

cost English edition of *Why Not Creation* in Russian speaking countries. It was approved to distribute Tom Barnes' new book on science and the Bible. The quarterly/editorial report by DeYoung was given as follows: a meeting was held with the printer and agreement was made on some cost cutting measures. It was passed that the Board express its appreciation to Editor DeYoung for five years of past service and Associate Editor Williams for ten years of past service in publishing the CRSQ.

The financial report by Zimmerman was given as follows: it was recommended that 1) the Board develop and follow procedures for responsible accountability: a) develop a line item budget for each activity, especially the Director of VARC, b) no spending of funds unless specifically authorized in the budget or with approval of Supervisor/Chairman, c) require full disclosure of all expenses; and 2) request Treasurer to develop a voucher for use in processing expenses including categories, budget reference, approval and documentation.

It was passed that the Secretary send a letter of appreciation to Dr. John Klotz for his past 30 years of service to the CRS and the cause of creation. It was

passed to nominate E. Chaffin, L. Lester, D. Rodabaugh and G. Wolfrom for the 1994 Board of Directors election. Dr. Richard D. Lumsden was also nominated for the above slate. A budget for the VARC for 1994 was passed. It was passed that the issue of joining the Evangelical Council for Financial Accountability be determined by the Executive Committee.

It was passed that officers be nominated and elected by secret ballot. The following officers were elected for 1993/94: President, W. Frair, Vice President: D. DeYoung, Secretary: D. Kaufmann, E. Chaffin was appointed Editor and G. Howe was appointed Associate Editor of the CRSQ for the 1994/95-1998/99 five year term.

It was passed that the 1994 Board of directors meeting be held at Chino Valley, Arizona. Rodabaugh was appointed Program Chairman for the Friday night Mini-Symposium at our 1994 meeting at Chino Valley, Arizona. It was passed to increase all categories of dues except patron and life by two dollars each effective 1994/95 publishing year.

The meeting was adjourned at 1520 hours.

David A. Kaufmann
Secretary.

FOSSIL WOOD OF BIG BEND NATIONAL PARK, BREWSTER COUNTY, TEXAS: PART III — CHEMICAL TESTS PERFORMED ON WOOD

EMMETT L. WILLIAMS, GEORGE T. MATZKO, GEORGE F. HOWE, RICHARD R. WHITE AND WILLIAM G. STARK*

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Abstract

Various tests were performed on samples of wood collected from the Dawson Creek region of Big Bend National Park. No radiohalos were found in the charcoaled material. No C-14 was detected in a charcoaled wood sample. The silica content of the silicified wood specimens was found to be generally greater than 90%. Comments and a discussion of the test results are offered on the nodular objects found in and around a clay mound. All data were interpreted within a Diluvialist model where possible.

Key Words: Charcoaled Wood; Silicified Wood; Energy Dispersive X-Ray Analysis; Dawson Creek, Big Bend National Park.

Introduction

The formations in which fossil wood was found in the Dawson Creek area of Big Bend National Park were discussed in Part I (Williams and Howe, 1993). Also the importance of bentonite deposits in relation to the silicification of wood was presented and applications were suggested within a tentative catastrophist model. A theoretical model for the silicification of wood was elucidated in Part II (Williams, 1993). Possible rapid burial and silicification were discussed within the framework of a young earth model. An examination of autochthonous and allochthonous deposition of wood at various locations was included in Part II.

This part contains the results of the tests conducted on the wood samples (a search for radiohalos, C-14 dating measurement and various chemical analyses).

*Emmett L. Williams, Ph.D., 5093 Williamsport Drive, Norcross, GA 30092; George T. Matzko, Ph.D., 2902 Edwards Road, Taylors, SC 29687; George F. Howe, Ph.D., 24635 Apple St., Santa Clarita, CA 91321; Richard R. White, B.A., 2421 Brown Deer Trail, Acworth, GA 30101; William G. Stark, A.S., 942 Traymore Drive, Norcross, GA 30093.

Charcoaled Wood Samples

A fossil wood limb or small diameter log (Figure 1) was found buried approximately 20 feet deep at the base of a bentonite mound. The outside of the limb was mineralized (Figure 1c) whereas the interior was charcoaled (Figure 1d). Other smaller pieces of charcoaled wood were found in the mound (Figure 2) in "lenses" or layers about four feet apart vertically.

A specimen of charcoaled wood was subjected to a standard carbon analysis by a combustion technique and found to contain 59.2% carbon by weight. No elements were detected in an EDX (energy dispersive x-ray) analysis.* Since the lower detection limit is atomic number 10, carbon, oxygen and hydrogen would not be indicated if present. However the mineralized exterior (Figures 1c and 2), when analyzed by EDX techniques, revealed the presence of silicon, iron, sulfur, calcium, potassium and aluminum (Figure 3).

*For an introductory explanation of this technique, see Vaughan, 1989.



Figure 1a. Location of charcoalified wood limb (?) in bentonite mound. Emmett L. Williams is pointing to the specimen—Dawson Creek area, Big Bend National Park. Photograph by George F. Howe.



Figure 1b. A closer view of the charcoalified limb (~4 inches in diameter). Photograph by George F. Howe.



Figure 1c. Another view of fossil site—charcoalified interior of limb with pieces of the mineralized exterior shown to the right of the 5.5-inch mechanical pencil. Photograph by George F. Howe.

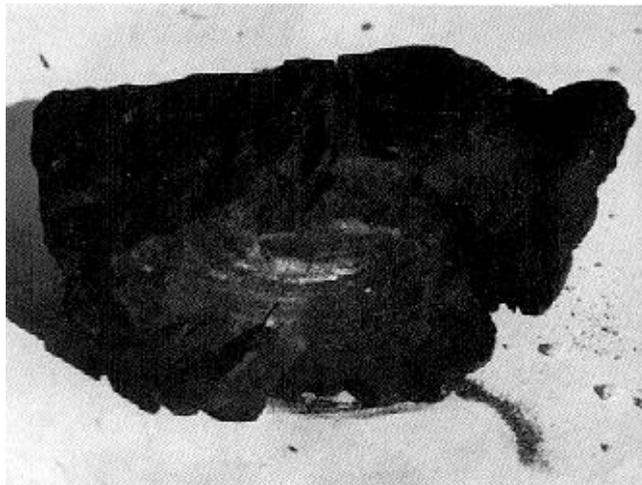


Figure 1d. Charcoalified interior of limb. Photograph by George F. Howe.

No Radiohalos Detected

Thin sections of various charcoalified wood samples were prepared and examined by Robert Gentry of Earth Science Associates. He found no radiohalos in any of the thin sections as was found in coalified wood samples he had examined in previous studies (Gentry, et al., 1976). He writes (1991):

... thin sections ... were microscopically examined for radioactive halos and/or radioactive staining ... no visual evidence of staining from radioactivity was found. The obvious conclusion is that uranium and its daughters are not present in the specimens in sufficient quantities to have caused discoloration as seen in many coalified wood specimens from the Colorado Plateau and Chattanooga shale.

Radiocarbon Age Measurement

A sample of charcoalified wood was subjected to a radiocarbon age determination. The specimen was cleaned to remove dirt and other foreign material and



Figure 2. Small piece of charcoalified wood with mineralized exterior seen above the hammer. This fossil was found higher in the same bentonite deposit as in Figure 1. Photograph by Emmett L. Williams.

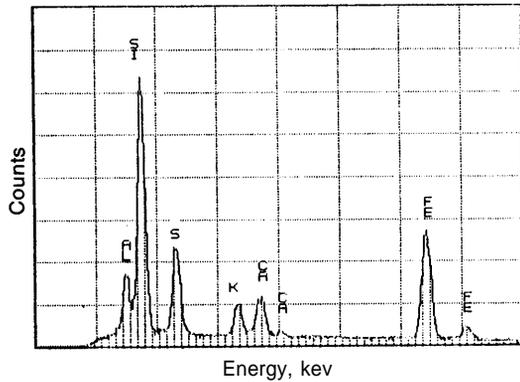


Figure 3. EDX spectrum of mineralized exterior of charcoalfied wood; Si—silicon, Al—aluminum, S—sulfur, K—potassium, Ca—calcium, FE—iron.

then was split into small pieces. It was treated with hot dilute hydrochloric acid to remove any carbonates and then treated with hot dilute sodium hydroxide to remove humic acids and other organic contaminants. After washing and drying, the pieces were combusted to recover carbon dioxide for the analysis. No C-14 was detected, thus the age according to the Libby method (equilibrium model) was greater than 42,000 C-14 years BP.* Using the nonequilibrium model, the age telescopes to approximately 5350 years BP (Brown, 1992). Also a recent article on the nonequilibrium model of C-14 age determination (Whitelaw, 1993) may be of interest to the reader.

Infrared Spectrum

An infrared spectrum was obtained from a sample of the charcoalfied wood dried for approximately 82 hours over calcium sulfate in a dessicator and then pressed into a KBr pellet. The resultant spectrum, shown in Figure 4, is similar to Cope's spectrum 5e (1979, p. 670) of a Mesozoic charcoalfied phytoclast,** except that there is more OH stretching absorption from our sample. A discussion of this spectrum is contained in Appendix I.

Speculations Concerning the Charcoalfied Wood Limb

The carbon content (59.2%) of our charcoalfied wood sample is lower than any of Cope's Mesozoic charcoalfied phytoclasts (Cope, 1979, p. 666) by about eight percent. Thus the presence of more oxygen and hydrogen in our sample would result in greater absorption of incident infrared radiation in the OH stretching frequency range.

When wood is pyrolyzed, gases such as carbon monoxide, methane and hydrogen as well as tars are produced in the temperature range of 280-500°C (Cope and Chaloner, 1985, p. 258). Likely our sample was not exposed to as high temperatures as the ones analyzed by Cope. Thus not as much oxygen and hydrogen were released during natural pyrolysis of the limb and this is reflected in a lower carbon content. The more decomposition of wood achieved during pyrolysis, the higher the carbon content of the remaining charcoal.

*Radiocarbon age determination was performed by Geochron Laboratories Division, Krueger Enterprises, Inc., Cambridge, MA.

**Organic particles which show evidence of plant origin and behave as discrete clasts during sedimentation.

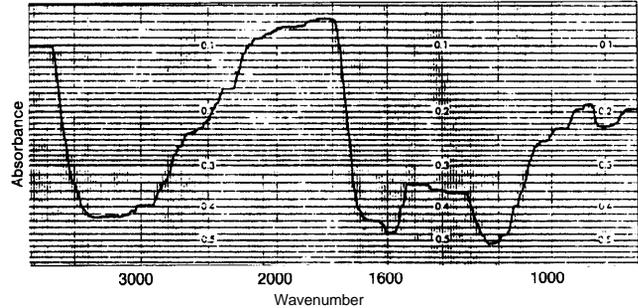


Figure 4. Infrared spectrum of charcoalfied wood sample.

In analyzing artificial charcoals produced from Sequoia wood (Cope, 1979, p. 667), the following carbon composition vs. pyrolysis temperatures were found (Table I). We can conclude from these data that the interior of the charcoalfied limb reached temperatures between 320 and 360°C during natural pyrolysis.*

Table I. Carbon Content of Dry Wood and Artificial Charcoal (Sequoia Wood) (Cope, 1979, p. 667).

Specimen	Carbon Content (weight percent)
Sequoia wood, dry	47.8
Sequoia wood pyrolyzed to 300°C	55.2
Sequoia wood pyrolyzed to 400°C	65.5

Assuming the reliability of the laboratory procedures in the determination of radiocarbon content and the accuracy of the nonequilibrium calculation, the charcoalfied limb (Figure 1a) possibly was from a pre-Flood or early post-Flood tree. It could have been deposited at or near the site of discovery by receding Flood water or during a period of post-Flood erosion and transport (after-effects of the Flood). Eventually (likely very quickly after deposition) the limb may have been exposed to hot volcanic gases and/or hot falling volcanic ash.** Absorbed water was expelled and the interior of the limb was baked at temperatures slightly above 300°C. The exterior of the limb was subsequently mineralized. This mineralization combined with burial under bentonite prevented water penetration and later silicification, preserving much of the interior structure of the wood. This speculation is offered as only one of the several possibilities of how the charcoalfied wood was formed and buried at this location.

Origin of Fossil Charcoalfied Wood

This type of fossil wood is referred to as fossil charcoal or fusain by Sander and Gee (1990) who stated that:

Although its origin was formerly in dispute, it is now clear that fusain is the result of wildfire and does provide an additional source of paleobotanical information. Through charring, wood is rendered into an excellent preservation state . . . (p. 269).

Herendeen (1991a; 1991b) labeled fusinized wood as charcoalfied wood and we prefer this designation.

*As can be observed in Figure 1c, a shrinkage of interior wood structure occurred probably during pyrolysis. See McGinnis et al., 1974 for an investigation of artificially charcoalfied wood and their discussion of the shrinkage of cellular dimensions as a result of pyrolysis.

**See Austin, 1984, pp. 87, 89 for a brief discussion of the temperatures that can be attained by ash blown from a volcano.

Earlier Schopf (1975, pp. 44-45), in discussing fusinized plant tissue, made the following comments on the concept that fusain is a result of fires:

The prevalence of the minor proportion of fusain and the fact that fusain is most abundant in Paleozoic coals (4-15 or 20%) and least abundant in Tertiary coals (1 or 2%) does not seem to favor origin by fires. The charcoal theory of origin of all fusain is principally objectionable because it is commonly taken to be an indication of periodic drouth [sic] and a susceptibility of vegetation to conflagration for which all other evidence is lacking. But if forest fires were such a consistent element of the ancient environment, surely other clear indications of heating also would be found. Instead of this we find resinous bodies, for example, variously preserved. Some of those which may even be closely associated with fusain are scarcely altered. Others obviously are fusinized, just like some of the cellulosic and lignocellulosic tissues. For some and probably for the majority of the occurrences of fusain, the forest fire origin seems ruled out (p. 45).

However, as noted at the beginning of this section, the generally accepted mechanism for the formation of fossil charcoal is wildfire. Also as noted there has been controversy concerning the origin of fusain. See Cope, 1979 for a brief discussion of the "fire" vs. "non-fire" origin proposals for fusinite. M. J. Cope and W. G. Chaloner have promoted the fire origin hypothesis for the material as well as performed many studies on charcoalfied wood (i.e., Cope, 1979; Cope and Chaloner, 1980; Cope and Chaloner, 1985; Chaloner, 1989). They claimed:

[Fossil] Charcoal results from incomplete combustion of plant tissues . . . and is a common product of natural wildfires (forest fires). . . . Such burning has three essential requirements: (1) a suitable fuel, (2) an ignition source, and (3) the necessary level of atmospheric oxygen to support combustion. Suitable natural ignition sources are lightning strike, volcanic activity, meteorite fall, spontaneous combustion and sparks due to a rock fall (Cope and Chaloner, 1980, p. 647).

Another piece of charcoalfied wood has been found about seven miles southwest of our collection site at Rattlesnake Mountains in Big Bend National Park and reported by Sander and Gee, 1990. We suggest that due to the post-Flood volcanic activity in the Big Bend area, the likelihood of finding fossil charcoalfied wood is high.

Chemistry of Silicified Wood

Sections (Figures 5 and 6) of silicified logs as well as fragments of disintegrating logs were found in the collecting area* (shown in Figures 1a and b of Williams and Howe, 1993, p. 49). A typical EDX spectrum of

*The silicified wood generally is located in steeply-sloped bentonitic clay deposits (mounds or rounded knobs) well above the desert pavement. During periods of erosion the logs are exposed as the sediment is washed away. Continued erosion causes the wood to slide or tumble down the steep slopes to the base of the mound. Sometimes the logs are located some distance away from the base of the clay mounds. Weathering causes the exposed logs to break into various-sized fragments.



Figure 5a. Silicified sections of logs at the base of a clay mound. Recent erosion caused the sections to be washed from a higher position in the mound—Dawson Creek area, Big Bend National Park. Photograph by Emmett L. Williams.



Figure 5b. Exposed end of silicified log found approximately 30 feet above the base of a clay mound—Dawson Creek area, Big Bend National Park. Photograph by George F. Howe.

pieces of this wood is given in Figure 7. The major constituent is silicon (indicative of a high SiO_2 content) with trace amounts of aluminum, sulfur, potassium, calcium and iron. The silica (SiO_2) content of these specimens varied between 94 and 96%. Quartz, containing 96-97% silica, was deposited in fissures in some of the silicified logs (Figure 8, this report; also see Figure 1, Williams, 1993). A translucent specimen of silicified wood with more visible structural detail (Figure 9) was studied. Only silicon was indicated on the EDX spectrum (Figure 10) and the silica content of the sample was found to be 93-95%.

Lighter-colored specimens were found in the collecting area shown in Figure 1c of Williams and Howe, 1993, p. 49. A typical disintegrating section of fossil wood can be seen in Figure 11. Specific pieces are shown in Figure 12. An EDX analysis revealed mainly silicon with traces of magnesium and aluminum. The silica content obtained from two determinations was



a.



b.



c.

Figure 6. Exposed disintegrating silicified logs—Dawson Creek area, Big Ben National Park. a. Photograph by Glen W. Wolfrom, b. and c. Photographs by Emmett L. Williams.

approximately 85 and 96%. The silica content of the various samples is given in Table II and the procedure for the analysis is given in Appendix II.

Calcified Wood or Mineral Nodules?

In the collecting area, shown in Figure 1c of Williams and Howe, 1993, p. 49, several rounded, nodular-like objects (Figures 13-15) were scattered over the desert pavement, evidently exposed by erosion of a clay mound. Assuming these objects to be specimens of silicified wood we found, however, that they contained only 4-5% SiO₂ (Table II). An EDX analysis (Figure 16)

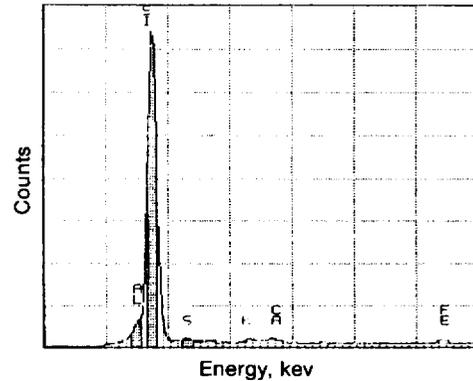


Figure 7. EDX spectrum of silicified wood fragments; Si—silicon, Al—aluminum, S—sulfur, K—potassium, Ca—calcium, Fe—iron.

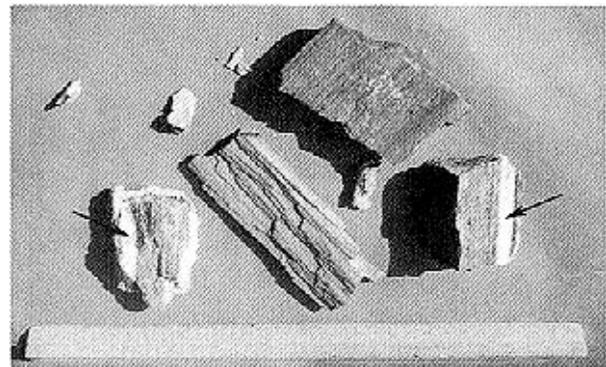


Figure 8. Fragments of silicified wood containing infiltrated quartz (white areas indicated by arrows). Photograph by Emmett L. Williams.

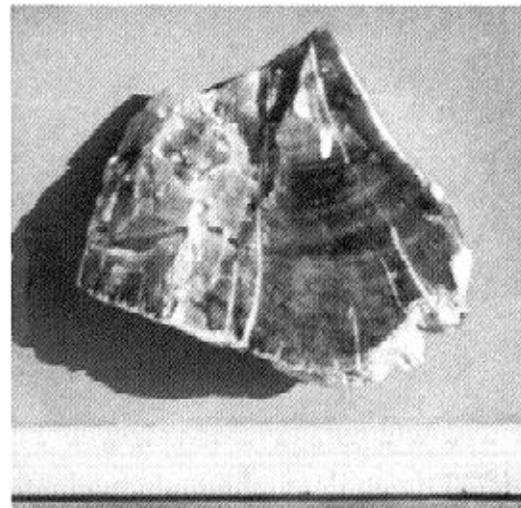


Figure 9. Translucent silicified wood fragment—Dawson Creek area, Big Bend National Park. Photograph by Emmett L. Williams.

Table II. Silica Content of Silicified Wood From the Dawson Creek Region of Big Bend National Park.

Specimen Designation	Reference Photographs	Weight Percent SiO ₂
19—dark brown pieces	Figures 5 and 6	94.85 ± 1.07
19—infiltrated quartz	Figure 8	96.82 ± 0.50
19—translucent specimen	Figure 9	94.12 ± 1.61
25—light brown fragments	Figures 11 and 12	90.72 ± 8.03
CN—calcified wood/nodules?	Figures 13,14 and 15	4.8 ± 0.5

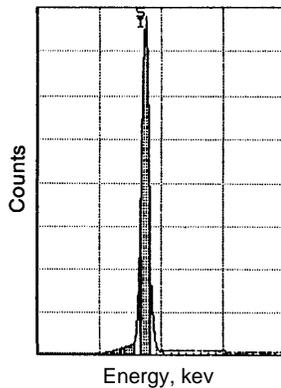


Figure 10. EDX spectrum of translucent silicified wood fragment.



Figure 11. Fragmented silicified wood—Dawson Creek area, Big Bend National Park. Photograph by Glen W. Wolfrom.

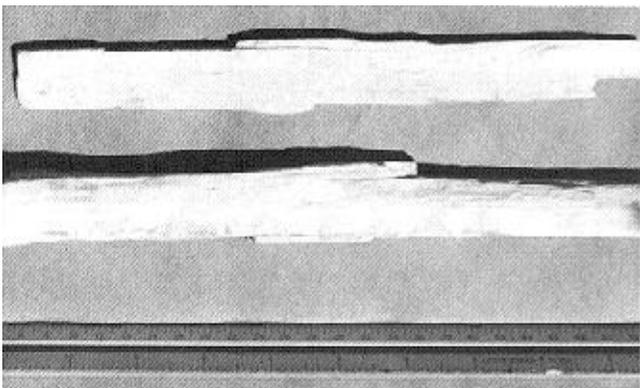


Figure 12. Individual pieces of the wood shown in Figure 11. Photograph by Emmett L. Williams.

showed an unusually high calcium content. Further chemical analysis indicated a calcium oxide content of 51-52% which converts to 91-93% CaCO_3 . Density measurements and dry ashing of samples at 900°C indicated that this 91-93% estimate is essentially correct. The procedure for the analysis for calcium oxide (CaO) is given in Appendix III.

Since the silica content of the rounded objects was low, initially it was decided they were indeed mineral nodules. Maxwell, et al. (1967, pp. 88, 91), in discussing the Javelina formation reported the presence of:



Figure 13a. Disintegrating rounded nodules on desert pavement near clay mound. Photograph by Emmett L. Williams.



Figure 13b. Fragments from another rounded nodule. Photograph by George F. Howe.

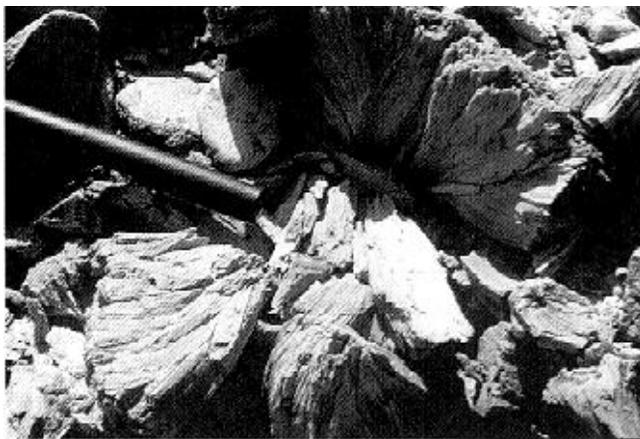
... impure concretionary-like nodules of calcium carbonate, $\frac{1}{4}$ inch to $2\frac{1}{2}$ inches across with a few up to 8 inches across. They have rough surfaces and some nodules have radiating interior structures or shrinkage cracks commonly filled with calcite.

The rounded nodules (?) we studied definitely have a radiating interior but some do not have a particularly rough surface. The nodules (?) examined are in various states of preservation—some can be broken apart by hand, whereas others can be broken apart only with the use of a hammer.

When pieces of the rounded objects were subjected to scanning electron microscopy at magnifications of 1000X, possible wood-like structures were detected. (A discussion of the microscopic structure of all of the specimens will be presented in Part IV of this series.) At this time we have reached no definite conclusions as to whether the material is fossil wood or mineral nodules. Representative samples of all of the various materials collected [charcoalified wood, silicified wood and calcified wood/nodules(?)] have been sent to Dr. Elisabeth Wheeler of North Carolina State University, an authority on the structure of wood, for identification.



a.



b.

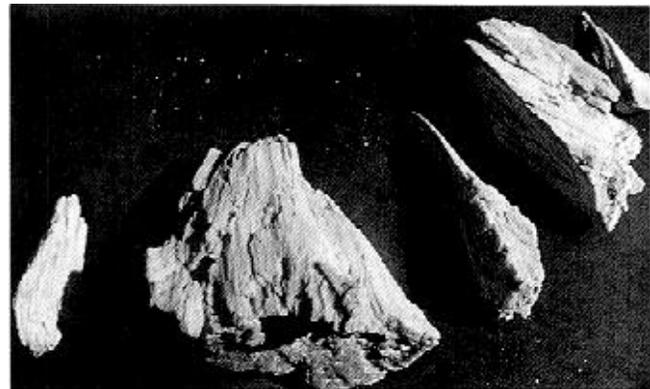
Figure 14. Close-up views of disintegrating nodules. Photographs by Glen W. Wolfrom.

Conclusions and Conjecture

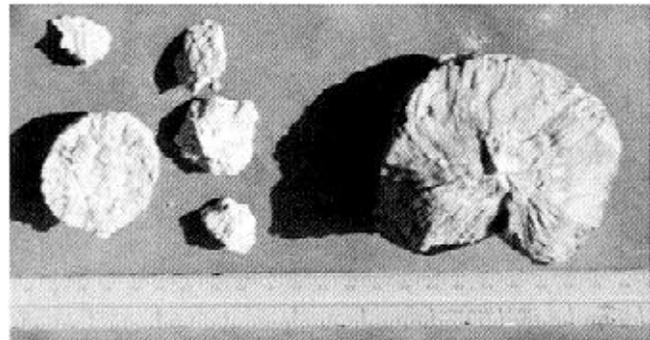
The chemical analyses of fossil wood samples from the Dawson Creek area of Big Bend National Park have been reported in this article. The silicified specimens usually contain over 90% silica. Smaller amounts of other elements present in the samples could have come from the overlying clay, or could have been introduced into the fossils during a period of intense volcanic activity after the Flood. For instance, sulfur could have entered the deposited wood as dissolved sulfur dioxide since SO₂ is emitted from active volcanos.

The carbon content of the charcoaled specimen we analyzed indicates that the interior of the wood was subjected to temperatures in the range of 300-400°C. An interesting riddle is why some of the wood in this area is silicified, while some is charcoaled. We attempt an answer based on a Flood model. Assuming all of the wood was transported to the Dawson Creek area by receding Flood water, some of the wood was left exposed (not covered by sediment) and was subjected to burning or baking (under a covering of settling hot volcanic ash) during a period of post-Flood volcanic activity. Later post-Flood reworking during possible transgression and regression cycles could have buried the once exposed wood.

Other logs could have been buried under silica-rich sediments by receding water and not exposed to any



a.



b.

Figure 15. Fragments from nodules. a. Photograph by George F. Howe, b. Photograph by Emmett L. Williams.

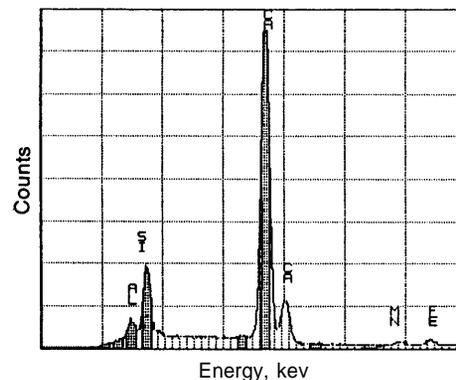


Figure 16. Typical EDX spectrum of calcified wood/nodule? CA—calcium Si—silicon, Al—aluminum, Mn—manganese, Fe—iron.

pyrolysis during the volcanic activity. These samples could have silicified later during a postulated post-Flood period of high precipitation. As noted in Part II of the series, rapid silicification of wood is definitely possible. The authors realize the tentative nature of these suggestions and that other explanations could account for the field evidence.

Acknowledgments

Bryan Vogt, Chemistry Department, Bob Jones University graciously performed the infrared spectroscopy on a sample of charcoaled wood. The following people offered helpful comments on the manuscript: Robert H. Brown, Larry Helmick, Glen Wolfrom and John Woodmorappe. The opinions expressed in this paper remain solely those of the authors. The authors

thank the many donors to the Creation Research Society Research Fund, interest from which financed a portion of these studies. Appreciation is expressed to personnel of the Southwest Region of the National Park Service and personnel of Big Bend National Park for allowing us to collect the various fossil wood specimens.

Appendix I

Analysis of Infrared Spectrum of Charcoalified Wood

The theory of absorption of infrared radiation by characteristic molecular vibrations can be studied in various treatises, e.g., Nakamoto, 1970. The principal absorptions shown in Figure 4 are likely a result of the following characteristic vibrations (Cope, 1979, p. 671; Nakamoto, 1970, p. 322):

3500-3000 cm ⁻¹	OH stretching
3050-2850 cm ⁻¹	CH stretching
2920 and 2850 cm ⁻¹	aliphatic CH ₂ stretching
1700 cm ⁻¹	C=O stretching
1600 cm ⁻¹	C=C stretching in aromatic rings and polyaromatic structures
~ 1200 cm ⁻¹	C-C skeletal vibrations, C-OR stretching, C-OH deformation
~ 800-740 cm ⁻¹	aromatic CH bending, out-of-plane CH bending

Cope (1979, p. 671) noted that "... charcoalified clasts ... differ from the coal fusinites by the presence of absorptions corresponding to aliphatic CH₂, C=O and OH groups." Thus infrared spectra along with other analytical data can be used to differentiate charcoalified wood from coal fusinite. Likewise an absorption of infrared radiation in the 800-740 cm⁻¹ range indicates charcoalified wood rather than natural or artificial charcoal.*

Appendix II

Analysis for Silicon Dioxide

1. Specimens were ground to a fine powder and dried at 110°C for one hour.
2. The mass of the powder analyzed ranged from 0.1 to 0.6g and was digested either in fuming nitric acid or aqua regia in a digestion bomb at 150°C for one hour.
3. After digestion, the liquid was transferred to a porcelain crucible and treated with concentrated hydrochloric acid.
4. The sample was evaporated to dryness at 150°C in order to dehydrate any soluble silicates.
5. The residue was redissolved in concentrated hydrochloric acid, filtered and rinsed with deionized water.
6. The sample and ashless filter paper were charred then ignited at 1000°C for one hour.
7. The sample was cooled and weighed. This remainder was reported as percent SiO₂.

*Dr. Larry Helmick (personal correspondence, 1993) offered the following comments:

A strong, broad IR absorption band from 2500 to 3666 cm⁻¹ is very typical of hydroxyl groups of carboxylic acids. Strong absorption at 1766 and 1266 is also typical of C=O and C-O stretching of carboxylic acids, which further supports the presence of a carboxyl group. Spectra with strong OH stretching absorption bands should also exhibit OH bending bands, which might account for the weak band at about 800 cm⁻¹.

Appendix III

Chemical Analysis for Calcium Oxide

1. Half-gram samples were weighed to the nearest 0.1 mg.
2. Ten ml of 12M HCl were added to each sample and the sample was sonicated until dissolution appeared to be complete.
3. A 10 ml aliquot of solution was transferred to a conical flask and 15 ml of NH₃-NH₄Cl buffer, 50 mg of ascorbic acid and 10 ml of a solution, 0.4 M in NaCN and 0.75 M in triethanolamine as well as 4 to 5 drops of 0.1% calmagite, were added.
4. This solution was titrated with a 0.015 M EDTA solution which had been standardized against primary standard CaCO₃.

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