

# Silicified Woods Consist with Malachite, Azurite, and Hematite in the Middle Eocene Çekerek Formation, Tokat—Turkey

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**Abstract**—In the vicinity of Yücepinar Village of Zile district of Tokat province, there are silicified wood formations in agglomerate levels in the Çekerek formation Middle Eocene aged. These formations consist of well-preserved tree trunks of about 1.5 m in diameter or branches and trunk parts in mm—1 m length. Generally, they are open-brownish cream; in some places they demonstrate dark brown, green, and blue colors. According to XRD and FT-IR analysis results of the samples, it is determined that the silicified wood formations are composed of quartz, cristobalite, malachite, azurite, hematite, graphite, and goethite minerals. According to XRF and ICP-MS analyzes of silicified woods, the high iron content ( $\text{Fe}_2\text{O}_3$  8.29–63.79%) in the samples causes red brown color while the increase in copper content ( $\text{Cu} > 10000$  ppm) causes blue and green colors. As a result of the cabochon cuts made from the silicified wood samples to be used for jewellery, products which have rich color composition and silky brilliance, keep the polish well and with high-strength are obtained. Particularly because of its color compositions, it is separated from similar silicified wood samples on the Earth. As a result of the surface studies carried out in the study area, it was observed that the silicified wood formations did not propagate much. In order to determine the reserves of these formations, which are thought to have significant economic value, it is necessary to carry out a more detailed exploration activity with trenching and drilling in the region.

**Keywords:** silicified wood, azurite, malachite, mineralogy, geochemistry

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## INTRODUCTION

Silicified woods are formed by the preservation of the original structure of root tissue through the accumulation of mostly silicate and quartz spheres (opal-A → opal-CT → quartz) in the cell walls and cell spaces of the trees as a result of the acidic hydrothermal cycle under the influence of silica rich fluids (Stein, 1982; Scurfield and Segnit, 1984; Mustoe, 2008; Pewklian et al., 2004; Mustoe, 2015; Mustoe and Viney, 2017).

The color formation in silicified woods (Mustoe and Acosta, 2016) results from the various elements that penetrate into the earth during the petrification process (Table 1). In the research area, the copper element included in the structure enabled the formation of blue and green colors and the iron element enabled the formation of yellowish-reddish-brown colors of the iron element.

The gemstone refers to different colored minerals, stones and organic materials, which are extracted from the Earth's crust, processed and used as ornaments by people (Sariiz and Nuhoglu, 1992; Eşme, 1994). Jewels and tools made with gemstones have had an important place in people's lives for centuries. Gem-

stones are formed by elements commonly found in nature such as oxygen, carbon, aluminum, silicon, calcium, and magnesium (Vieil et al., 2004). Gemstones are rarely found due to silicified wood formations observed in different colors and textures or, in commercial terms, the difficulties in the formation conditions of wood opals. The silicified woods found in the study area are rare formations which can be used as gemstones due to their physical properties as they are composed of a mixture of many colors in different tones such as red, brown, blue, green, and yellow with the effect of the different elements such as iron and copper along with silica.

## MATERIALS AND METHODOLOGY

Mineralogical determinations (mineral paragenesis) were made by examining the thin sections of the silicified woods and side rocks taken from the area and prepared at Mersin University, Geological Engineering Department and Thin Section Laboratory under an illuminated polarizing microscope at Ahi Evran University Geological Engineering Mineralogy-Petrography Laboratory. In order to determine the

**Table 1.** Elements causing coloring in silicified wood

Carbon	Black
Cobalt	Green/Blue
Chrome	Green/Blue
Copper	Green/Blue
Iron Oxides	Red, Brown and Yellow
Manganese	Pink/Orange/Blackish/Yellow
Nickel	Green

mineralogical compositions of the samples, XRD analyses were carried out in Rigaku RadB-DMAX II Computer Controlled X-Ray Diffractometer and FT-IR analyses were carried out in Fourier-transform infrared spectroscopy of Perkin Elmer brand and Frontier model in the XRD Analysis Laboratory of Mersin University. In order to determine the major oxides and trace elements of the samples XRF and ICP-MS analysis were performed in Acme Analytical Lab. (Canada).

## GEOLOGY

The geological map of the study area was drawn by rearranging MTA (Mineral Research And Exploration General Directorate) (2002) geological map (Fig. 1). In the research area, the observed formations were Tokat Massif of Permo-Triassic, Amasya Group of Late Jurassic-Early Cretaceous, Çekerek formation of Middle Eocene and Kemerkaş formation of Miocene-Pliocene, respectively from late to early ages (Akyazı and Tunç, 1992, 2003, Yolcubal et al., 2014). Tokat Massif consists of a metamorphic matrix composed of quartzite, calcschist, epidote schist, milonitgniss, micaschist, metaclastic, and metacircus sandstone with low-grade metamorphism and recrystallized limestone levels in this matrix (Akyazı and Tunç 1992; Yolcubal et al., 2014). Upon Tokat Massif, Amasya Group, which consists of medium-bedded limestone levels beginning with conglomerates including unconformably metamorphic pebbles, takes place (Akyazı and Tunç, 1992; Üstüntaş and İnceöz, 1999). Çekerek Formation consists of conglomerate, sandstone, mudstone, claystone, marl alternation and limestone, and agglomerate levels (Akyazı and Tunç, 1992, Üstüntaş and İnceöz, 1999, Akpınar et al., 2003; Yolcubal et al., 2014). Gypsum intercalations, coal bands and silicified wood fossils were observed in the unit (Üstüntaş and İnceöz, 1999). Kemerkaş Formation taking place on Çekerek formation with an incompatible contact generally consists of conglomerate, pebble, coarse sandstone alternation, mudstone, gypsum interlayers and travertines (Üstüntaş and İnceöz, 1999). The earliest unit in the research area was the Quaternary alluvium. The silicified wood fossils, which are the main subject of the present.

## FINDINGS

### *Field Studies*

There is a matrix consisting of generally volcanic materials within Çekerek formation of Middle Eocene around Yücepınar village of Zile district of Tokat province and there are silicified wood fossils in the agglomerate levels of basalt and andesite pebbles and blocks in this matrix (Üstüntaş and İnceöz, 1999). These formations consist of well-preserved tree trunks (Fig. 2) or branches and trunks with the length of mm—1 m at a diameter of about 1.5 m (Fig. 3). Silicified wood fossils are generally made up of a light brownish cream color and sometimes dark brown consisting of the mixture of green and blue colors (Fig. 4).

### *Mineralogy-Petrographic Investigations*

Thin section investigations made from silicified wood samples clearly revealed residual wood texture (Figs. 5, 6). The quartz forming the dominant mineral was observed in the form of spherulitic textured fibrous structures which were in conformity with the texture as fracture-crack filling between the wood textures and microcrystalline texture (Fig. 7). Presence of iron oxides and malachites (azurites) as opaque minerals was extensively detected in the sections (Fig. 8). These opaque minerals were observed only in some sections, but in some sections they could also be observed as iron oxides surrounding the outer walls of the malachite in a thin line (Fig. 9).

### *XRD and FT-IR Investigations*

According to the results of XRD and FT-IR analysis, it was determined that the silicified wood formations consisted of quartz minerals and some samples of quartz minerals were accompanied by cristobalite, malachite, azurite, graphite, hematite and goethite minerals (Figs. 10, 11). According to the XRD and FT-IR analysis results, it was observed that, the quartz mineral in the silicified wood formations in the region was accompanied by malachite in green samples, azurite in blue samples, hematite-goethite-graphite in red-brown samples and cristobalite mineral in white samples.

### *Geochemistry Investigations*

The main oxide analyzes from silicified wood samples (Fig. 12) taken from the study area are given in Table 2. SiO<sub>2</sub> content was measured as 96.98–98.29% in the samples consisting only of quartz and cristobalite which white color is dominant (3k, 7ky, and 13). SiO<sub>2</sub> content was measured as 24.09–83.71% and Fe<sub>2</sub>O<sub>3</sub> content was measured as 8.29–63.79% in dark reddish brown color samples consist of quartz, cristobalite, hematite, goethite, and graphite (12kk and 16k). In the green and blue colored samples (16y and

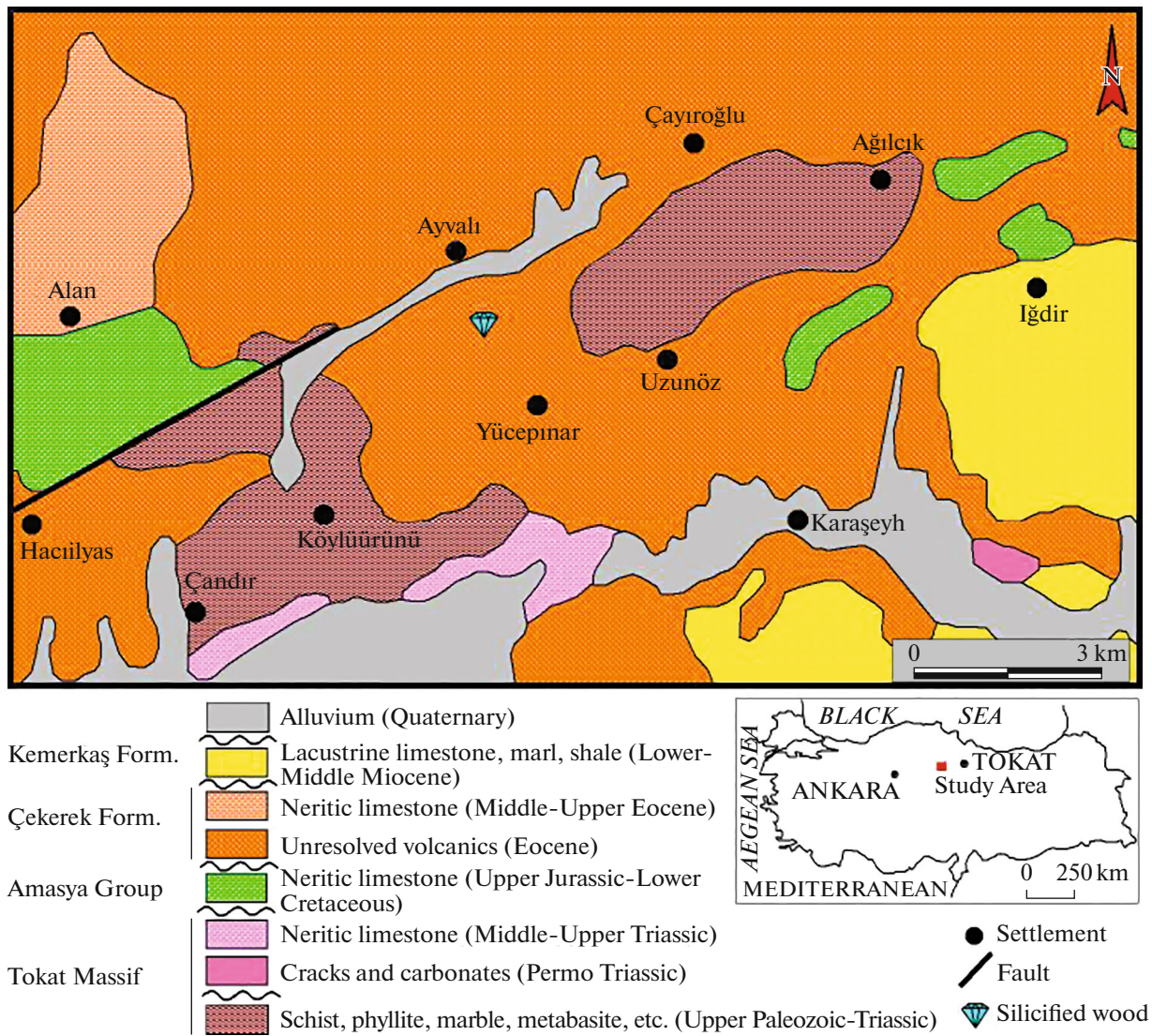


Fig. 1. Geological map of the study area (MTA, 2002).

22ma) composed of quartz, malachite, and azurite, as expected, the amount of loss in the fire is high due to copper carbonate minerals, therefore  $\text{SiO}_2$  was measured as 58.68–69.55%.

The trace element analyzes from silicified wood samples (Fig. 12) taken from the study area are given in Table 3. In silicified woods, significant enrichments are observed in Mo, Cu, Pb, Zn, Ni, Ag, Co, Mn, As, Sr, Sb, V, Ba, and W elements. In particular, these enrichments in Cu, Ag and V have increased above the detection limit.

## CONCLUSION AND RESULTS

The fossilization process involves a variety of physicochemical, biological, and geological mechanisms, which depend on the burial environment (Bardet and Pournou, 2017). Certain minerals (mainly quartz,

opal, or moganite) crystallize or precipitate in the hollow cavities and cells of the woods in a fossilization process (Saminpanya, 2015). Therefore, fossil wood can be found in a variety of forms and preservation conditions (Taylor et. al., 2009; Bardet and Pournou, 2017).

The silicified woods around Yücepinar Village of the Zile district of Tokat province are in agglomerate levels within Çekerek formation of Middle Eocene age. The silicified woods in the region are similar to the formation mechanism of silicified woods in Xinchang Geopark eastern South China (Zhang et al., 2014), in volcanosedimentary rocks, due to the effect of volcanism. The silicified woods are not entirely preserved, they have a trunk with axial diameters of up to one and a half meters and branches and trunk pieces in mm–1 m in length. The silicified woods usually have a color in the shades of brown, and con-



Fig. 2. A well-preserved tree trunk about 1.5 m in diameter of silicified woods in agglomerate levels in The Çekerek Formation.

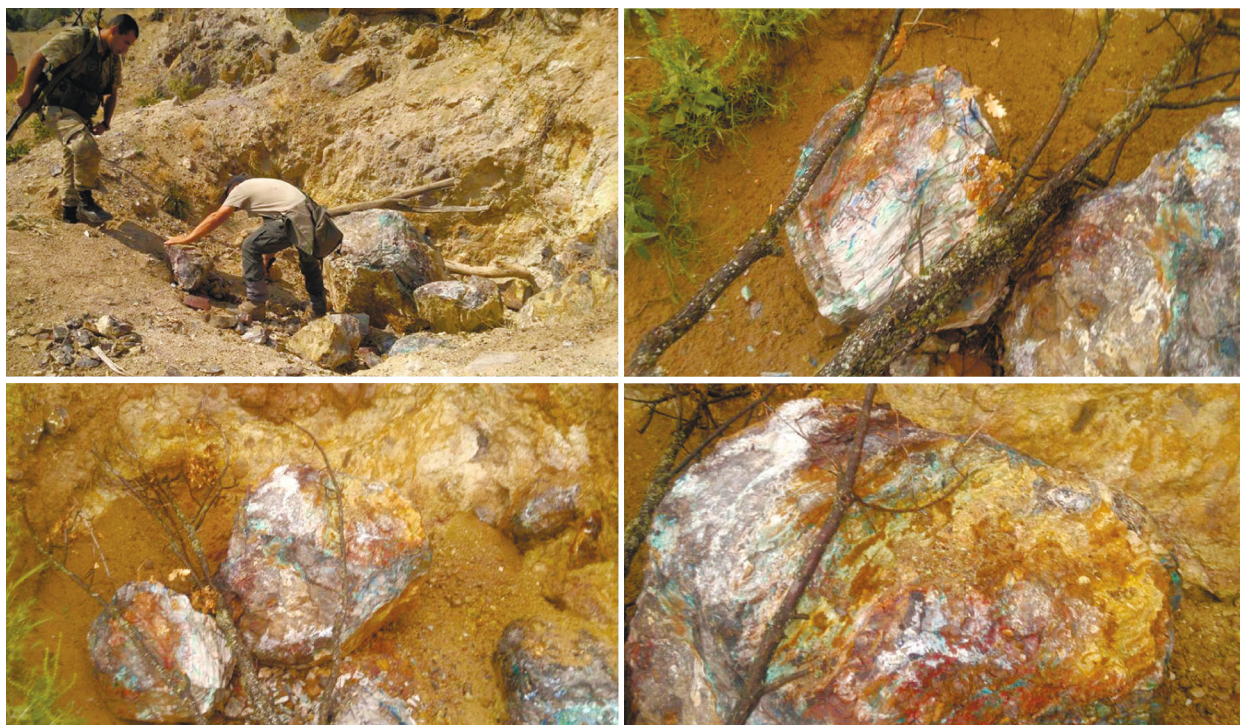


Fig. 3. Branches and trunk parts about mm—1 m in length of the silicified woods in the agglomerate levels of the Çekerek Formation.



Fig. 4. Examples of silicified wood in different colors and textures from the study area.

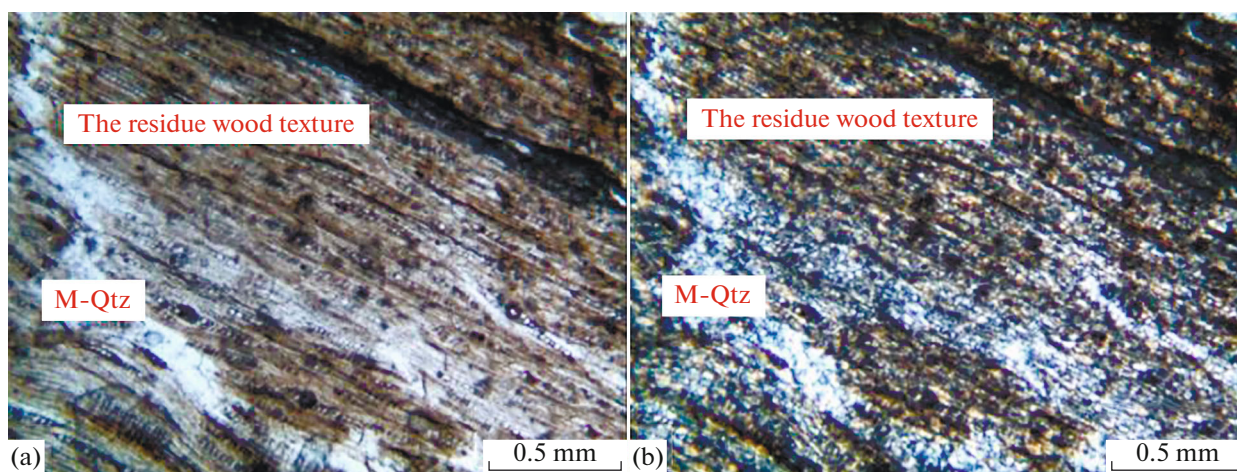


Fig. 5. Residual wood texture and microcrystalline quartz minerals in the silicified wood. (M-Qtz: Macro quartz, (a) plane-polarized light, (b) crossed polars).

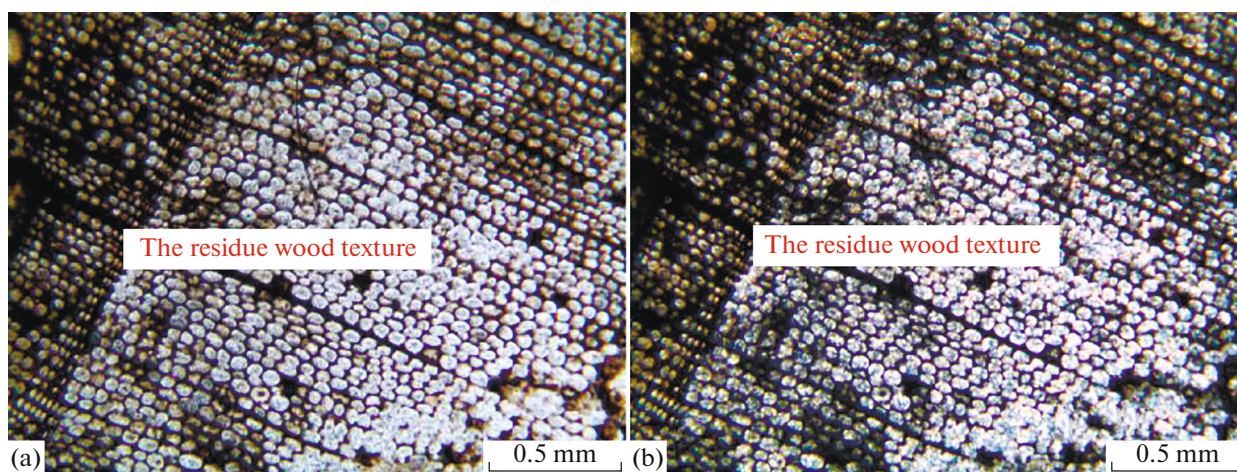
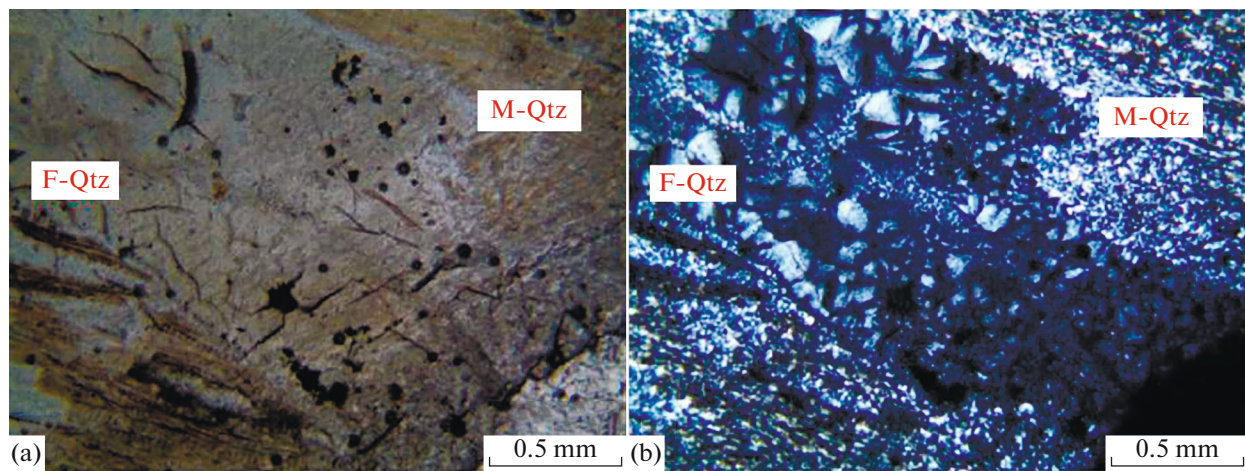
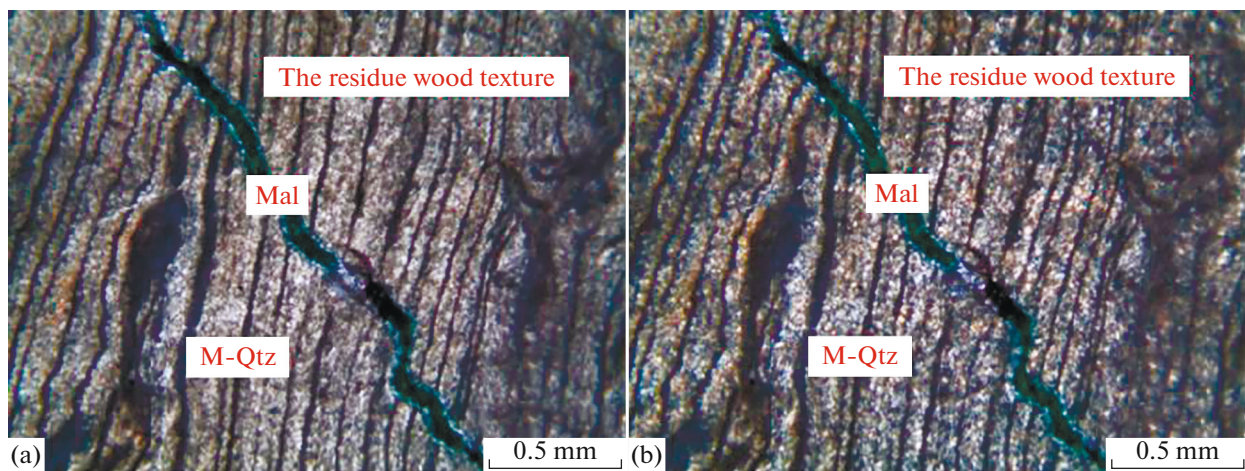


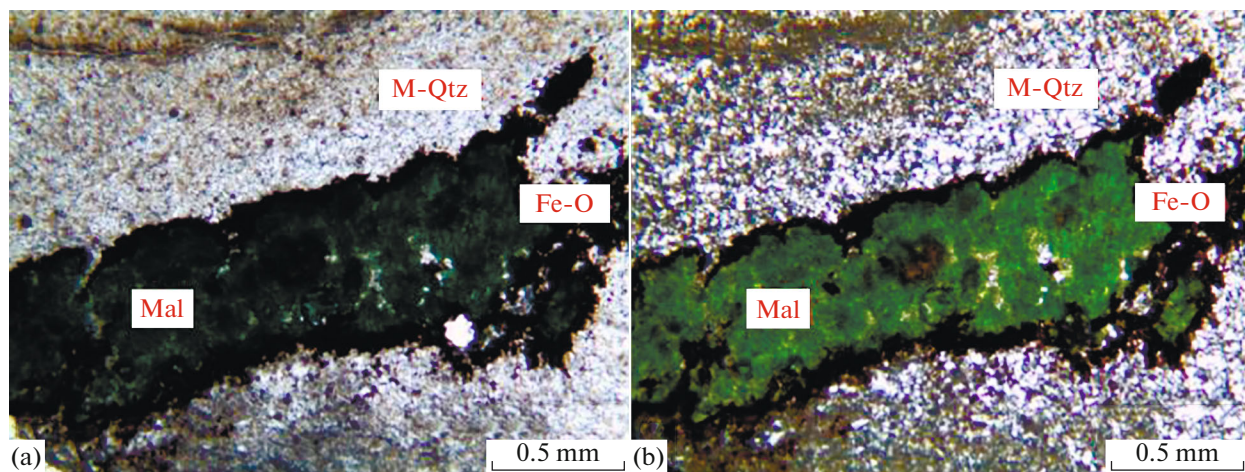
Fig. 6. Residual wood texture in the silicified wood. ((a) plane-polarized light, (b) crossed polars).



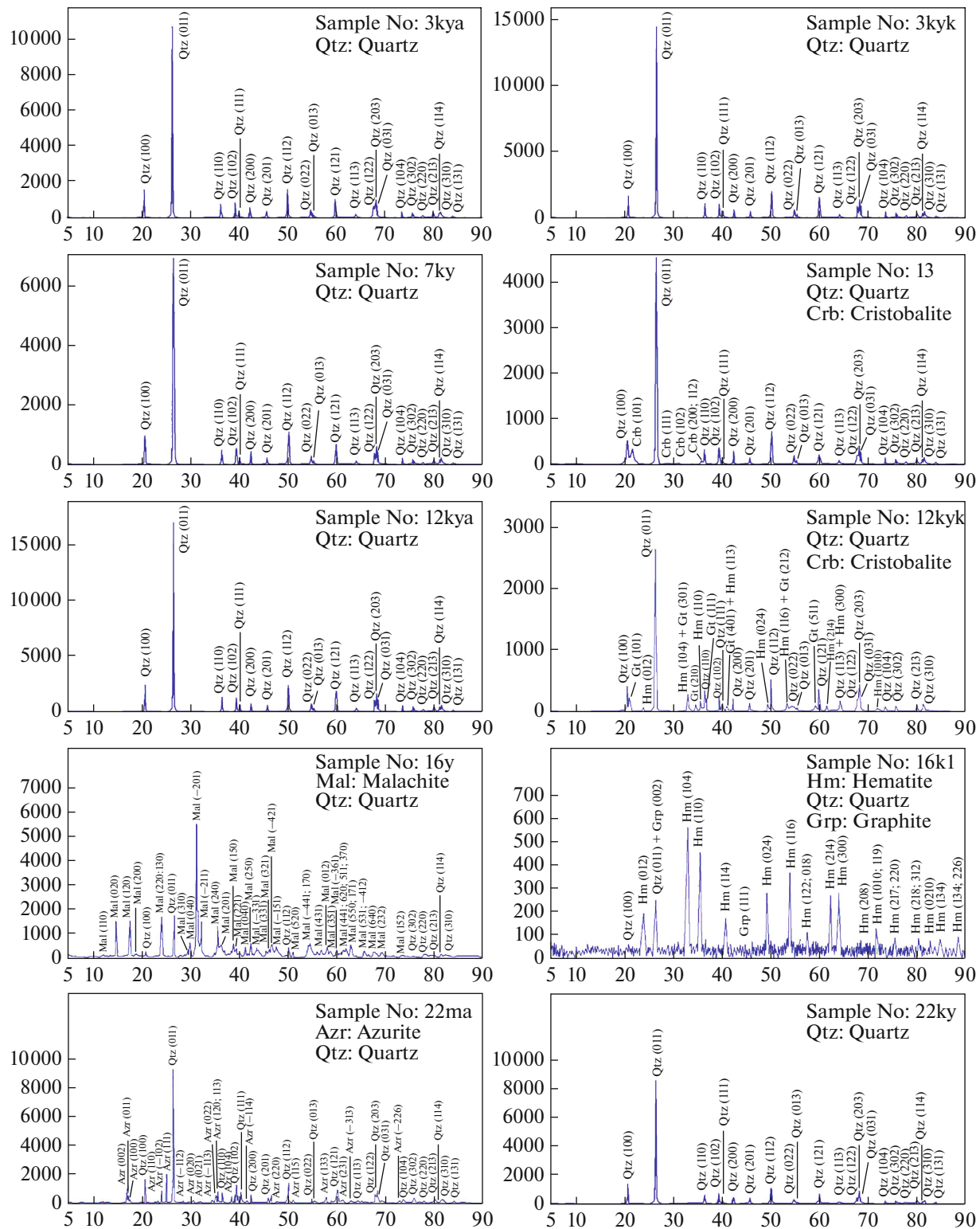
**Fig. 7.** Spherulitic textured lysine and microcrystalline quartz minerals (M-Qtz: Macro-quartz, F-Qtz: Microquartz, (a) plane-polarized light, (b) crossed polars).



**Fig. 8.** Residual wood texture, microcrystalline quartz, and crack-filling malachite minerals in the sample of silicified wood. (M-Qtz: Macro-quartz, Mal: Malachite, (a) plane-polarized light, (b) crossed polars).



**Fig. 9.** Microcrystalline quartz, iron oxide, and malachite minerals in the sample of silicified wood. (M-Qtz: Macroquartz, Mal: Malachite, Fe-O: Iron oxide, (a) plane-polarized light, (b) crossed polars).



**Fig. 10.** XRD shots of silicified wood samples with different color, crystal grain size, and mineral content in the examination area.

tain veins of blue and green. Microscopic quartz crystals, fibrous quartz in pores, fracture crack filling and dark green opaque malachite in the pores and iron oxide (hematite, goethite) minerals were

observed as dominant residues in thin sections made of the silicified woods.

According to XRD and FT-IR analysis results of the silicified wood samples, it was determined that the

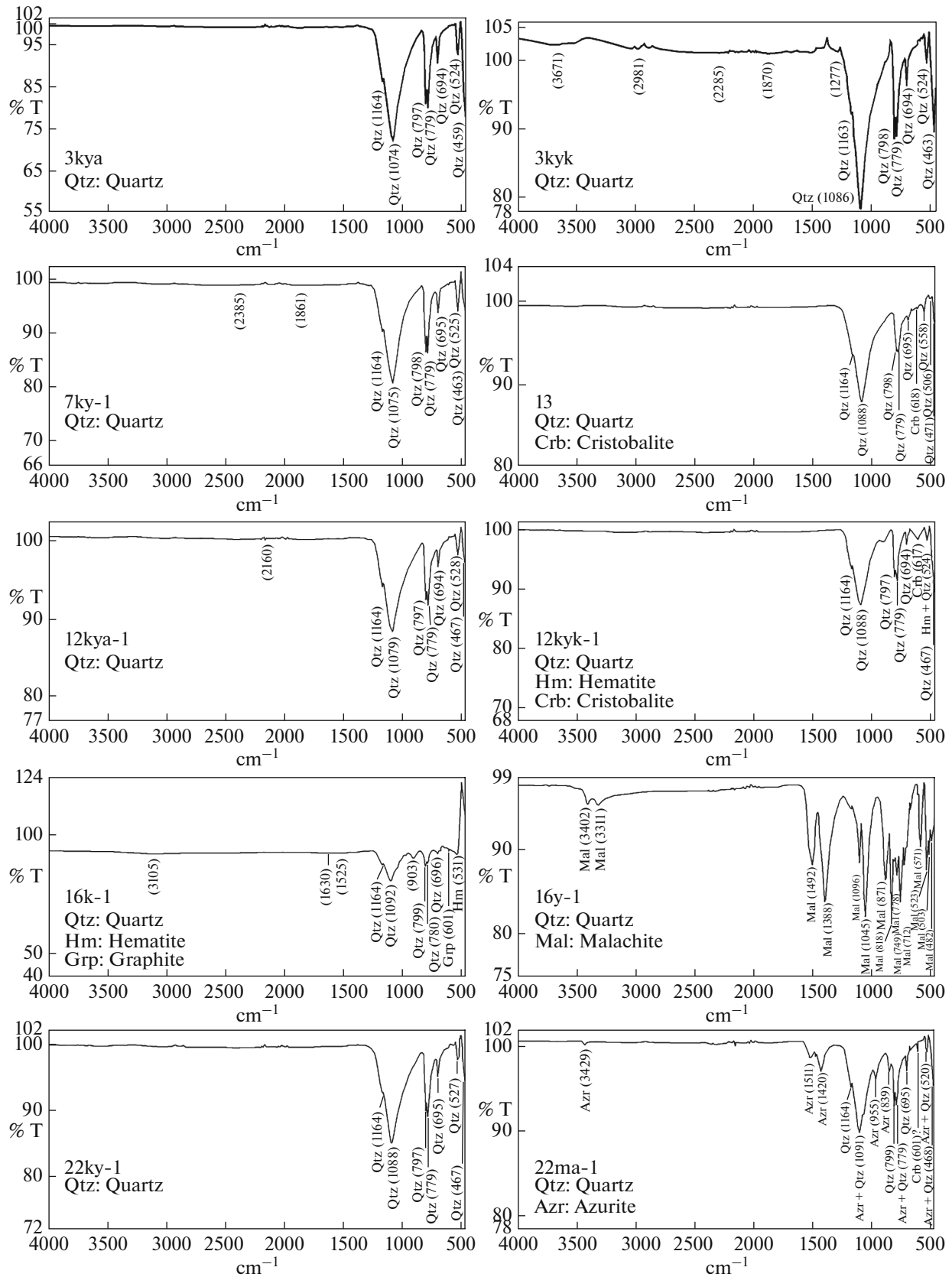


Fig. 11. FT-IR shots of silicified wood samples with different color, crystal grain size, and mineral content.

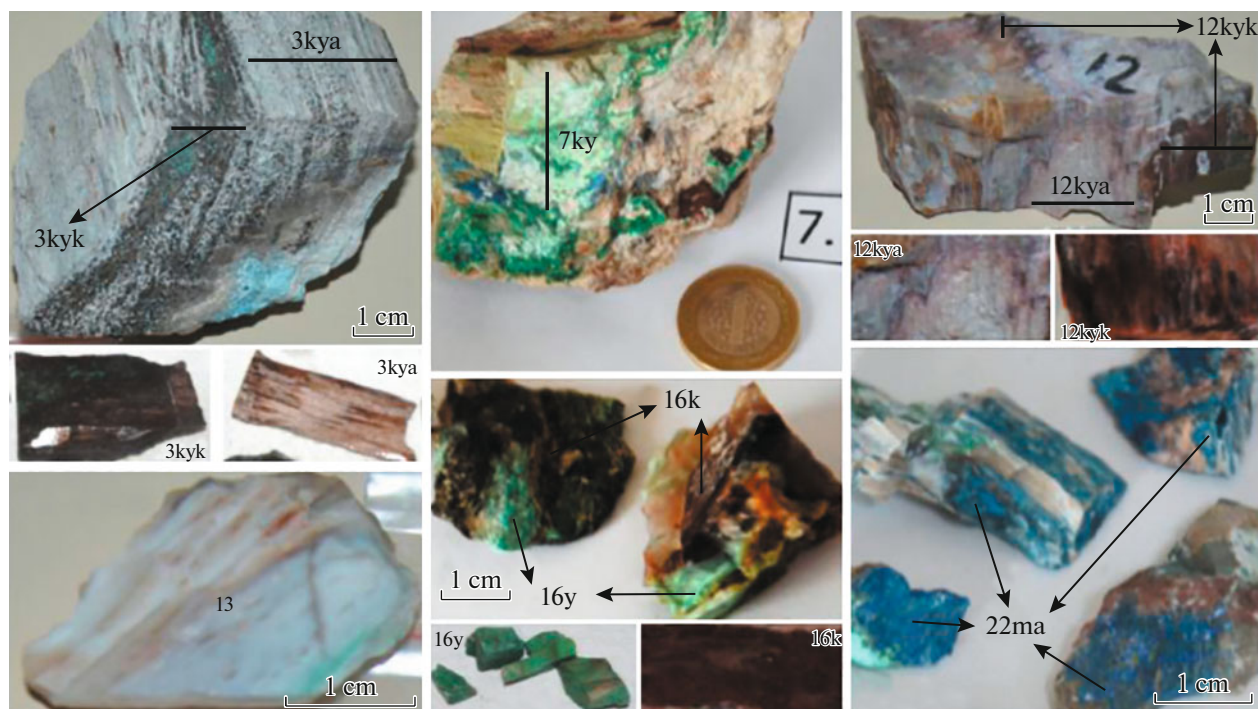


Fig. 12. Examples of silicified wood in different colors and textures from the study area.








silicified wood formations consisted of quartz minerals and some samples of quartz minerals were accompanied by cristobalite, malachite, azurite, graphite, hematite and goethite minerals. Color of silicified

wood may be influenced by the presence of relict organic matter, but the most significant contribution comes from trace metals (Kuczumow et. al., 2000). In study of fossil woods in Arizona (USA) and Zimbabwe

Table 2. XRF Main Oxide Analysis Results of Silicified Wood Samples

	3kya (Qtz)	7ky (Qtz)	12kyk (Qtz + Hm + Gt + Crb)	13 (Qtz + Crb)	16y (Qtz + Mal)	16k (Hm + Qtz + Grp)	22ma (Qtz + Azr)
SiO <sub>2</sub>	96.98	98.29	83.71	97.88	69.55	24.09	58.68
Al <sub>2</sub> O <sub>3</sub>	<0.01	<0.01	<0.01	0.02	0.02	0.03	0.03
Fe <sub>2</sub> O <sub>3</sub>	0.57	<0.04	8.27	0.04	<0.04	63.79	0.31
MgO	<0.01	<0.01	0.02	<0.01	0.04	<0.01	<0.01
CaO	0.05	0.03	0.08	0.02	0.02	1.33	0.07
Na <sub>2</sub> O	0.01	0.01	<0.01	0.03	0.01	0.03	0.01
K <sub>2</sub> O	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
TiO <sub>2</sub>	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
P <sub>2</sub> O <sub>5</sub>	0.01	<0.01	0.03	0.01	0.06	0.54	0.07
MnO	<0.01	<0.01	<0.01	<0.01	<0.01	0.03	<0.01
Cr <sub>2</sub> O <sub>3</sub>	<0.002	<0.002	0.005	<0.002	<0.002	0.006	0.002
LOI	1.2	1.2	N.A.	2.0	10.0	3.0	13.6
Sum	98.80	99.58	92.19	100.00	79.65	93.18	72.86

**Table 3.** ICP-MS Trace Element Analysis Results of Silicified Wood Samples

	3kya (Qtz)	7ky (Qtz)	12kyk (Qtz + Crb + Hm)	13 (Qtz)	16y (Qtz + Mal)	16k (Hm + Qtz + Grp)	22ma (Qtz + Azr)
							
Mo ppm	13.0	<0.1	4.0	<0.1	0.5	818.6	2.1
Cu ppm	9078.2	3380.3	3854.3	213.7	>10000.0	>10000.0	>10000.0
Pb ppm	20.5	7.1	25.3	0.1	44.9	1870.7	144.6
Zn ppm	6	8	80	2	32	256	6
Ag ppm	>100.0	>100.0	48.5	6.7	>100.0	9.6	9.5
Ni ppm	0.9	0.6	438.7	0.3	50.8	725.1	312.7
Co ppm	0.4	0.6	253.8	<0.1	5.0	81.9	1.3
Mn ppm	2	1	25	<1	18	160	6
Fe %	0.37	<0.01	6.06	<0.01	0.02	>40.0	0.22
As ppm	135.3	3.3	186.0	2.3	768.4	6022.3	528.5
Au (ppb)	3.1	2.1	2.7	230.7	8.2	51.1	14.1
Th ppm	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Sr ppm	2	<1	31	<1	2	346	9
Cd ppm	<0.1	<0.1	<0.1	<0.1	0.6	8.5	0.2
Sb ppm	0.8	<0.1	22.9	2.5	0.3	55.8	1.8
Bi ppm	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
V ppm	68	12	6142	<2	932	>10000	848
Ca %	0.03	0.02	0.06	<0.01	0.02	0.86	0.04
P %	0.002	<0.001	0.009	<0.001	0.026	0.180	0.030
La ppm	<1	<1	<1	<1	<1	8	<1
Cr ppm	<1	<1	21	<1	2	2	<1
Mg %	<0.01	<0.01	<0.01	<0.01	0.02	<0.01	<0.01
Ba ppm	17	1	84	<1	11	1930	96
Ti %	<0.001	<0.001	<0.001	<0.001	<0.001	0.002	<0.001
B ppm	<20	<20	<20	<20	<20	<20	<20
Al %	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Na %	0.001	0.002	0.002	0.001	0.002	0.020	0.002
K %	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
W ppm	5.4	<0.1	5.1	<0.1	<0.1	75.8	1.0
Hg ppm	0.05	<0.01	0.09	0.03	0.08	0.04	0.19
Sc ppm	0.3	<0.1	<0.1	0.1	1.2	1.9	0.7
Tl ppm	<0.1	<0.1	<0.1	<0.1	<0.1	0.2	<0.1
S %	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Ga ppm	<1	<1	<1	<1	<1	<1	<1
Se ppm	<0.5	<0.5	<0.5	<0.5	1.7	4.2	2.3
Te ppm	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2

(Africa) by Kuczumow et. al., (2000) is defined that the most important of these metals is Fe (Mustoe and Viney, 2017), which can produce a rainbow of hues depending on its abundance and oxidation state, Cr is the dominant colorant for bright green fossil wood. According to Saminpanya (2015), the rough surfaces of petrified wood may have been altered and stained by soil or iron oxides, resulting in black, brown, cream, white, and red coloration. According to the XRD and FT-IR analysis results, it was observed that the quartz mineral in silicified wood formations in the region was accompanied by malachite in green samples, azurite in blue samples, hematite-goethite-graphite in red-brown samples and cristobalite mineral in white samples. According to XRF main oxide analyzes from white coloured silicified wood samples, SiO<sub>2</sub> content was measured high (96.98–98.29%), red-brown coloured silicified wood samples Fe<sub>2</sub>O<sub>3</sub> content was measured high (8.29–63.79%). According to ICP-MS Trace Element Analysis from green and blue coloured silicified wood samples, Cu content was measured high (>10000 ppm). Therefore, the formation of green and blue colors is associated with Cu and the formation of red-brown colors with Fe and its oxidation.

Silicified woods have long been used as a gem and ornamental material due to their beauty, luster, durability, and relative rarity (Saminpanya, 2015). The silicified woods in the study area take part in the group of the gemstones with good visibility and color compositions with silky brilliance, high strength, and good polish retention. As a result of the surface studies carried out in the study area, it was observed that the silicified wood formations did not extend to a great area. As a result of these studies, evaluating the region as a precious mineral and stone site will be able to bring significant contributions to both the region and the country's economy.

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