Mineralogical and paleobotanical investigations of Oligo-Miocene petrified wood from the southwest of Thrace Basin (NW Turkey)

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Abstract: Petrified wood samples are found within terrestrial sediments belonging to the Late Oligocene-Early Miocene Danişmen Formation in Malkara-Keşan located in the southwest of the Thrace Basin. The petrified wood in both regions is usually silicified and partly coalified. The silicification of the Tertiary wood in the Malkara-Keşan region is associated with volcanic activity and coeval sedimentation. Thin sections from petrified wood samples were taken as transverse, tangential and radial sections. The mineralogical-petrographic-botanical studies were carried out under a polarizing and botanical microscope. Opal-moganite-chalcedony-quartz, which are different polymorphs of silica, were detected under the microscope in the petrified wood. Results were supported by X-Ray Diffractometer (XRD), Confocal Raman Spectroscopy, Fourier Transform Infrared Spectroscopy (FT-IR) analysis and measurement of density in a total of five samples. In addition, Scanning Electron Microscopy (SEM/EDS) was performed for textures and to determine the average elementary composition of wood samples. Results showed that while crystalline quartz and chalcedony were well defined, opal-A and other polymorphs of silica could be partly examined due to isotropic features. As a result of XRD studies of petrified wood samples from the Keşan and Malkara regions, the peaks of the crystalline types of silica were well defined in the diffractogram patterns. As a result of FT-IR analysis, polymorphs of silica such as quartz-chalcedony-moganite and mineralogical elements similar to carbon and graphite were detected. In two samples, the densities of chalcedony and quartz composition were 2.35 and 2.27 g/cm$^3$, respectively. Furthermore, the average elementary composition was detected with SEM-EDS analysis as O, Si, S, Ca, Cr and Fe elements in the Keşan region samples and O, Si, S and Fe elements in the Malkara region samples. The results of all
investigations and analysis were interpreted to understand the geodynamic evolution and paleobotanical properties of the region.

**Key words:** Petrified wood, Thrace, mineralogy, geochemistry, paleobotany

1. **Introduction**

Petrified wood is a fossil formed due to burial of trees by sediments in areas close to volcanic activity and is an important resource for understanding biodiversity and paleogeography. The petrification of wood occurs in the form of replacement of organic parts by inorganic materials in waters affected by volcanism or the permineralization of inorganic material in tissues (Mustoe, 2017; Mustoe and Viney, 2017; Viney et al., 2019). During the silicification process, organic substances in the tissues of the tree are removed and are replaced by silica and/or some other elements (Ca, Cu, Fe etc.). Since the woody structures can be partially or completely preserved in fossil wood with different chemical composition, texture and color, genus/species determinations can be made. Thus, important information about the geology, paleogeography and paleobotanic characteristics of the region is obtained.

In many parts of the world (such as Indonesia, America, Germany, Egypt, Iran, etc.) there are petrified wood forests formed at different times by volcanic activities (Voudouris et al., 2007; Dietrich et al., 2013; Mustoe, 2017; Mustoe and Viney, 2017; Hassan, 2019; Lukens et al., 2019; Mustoe et al., 2019; Pe-Piper et al., 2019). Various fossil forest locations were identified in Turkey, mainly in central Anatolia (Ankara-Çamlıdere-Kızılcahamam, Bolu-Seben, Tokat-Zile etc.) (Hatipoğlu and Türk, 2009; Akkemik et al., 2016; Kaydu Akbudak et al., 2017; Acarca Bayam et al., 2018; Akkemik et al., 2018; Akkemik and Acarca Bayam, 2019; Denk et al., 2019), western
Anatolia (İzmir-Aliağa, Manisa-Yunusemre, Uşak-Banaz, Kütahya-Tavşanlı) (Yurtseven, 2018; Polat et al., 2019) and northwestern Anatolia (Edirne-Keşan, Tekirdağ-Malkara-Çorlu, Çanakkale-Gökcèada, İstanbul-Sarıyer-Beykoz-Beylikdüzü-Çatalca) (Aras et al., 2004; Akkemik et al., 2005; Güngör et al., 2019; Çevik Üner et al., 2020). Most of the petrified wood in Turkey is generally silicified, partially carbonated and carbonized. Among these, fossil wood located in the Thrace region (NW Turkey) is observed in terrestrial sediments associated with volcanic activity in the region during the Tertiary period. In this study, conducted in the Keşan-Malkara regions (SW Thrace), petrified wood samples are located in sediments belonging to the Danişmen Formation and are generally observed in areas close to coal formations or inside coal deposits. Despite many studies about the geology of basin formation, coal deposits, natural gas potential and oil in Thrace, the number of studies about petrified wood is more limited. Paleobotanical and paleogeographic interpretations for the region used data obtained as a result of these studies (Şanlı, 1982; Aras et al., 2004; Akkemik et al., 2005; Akkemik and Sakınç, 2013; Akkemik et al., 2019a, 2019b).

The fossil wood materials studied here were identified and published by Çevik Üner et al. (2020). They are *Glyptostroboxylon rudolphii* Conwentz, 1884 (all from Keşan), *Taxodioxylon gypscæum* (Göppert) Krausel, 1949 (one from Keşan and one from Malkara), *Ginkgoxylon lesboense* Süss, 2003 (one from Keşan), and *Quercoxylon caucasicum* (Gajvoronskij) Madel-Angeliewa, 1968 (all from Keşan). The paleoenvironment of this assemblage was suggested to belowland riparian and swamp conditions together with well-drained lowland forests (Çevik Üner et al., 2020).

The purpose of this study is to describe the petrified wood samples in the Malkara (Tekirdağ)-Keşan (Edirne) region from the point of view of mineralogical, geochemical
and paleobotanic features. Some species of petrified woods, such as *Taxodioxylon gypsaceum* and *Glyptostroboxylon rudolphii* from the Malkara (Tekirdağ) - Keşan (Edirne) region, were already described by Çevik Üner et al. (2020). The aim is to identify the silica content and density of silica polymorphs in these petrified wood samples and to interpret the geodynamic evolution and palaeobotanical features of the region as a result of this data.

2. **Geological Setting**

The study area is located in the Malkara and Keşan regions in the southwest of the Thrace Basin (Figure 1). The basin is represented by the units of the western Pontides, namely crystalline rocks of the Strandja Massif. This basement is covered by sedimentary rocks of the Thrace Basin in the south (Okay et al., 2001; Figure 1). The Strandja Massif consists of Precambrian rocks intruded by Precambrian metagranitoids and the early Paleozoic metamorphic rocks that are intruded by plutonics ranging from late Carboniferous to early-late Permian in age (Okay et al., 2001; Sunal et al., 2011; Yılmaz Şahin et al., 2014; Aysal et al., 2018; Yılmaz et al., 2021). All of the units mentioned so far are unconformably overlain by Triassic-Jurassic metasedimentary rocks (Çağlayan et al., 1988; Okay et al., 2001; Natal’ in et al., 2005a, 2005b; Sunal et al., 2006; Sunal et al., 2011). Late Cretaceous unmetamorphosed sedimentary and volcanic rocks unconformably overlie these metamorphic basement rocks (Okay et al., 2001; Sunal et al., 2011). The late Cretaceous interval is represented by arc magmatism, which formed due to the subduction of the Neo-Tethys Ocean under the Pontides (Görür, 1988; Okay et al., 2001).
Sedimentation in the Thrace Basin started with a transgressive sequence in the early Eocene and continued reggressively until the middle Oligocene-early Miocene period (Keskin, 1974; Turgut et al., 1983; Saner, 1985; Perinçek et al., 2015). While the middle Eocene-early Oligocene period includes turbiditic deposits in the south, carbonate sedimentation occurred in the north of the basin at the same time (Keskin, 1974; Turgut et al., 1983; Figure 1). It was suggested that the Thrace Basin was under the influence of a delta system formed by a large river in this period (Turgut et al., 1983). In the late Eocene-early Oligocene period, dacitic and andesitic ash was intercalated with the basin sediments. Miocene and younger units in the region cover the Eocene-Oligocene sequence (Figure 1). Tertiary units throughout the basin are generally composed of clastics and also contain local carbonate rocks (Perinçek et al., 2015).

Although sedimentation was interrupted locally at the margins of the basin, there is a thick pile in the central parts where sedimentation was continuous (Burke and Uğurtaş, 1974; Perinçek, 1987; Turgut et al., 1991; Perinçek et al., 2015). In the Thrace Region, the areas where coal formations (mostly lignite) are densely observed are generally located on the foothills of the Strandja Massif, and the coal seams get thicker towards the middle of the basin. Coal, which outcrops as a zone in the north and in the south, is found at depths of more than 600 meters in the sedimentary pile, which reaches 10,000m thickness in the central parts of the basin, and is accompanied by petrified wood formations (Şengüler, 2013; Erarslan and Örgün, 2017; Erarslan, 2018).

Early-middle Eocene aged units located on the basement rocks are represented by turbiditic Gaziköy and Keşan Formations in Malkara and Keşan regions, and Fıçtepe, Karaağaç and Hamitabat Formations containing clastic and carbonate rocks in northern Thrace (Perinçek et al., 2015; Figure 2). The shallow depth environment in the middle
Eocene-early Miocene is represented by Koyunbaba and Soğucak Formations (Perinçek et al., 2015; Figure 2). Then, the Ceylan Formation, representing the marine environment, was deposited with the deepening of the basin (Siyako, 2006; Perinçek et al., 2015; Figure 2). The Late Eocene-Early Miocene Yenimuhacir Group overlies the Ceylan Formation conformably (Kasar et al., 1983; Siyako, 2005; Siyako, 2006). The Yenimuhacir Group, which was deposited in the delta environment, consists of the Mezardere, Osmancik and Danişmen Formations from bottom to top (Siyako, 2006; Perinçek et al., 2015; Figure 2).

In the Yenimuhacir Group, there are some tuff-tuffite intercalations and coal seam formations within the alternation of shale, claystone, sandstone, and conglomerate. At the end of the early Miocene, the region became land and the early-middle Miocene Hisarlıdağ volcanics formed unconformably above the group in the southwest of the basin. The Hisarlıdağ volcanics are 35.0 ± 0.9 My old according to K/Ar dating (Sümengen et al., 1987) and are the products with acidic-intermediate volcanic composition forming abundant pyroclastic rocks in general (Saner, 1985; Ercan, 1992; Siyako, 2006; Güçtekin, 2017). The Miocene Çanakkale and Ergene Formation and Çekmece Group unconformably overlies all units in the region. The Çanakkale Group, located in the southern part of the basin, consists of Gazhanedere, Kirazlı, Çamrakdere and Alçitepe Formations. The Ergene Formation is located in the central parts of the basin and the Çekmece Group consists of the Çukurçeşme, Güngören and Bakırköy Formations around İstanbul (Siyako, 2006; Figure 2). The youngest unit deposited in the Thrace basin is the Kircasalih Formation with Pliocene age. (Siyako, 2006; Perinçek et al., 2015; Figure 2).
The Danişmen Formation containing petrified wood, which is the subject of the study, has gradual contact with the underlying Osmancık Formation and is unconformably covered by the younger Kırcasalih Formation. The unit was first named after Pınarhisar Danişmen Village (Kırklareli) by Ünal (1967) (Kesgin and Varol, 2003). The thickness of the unit, which is around 1000 meters on average, reaches 1600 m and decreases to 0-300 m at its thinnest point (Siyako, 2006; Perinçek et al., 2015). According to Perinçek et al. (2015), the formation consists of the Taşlısekban, Pınarhisar and Armutburnu Members. The late Oligocene-early Miocene formation, representing lake, swamp, flood plain and stream sediments, contains shale, claystone, sandstone, conglomerate, rarely tuff and occasionally coal (Figure 2). The Danişmen Formation has a special importance for the basin as it contains oil, coal (lignite) and natural gas (Ünal, 1967; Kasar et al., 1983; Batı et al., 2002; Siyako, 2006). Moreover, it provides important data for the paleogeography for the region, as it contains fish fossils in the northwestern part of Thrace and petrified wood and plant fossils in southwestern Thrace. Some examples of this wood, which were identified in various sizes, can reach up to several meters tall and more than one meter in diameter.

In the Keşan region, around Muzalı/Çobançeşme pond, the greenish-gray colored Danişmen Formation, approximately 300 m thick, comprises alternations of sandstone-claystone-marl and rarely thin coal seams. Here bedding is generally sub-horizontal with dips of ~10-15° (Figures 3A-4B, 4A-4B). The petrified wood fossils are located close to the coal seams located parallel to the layers forming the unit (Figures 3C-D, 4A-4B). While the trunks of the trees are generally perpendicular to the dip direction of the beds, thin branches are observed parallel to the slope dip direction (Figures 3A-B, 4A-4B). The elements with woody texture can be seen at macro scale in well preserved
and petrified tree trunks. In addition to silicification, partial and/or complete carbonization occurred in samples close to the coal layers (Figure 3D). While silicified wood is generally observed in local outcrops in the study area, some samples are found in coal mines and accumulated else where. In the local outcrops, fossil wood with a height of approximately 80-290 cm and a diameter of 30-60 cm can be seen, while fossil wood with a height of approximately 300 cm and a diameter of 150-200 cm and well-preserved texture were found in samples collected near the quarries (Figure 3).

In the Malkara region, the Danişmen Formation units are composed of fine-grained, grayish-greenish colored, thinly laminated sandstone-claystone alternations and coal seams (Figure 5C, 6A-6B). The petrified wood is frequently found at coal-bearing levels and at levels of sandstone-claystone alternations, perpendicular to the dip directions of bedding (Figure 6A-6B). The recorded dimensions of this fossil wood are between approximately 75 and 270 cm long and between ~55 and 130 cm in diameter (Figures 5A-B). However, there are also samples that were broken and reduced in length during the extraction and transportation processes from the coal mine. The wood texture is well observed at macro scale in the samples of well-preserved silicified wood (Figure 5D).

3. Material and Methods

Samples were taken for geological and paleobotanical study from two study areas, Keşan and Malkara. Numerous petrified wood, partially carbonized wood and rock samples were collected from six locations in total. The samples collected were coded with ‘K’ for the Keşan region and with ‘M’ for Malkara. First of all, they were studied at macro size and then three oriented thin sections were made from each sample: transverse section, radial section, and tangential section. The 36 thin sections were
prepared from a total of 12 fossil wood samples, and identification results of all these samples were published by Çevik Üner et al. (2020). The samples coded as K4 (Glyptostroboxylon rudolphii Conwentz, 1884), K12 (Taxodioxylon gypsaceum (Göppert) Krausel, 1949), K14 (Glyptostroboxylon rudolphii Conwentz, 1884), M7 (Taxodioxylon gypsaceum (Göppert) Krausel, 1949) and M9 (Taxodioxylon gypsaceum (Göppert) Krausel, 1949) were used for the following analysis.

X-ray Diffraction (XRD) analysis was carried out at İstanbul University-Cerrahpaşa Geology Engineering Division of Mineralogy-Petrography with GNR APD 2000 Pro model in Cu-Kα radiation, 40 kV voltage and 30 mA current and 2θ=1°/dk goniometer speed. Measurement was taken between 0°–55° and evaluated by using the Philips X’pert Highscore program. Confocal Raman Spectroscopy (CRS) was performed in Earth Sciences Application and Research Center (YEBİM) Ankara University with a Thermo Scientific brand DXR model device. For point measurements, 25 micrometer slit reading was taken by using 633 nm laser. Samples were studied in the range between 100-1200 cm⁻¹ and 100-2000 cm⁻¹. Samples were analyzed with FTJASCO brand FT/IR 4700 model Fourier Transform Infrared Spectrometer (FT-IR) at İstanbul University-Cerrahpaşa Central Laboratory (MERLAB). Analysis was carried out with 35,000:1 S/N ratio and 0.4 cm⁻¹ maximum resolution. Specific gravity values were obtained at the İstanbul Chamber of Jewelry Gemological Laboratory of Turkey (GLT) with Mettler Toledo JP303G model digital device in an environment of 21.5 °C and 38% humidity. Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) used a Joel- JSM 5600 device and I-XRF 500 device in İstanbul University-Cerrahpaşa Department of Metallurgical Engineering SEM Laboratory.
4. Petrological Identifications

4.1. Optical Microscope Investigations

After the petrified wood was taken from Malkara-Keşan in the Thrace region, the samples were firstly examined with a polarizing microscope. Then, the obtained mineralogical compositions and textural features were supported by other studies such as XRD, Raman spectroscopy and FT-IR.

Geologically, petrified wood samples located in clastic and volcano-clastic rocks in the Malkara-Keşan regions differ from each other in terms of textural and mineralogical features. The basic lithological unit containing petrified wood is the Danişmen Formation, which consists of claystone-sandstone-marl and volcano-clastic/pyroclastic levels in places. Within this formation, the samples of petrified woods were silicified in places, were carbonated in places or both are observed together and described.

Banded siltstones in the Danişmen Formation are light gray-cream colored and contain opaque minerals and carbonate cement. In addition, they include dark-colored carbonization and light-colored silicification with the coal formations. The samples are very fine grained and lithic textured rocks (Figure 7).

Silica polymorphs in petrified woods from the Malkara–Keşan regions were recognized with transmitted polarized light microscopy. While crystalline quartz was well defined, opal-A and other polymorphs of silica were partly examined due to isotropic features (i.e. opaque black). Weak crystallinity of opal-CT showed interference colors, in contrast to the brighter colors that are characteristic of chalcedony and quartz. Optical microscopy also provides anatomic information about samples where cell features can be distinguished based on color variations.
When the sandstones in the Danişmen Formation are examined in terms of their mineralogical properties, they have fine-medium grained and good gradation. In terms of textural maturity, the grains consist of less angular-round components. Mineralogically it can be defined as mature due to the low amount of clay and high quartz content. In microscopic studies, mineralogical composition is mainly composed of quartz, feldspar, mica and epidote minerals, sedimentary (limestone) and metamorphic (quartzite, schist) rock fragments cemented with carbonate. Sandstones from the Danişmen Formation are defined as lithic-arkose, subarkose type sandstone according to the classification of Folk et al. (1970). The abundance and orientation of muscovites and the metamorphic rock fragments indicate that the sandstones were derived from metamorphic rocks (Strandja Massif). In the formation, claystone levels are also intercalated as well as sandstones. Petrified wood fossils are frequently found in these units, which are light gray-cream colored, very fine-grained and have opaque minerals and carbonate cement. The petrified wood samples taken from levels close to the coal bands are examples with dark-colored and well-preserved wood texture. Carbonization and silicification are observed in thin sections. As a result of the examination of petrified wood samples under a polarizing microscope, opal, chalcedony and quartz were identified, which are different products of silica. But the precise distinction between them could not be made very well and the presence should be confirmed with XRD, Raman, FT-IR and other studies. *Keşan Region:* While quartz and chalcedony crystals are observed under polarized light in the radial section of the petrified wood samples from the Keşan region (K5b), the structural elements in the wood such as wood parenchyma, tracheid and ray are
observed in transmitted light (Figures 8, 1A-1B). Similar minerals and their textural
features are observed in the tangential section (K5c) of the petrified wood (Figures 8,
2A-2B).

Petrified wood samples can be separated from each other due to the difference in coal
levels and wood tissues under plane polarized light (PPL). Fossil wood, which has
interference colors of gray shades, offer a wide range of crystalline textures from fine-
grained to coarse-grained ones. While some of them show very good crystallization to
form medium-coarse-grained quartz crystals (Figure 8, 1A), some are in the form of
microcrystalline chalcedony and some of them are observed as more amorphous silica
(Figure 8, 2A). While wood-structure components are partly or completely preserved in
fine-grained wood samples, the resulting silica formations generally developed in
accordance with these building elements. While the quartz crystals and chalcedony fill
in tracheids seen in the cross section (Figure 8,1A), chalcedony also developed on the
tangential section (Figure 8, 2A).

Chalcedony is typically distinguished from microcrystalline and crystalline quartz and
fine-grained or amorphous opal by fibrous crystals and their radial arrays. But
chalcedony and microcrystalline quartz have similar interference colors.

The petrified wood samples from Malkara-Keşan (SW Trakya) were identified by Çevik
Üner et al. (2020). However, in some cross sections, the juxtaposition of quartz crystals
in the tracheid and / or roundish cavities in the tracheids make it easy to identify. Silica
crystallization may have occurred in several stages in the woods of the Keşan region.
Recent studies about this subject found that silica may be in the form of opal-A, opal-
CT (chalcedony-tridymite) and quartz, respectively, during diagenesis in aqueous
sediments (Mustoe, 2017; Viney et al., 2019). It is a common belief that silicification
occurs in this order in fossilized wood, but in many studies the fossilization of woods may involve multiple phases of mineralization. These coarse quartz crystals are considered to be the primary occurring mineral. This feature is supported by both the observation of abundant quartz crystals under polarizing microscope and good observation of the peaks for quartz in XRD evaluations (Figure 10).

*Malkara Region:* Although petrified wood from the Malkara region resembles the Keşan fossil wood, some properties differ such as wood parenchyma and tracheids (Figure 9, 1A).

The crystallization level of silicified wood was determined by examining them under a polarizing microscope and quartz crystallization with fine-medium grain size was well observed in two-directional sections (Figures 9, 1A-2A). In addition, tracheids and rays, which are among the structural elements of wood, were observed well under plane polarized and crosspolarized light. In silicified woods, which offer an extremely cellular structure, the cell walls are observed to be brown-black while the interior of the cell is colorless. While the cell walls are considered carbonated derivatives of organic material, the inner parts are identified to be filled with silica (Figures 9, 1B-2B). In some sections, quartz is observed as coarse crystals showing intense crystallization properties, while it resembles a single mineral rock (such as quartzite), but the preservation of the wood texture under the single Nicol indicates that these samples are petrified wood. Chalcedony and opal formations, observed to be microcrystalline or amorphous, are relatively limited in some samples.

### 4.2. X-Ray Diffraction (XRD)

X-Ray Diffraction (XRD) is an important and common method for identifying polymorphs of silicain petrified wood research, but it is not sufficiently effective in
identifying species such as opal-A and opal-CT. However, polymorphs of silica in petrified wood do not occur with a single color, and both crystalline and amorphous types can coexist in the cell structure. Therefore, crystalline quartz peaks may be weaker than expected. In the case of microcrystalline-crystalline quartz, it provides diffraction peaks.

As a result of XRD studies of petrified wood samples from the Keşan and Malkara region, the peaks of the crystalline types of silica were well defined in the diffractogram patterns (Figure 10). Quartz peaks were identified at 2θ between 21° and 26° on the diffractogram for both samples (K-4, M-7) from Malkara-Keşan areas (Figure 10). Especially opal-A is not well recognized in XRD patterns but it appears as an amorphous mineral in optical and SEM microscopy of some samples of Malkara-Keşan region petrified wood. On the other hand, opal-A formed in petrified wood cells that contain a small quartz-filled fracture produces a pattern that appears to indicate quartz composition (Mustoe et al., 2020).

4.3. **Confocal Raman Spectroscopy (CRS)**

In confocal Raman spectroscopy studies performed on thin sections of samples (K14 and M7) from the Malkara-Keşan region, readings were made from cell (tracheid) walls (Figures 11, a-c) and cell centers (lumen) (Figures 11, b-d). While peaks for types of silica and carbon were identified in the analysis of the walls, only silica peaks were detected within the cell. While quartz is characterized by Raman peaks at 354, 395-7, 464 and 465 cm⁻¹, quartz polymorphs, i.e. monoclinic SiO₂ phase moganite, are observed at 503-6 and 504 cm⁻¹ (Saminpanya and Sutherland, 2013; Figure 11). Opal, the other type of polymorphous SiO₂, is seen as bands at 1587 and 1607 cm⁻¹ but carbon (graphite) and silica were obtained in the same band gap. It is believed that the
carbonaceous parts may be in the form of thin bands and were read by the laser simultaneously with the silica around them (Figure 11). This situation can be evaluated as indicating that both fine carbon structures and silica polymorph structures occur together within the Raman peaks where the laser falls and the spectrum reflects this combination (Figure 11).

In two samples (K14 and M7) from the Malkara-Keşan region, mineralogically the graphite form of carbon and quartz and chalcedony polymorphs of silica, as well as moganite crystallized in the orthorhombic system were detected as a result of Raman studies (Figure 11).

4.4. Fourier Transform Infrared Spectroscopy (FT-IR)

FT-IR analyses were performed on two petrified wood samples from the Malkara-Keşan regions. The two samples (K14 and M9) are characterized by silica mineralizing processes in the FT-IR spectra (Figure 12). The typical peaks for quartz and microcrystalline chalcedony were seen in FT-IR diffractometry patterns. As a result of these analyses, polymorphs of silica such as quartz-chalcedony and moganite and mineralogical elements similar to carbon and graphite were detected in the petrified wood samples.

4.5. Density Measurement

One of the physical properties of petrified wood is density (specific gravity). The measurement of density is a simple method for identification of silica polymorphs in petrified wood. This simple gravimetric method can provide evidence for the study of fossil woods in Malkara-Keşan areas. It can be performed rapidly and requires minimal laboratory facilities. Samples mineralized with opal have densities of 1.9–2.1 g/cm³, compared to 2.3–2.6 g/cm³ for woods mineralized with chalcedony or quartz. The
density of two petrified wood samples from the Keşan-Malkara region was measured. As shown in the table, both samples (K4 and M7) have chalcedony and quartz composition and their densities are 2.35 and 2.27 g/cm³ respectively (Table and Figure 13). These intermediate densities may be the result of petrified wood with mixed silica and carbon due to coalification. This is why density can be analyzed with loss on ignition (LOI) of petrified woods. Although calculation of relict organic matter based on 450°C LOI yields only an approximation of the actual value, the results are useful for evaluating the degree of permineralization (Mustoe, 2016). For the density of the fossil wood, % weight loss occurs when a powdered sample is heated for several hours at 450°C to destroy organic constituents. Another possibility is that the petrified wood contains a mixture of opal and quartz/chalcedony. Similar evidence from XRD patterns, optical microscopy and SEM supports this view about the composition of fossil wood.


Silica precipitation in fossil wood may occur in two stages, such as permineralization and replacement that form different silica polymorphs deposited in separate episodes during diagenetic transformation. These polymorphs of silica are amorphous opal-A, microcrystalline opal-CT, and chalcedony. If wood is fully petrified, silicified wood has dense texture and homogeneous silica polymorphous. But wood specimens that contain partial mineralization may have cavities on their surfaces. This type of specimen is suitable for investigation with scanning electron microscopy (SEM).

Two different wood types were identified in Malkara-Keşan region. The vertical and horizontal tracheids and pits in silicified wood are not well-preserved and detected in Figure 14. The textures of petrified wood are not seen very well in SEM photographs.
(K4, K14 and M-7 samples). However, in the SEM photo of the Malkara region sample M7, less distinct tracheids are observed and in the woody tissues called lumens are also well preserved and filled with opal and microcrystalline quartz crystals (Figure 14 c).

The average elementary composition measured in the target areas in each sample consists of approximately O, Si, S, Ca, Cr and Fe elements for Keşan region samples K4 and K14. The small peak to the left of the oxygen peak in spectra K4 and K14 is the carbon peak (Figure 14, a-b). The presence of weak carbon peaks in SEM diffractograms usually show that carbon is enriched in relict cell walls relative to silica-filled lumina. There is not a lot of carbon in any of the samples, but the carbon abundance varies, with M7 having almost none.

For all of the samples, the Ca and S values suggest a small amount of gypsum. This is not common in fossil wood, but some petrified wood specimens from arid regions include gypsum. The presence of this mineral in silicified wood from the Malkara-Keşan region probably represents a time when ground water contained dissolved sulfate, causing Ca to precipitate as CaSO₄ rather than as CaCO₃ or Ca₅(PO₄)₃ (Mustoe et al., 2020). If gypsum is present, the Ca:S ratio should be 1:1 (Mustoe, 2021). For sample K14, 2.62% Cr could make this a possible pigment as this is a very high level in terms of the amount needed to produce color in fossil wood. It is hard to understand the presence of S in this sample. The most common sulfide minerals found in fossil wood are iron pyrite and gypsum, but this spectrum does not contain peaks for Fe or Ca. Chromium would be more likely to be present as an oxide, and there are a few possibilities. Ordinarily, it is expected that trace metal colorants might be in the form of
individual atoms substituting in lattice positions in other minerals, but 2.62% seems to be high for this explanation (Mustoe, 2021).

The high Cr value in K-14 sample may be due to a local fault zone that developed within the previously-defined "Thrace Fault System" (Perinçek, 2015) in the region. Along the fault zone, hydrothermal solutions may dissolve some elements such as Cr, Ni, Co from ultramafic rocks that are thought to exist at depth and these elements may be included in silicified wood during petrification. This assumption may be supported by the high content of some elements such as V, Cr, Co, Ni, Zn, As, Rb, Sr, Mo, Cs, Ba, W and U detected in coal ash in some studies about coal in the Thrace region (Erarslan and Örgün, 2017; Erarslan, 2018). It is thought that hydrothermal solutions may bring these elements along the fracture zones and there may be local enrichment, which may explain the excess Cr element in petrified wood located near the coaly levels especially.

The elementary composition represents original organic constituents and elementary mobility during petrification.

In the Malkara sample, the chemical composition of the areas that appear to be opal consists of only O and Si elements. The SEM-EDS examination of the petrified wood samples revealed that the pits between tracheids are also filled with opal and microcrystalline quartz crystals. The elemental composition of these quartz microcrystals filling the cell walls, pits and lacunae indicate that there are two possible sources of silica required for the petrification process. These sources are those derived from hydrothermal fluids or due to weathering of feldspars in late Oligocene-early Miocene sediments.

In the Malkara-Keşan region, periods of sedimentation accompanied by volcanic activity occurred in mid-Tertiary time, followed by uprise of hot siliceous fluids that
carried S, Ca, Cr, Si, O and other elements. The high concentrations of these elements in Oligo-Miocene petrified wood samples may be due to hydrothermal solutions related to volcanic activity (Hisarlıdağ Volcanics) in the southwestern Thrace basin. Fossil forests that develop due to volcanic activity are observed at different locations in Thrace, as well as in the east of Greece on Evros, and some islands such as Limnos and Lesvos (Velitzelos and Zouros, 1997; Voudouris et al., 2007).

5. Biodiversity and Paleogeography of Keşan-Malkara Regions

The fossil wood materials studied here were identified and published by Çevik Üner et al. (2020). They are Glyptostroboxylon rudolphii Conwentz, 1884 (all from Keşan), Taxodioxylon gypsaceum (Göppert) Krausel, 1949 (one from Keşan and one from Malkara), Ginkgoxylon lesboense Süss, 2003 (one from Keşan), and Quercoxylon caucasicum (Gajvoronskij) Madel-Angeliewa, 1968 (all from Keşan). G. rudolphii and T. gypsaceum are common fossil woods identified in Turkey (Figure 15). They are found mainly in Oligocene to Pliocene deposits and mainly from early-middle Miocene fossil sites. In Thrace basin, Özgüven Ertan (1971), Kayacık et al. (1995), Aras et al. (2004), Akkemik et al. (2005), Akkemik and Sakınç (2013) and recently Akkemik et al. (2019a) reported the presence of fossil wood from Taxodium (=Sequoioxylon) gypsaceum. The presence of the fossil wood of Glyptostroboxylon rudolphii was determined by Çevik Üner et al. (2020) for the first time in Thrace (Figure 15, 1-3).

Denk et al. (2017) assessed both these genera as members of swamp (vegetation unit 3 “VU3”) and riparian forests (vegetation unit 4 “VU4”). All studies about fossil wood revealed that lowland riparian and swamp conditions were common through Turkey.
from late Oligocene to Pliocene (e.g. Özgüven Ertan, 1971; Kayacık et al., 1995; Akkemik et al., 2005; Sakınç et al., 2007; Akkemik et al., 2009; Akkemik and Sakınç 2013; Acarca Bayam et al., 2018; Akkemik, 2019; Akkemik and Acarca Bayam 2019; Güngör et al., 2019; Polat et al., 2019; Çevik Üner et al., 2020).

The other two genera, *Quercoxylon* Sect. *ilex* and *Gingkoxylon*, may be evaluated as representatives of well-drained lowland (VU5) and upland (VU6) conditions. The species composition shows that the environmental conditions were more humid than today, rainfall was high and that there were swamps and riparian areas in the plains together with well-drained lowland and/or upland areas in Thrace (Çevik Üner et al., 2020).

6. Discussion

Fossil wood occur via permineralization when solutions rich in minerals permeate porous tissue. Minerals fill the pores and empty spaces. Petrification occurs when cellulose, hemicellulose, and lignin within the cell walls of the woody tissue act as a framework to preserve cell structures. Silicates, iron oxides, metal sulfides, native elements, carbonates, and sulfates can be involved in permineralization. Silicified wood is the most common petrification type and provides the most detailed preservation of cell structure (Viney, 2014).

The formation of petrified wood includes permineralization, replacement and recrystallization stages. When wood is permeated by silica solutions, hydrogen bonding links silicic acid (H$_4$SiO$_4$) to cellulose making up the inner cell walls (Viney, 2014). Silicic acid is polymerized into opal through water loss. Silica is firstly amorphous in the wood structure and later on it crystallizes to a more stable form. Silicification
includes a transformation of the initial silica to increasingly more stable forms from opal-A to opal-CT to chalcedony, moganite (α-quartz) and finally to quartz. However, evidence for silica recrystallization is lacking in some specimens, suggesting more than one pathway for silicified wood formation (Mustoe, 2008; Viney, 2014). The rates of change can be perturbed by heating, weathering and dissolution of deposited silica. However, moganite seems indicative of the influence of volcaniclastic material during silicification (Matysová et al., 2010). Moganite (α-quartz) is a meta-stable silica polymorph that is intergrown cryptocrystalline quartz forming chalcedony (Florke et al., 1976). This mineral is usually buried by volcanic material (Hatipoğlu and Türk 2009; Saminpanya et al., 2013).

The silicification mechanisms outlined here represent the first step in understanding the variables involved in the wood preservation processes in the Malkara-Keşan sedimentary deposits. These areas are characterized by widespread occurrences of petrified forests, mainly in the volcanic environments of the northeastern Thrace basin (Çevik Üner et al., 2020). The Danişmen Formation, which contains petrified wood, represents a typical terrestrial-delta environment, containing sandstone-claystone-shale alternations and rarely limestone levels and parallel coal (lignite) formations. Fossil woods with different thicknesses and levels, which cut these nearly horizontal units in vertical positions, can be found in the environment by burial. Petrified wood is identified at different levels of the Danişmen Formation in Malkara-Keşan regions, but it is thought that the Hisarlıdağ Volcanics and their hydrothermal solutions, which are located in the vicinity and outcrop east of the study area, are sources that affected sedimentation and fossilization (petrification).
Permineralization and replacement are not independent processes; instead, they commonly occur concurrently. The fidelity of anatomical preservation depends on the relative rates of these processes. Rapid rates of mineral deposition under relatively mild Eh and pH conditions favor the preservation of organic matter. These conditions appear to be more common for calcium carbonate deposition than for silicification, as evidenced by observations of permineralized wood specimens from many localities. SEM images and HF-etched specimens indicate silicification and it commonly begins in the cell walls, but subsequent mineralization may occur.

The silicified woods in the Malkara-Keşan region were caused by the effect of volcanic activity on the silica content of the environment which increased in some stage of sedimentation while the Danişmen Formation units were deposited, and trees in the region may have silicified in this environment (Batı, 1996; Siyako, 2005; Akkemik and Sakınç, 2013). It is also suggested that the faults observed in the region may affect carbonization and silicification that developed in this formation. While the structural elements that make up the Thrace fault system cause some parts to rise, in some parts they caused the basin to form with erosion.

In many parts of the world, such as Indonesia, America, Germany, Egypt, Iran and China, there are petrified wood forests formed at different ages with similar volcanic activity and sedimentation. Rare conditions, acidic environment and silica-rich fluids are required for all fossil forest formations.

Trees buried in fine-grained claystones and siltstones in the Danişmen Formation under went the silicification phase with the effect of hydrothermal solutions with acidic composition. Silicification events that develop due to volcanism in the Aegean region, on the other hand, formed by the exposure of trees in pyroclastic sediments to
petrification by hydrothermal solutions (Voudouris et al., 2007; Pe-Piper et al., 2019).

The formation process of silicified wood in the Malkara-Keşan region is related to the
Hısrıludağ Volcanics outcropping in the region. The volcanics consist of andesitic and
dacitic rocks and tuff alternations such as rhyodacitic tuffs, andesite, altered andesitic
tuffs and reddish green lahar flows (Güçtekin, 2017). It has acidic to intermediate and
high-K, shoshonitic characteristics geochemically. The age of these volcanics was
determined as 35.0 ± 0.9 Mausing the K/Ar method on andesitic rocks from the upper
levels of the Hısrıludağ volcanics (Sümengen et al., 1987). There is a relationship
between silicified wood and hydrothermal solutions from the Hısrıludağ Volcanics
during the silicification process in Malkara-Keşan area. The magmatic-hydrothermal
systems cover extended areas in this region. In addition, similar relations were
identified in some areas such as Sigri Petrified Forest and silicified Evros and Limnos
Islands in Greece (Voudouris et al., 2007; Pe-Piper et al., 2019).

According to an experimental study, the silicification of petrified wood in volcanic ash
is possible if the hydrothermal fluids bring the pH of the environment from around 7.8
to an acidic state of around 4 and the temperature is around 100°C (Ballhaus et al.,
2012). In some experimental studies, the temperature and H₂O pressure conditions in
the environment must rise from 100°C to 150°C (in rhyolitic volcanism) and the
pressure should be around 1 atm for silicification to occur (Läbe et al.,2012). In these
studies, it was observed that in deep environments where trees are buried, organic parts
of lignin containing macro-molecule grains are liberated over time with the effect of hot
water providing an acidic environment, and silicification can take place.
Paleobotanical research in the study area indicates that the environmental conditions of the petrified wood species were more humid than today, rainfall was high and marshes and riparian areas existed in the plains (Çevik Üner et al., 2020).

7. Conclusion

- Petrified wood is located in clastic and volcano-clastic rocks in Malkara-Keşan regions.
- From the mineralogical studies of petrified wood, it was concluded that silicification is a versatile event and can develop with different forms of silica.
- Silica forms in samples are generally developed in accordance with structural elements of wood (tracheid, ray etc.) or cracks in the structure.
- The examination of the fossil wood samples under a polarizing microscope revealed that opal, chalcedony, moganite and quartz were present as different silica products.
- XRD studies of wood samples from the Keşan and Malkara regions found the peaks of crystalline types of silica were well defined in the diffractogram patterns.
- Raman analysis shows that petrified wood samples from the Malkara-Keşan region contain the graphite form of carbon and quartz and chalcedony polymorphs of silica.
- As a result of FT-IR analysis, quartz-chalcedony-moganite and mineralogical traces similar to carbon and graphite were detected in the petrified wood samples.
- According to specific gravity values, which is one of the physical properties, chalcedony and quartz were determined in fossil wood samples.
- In SEM photographs of thin sections, the textural features such as cell wall, tracheids of petrified wood were weakly seen. The average elementary composition in EDS
analysis comprised O, Si, S, Ca, Cr and Fe elements in the Keşan region and O, Si and Fe elements in the Malkara region samples.

In conclusion, in the Malkara-Keşan region in mid-Tertiary time, there were periods of sedimentation accompanied by volcanic activity and followed by uprise of hot siliceous fluids that carried S, Ca, Cr, Si, O, Fe and other elements. As a result, trees living during this period turn into petrified wood with the action of silica-rich fluids. Similarly, evidence from XRD patterns, optical microscopy, Raman, FT-IR and SEM/EDS studies support this view about the composition of petrified wood.

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Table. Densities of silicified wood samples.

<table>
<thead>
<tr>
<th>Age</th>
<th>Location</th>
<th>Mineralogy</th>
<th>Genus</th>
<th>Density g/cm³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Late Oligocene</td>
<td>Keşan</td>
<td>Chalcedony/Quartz</td>
<td>Glyptostroboxylon rudolphii</td>
<td>2.347</td>
</tr>
<tr>
<td>Late Oligocene</td>
<td>Malikara</td>
<td>Chalcedony/Quartz</td>
<td>Taxodiodyxylon gypsaceum</td>
<td>2.267</td>
</tr>
</tbody>
</table>
Figure 1. The areas studied and geological map of Thrace basin (Modified according to Siyako, 2006).
Figure 2. Generalized stratigraphic section for the Tertiary sequence in Thrace (Modified from Siyako, 2006).
Figure 3. A-B) The view of the horizontal or nearly horizontal layers of the Danişmen Formation in the Keşan region and tree trunks perpendicular to these layers. C) The view of the layers forming the formation and the coal layer in the coal mine. D) View of the carbonated tree trunks extracted from near the coal layer.
Figure 4. General view (A) and cross section (B) showing the location of coal bands and silicified wood layers within the Danişmen Formation in the Keşan region (PW: Petrified Wood).
Figure 5. A-B) Silicified wood samples of various sizes extracted from the mine in Malkara region. C) General view of the coal mine where some of the silicified wood samples belonging from the Malkara region were identified. D) Macro view of well-preserved woody texture in silicified wood.
Figure 6. Field photograph (A) and cross section (B) showing the location of layers in the Danişmen Formation, coal bands and silicified wood samples in the Malkara region (PW: Petrified Wood).
Figure 7. General view of siltstones from the Danişmen Formation, which are very fine grained and include some calcite veins, PPL (left: Keşan region [L], right: Malkara region [R]).
Figure 8. For each photo pair of Keşan region samples, image A is ordinary polarized light view, image B is transmitted light view. Sample K5, radial section (1A-1B) and tangential section (2A-2B) showing an area where tracheids (T), rays (R) and wood parenchyma (WP) are mineralized with quartz (Q) and chalcedony (Ch). 2A-2B. Radial section with tracheid (T), ray (R), wood parenchyma (WP).
Figure 9. For each photo pair of Malkara region samples, image A is ordinary polarized light view, image B is transmitted light view. Radial section (1A-1B) and tangential section (2A-2B) showing quartz (Q) and chalcedony (Ch) filled tracheids (T), rays (R) and wood parenchyma (WP) in sample M7 (Malkara region).
Figure 10. X-ray diffraction patterns for two typical specimens from Keşan (K4) and Malkara (M7) regions. Optical microscope images of these specimens show amorphous opal-A, microcrystalline chalcedony and crystalline quartz polymorphs of SiO$_2$ in petrified wood but X-ray patterns only show peaks for quartz minerals.
Figure 11. Raman spectra of the cell wall (a-c) and the lumen (b-d) from Keşan (K14)-Malkara (M7) petrified wood samples.
Figure 12. FT-IR spectra of two silicified wood samples (Samples K14 and M9).
Figure 13. Silicified wood samples from Keşan-Malkara region are included in one density category (Chalcedony/Quartz) (Data are from Table).
Figure 14. SEM images of silicified wood specimens from Malkara-Keşan region. a) Areas of white and black include opal type silicification where conchoidal fractures are the most obvious topographic feature. b) K14 contains many small silicified areas, two samples consist of O, Si, S, Ca, Cr and Fe elements. c) Sample M-7 radial orientation, showing tracheids partly/unclear crystallizations and consists of O, Si and Fe elements.
Figure 15. 1-3) Wood sections of *Glyptostroboxylon rudolphii*. 4-7) Wood sections of *Taxodioxylon gypsaceum*. 