Wood opals from Yakuplu, Turkey: their properties and genesis

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Fossil driftwood from Sarmatian (Late Miocene) gravel deposits near Yakuplu, Turkey, ranges between lignitic and opaline. Opalization occurred in various stages of decay. The stage of decay of the wood and the eventual admixture of detritic clay influenced the crystallinity and the dehydration characteristics of the opal. Opals influenced by the host rock seem to have montmorillonitic suprastructures. Opalization was probably the result of the weathering of volcanic ash layers in the overlying strata.

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Introduction

Wood opals are opaline pseudomorphs after wood. Wood opals generally show an excellent preservation of the original wood structure and they have been studied by palaeobotanists for a long time.

Although the mineralogy of wood opals was sometimes included in investigations on precious opals (e.g. Segnit et al., 1965), and was more recently studied by Buurman (1972) and Mitchell & Tufts (1973), its genesis was hardly ever discussed and it is still poorly understood.

Wood opals are known from all over the world. Classical sites are located, among others, in Hungary.

Schréter (in Andreánszky & Schréter, 1959) described the relation between rhyolitic tuffs and opalized wood in Hungary. He supposed that silica, liberated by the weathering of rhyolite, caused the opalization of wood in the underlying strata.

In order to study genetic relations between host rock and wood opals, the author visited classic wood opal sites in Austria and Hungary, and in Turkey an occurrence of wood opals that was recently discovered by Mr J. Buurman, an astronomist of Utrecht University.
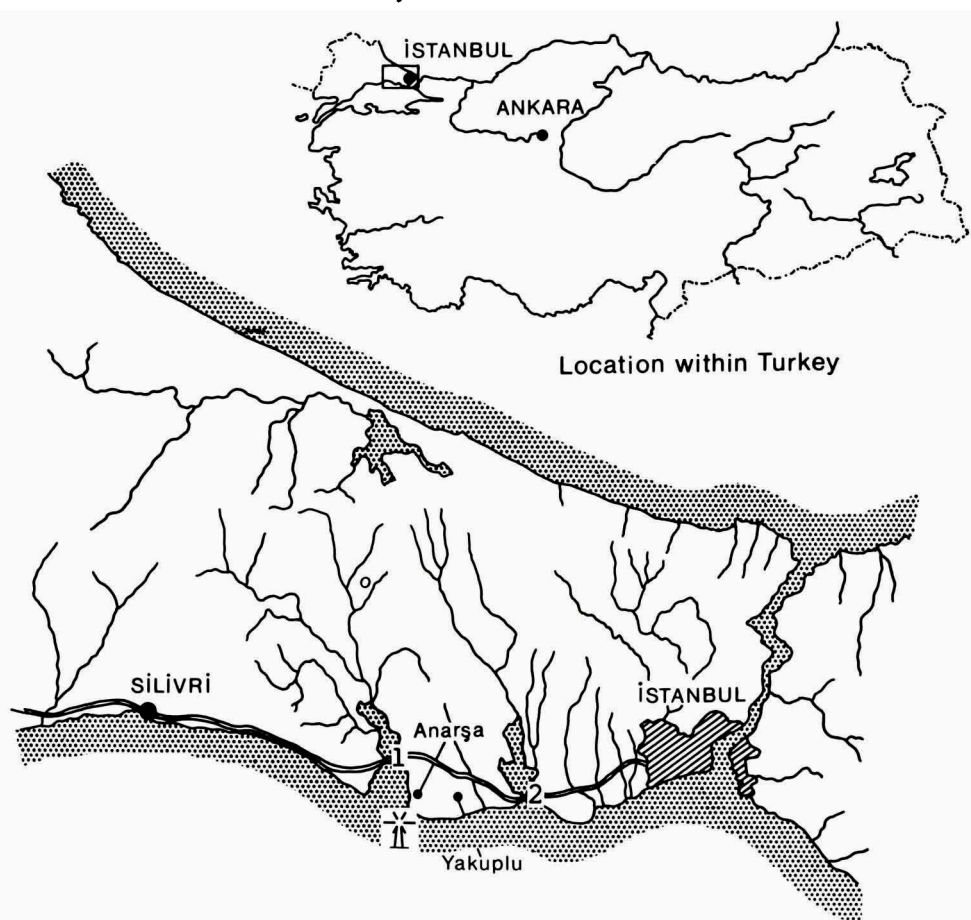

Fig. 1. Location map. 1= Büyük Çekmece; 2= Küçük Çekmece.

Although collecting was succesful in Hungary, thanks to the aid of Dr I. Pálfalvi of the Hungarian Geological Institute, and in Austria, conditions of the exposures visited were not suitable for detailed study. The exposures in the cliffs south of Yakuplu and Anarsa, Turkey (Fig. 1), however, were well accessible and could be studied.

Part of the collection is still in the possession of the author, the other part is stored in the Rijksmuseum van Geologie en Mineralogie (the Netherlands National Museum of Geology and Mineralogy) in Leiden.

Acknowledgements

Fig. 2. Cliff with gravel bank, south of Yakuplu.

Geological outline

The coast of the peninsula between Büyük Çekmece and Küçük Çekmece, south of the villages of Yakuplu and Anarsa consists, according to the Geological Map of Turkey, Sheet Istambul (1964), of Sarmatian (Late Miocene) and Pliocene deposits.

A reconnaissance along the coast learned that these deposits, from the lighthouse eastward, consist of marine limestones with shell remains (oldest) and whitish gravelly kaolinitic deposits with a single cobbly level of about 5 m thick, about 1.5 km east of the lighthouse. The strata are dipping eastward.

Along the shore, cliffs in the marine limestones are low but well exposed. The limestones do not show any wood remains. Most of the cliffs in the gravel deposits are obscured, but for about 200 m on each side of the cobbly level 5-10 m high cliffs are well exposed (Fig. 2).

In the cobbly layer two kinds of fossil wood are found: chalcedonic and quartzous rounded fragments, up to 0.5-1 m in length occur; opaline, black and brown not-rounded specimens were found in both the cobbly layer and in the over- and underlying finer grained deposits. The opaline wood occurred in pieces up to one metre long and 40 cm across.

Fig. 3. Conglomerate with opaline cement. Length of hammer = 33 cm.

This investigation was concentrated on the opaline wood, because its angular habit suggested in situ opalization, while the rounded woods in the cobbly level have been transported after silicification.

THE OPALINE WOODS

The in situ woods show a complete range between lignitic and opaline. The essentially lignitic woods are easily broken, show evidence of burrowing, and have dark brown colours.

Some woods are partially lignified and partially opalized. The opal in these woods has on oily appearance and a somewhat splintery fracture. The colour of these fossilizations is pitch black, generally with lighter, yellowish or greenish transitions towards the host rock.

The next stage is fully opaline, pitch black and glassy, and has a conchoidal fracture. Specimens of this group show caves and veins filled with chalcedony and quartz.

A last group of wood opals shows concentric structures in the opaline material: a brown core with distinct structure, followed by a pitch black glassy rim, a white or yellowish green glassy rim, and finally, a yellowish green, granular rim that gradates into the host rock.

Wood structures in the black opals are hardly recognized macroscopically.

There is no difference between the woods extracted from the cobbly level and those from the adjacent layers. A most remarkable feature is the cementation of parts of the cobbly layer with yellowish green opaline material. These layers have a conglomeratic appearance and a brittle consistence (Figs. 3, 4). They occur randomly in the cobbly level. Their thickness varies, but may reach more than one metre.

Fig.4. Conglomerate with opaline cement, detail; x 1/3.

The following samples were taken for further investigation:

Group 1 — lignitic wood with little opalization, nr. 258, RGM 173 725.

Group 2 — partially lignitic, partially opaline, not glassy, nrs. 252, 253, 255, RGM 173 717, 173 714, 173 726.

Group 3 — predominantly opaline, glassy, with veins of chalcedony, nrs. 254, 256, 257, 260, 262, 263, 288, RGM 173 716, 173 718, 173 713, 173 722, 173 719, 173 712, 173 723.

Group 4 — zoned wood opals, nrs. 261, 289, RGM 173 715, 173 724; brown core, nr. 188; black rim, nr. 189; yellowish rim, nr. 190; greenish yellow, granular passage to host rock, nr. 191.

Group 5 — yellowish green cast of woody stem with little macroscopically detectable wood structure, nr. 259, RGM 173 721.

Group 6 — opaline cement in conglomerate, nr. 290, RGM 173 720.

Opals of groups 2 through 5 have yellowish green outer rims, merging into the host rock. Thickness of these rims varies between several millimetres and several centimetres.

Investigation

METHODS

All specimens were studied with the aid of X-ray diffraction, thermal analysis and thin sections. Some samples were subjected to chemical analysis.
    X-ray diffraction analysis was carried out with a quadruple Guinier-de Wolff camera and with a diffractometer, both using Fe-filtered Co-K alpha radiation.
    Differential thermal analysis (DTA) was carried out with a DuPont 900 apparatus in combination with a 550° Cell; for thermogravimetry (TGA) a DuPont 950 thermobalance was used in combination with a DuPont 990 unit.
    Chemical analysis was carried out by way of X-ray fluorescence (XRF).

X-RAY DIFFRACTION ANALYSIS

The XRD patterns from the Yakuplu wood opals fall apart in two distinct groups.
    The first group, the brown and black opalizations, shows an X-ray pattern (Fig. 5a) characteristic for opal-CT (Jones & Segnit, 1971). The second group, consisting of yellowish green opalizations both within black opals and as rims on opals of groups 2 through 5, shows the pattern of opal-CT with strong additional

lines: (d=) 14, 10, 4.45, 1.51 Å (Fig. 5b).

The opaline cement of the host rock (sample 290) gave an X-ray diffraction pattern very similar to that of the yellowish green opals, but with a less distinct 4.35 Å reflection. This indicates a lesser amount of tridymitic stacking in this opal.

Most opals, some of group 4 (188, 189) excepted, contain some quartz.

The additional lines in the greenish opaline materials correspond with those of clay minerals of the mica and smectite groups. The 14 Å (7° 2 θ) reflection shifts to 17 Å upon treatment of the sample with glycerol. It should be noted, however, that randomly oriented powders were used in the X-ray diffraction, and that strong (001) reflections of clay minerals in randomly oriented samples are unusual.

The zoned opals (188-191) show opal-CT in the centre and in the black rim. The yellowish rim and the outer part have equally strong 14 Å reflections,
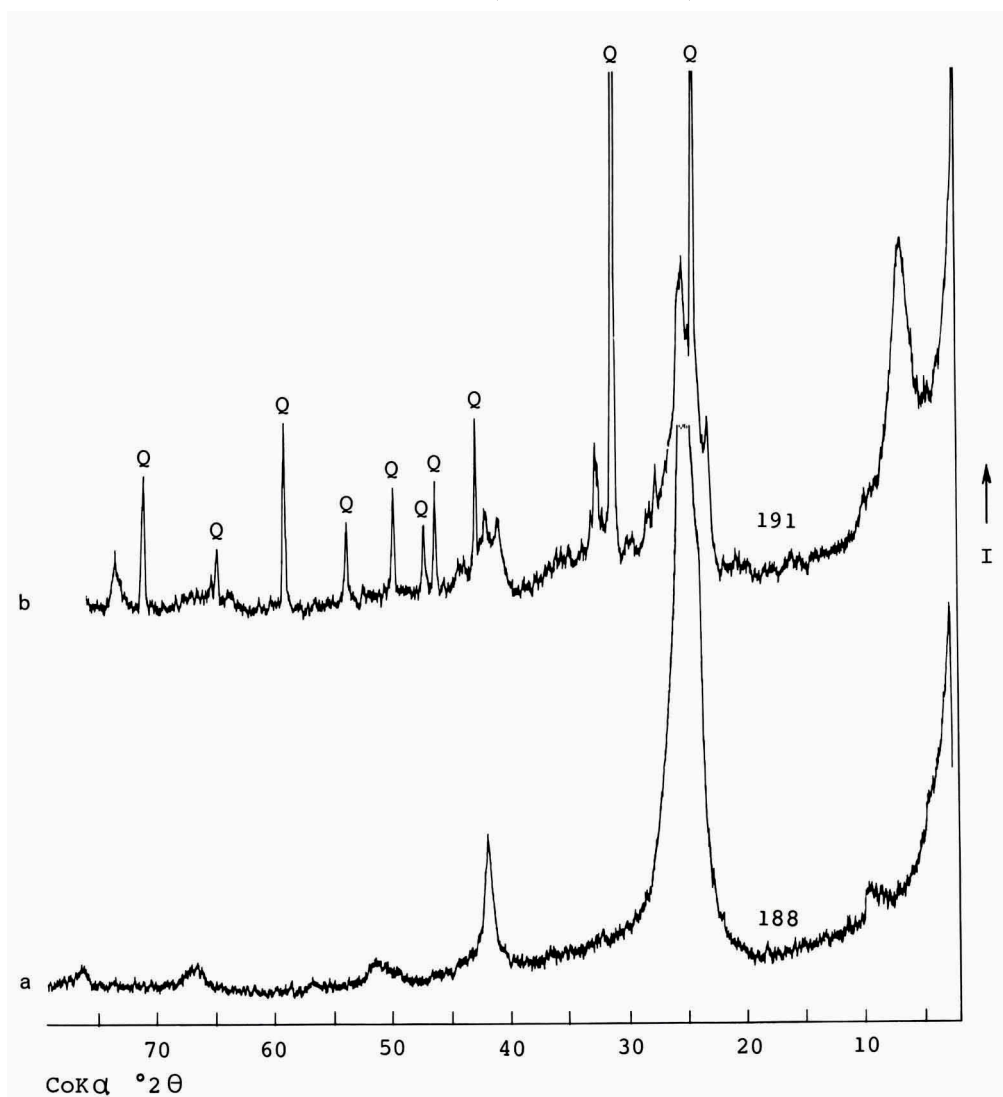

Fig. 5. Diffractometer traces of samples 188 (brown) and 191 (greenish). Co-K alpha radiation. Q = quartz. Unoriented.

while the opal-CT reflections are less intense in the outer sample. Quartz is present in samples 190 and 191. A weak 10 Å reflection is found in sample 188 (core).

THERMAL ANALYSIS

Just as in X-ray diffraction, greenish yellow opaline material gave results quite different from those of brown and black samples. For comparison, the DTA and
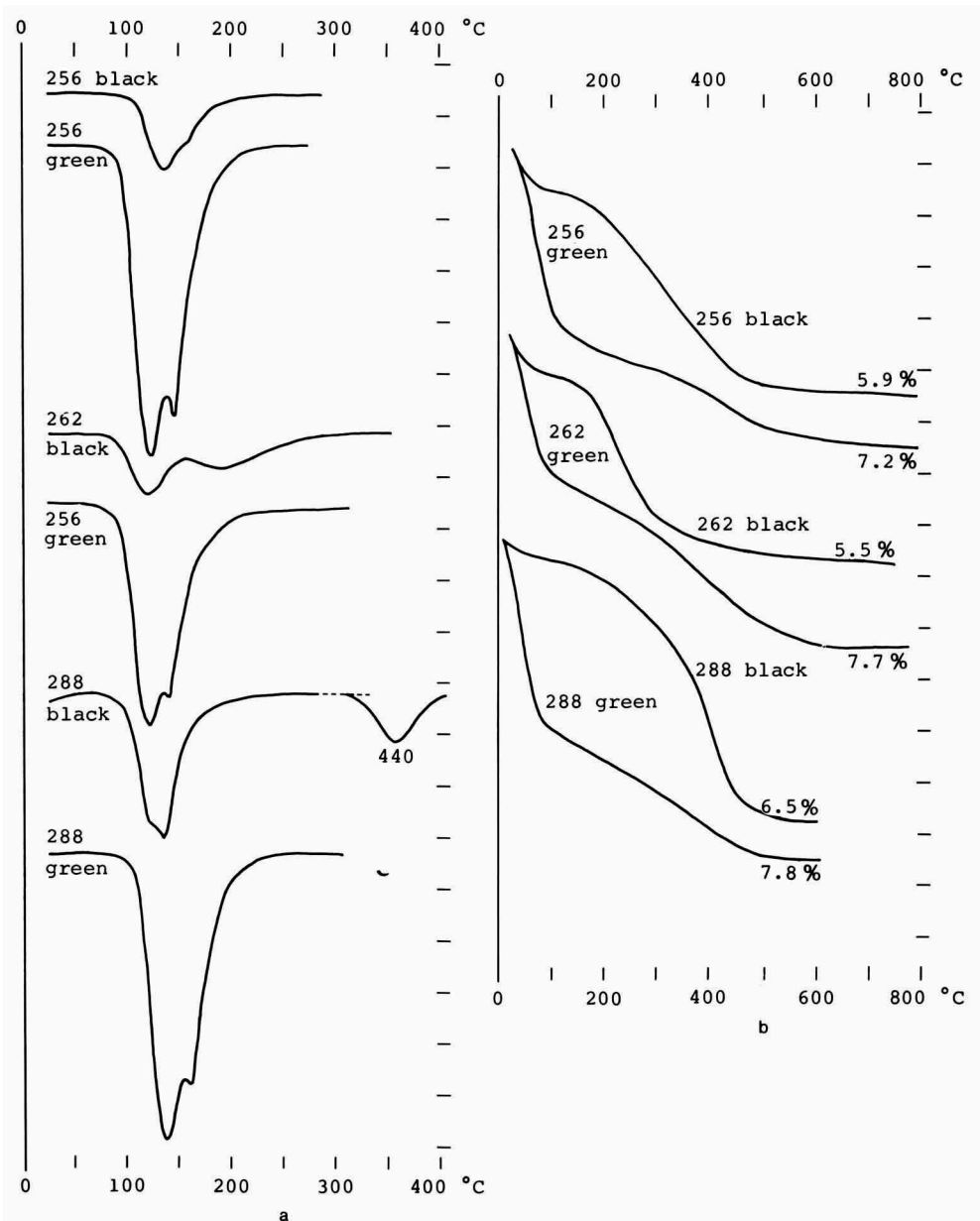

Fig. 6. a. DTA traces of samples 256, 262 and 288, weighing about 30 mg each; vertical scale 0.5 °C/unit. b. TGA traces of samples 256, 262 and 288, weighing 16 mg each; vertical scale 0.2 mg/unit. N_2 atmosphere.

TGA curves of differently coloured parts of samples 256, 262 and 288 are given in Fig. 6a, b, while the curves for the four zones of samples 188-191 are given in Fig. 7a, b. DTA curves are recorded up to 300 °C, while between 300 and 550 °C no reactions were encountered.

All DTA curves show endothermic reactions with maxima between 100 and 170 °C, generally consisting of two steps. Endothermal reactions are always stronger in greenish opals. This corroborates well with the fast initial dehydration, observed in TGA traces of these samples. Dehydration in black and brown opals
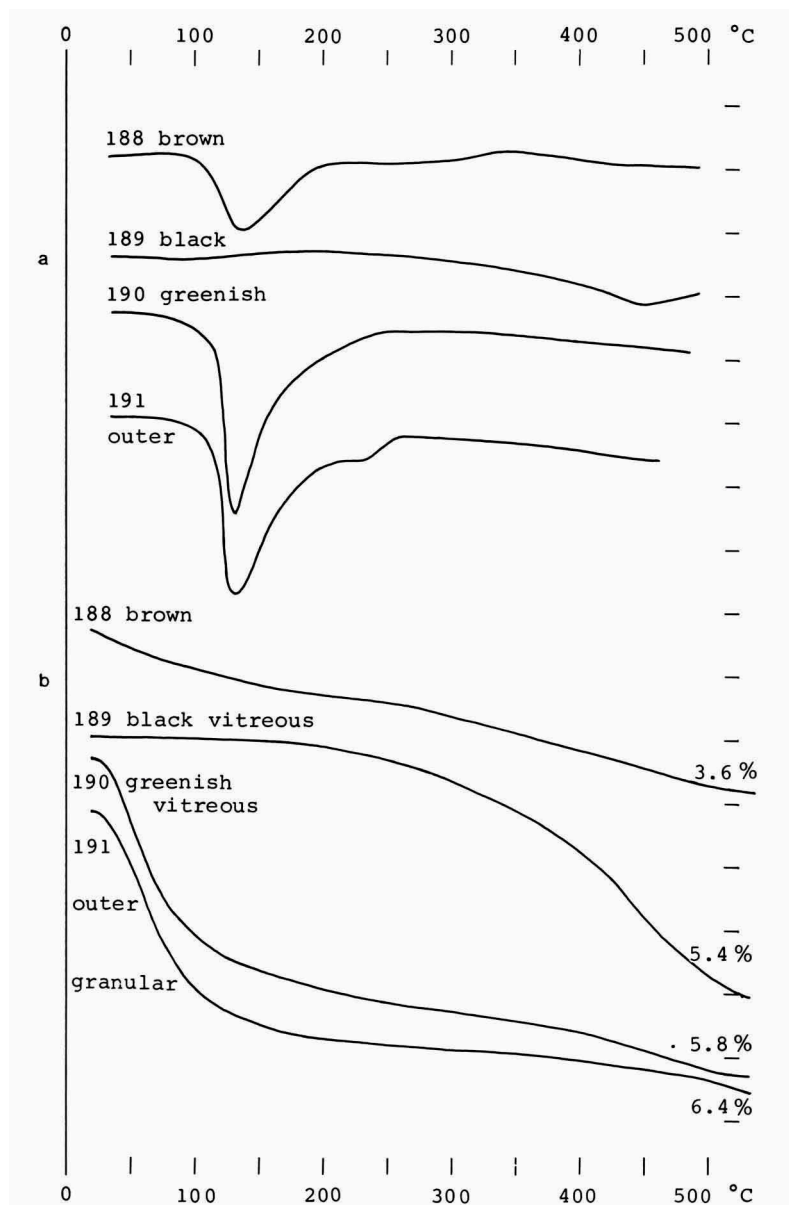

Fig. 7. a. DTA traces of samples 188 through 191, weighing about 5 mg each; vertical scale 0.5 °C/unit for 188 and 189; 1.0 °C/unit for 190 and 191. b. TGA traces of samples 188 through 191, weighing 16 mg each; vertical scale 0.2 mg/unit. Air.

Table 1.   Chemical analysis of the zones of opaline wood sample 289 (oven dry samples).

	188 core brown	189 black vitreous	190 greenish yellow vitreous	191 outer part yellow, granular	foreign compounds ratio in samples 191/190
SiO_2	95.0	93.6	88.8	84.4	
Al_2O_3	0.0	0.0	3.5	7.3	2.1
Fe_2O_3	0.1	0.0	2.7	2.0	
MnO	0.0	0.0	0.01	0.01	
MgO	0.0	0.1	0.5	0.6	1.2
CaO	0.13	0.11	0.36	0.65	1.8
Na_2O	0.1	0.3	0.3	1.1	3.6
K_2O	0.02	0.01	0.25	1.15	4.6
TiO_2	0.0	0.01	0.13	0.32	2.5
P_2O_5	0.0	0.0	0.0	0.0	
H_2O+	3.77	5.77	2.95	2.55	
C	0.65	0.37	0.12	0.07	
	99.8	100.3	99.6	100.2	
Foreign compounds	0.35	0.53	7.75	13.13	

occurs at higher temperatures and is generally slower. Similar tendencies are observed in samples 188-191 (Fig. 7).

According to Jones et al. (1963) and Segnit et al. (1965), most of the water in opals is not bound chemically, and dehydration characteristics depend on the size-distribution of pore systems in the opal and on the internal surface (silanol-bound water). According to this model, greenish opals will have wider pore systems than have black and brown opals. Water content is always higher in greenish parts than in brown or black parts of the same specimen. The cement of the host rock (290) (potch opal) shows curves similar to those of the other greenish opals.

Almost all greenish opals have DTA curves with two distinct maxima in the first endothermic reaction. One of these maxima might be due to the dehydration of admixed clay of the montmorillonite group.

The dehydration of sample 189 (black, vitreous) is so slow, that there is no initial endothermic reaction. This reflects an absence of larger pores. An endothermic reaction above 400 °C is found both in this sample and in sample 288 (black). Both samples show a rapid dehydration in this traject, indicating a certain amount of smaller pores of uniform size.

The weight loss characteristics of brown and black opals are similar to those reported by Jones & Segnit (1971), but those of the greenish opals are quite distinct. No phase transitions in the tridymitic structure were observed.

CHEMICAL ANALYSIS

The zones of samples 188-191 were analyzed chemically. The results are given in Table 1.

The analyses reveal that the amount of foreign compounds (not SiO_2, C, or H_2O) increases from the brown core outward. This is reflected in increasing amounts of Al_2O_3, MgO, CaO, Na_2O, K_2O and TiO_2. Amounts of iron and

manganese are influenced by redox equilibria and react differently from the compounds mentioned above. Organic carbon decreases tenfold from the core outward. Water contents are given with respect to oven dry (105 °C) material and do not reflect the higher contents of air-dry greenish parts.

Amounts of foreign compounds are approximately equal in brown and black parts, while they are considerably higher in the greenish outer rims.

Although the distribution of foreign compounds will be partially due to an admixture of e.g. clay, the changing proportions of these show, that their presence is not due to an admixture alone. It is likely, that part of the Mg and Ca for example occur in the opal and have entered by diffusion.

Relative amounts of some foreign compounds in the samples 190 and 191 are given in the last column of Table 1. When the amount of TiO_2 is taken as a measure for the amount of admixture in both samples, there seems to be a depletion of monovalent cations and an excess of divalent cations in sample 190 with respect to sample 191.

MORPHOLOGY

Thin sections were prepared of samples 252 through 263, 288 and 289. Microscopic examination shows a range of mineralizations from lignified to opalized wood, and also opaline material without discernible wood structure.

Opalized wood tissue is generally well preserved in specimens of all groups. Brown or black opalized tissue remains in groups 2 and 3 appear generally in massive units that are isotropic when viewed with crossed nicols (Fig. 8). Yellowish or greenish opalized tissue fragments in groups 2, 3 and 4, which occur as small fragments in crevasses in the brown and black tissues, are slightly anisotropic (Fig. 9a, b).
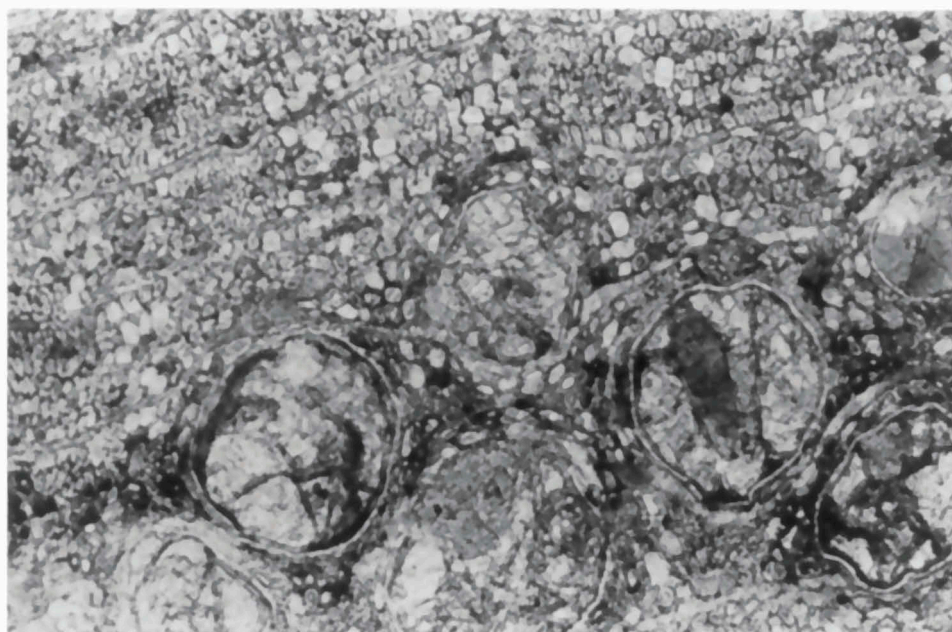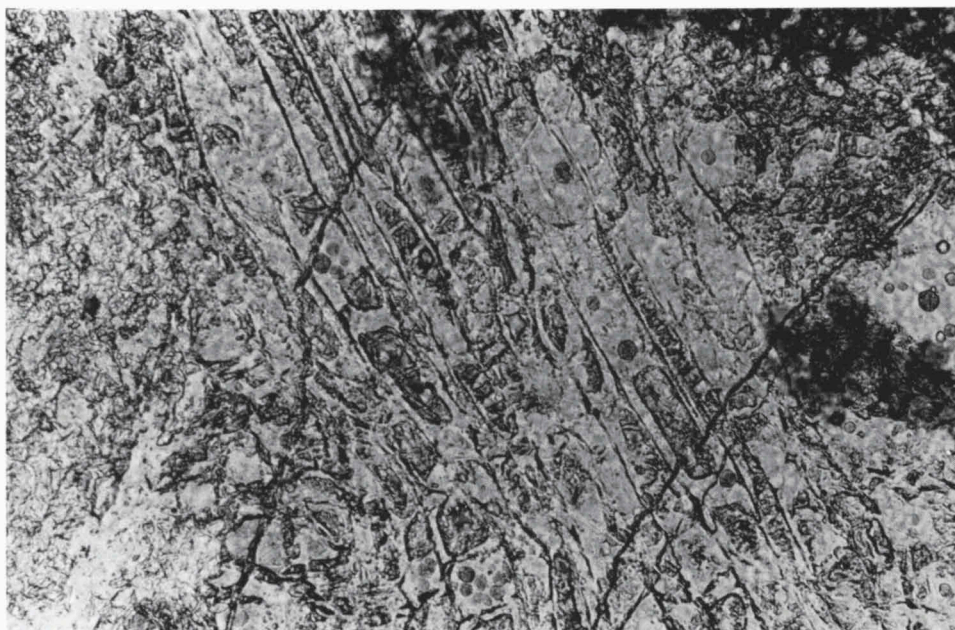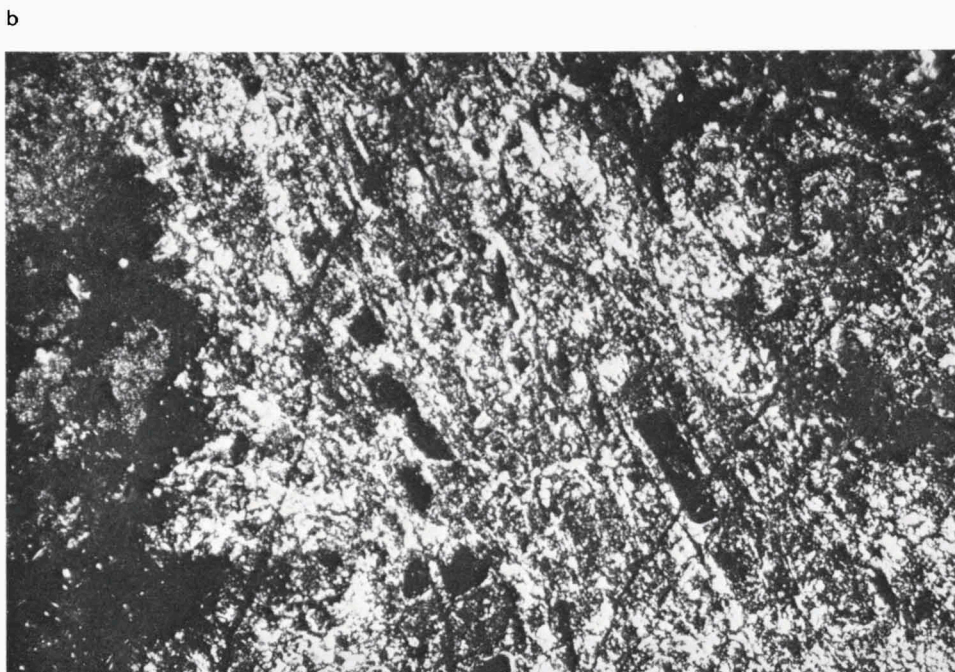

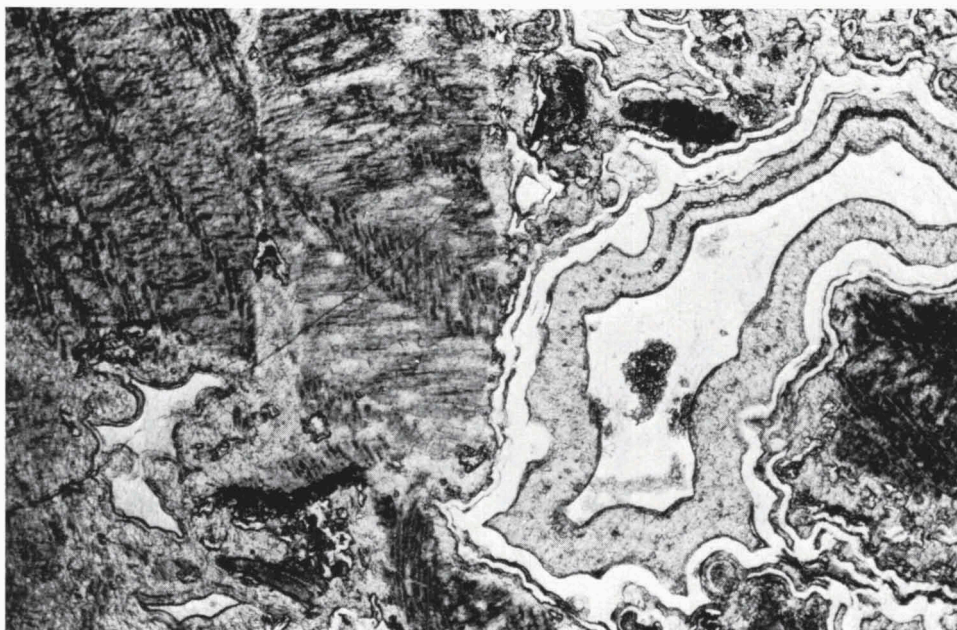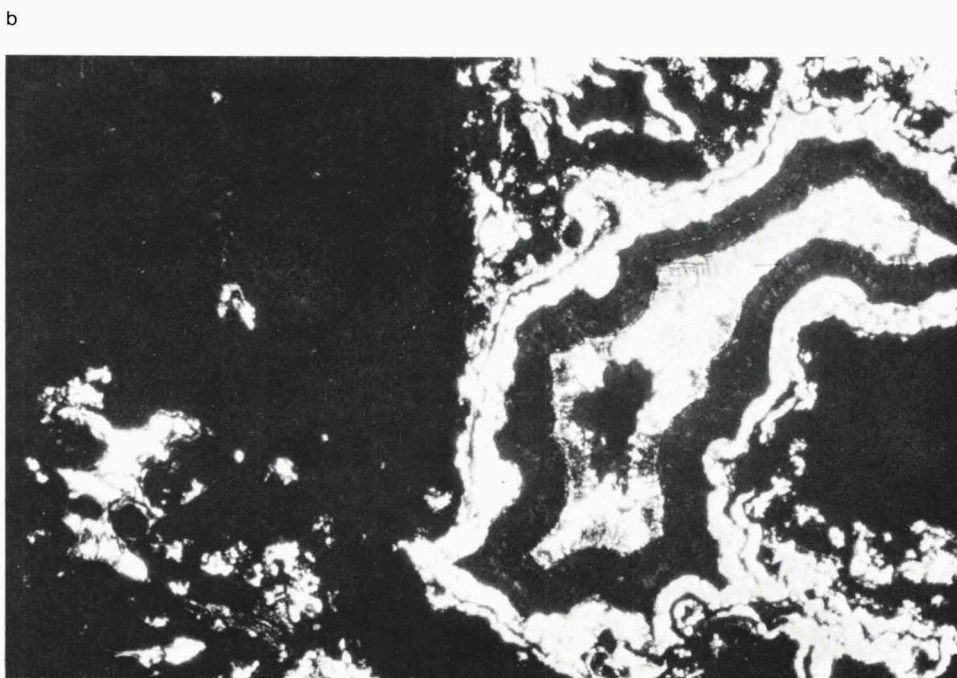Fig. 8. Thin section of the isotropic, brown core of sample 289. Normal light, 200 x.

Fig. 9. Thin sections of yellowish, anisotropic opalized wood tissue in sample 256; a. normal light; b. crossed nicols. Both 200 x.

Fig. 10. Thin section of chalcedonic inclusions in sample 254; a. normal light; b. with crossed nicols. Both 50 x. Note isotropic wood tissue at upper left and isotropic opaline bands in the chalcedonic inclusion.
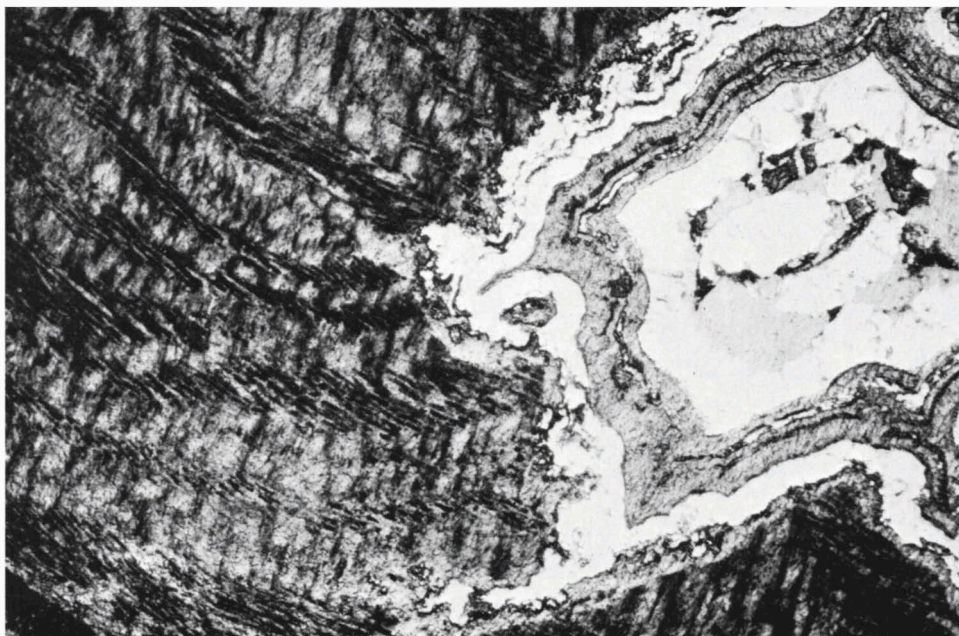
Fig. 11. Thin section of a chalcedonic inclusion in sample 254; nicols at 80⁰. Magnification 50 x.

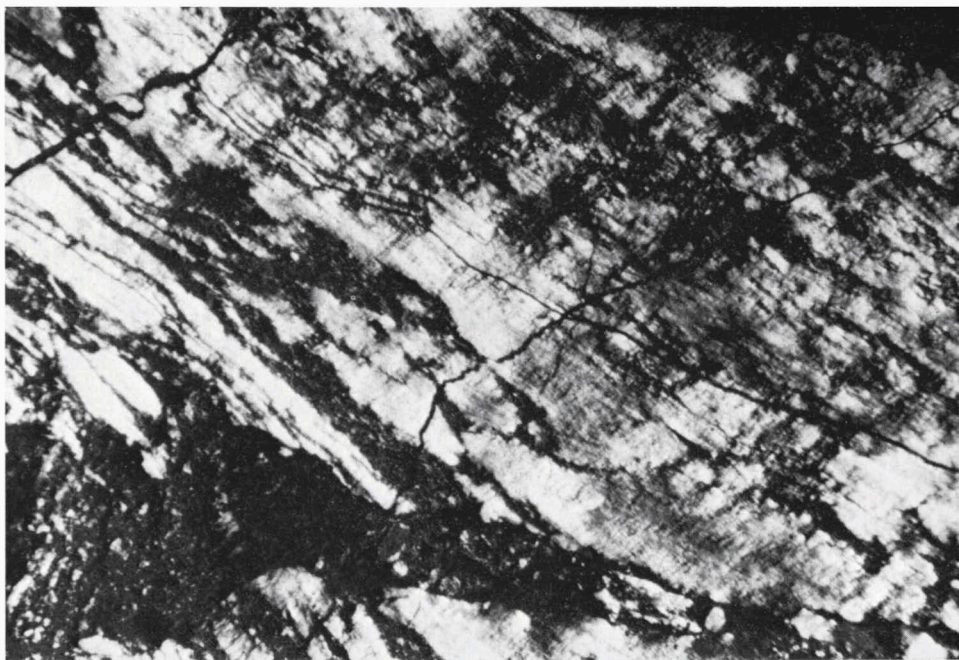Fig. 12. Thin section of anisotropic and isotropic zones in structureless opal of sample 255. Magnification 50 x; crossed nicols.
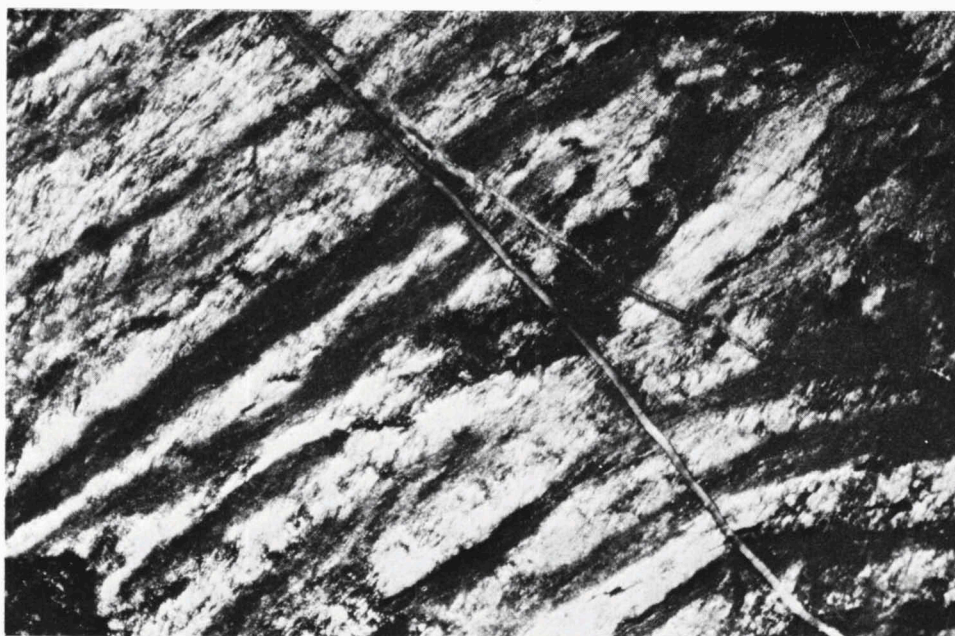
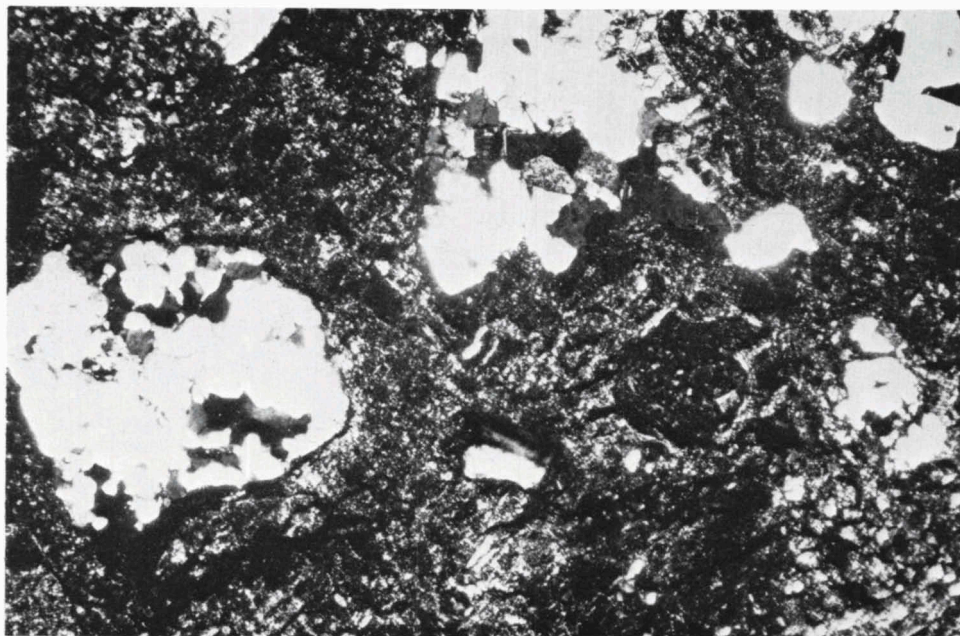Fig. 13. Thin section of isotropic and anisotropic zoning in sample 257. Magnification 50 x; crossed nicols.

Fig. 14. Thin section of part of the host rock with opaline cement. Sample 257. Magnification 50 x; crossed nicols. Note absence of zoning in cement. Light parts are detritic quartz grains.

Most of the specimens of groups 2 and 3 show chalcedonic veins (Figs. 10a, b, 11) that are randomly oriented. In these black specimens, wood structure is hardly discernible macroscopically, but thin sections reveal its presence in all specimens.

The sample of group 5 (259) consists almost entirely of opal without a tissue structure. Macroscopically, greenish fragments with tissue remains are observed in structureless masses. Microscopic examination shows that tissue remains are slightly anisotropic, while the parts without tissue structure show distinct zoning of isotropic and anisotropic parts (Figs. 12, 13). Notwithstanding the lack of tissue structure, the opaline material of this sample 259 is almost free of detritic material.

Thin sections of cemented host rock reveal that the cementing opal is slightly anisotropic. It does contain detritic fragments, but usually less than 50% (Fig. 14).

The zoned sample 289 shows an isotropic, brown core with excellent structure preservation; no tissue structure whatsoever has been found in the isotropic black glassy rim; ghosts of tissue structure occur in the slightly anisotropic yellowish green zone (Fig. 15), grading into the cement of the host rock.

Sample 258, which was almost completely lignified, showed rounded lignitic pellets without any structure, surrounded by sediment with opaline cement.
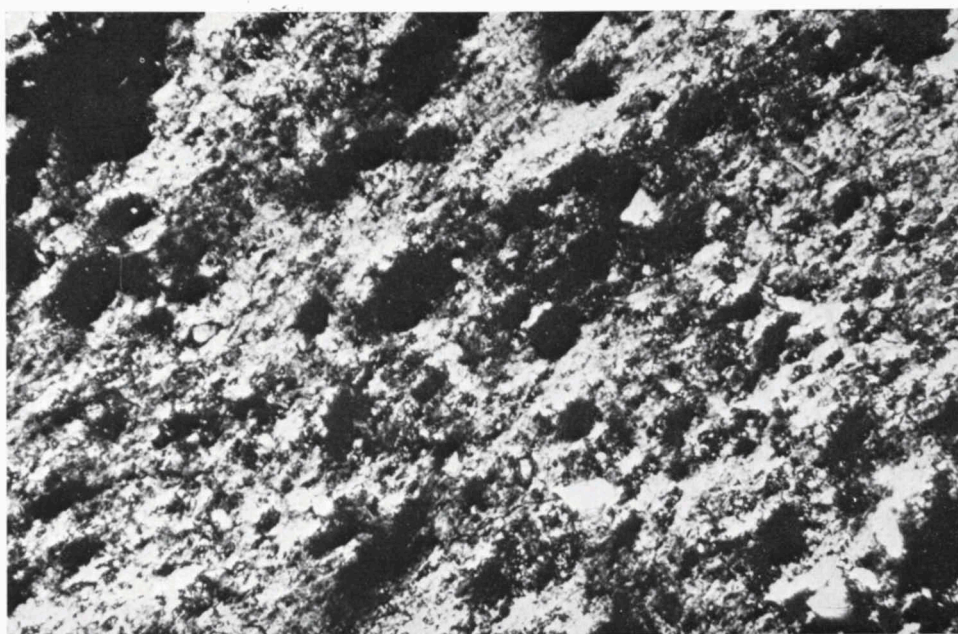

Fig. 15. Ghosts of tissue structure in anisotropic yellowish green rim of sample 289. Magnification 200 x; crossed nicols.

Discussion

The angular habit of the opaline wood, and its occurrence in both coarse and fine layers in equally large pieces underline its driftwood nature.

Thin sections reveal that the wood occurred in varying states of preservation when opalization took place. Some pieces were fully lignitized, while others were practically unaltered and have turned into wood opals with excellent preservation of wood structures. The opalizing agent solidified both wood and host rock.

The state of decay of the wood upon opalization seems to have influenced the crystallinity of the opal. Massive pieces of wood show isotropic opalizations, while anisotropic opalizations are found in loose wood fragments. Anisotropic wood tissues generally have greenish of yellowish colours.

In some cases, wood has decayed more rapidly than opalization occurred, and structureless greenish opaline stem casts are formed.

The wood opals of Yakuplu are mineralogically opals with mixed cristobalitic and tridymitic stacking (opal-CT). This kind of stacking is usually found in opals (Mitchell & Tufts, 1973) and according to Flörke (1967) and Jones & Segnit (1972) opal-CT will form from amorphous silica under low energy conditions.

Greenish opalizations, both in the host rock and in the wood, show X-ray diffraction and thermal characteristics distinctly different from those of black and brown opalizations. These differences will be partly due to impurities in the greenish opals (detritic clay). However, the (001) reflections at d= 14 Å in the greenish opals are much too high to result from about 10-20% of randomly oriented montmorillonitic clay (compare analyses of samples 190 and 191). It might be possible that the silica supplied in solution by the percolating water built on the silica sheets of montmorillonitic clay and extended these, and that these silica plates have been supported by scattered brucite or gibbsite units, thus creating an open montmorillonitic suprastructure in the opal.

Such a suprastructure would be randomly oriented because of the random orientation of the clay in the host rock, and it would enhance the (001) reflection of smectite clay. It would also create a pore system with dehydration characteristics comparable to those of the greenish opals. The comparatively high Mg content of sample 190 would than be due to brucite units.

In the light of the foregoing, it might be questioned whether the high-angle reflections in opals mentioned e.g. by Frondel (1962) are due to particulate structures or to impurities.

Although according to Jones et al. (1963) opals from one site use to have similar thermal and X-ray characteristics, in this case different structures seem to exist within one specimen.

Mitchell & Tufts (1973) observe that in their wood opals those with an opal-CT structure contain less impurities than those with an opal-C structure. This was not the case in the present investigation. All opals show distinct opal-CT structures, and some contain considerable amounts of impurities. Presumably, the amount of impurities depends on the host rock.

According to Sato (1962, 1964), impurities favour the formation of tridymitic stacking above that of cristobalitic stacking.

Structureless opaline casts of wood stems may form in the way described by Jones & Segnit (1966) for opaline veins in Coober Pedy and Andamooka (Australia). Silica-rich water percolates through open channels in the host rock.

Water is adsorbed by the walls and silica is deposited on the walls. When this process proceeds, the walls adjacent to the open space will be fully cemented by opal (potch opal) and the open space will fill up with more pure opaline material. When part of the decaying wood is still present, occasional fibers of opalized wood will be incorporated in the filling of the central part. Thus, unlike the statement by Mitchell & Tufts (1973), impurities in the outer part of wood opals are not the results of processes subsequent to opalization, but of infiltration or inclusion of foreign material during opalization.

The geological setting of the wood opals in Yakuplu seems similar to that of some Hungarian wood opals. The deposits of Yakuplu, and those of Mount Szókehégy near Mikófalva in Hungary are of the same age (Sarmatian, Late Miocene) and are very much alike. Volcanic tuffs are known to be intercalated in the strata of Mikófalva; although they have not been unequivocally identified in the cliffs of Yakuplu, they may be present in the higher strata, where their weathering may have caused the liberation of silica and its percolation through the adjacent rocks.

The silicification of the host rock in Yakuplu, points to an enormous excess of silica, since at most other localities only the wood is opalized.

Summary

Wood opals in Sarmatian and Pliocene sediments from Yakuplu, Turkey, have been formed in situ by the alteration of driftwood in gravelly deposits. This is very much like the genesis of wood opal in some sites in Hungary.

Driftwood was lignitized and/or opalized. Lignitic specimens do not show opalization apart from filling in of crevasses. The state of preservation of the wood seems to have influenced the crystallinity of the opal.

All opals show characteristics of opal-CT: broad reflections at $d = 4.35$, 4.10, 2.50 Å and at higher angles. Part of the opalized wood, especially greenish scattered fragments in crevasses of massive parts and greenish potch-opal transitions towards the host rock, show reflections that can be attributed to clay minerals. The intensity of these reflections, however, suggests a sheet-like structure in the opaline material, as a result of the extension of silicon tetrahedral sheets of clay minerals, especially of the smectite group.

Greenish wood opals and potch opals have wider pore systems than black and brown wood opals. This is reflected in the dehydration characteristics. Greenish opaline material dehydrates at lower temperatures and has higher water contents than black and brown opals.

Black and brown opals have higher contents of SiO_2 and low amounts of foreign compounds. Their carbon percentage is considerably higher than that of the greenish opals.

Black and brown opals are isotropic, while greenish ones tend to show anisotropic and isotropic zoning.

Most of the layered chalcedonic veins in black opals show alternating chalcedonic and isotropic opaline bands.

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Manuscript received 27 January 1975.