

REPLACEMENT OF QUARTZ BY OPALINE SILICA DURING WEATHERING OF PETRIFIED WOOD

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Abstract—A mineralogical investigation by X-ray powder diffraction and optical, scanning, and transmission electron microscopy of partially weathered petrified wood in the Yegua Formation (Eocene) of east-central Texas revealed that microcrystalline quartz present in the unaltered petrified wood has been gradually dissolved and replaced by disordered silica polymorphs (mainly opal-CT) as a result of weathering. This replacement suggests that the reaction sequence: opal-A → opal-CT → quartz, which has been described elsewhere to occur during diagenetic alteration of petrified wood, is apparently reversed when the petrified wood is exposed to low-energy weathering conditions. The relatively high rate of dissolution of the quartz in the petrified wood appears to be related to its small crystallite size. The silica released by the dissolution of the quartz is subsequently reprecipitated as disordered cristobalite-tridymite (opal-CT) and poorly crystalline silica (opal-A) that, in turn, probably converts to opal-CT on aging. Opal-CT is the major silica phase in the completely altered powdery material enclosing the partially weathered petrified wood. The intermediate zone between the altered and unaltered zones contains both quartz and opal-CT.

Key Words—Opal-A, Opal-CT, Petrified wood, Quartz, Silica, Weathering.

INTRODUCTION

Previous investigations of petrified wood have mainly dealt with mechanisms of silicification and the mineralogical transformations associated with petrification of fossil wood (Scurfield and Segnit, 1984; Buurman, 1972). It is generally accepted that microcrystalline quartz is the most common silica mineral in petrified wood (Stein, 1982), although poorly crystalline forms of silica (opal-A) and disordered cristobalite-tridymite (opal-CT) also occur. Conversion of opal-A to opal-CT and eventually to quartz has been experimentally demonstrated (Mizutani, 1977), and field observations have confirmed the significance of this reaction sequence during diagenetic alteration of both petrified wood and biogenic siliceous sediments (Stein, 1982). In the present report, evidence is presented that suggests a reversal of the above reaction sequence during weathering of petrified wood. Microcrystalline quartz was found to have gradually dissolved, releasing silica which reprecipitated as poorly crystalline silica (opal-A) that, in turn, probably converted to opal-CT during aging. The relatively high weatherability noted here for microcrystalline quartz may explain (1) the general absence of fine clay size ($<0.2 \mu\text{m}$) quartz in many soils (Wilding *et al.*, 1977) and (2) the origin of zoned chert concretions having white surficial zones of cristobalite that enclose cores of microcrystalline quartz (Kovnurko, 1970).

LITHOLOGY AND OCCURRENCE

Petrified wood is abundant in the Yegua Formation (Eocene) sediments exposed at College Station, Texas.

These sediments were deposited mainly in deltaic and fluvial types of environments (Berg, 1970). The basal unit of the Yegua (the Bryan Sandstone) consists of predominantly fluvial sandstones of deltaic origin. The Easterwood Shale, which contains volcanic strata (bentonite and tonstein) described by Senkayi *et al.* (1984), overlies the Bryan Sandstone. A considerable quantity of petrified wood is embedded in both the Bryan and the Easterwood rock units (Mathews, 1950).

The petrified wood shown in Figure 1 is part of a larger piece excavated from a depth of about 2 m below the tonstein and bentonite strata (Figure 2) at one of the three locations (Site 3) previously described by Senkayi *et al.* (1984). The volcanic ash from which these strata were derived apparently provided a ready source of soluble silica which was necessary for the initial silicification process. This particular piece of petrified wood is about 60 cm in length and 20 cm in diameter. It was partially exposed along the bank of a small creek although a larger portion of it was still deeply embedded in the unconsolidated sandy layer shown in Figure 2. The petrified log consists of a white powdery exterior zone (1–3 cm thick) which grades into a hard, consolidated core. The white powdery material also occurs in thin veinlets (which extend into the surrounding host rock for several centimeters) and along the joint plane shown in Figure 1 where it forms a thin surficial coating (indicated by WC).

ANALYTICAL PROCEDURES

Whole samples of the white, powdery exterior zone of the petrified log, the partially altered intermediate

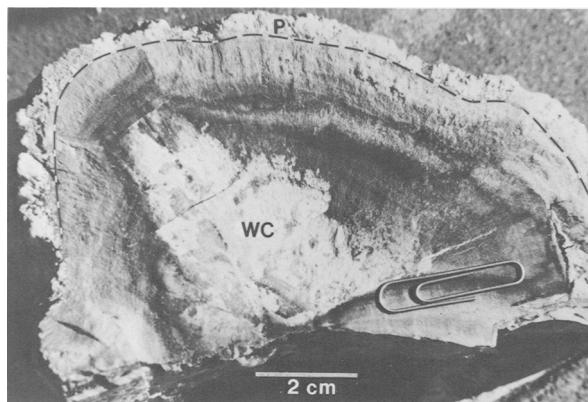


Figure 1. Hand specimen of partially altered petrified wood showing powdery exterior zone (P) and thin white coating (WC), both of which consist mainly of opal-CT.

zone, and the hard material near the center of the log were fractionated into sand- ($> 50 \mu\text{m}$), silt- ($50\text{--}2 \mu\text{m}$), and clay-size ($2\text{--}0.2$ and $< 0.2 \mu\text{m}$) fractions according to the procedures described by Jackson (1974). Dispersion of the two consolidated samples was achieved by wet grinding and repeated ultrasonic dispersion in water. The mineralogy of the whole samples and the various size fractions was determined by X-ray powder diffraction (XRD) using a Philips diffractometer with a graphite monochromator and $\text{CuK}\alpha$ radiation. The fine ($< 0.2 \mu\text{m}$) clay fractions were also investigated by transmission electron microscopy (TEM). Thin sections for optical microscopy investigations were cut to reveal the transition from the loose exterior to the unaltered consolidated zone. For scanning electron microscopy (SEM), small chips were broken from the petrified log to expose the transitional zone between the altered and unaltered zones of the petrified wood. The samples were examined with a JEOL JSM 25 microscope after they were coated with carbon.

RESULTS

Mineralogical composition

Opal-CT is the major phase in all size fractions of the powdery exterior zone (Table 1). It is also the major component of the fine-clay size ($< 0.2 \mu\text{m}$) fraction from the intermediate zone as indicated by the XRD data in Figure 3. According to Jones and Segnit (1971), opal-CT is characterized by a strong XRD peak at 4.07 \AA (with a shoulder near 4.3 \AA) and a weaker peak at 2.49 \AA (Figure 3). Identification of opal-A from XRD data is difficult particularly in the presence of large quantities of opal-CT. The broadening of the peak at about 4.1 \AA , however, suggests the presence of at least a small amount of opal-A in the soft exterior and intermediate zones (Figure 3). The fine clay from the unweathered, consolidated inner zone contains quartz as the only crystalline phase. Quartz (characterized by

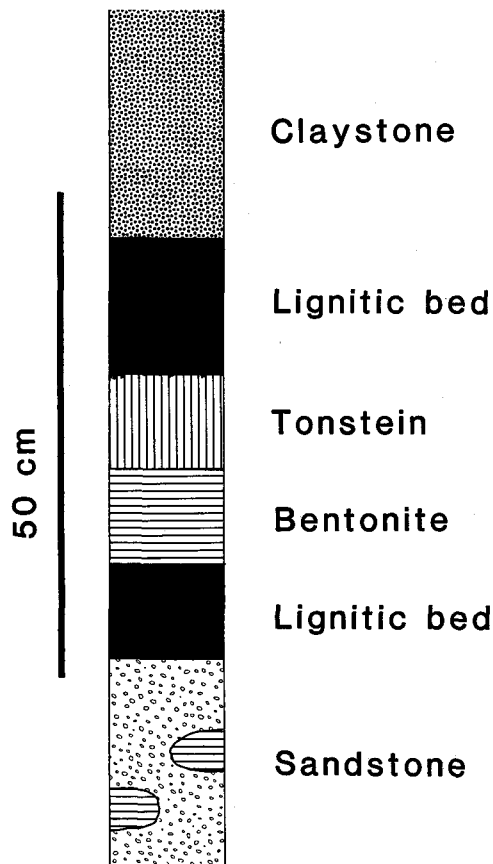


Figure 2. Section showing major strata of Easterwood Shale (Yegua Formation) at College Station, Texas. Petrified wood specimen shown in Figure 1 was exhumed from sandstone layer, 2 m below tonstein/bentonite layers.

$4.26\text{--}, 3.34\text{--},$ and 2.459-\AA peaks in Figure 3) is absent in the fine clay fraction from the soft exterior zone although it is present in the same size fraction from the intermediate zone. The TEM data (Figure 4) are consistent with the XRD data. Microcrystals of both quartz and opal-CT are present in the $< 0.2\text{-}\mu\text{m}$ fraction from the intermediate zone, whereas only crystallites of opal-CT were noted in the same size fraction from the soft, completely altered exterior zone.

Micromorphological relationships

The optical microscopy data (Figure 5) show a gradual disappearance of the quartz from the unaltered (U) to the altered (A) zone of the petrified wood which contains opaline silica (mainly opal-CT). Although the opal-CT is weakly birefringent, the altered zones in micrographs 5b, 5d, and 5f are isotropic due to the very small particle size of the opal-CT crystallites. The intermediate zones (T) between the altered and unaltered zones in Figure 5b, 5d, and 5f contain both opal-CT and quartz. The gradual replacement of quartz by

Table 1. Mineralogical composition of partially altered petrified wood in the Eocene Yegua Formation at College Station, Texas.

| Sample | Powdery exterior | Intermediate zone | Consolidated interior |
|---------------------|------------------|-------------------|-----------------------|
| <0.2 μm | C | C > Q | Q |
| 2-0.2 μm | C | Q | Q |
| 50-2 μm | C > Q | Q | Q |
| >50 μm | C > Q | Q | Q |
| Whole | C >> Q | Q >> C | Q |

C = opal-CT; Q = quartz.

opal-CT along the weathering front without disruption of the cellular structure strongly suggests a dissolution and reprecipitation mechanism. Dissolution of the quartz probably occurred during periods of excess moisture. Subsequent drying raised the concentration of silica in the solution and then caused precipitation of the disordered silica polymorphs in the altered zone and in the veins within the enclosing sedimentary material. Initially, the dissolution process did not affect the microfabric, integrity, or continuity of the cellular structure of the petrified wood. This preservation was likely due to islands (I) and veinlets (V) containing larger crystals of quartz (Figure 5d and 5f) which persisted in the partially altered zone and acted as pillars, helping to maintain the integrity of the cellular structure. Eventually, these supports also dissolved and were replaced by secondary precipitation products. The altered zone then lost its rigidity and became soft and powdery.

SEM data (Figure 6a and 6b) show the initial stages of the dissolution process. The cell wall structure initially resisted the dissolution process and clearly defines the original cellular morphology of the wood in the area that has been partially affected by the dissolution process (Figure 6b). Most of the cells in the completely altered soft zone are filled with spherical bodies (Figure 6d) which are characteristic of the opaline silica (Pollard and Weaver, 1973), whereas euhedral crystallites of quartz (Figure 6c) were commonly observed in the unaltered consolidated zone.

DISCUSSION

The relatively high solubility of the quartz in the petrified wood appears to be related to its small crystal size and, therefore, large surface area. According to Lidstrom (1968), the solubility of quartz greatly increases as the particle size decreases below 0.1 μm . Apparently, most of the quartz in the petrified wood occurs as very tiny crystals and would, therefore, readily dissolve. The optical microscopy data provided the most conclusive evidence to support the dissolution hypothesis. Under the optical microscope, veinlets of quartz can be traced from the unaltered to the altered

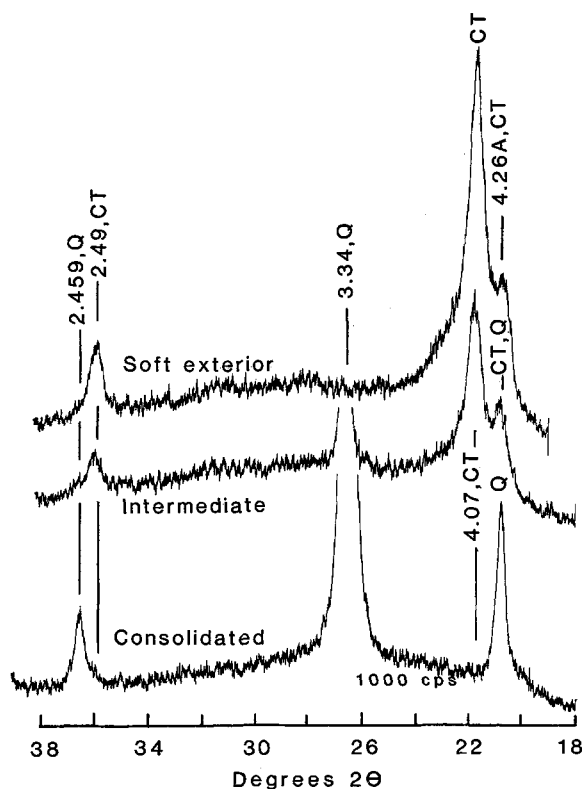


Figure 3. X-ray powder diffraction patterns of fine (<0.2 μm) clay fractions showing variations in relative contents of opal-CT (CT) and quartz (Q) from most altered soft exterior to unaltered, consolidated zone of petrified wood.

zones. These veins contain much larger crystals of quartz which tend to resist the dissolution process (Figure 5d and 5f).

Dissolution and reprecipitation may also explain the origin of the zoned chert concretions (as large as 20 cm in diameter) which were described by Kovnurko (1970). These concretions were reported to occur in an environment similar to that described for the petrified log investigated in this study. They occur in sedimentary strata exposed along the bank of a river. Many of these concretions are surrounded by a white isotropic crust (1-2 mm thick) consisting of mainly α -cristobalite (probably opal-CT). The white crust encloses a dark gray core which consists of microcrystalline quartz. Although Kovnurko (1970) proposed a different mechanism for the origin of these zoned chert concretions, it is possible that the microcrystalline quartz in the cores of these concretions gradually dissolved and released silica which reprecipitated around the core. Wilding *et al.* (1977) proposed two hypotheses to explain the apparent lack or absence of quartz in the fine clay fractions of moderately weathered soils. These are: (1) high solubility rates of the <0.2- μm quartz particles due to their small particle sizes, and (2) physical in-

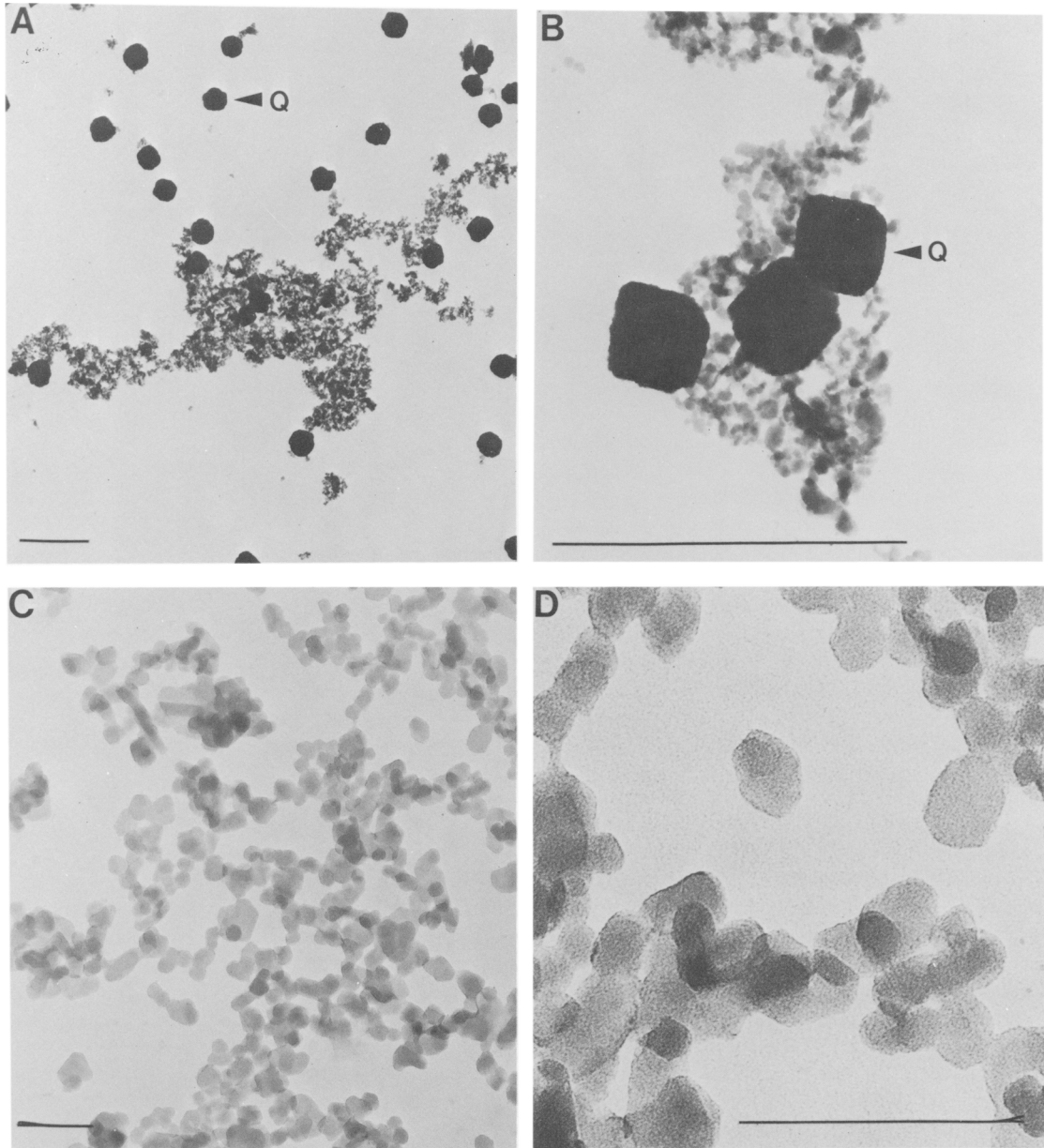


Figure 4. Transmission electron micrographs of fine clay ($<0.2 \mu\text{m}$) fractions showing (a and b) microcrystals of opal-CT and quartz (Q) from partially intermediate zone and (c and d) opal-CT from completely altered exterior zone. Bar represents $1 \mu\text{m}$ in (a) and (b) and $0.1 \mu\text{m}$ in (c) and (d).

ability to comminute quartz to particles of $<0.2\text{-}\mu\text{m}$ diameter.

For the petrified log investigated in the present study and the zoned chert concretions described by Kovnurko (1970), most of the silica released was not leached out of the system as it may have been in a soil weathering environment. As the concentration of silica in the solution increased during the drying cycle, poorly crystalline forms of silica (opal-A and opal-CT) precipitated instead of quartz. The opal-A was probably

converted to opal-CT on aging. According to Jones and Segnit (1972), the formation of disordered cristobalite-tridymite phases (having a sheet structure consisting of coplanar six-membered rings of tetrahedral units) is kinetically favored over the formation of well-crystallized quartz under the low-energy, surface-weathering conditions and high silica concentrations.

Oxygen isotope data (Table 2) indicate that if these samples were in equilibrium with water of seawater isotopic composition ($\delta = 0\%$), the equilibrium tem-

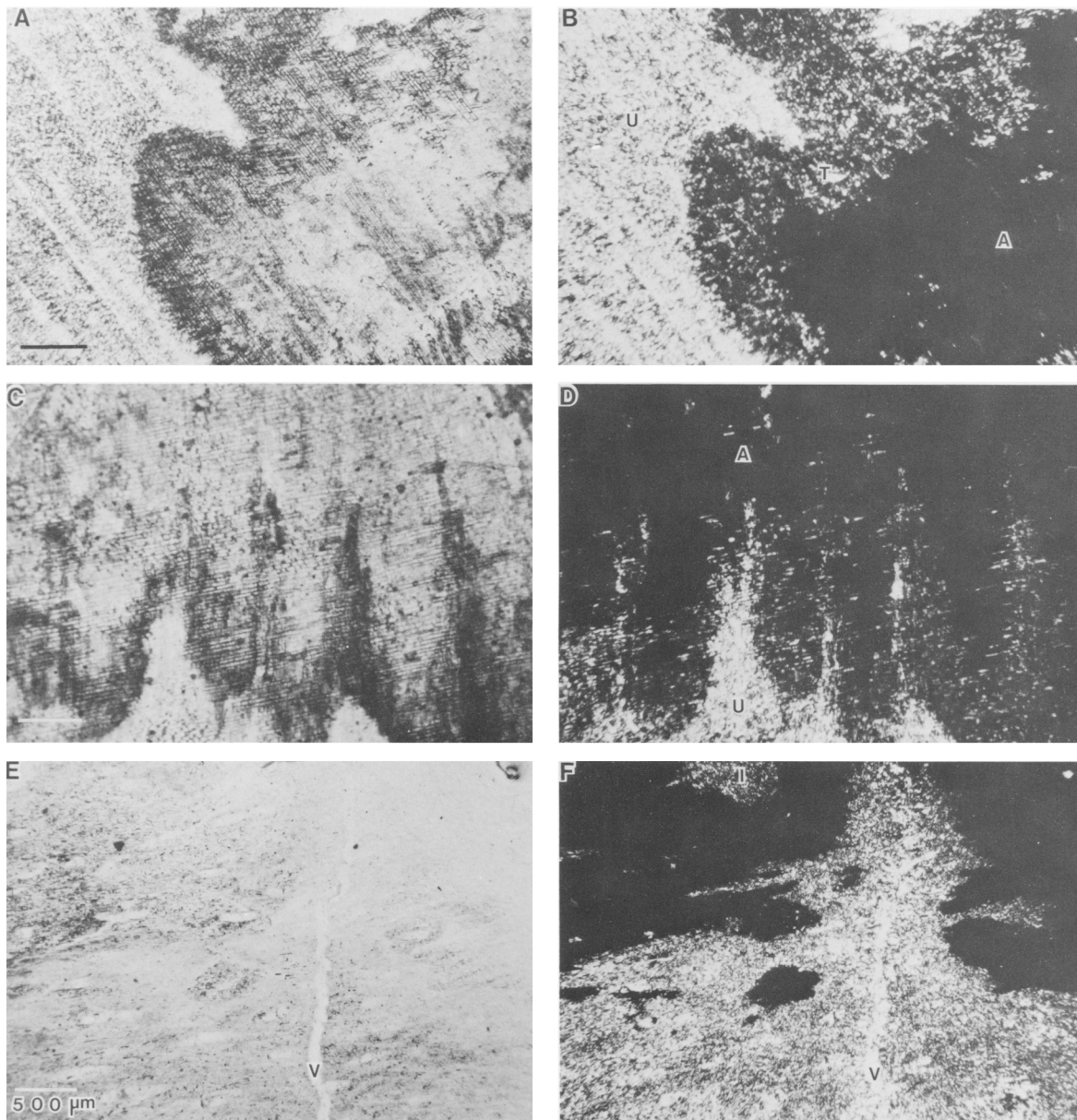


Figure 5. Photomicrographs of thin sections cut across the boundary between altered (A) and unaltered (U) zones. The zones are barely distinguishable in plane polarized light (a, c, and e). Under crossed polarizers (b, d, and f), altered zone is isotropic and is represented by black areas. Bar is 500 μm .

peratures were in the range of 30°–50°C (R. N. Clayton, The Enrico Fermi Institute, University of Chicago, Illinois 60637, personal communication, 1985). All the samples appear to have a $\delta^{18}\text{O}$ value of about +30‰ relative to the SMOW standard. These data support the hypothesis that both the initial silicification process that resulted in the formation of the petrified wood and the subsequent weathering phenomenon occurred under relatively mild temperatures (30°–50°C).

Table 2. Isotopic composition of minerals in the coarse clay size (2–0.2 μm) fractions from altered and unaltered zones of petrified wood.

| Sample | $\delta^{18}\text{O}^1$ (‰) |
|-----------------------|--------------------------------|
| Powdery exterior | +31.8 ² |
| Intermediate zone | +30.4 |
| Consolidated interior | +28.7 |

¹ Vs. SMOW.

² Averages of 2 analyses.

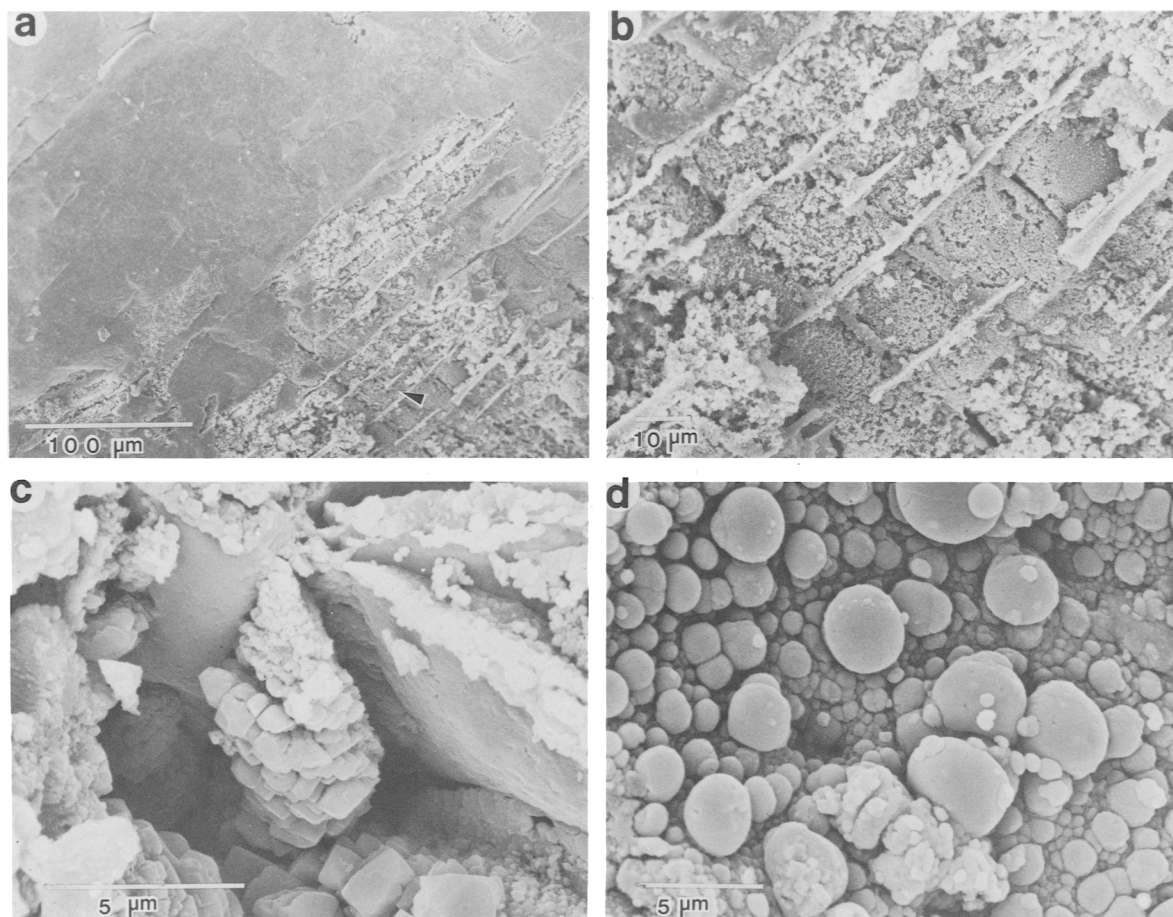
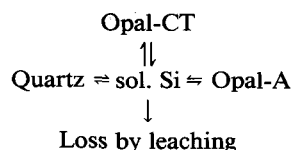


Figure 6. Scanning electron micrographs showing (a) initial stages of dissolution process, (b) original cellular morphology of wood in zone (indicated by arrow in (a)) that has been affected by dissolution, (c) euhedral microcrystals of quartz common in unaltered zone and (d) spherical opaline bodies characteristic of altered zone.

SUMMARY AND CONCLUSIONS

When subjected to alternating wetting and drying cycles, the silica minerals present in the unaltered consolidated petrified wood dissolved to release Si, as follows:



Some of the silica released may have been lost from the system by leaching or reprecipitated (during the subsequent drying cycle) either as opal-CT or opal-A which probably converted to opal-CT on aging. The resulting high concentrations of silica in the solution favored precipitation of disordered silica phases rather than well crystalline quartz. Formation of quartz would have been favored by higher temperatures associated

with diagenesis or slow rates of precipitation from dilute solutions under normal surface conditions (Jones and Segnit, 1971). The weathering process resulted in a gradual disruption of the cellular structure of the petrified wood. The hard consolidated wood was eventually transformed into the soft, powdery material consisting chiefly of disordered silica phases. Although data for only one specimen have been discussed in this report, many other petrified wood specimens from the College Station area show the same weathering features.

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