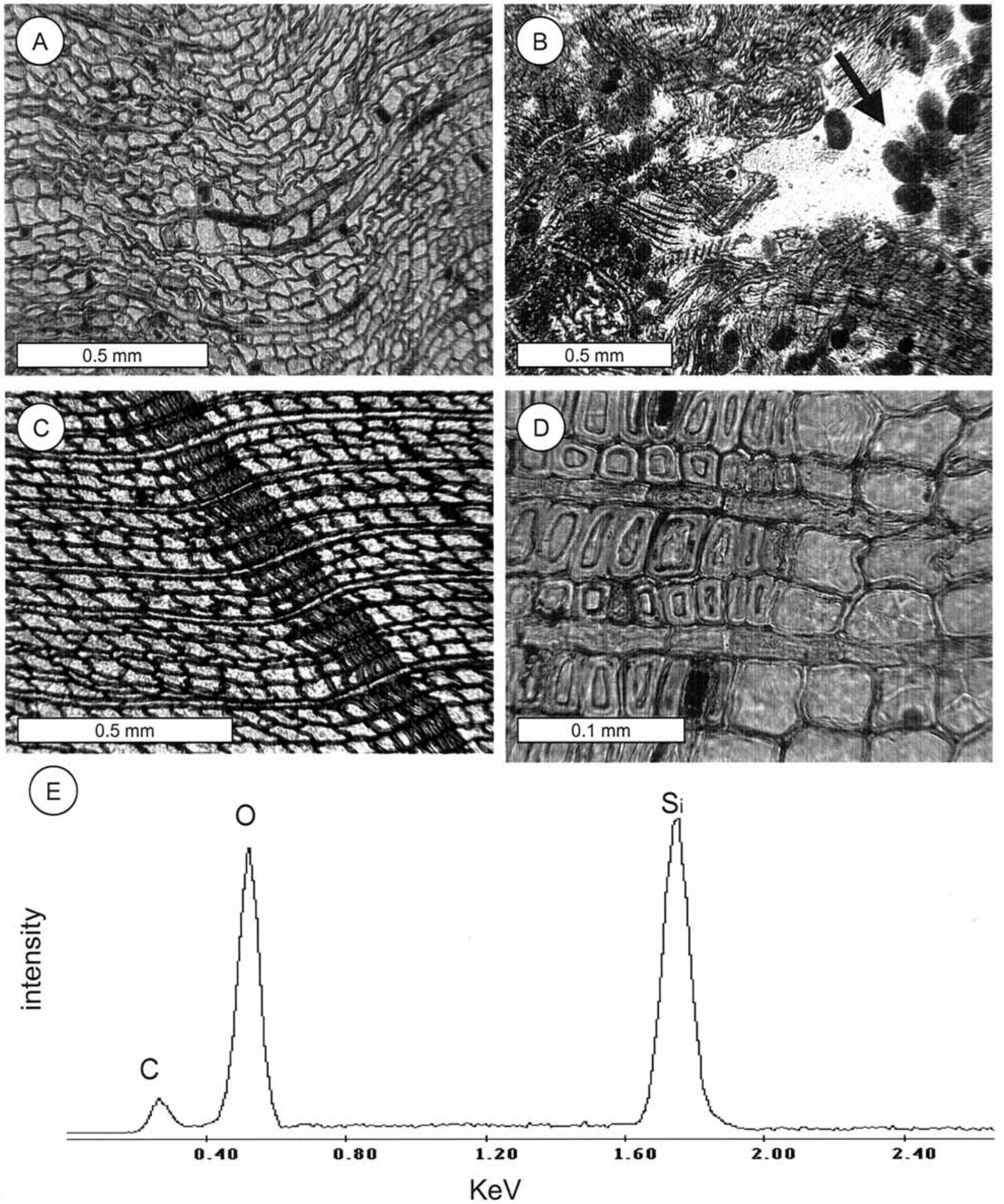

Figure 7. Transmitted-light thin-section photomicrographs showing transverse views of Florissant petrified *Sequoioxylon* wood. (A, B) Specimen P-16b contains chalcedonized wood in a region of the stump where the cells were distorted and locally decayed prior to petrifaction. Note the preservation of probable insect fecal pellets (arrow in B). (C) Undamaged wood in parts of this same specimen is mineralized with a mixture of chalcedony and opal-CT. (D) Chalcedonized wood typical of specimen P-55. In photos C and D, the thin-walled earlywood and thick-walled latewood of successive growth rings are consistent with seasonality in the local paleoclimate. (E) SEM/EDX spectrum of P-16d shows a strong carbon peak, indicative of the preservation of relict organic matter within the dark-colored cell walls.

and silicon in a polished slab of silicified wood that contains two ovoid inclusions, presumed to be fossilized insect fecal pellets. Their dark brown color under transmitted light suggests a carbonaceous composition, and microbeam analysis reveals the presence of carbon as a constituent of these particles. However, X-ray mapping of the full field of view fails to reveal variations in carbon content. The EDX maps show a deficiency of both oxygen and silicon in the ovoid regions, as compared to the abundance of both elements in the adjacent matrix. Note that as the atomic number increases, elements are mapped with greater precision. Thus, carbon (atomic number 6) was not detected, and compositional boundaries are less sharply defined for oxygen (atomic number 8) than for silicon (atomic number 14). As noted above, X-ray maps are most likely to be successful when samples contain a combination of elements that have markedly different atomic numbers, a characteristic not typical of Florissant silicified wood. Boyce et al. (2001) successfully mapped carbon distributions in several types of permineralized fossils by taking advantage of the higher electron beam currents and greater resolution of the electron microprobe, but at present ordinary transmitted light microscopy remains the simplest method for observing the distribution of relict carbon in silicified wood.

Optical microscopy also provides a valuable tool for studying the relationship between opal-CT and chalcedony in specimens where both minerals are present. Cross-polarized light views show opal-CT to have very low interference colors, in contrast to the brighter colors typical of chalcedony. In thin sections prepared for this study, no samples showed evidence of transformation of opal-CT to chalcedony. Instead, when they were present together the two minerals showed very well-defined boundaries. Most often, chalcedony is present as a vein material in fissures that penetrate opalized wood, providing evidence of late-stage silica deposition that occurred after the wood had been petrified (Fig. 6E). A very different type of opal/chalcedony association occurs in samples where tiny hemispheres (“lepispheres”) are attached to the interior surfaces of cell walls, where they are enclosed within clear chalcedony that later permineralized the cell lumina (Fig. 6A

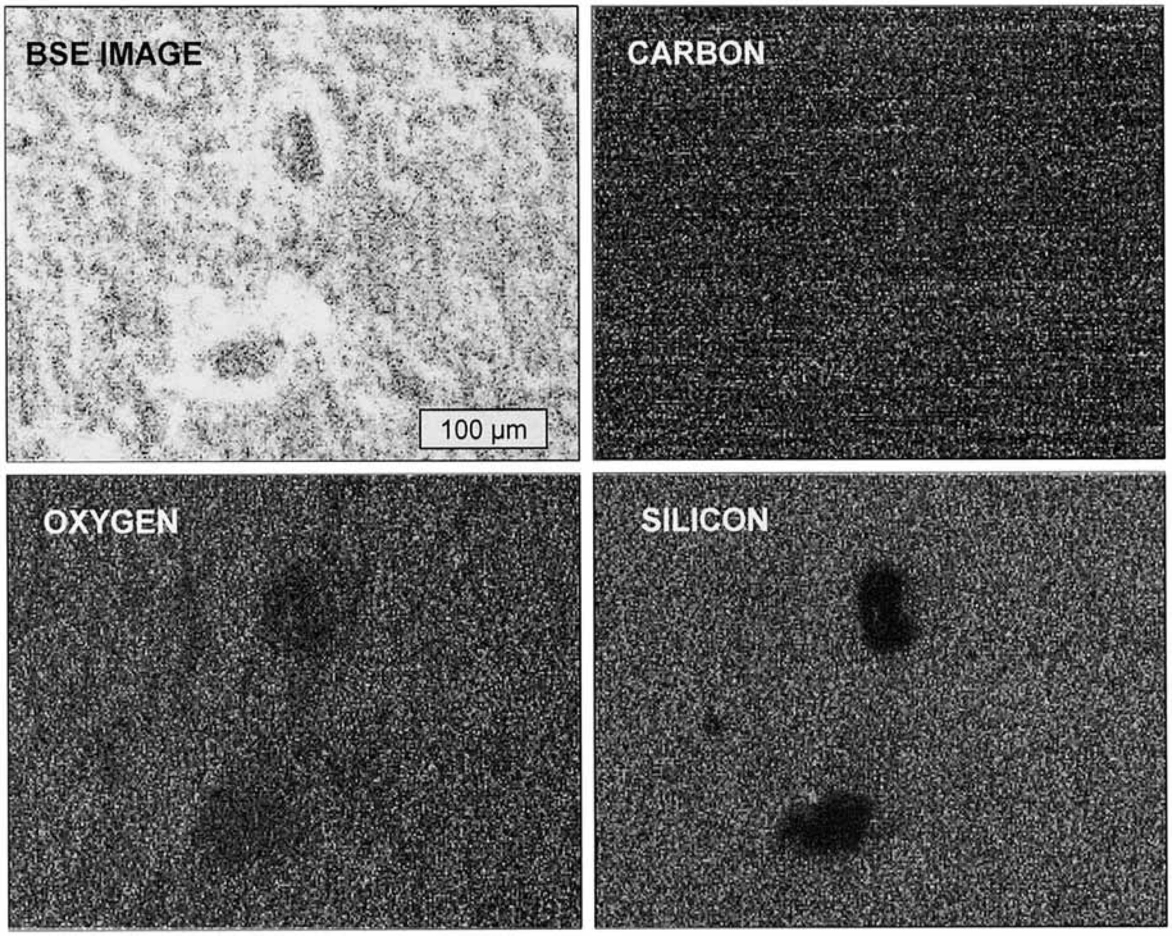

Figure 8. Back-scattered electron SEM image and EDX element distribution maps for carbon, silicon, and oxygen obtained from a polished slice of silicified wood from stump P-16 that contains two ovoid inclusions, possibly fossilized insect fecal pellets. Dark zones in each EDX images represent areas of the specimen where a particular element either is absent or is present only at undetectable levels. (Fig. 7B shows an optical photomicrograph of this specimen; see text for discussion.)

and 6B). These opal masses show no evidence of alteration at their contacts with the adjacent chalcedony, suggesting that the chalcedony did not originate from transformation of an opal-CT precursor, and that the two polymorphs instead developed independently during successive stages of silicification. In a few specimens, chalcedony is sparsely present as a filling material in individual cells within opalized wood (Fig. 6d), but this texture is uncommon.

DISCUSSION

Florissant specimens have great importance for helping geoscientists to understand the nature of the petrifaction process energy better. Unfortunately, some aspects of the early stages of fossilization are enigmatic. To have a complete understanding of the silicification processes that caused wood specimens at Florissant to become permineralized, it would be helpful to know the physical state of silica in the mineralizing fluid, and the environmental conditions that existed at the time of silicification. Was the silica a colloid or sol? Did silica form short or long-chain polymers? Was temperature an important factor in determining the physical state of silica, and the resultant mineralogy? Unfortunately, none of these questions can be answered by presently available evidence, though perhaps one day additional evidence may shed light on these mysteries.

Although the initial silicification processes remain imperfectly understood, other mineralogic features can be interpreted with greater certainty. The presence of tree trunks mineralized with opal-CT, chalcedony, or a mixture of the two is a particularly important and previously unrecognized feature of the Florissant fossil forest. One possible explanation for the presence of both minerals is that the silica mineralogy is evidence of local variations in the rates of diagenetic transformation. This hypothesis assumes that all of the wood was initially permineralized with opal, and that some of the specimens later became at least partially converted to chalcedony.

Mizutani (1970, 1977) described the successive transformation of amorphous biogenic silica (opal-A) to opal-CT and quartz as primarily being a function of geologic age and burial temperature. Neither factor can account for differences in silica mineralogy at Florissant, where stumps were buried within a single stratum of very limited geographic extent. Instead, mineralogic heterogeneity might have been produced by highly localized conditions, e.g., variations in permeability or chemical composition of groundwater. A particularly vexing problem for the mineralogic transformation hypothesis is the apparent absence of “missing link” specimens, where opal is in the process of being altered to chalcedony. Instead, in specimens where both minerals are present, the two phases appear to be coexisting as primary minerals.

Rather than supporting the transformation hypothesis, evidence from Florissant specimens suggests that some buried trees were directly mineralized with chalcedony, without an opal-CT precursor. Under epithermal conditions, opal is precipitated when concentrations of dissolved silica are relatively high, but lower silica concentrations may result in direct precipitation of chalcedony. Crystalline quartz precipitates only from extremely dilute solutions (Iler, 1979; Fournier, 1985). These geochemical characteristics may explain the mineralogy of Florissant fossil wood.

Initial silicification of cell walls probably followed the organic templating model, as evidenced by the presence of silicified cell walls that retain appreciable amounts of relict organic matter (Fig. 7C). Subsequent steps in the silicification process may have followed more than one pathway. Opalized specimens may have originated in woods that were exposed to solutions containing relatively high levels of dissolved silica, allowing cell lumina and intracellular voids to become impregnated with opal-CT (or perhaps opal-A that was later transformed to opal-CT). In contrast, wood mineralized with pure chalcedony may have originated in areas in the deposit with lower silica concentrations, perhaps as a result of small scale hydrologic or lithologic effects within the sedimentary matrix that caused concentrations to vary as groundwater passed through the deposit. Also, permeability and moisture content variations within the wood may have influenced silica mineralogy. Given the large diameters of the buried trees, seepage of silica-bearing groundwater through the tissue may have produced a concentration gradient, by which precipitation of silica in the outer tissues led to a reduction in dissolved silica in the remaining solution, affecting the type of silica that was subsequently deposited in inner regions of the same tree. Anatomical variations among different tree genera may have played a role during fossilization, and within a single trunk differences in physical properties between earlywood and latewood may have led to geochemical differences. Kuczumow et al. (2001) reported microspectrometric evidence of compositional variations in silicified wood from Poland that correlated with relict annual rings, and it would not be surprising to find similar characteristics in specimens from other localities. Although data obtained from the present reconnaissance study are insufficient for recognizing subtle compositional variations that may occur within individual stumps, the Florissant fossil forest is an excellent site for more detailed future research.

Geochemical and mineralogic characteristics are important factors to be considered during development of strategies for mitigating weathering damage to the silicified stumps that are a major feature of Florissant Fossil Beds National Monument. Microscopic observations are particularly useful for explaining why the silicified wood is so susceptible to weathering. Regardless of whether they are mineralized with opal-CT or chalcedony, Florissant fossil woods are typically composed of cells that are separated from each other by narrow (<1 µm) open spaces, causing the fossilized tissue to have cleavage characteristics much like that of modern wood. Florissant specimens readily cleave along radial planes because of the weak interface between longitudinal tracheids and latitudinal rays. Tangential fracturing also occurs because of parting along growth ring boundaries where there is a marked difference in texture between the wood of successive rings. Unlike modern wood, specimens of Florissant fossil wood are prone to fracture in the cross-grain (transverse) direction. Although Florissant fossil stumps are resistant to chemical decomposition because of their siliceous compositions, they are susceptible to damage by frost wedging because of the blocky fracture. These phenomena are discussed in detail by Young et al. (this volume).

CONCLUSIONS

The mineralogic, microscopic, and geochemical properties of Florissant silicified wood are significant for several reasons. From a conservation standpoint, these characteristics are important factors to be considered during development of possible conservation strategies for reducing weathering rates of the petrified stumps. In addition, data from this reconnaissance study shed new light on the fossilization processes that produced these spectacular specimens. The coexistence of opal-CT and chalcedony in some fossil stumps conflicts with the widely accepted hypothesis that chalcedonized wood results from transformation of an opaline precursor. Instead, wood silicification appears to have resulted from a combination of processes rather than following a single transformation pathway. This discovery demonstrates that the Florissant fossil forest is an important locality for studying the petrifaction process. The data presented here, based on analyses of only 15 specimens collected from six fossil stumps, provide only a tantalizing glimpse into possible geochemical processes that caused tree remains to become silicified. Perhaps the greatest significance of this investigation is that it points the way for possible future research. Analyses of a larger number of samples are needed to clarify the range of mineralogic and compositional variation among the more than 30 known fossil logs and stumps. Possible causes of these variations include local differences in groundwater flow rates and dissolved-element concentrations, and environmental factors such as pH and burial temperature. Within an individual stump, mineralization may be related to anatomical characteristics (e.g., cell diameter, presence or absence of open vessels) and to structural features (e.g., voids caused by decay or fissures produced from desiccation or mechanical damage). More extensive microscopic study is needed to understand better how these factors influence petrifaction. Do woods from different tree species become fossilized in the same manner? Present data are inadequate to address this issue.

Florissant Fossil Beds National Monument provides an ideal location for resolving these paleontologic uncertainties. Fossil wood occurs in an ancient lahar deposit that has been the subject of considerable past study, and this research has produced detailed geologic maps and stratigraphic columns, as well as a wealth of paleoenvironmental information. Silicified tree remains have been carefully surveyed, and many of them have been identified taxonomically. Furthermore, the protection efforts by the National Park Service ensure that the site will remain accessible for future scientific research, an important consideration given the sad reality that many other petrified wood localities have suffered from the effects of overzealous collecting, unskilled excavation, or access restrictions related to changes in land ownership or commercial development.

Florissant Fossil Beds National Monument is also an excellent location for studying possible strategies for reducing damage to silicified fossils caused by exposure to natural weathering. As discussed earlier in this report, the mineralogic compositions and microscopic physical characteristics of this silicified wood help to explain why Florissant specimens are susceptible to rapid freeze-thaw weathering in the harsh cold-season climate. Analytical information obtained in this study provides a starting point for developing conservation procedures aimed at reducing weathering rates, and the data and the analytical methods used to obtain them set a helpful precedent for establishing research protocols for conducting future research at fossil sites in other regions.

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REFERENCES CITED

Andrews, H.N., 1936, A new *Sequoioxylon* from Florissant, Colorado: Annals of the Missouri Botanical Garden, v. 23, p. 439–446, doi: 10.2307/2394162.

Augustithis, S.S., 1982, Atlas of sphaeroidal textures and their genetic significance: Athens, Theophrastus Publications, p. 71–73, 241–250.

Boyce, C.K., Hazen, R.M., and Knoll, A.H., 2001, Nondestructive, *in situ*, cellular-scale mapping of elemental abundances including organic carbon in permineralized fossils: Proceedings of the National Academy of Sciences of the United States of America, v. 98, p. 5970–5974, doi: 10.1073/pnas.101130598.

Buurman, P., 1972, Mineralization of fossil wood: Scripta Geologica, v. 12, p. 1–43.

Correns, C.W., 1950, Zur Geochemie der Diagenese: Geochimica et Cosmochimica Acta, v. 1, p. 49–54, doi: 10.1016/0016-7037(50)90008-1.

Daniels, F.J., and Dayvault, R.D., 2006. Ancient forests: A closer look at fossil wood: Grand Junction, Colorado, Western Colorado Publishing, 450 p.

Davis, E.F., 1918, The radiolarian cherts of the Franciscan Group: University of California Department of Geology Bulletin, v. 11, p. 235–432.

Dernbach, H., 1996, Petrified forests: Heppenheim, Germany, D'Oro-Verlag, 188 p.

Dietrich, D., Frosch, G., Röbler, R., and Marx, G., 2000, Analytical X-ray microscopy on *Parsonius* sp.—A contribution to permineralization process studies: Mikrochimica Acta, v. 133, p. 279–283, doi: 10.1007/s006040070105.

Ernst, W.G., and Calvert, S.E., 1969, An experimental study of the recrystallization of porcellanite and its bearing on the origin of some bedded cherts: American Journal of Science, v. 267A, p. 114–133.

Evanoff, E., McIntosh, W.C., and Murphey, P.C., 2001, Stratigraphic summary and $^{40}Ar/^{39}Ar$ geochronology of the Florissant Formation, Colorado, *in* Evanoff, E., Gregory-Wodzicki, K.M., and Johnson, K.R., Fossil flora and stratigraphy of the Florissant Formation, Colorado: Proceedings of the Denver Museum of Nature & Science, ser. 4, no. 1, p. 1–16.

Felix, J., 1897, Unterschungen über den Versteinerungsprozess un Erhaltungszustand planslicher Membranen: Zeitschrift der Deutsche Geologische Gessellschaft, v. 49, p.182–192.

Flörke, O.W., Graetsch, H., and Jones, J.B., 1990, Hydrothermal deposition of cristobalite: Neues Jahrbuch für Mineralogie, Geologie, und Paläontologie, v. 2, p. 81–95.

Fournier, R.O., 1985, The behavior of silica in hydrothermal solutions, *in* Berger, B.R., and Bethke, P.M., eds., Geology and geochemistry of epithermal systems: Reviews in Economic Geology, v. 2, p. 45–61.

Gregory, K.M., and Chase, C.G., 1994, Tectonic and climatic significance of a late Eocene low-relief, high-level geomorphic surface, Colorado: Journal of Geophysical Research, v. 99, p. 20,141–20,160, doi: 10.1029/94JB00132.

Gregory-Wodzicki, K.M., 2001, Paleoclimatic implications of tree-ring growth characteristics of 34.1 Ma *Sequoioxylon pearsallii* from Florissant, Colorado, *in* Evanoff, E., Gregory-Wodzicki, K.M., and Johnson, K.R., Fossil flora and stratigraphy of the Florissant Formation, Colorado: Proceedings of the Denver Museum of Nature & Science, ser. 4, no. 1, p. 163–186.

Guidry, S.A., and Chafetz, H.S., 2003, Depositional facies and diagenetic alteration in a siliceous hot-spring accumulation: Examples from Yellowstone National Park, U.S.A: Journal of Sedimentary Research, v. 73, p. 806–823.

Harding, I.C., and Chant, L.S., 2000, Self-cemented diatom mats as agents of exceptional preservation in Oligocene Florissant lake beds, Colorado, United States: Geology, v. 28, p. 195–198, doi: 10.1130/0091-7613(2000)28<195:SDMAAO>2.0.CO;2.

Herdianita, N.R., Browne, P.R.L., and Rodgers, K.A., 2000, Mineralogical and textural changes accompanying ageing of silica sinter: Mineralium Deposita, v. 35, p. 48–62, doi: 10.1007/s001260050005.

Iijama, A., and Tada, R., 1981, Silica diagenesis of Neogene diatomaceous and volcaniclastic sediments in northern Japan: Sedimentology, v. 28, p. 185–200, doi: 10.1111/j.1365-3091.1981.tb01676.x.

Iler, R.K., 1979, The colloid chemistry of silica and silicates: New York, Wiley, 866 p.

Jefferson, T.H., and McDonald, D.I., 1981, Fossil wood from South Georgia: British Antarctic Survey Bulletin, v. 54, p. 57–64.

Johnson, D.M., Hooper, P.R., and Conrey, R.M., 1999, XRF analysis of rocks and minerals for major and trace elements on a single low dilution Li-tetraborate fused bed: Advances in X-ray Analysis, v. 41, p. 843–867.

Karowe, A.L., and Jefferson, T.H., 1987, Burial of trees by eruptions of Mount St. Helens, Washington: Implications for the interpretation of fossil forests: Geological Magazine, v. 124, p. 191–204.

Kastner, M., Keene, J.B., and Gieskes, J.M., 1977, Diagenesis of siliceous oozes. I. Chemical controls and the rate of opal-A to opal-CT transformation—An experimental study: Geochimica et Cosmochimica Acta, v. 41, p. 1041–1059, doi: 10.1016/0016-7037(77)90099-0.

Kuczumow, A., Chevallier, P., Ro, C., Wajnberg, P., Kalita, J., and Siurek, J., 2001, Microspectrometric investigation of petrified wood from southeastern Poland: Mikrochimica Acta, v. 137, p. 173–183, doi: 10.1007/s006040170009.

Leo, R.F., and Barghoorn, E.S., 1976, Silicification of wood: Harvard University Botanical Museum Leaflets, v. 25, no. 1, p. 1–47.

Meyer, H.W., 2003, The fossils of Florissant: Washington, D.C., Smithsonian Books, 258 p.

Mitchell, R.S., and Tufts, S., 1973, Wood opal—A tridymite-like material: American Mineralogist, v. 58, p. 717–720.

Mizutani, S., 1970, Silica minerals in the early stages of diagenesis: Sedimentology, v. 15, p. 419–436.

Mizutani, S., 1977, Progressive ordering of cristobalite in early stages of diagenesis: Contributions to Mineralogy and Petrology, v. 61, p. 129–140, doi: 10.1007/BF00374363.

Murata, K.J., 1940, Volcanic ash as a source of silica for the silicification of wood: American Journal of Science, v. 238, p. 586–596.

Murata, K.J., and Nakata, J.K., 1974, Cristobalitic stage in the diagenesis of diatomaceous shale: Science, v. 184, p. 567–568, doi: 10.1126/science.184.4136.567.

Murata, K.J., and Norman, H., 1976, An index of crystallinity for quartz: American Journal of Science, v. 276, p. 1120–1130.

Mustoe, G.E., 2004, Microscopy of silicified wood: Microscopy Today, v. 11, no. 6, p. 34–37.

O'Brien, N.R., Meyer, H.W., Reilly, K., Ross, A.M., and Maguire, S., 2002, Microbial and taphonomic processes in the fossilization of insects and plants in the late Eocene Florissant Formation, Colorado: Mountain Geology, v. 37, no. 1, p. 1–11, doi: 10.2113/gsrocky.37.1.1.

O'Brien, N.R., Meyer, H.W., and Harding, I.C., 2007, this volume, The role of biofilms in fossil preservation, Florissant Formation, Colorado, *in* Meyer, H.W., and Smith, D.M., eds., Paleontology of the upper Eocene Florissant Formation, Colorado: Geological Society of America Special Paper 435, doi: 10.1130/2007.2435(02).

Oehler, J.H., 1976, Hydrothermal crystallization of silica gel: Geological Society of America Bulletin, v. 87, p. 1143–1152, doi: 10.1130/0016-7606(1976)87<1143:HCOSG>2.0.CO;2.

Schopf, J.M., 1971, Notes on plant tissue preservation and mineralization in a Permian deposit of peat from Antarctica: American Journal of Science, v. 271, p. 522–543.

Scott, A.C., and Collinson, M.E., 2003, Non-destructive multiple approaches to interpret the preservation of plant fossils: implications for calcium-rich permineralizations: Journal of the Geological Society [London], v. 160, p. 857–862.

Scurfield, G., 1979, Wood petrifaction: An aspect of biomineralogy: Australian Journal of Botany, v. 27, p. 377–390, doi: 10.1071/BT9790377.

Scurfield, G., and Segnit, E.R., 1984, Petrifaction of wood by silica minerals: Sedimentary Geology, v. 39, p. 149–167, doi: 10.1016/0037-0738(84)90048-4.

Siurek, J., Chevallier, P., Ro, C., Chun, H.Y., Youn, H.S., Zięba, E., and Kuczumow, A., 2004, Studies on wood tissue substitution by silica and calcite during preservation of fossil wood: Journal of Alloys and Compounds, v. 362, p. 107–115, doi: 10.1016/S0925-8388(03)00570-X.

Smith, B.Y., Campbell, K.A., Rodgers, K.A., and Browne, P.R.L., 2001, Morphological changes accompanying the opal-A to opal-CT silica phase transition in silica sinters, from Orakei Korako and Te Kopia, Taupo Volcanic Zone: Geological Society of America Abstracts with Programs, v. 33, p. 384–385.

Stein, C.L., 1982, Silica recrystallization of petrified wood: Journal of Sedimentary Petrology, v. 52, p. 1277–1281.

St. John, R.N., 1927, Replacement vs. impregnation in petrified wood: Economic Geology and the Bulletin of the Society of Economic Geologists, v. 22, p. 729–739.

Sutherland, J., 1994, Some aspects of petrification of Miocene wood from Kaipara Harbour, New Zealand: Geoscience Reports of Shizuoka University, v. 20, p. 143–151.

Wang, X., Xu, H., and Bryan, C., 2001, Formation of petrified woods: An organic molecule-templated silica precipitate in nature: Geological Society of America Abstracts with Programs, v. 33, no. 6, p. 234.

Wheeler, E.A., 2001, Fossil dicotyledonous woods from Florissant Fossil Beds National Monument, Colorado, *in* Evanoff, E., Gregory-Wodzicki, K.M., and Johnson, K.R., eds., Fossil flora and stratigraphy of the Florissant Formation, Colorado: Proceedings of the Denver Museum of Nature & Science, ser. 4, no. 1, p. 187–203.

White, D.E., Thompson, G.A., and Sandberg, C.H., 1964, Rocks, structure, and geologic history of Steamboat Springs thermal area, Washoe County, Nevada: U.S. Geological Survey Professional Paper 458-B, 63 p.

White, D.E., Heropolous, C., and Fournier, R.O., 1992, Gold and other minor elements associated with hot springs and geysers of Yellowstone National Park, Wyoming, supplemented with data from Steamboat Springs, Nevada: U.S. Geological Survey Bulletin 2001, 19 p.

White, J.F., and Corwin, J.F., 1961, Synthesis and origin of chalcedony: American Mineralogist, v. 46, p. 112–119.

Williams, L.A., and Crerar, D.A., 1985, Silica diagenesis. II. General mechanisms: Journal of Sedimentary Petrology, v. 55, p. 312–321.

Williams, L.A., Parks, G.A., and Crerar, D.A., 1985, Silica diagenesis. I. Solubility controls: Journal of Sedimentary Petrology, v. 55, p. 301–311.

Young, J.L., Meyer, H.W., and Mustoe, G.E., 2007, this volume, Conservation of an Eocene petrified forest at Florissant Fossil Beds National Monument: Investigation of strategies and techniques for stabilizing in situ fossil stumps, *in* Meyer, H.W., and Smith, D.M., eds., Paleontology of the upper Eocene Florissant Formation, Colorado: Geological Society of America Special Paper 435, doi: 10.1130/2007.2435(10).

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