

Silica polymorphs in the mineral assemblage of fossil plant samples from Lesvos Petrified Forest

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The Lesvos Petrified Forest was formed by silicification process of plants during the Lower Miocene era, when intense volcanic activity occurred in that region. It is situated in the western part of Lesvos Island (NE Greece) and consists of hundreds of standing and lying fossilized tree trunks, covering an area of 150 km². It is one of the most important natural heritage monuments in the world and in 2004 the area was included in the Global Geoparks Network. The Natural History Museum of the Lesvos Petrified Forest is the management body of Lesvos Geopark (Zouros, 2010). During the last three decades, a great number of excavations are taking place in the area, revealing important fossil plants and providing crucial palaeobotanical and volcano-sedimentological information. Despite its significance, the conduction of extensive geochemical and mineralogical analyses on fossil plant samples from this area has merely commenced (Pe-Piper et al., 2019), providing information on the permineralization process.

The present study aims to shed light on the silicification of the Lesvos fossil woods, by analyzing the silica polymorphs comprising the latter samples. Seventeen fossil plant samples were collected from the Sigrí pyroclastic formation within the Lesvos Petrified Forest. Several analytical techniques were employed. A Philips QUANTA 200 Environmental Scanning Electron Microscope (ESEM), coupled with an Oxford INCA Energy 200 Energy Dispersive System (EDS) was used for imaging and chemical analyses. For the Raman spectroscopy, a Thermo Scientific DXR Raman Microscope with a 780 nm laser beam was employed. The power value of the sample irradiation was ranging from 6 mW to 12 mW. The average spectral resolution in the Raman shift range of 100-3000 cm⁻¹ was 5cm⁻¹ (grating 400 lines/mm, spot size 2µm). Cathodoluminescence (CL) spectra were collected on polished slabs, at low vacuum mode without coating, using a Gatan MonoCL3 detector with a PA-3 photomultiplier attached to the SEM. For the X-ray diffraction (XRD), a Phillips PW1710/00 diffractometer was used with a CuKα radiation source, equipped with a graphite monochromator. The XRD patterns were obtained by step scanning from 2° to 64° (2θ in steps of 0.020°; 4 s per step). Block sections (Figure 1) of each sample were used for the ESEM-EDS, SEM-CL and Raman spectroscopy analyses, while a ground to powder portion of the same samples was used for the XRD analysis.

SEM imaging and EDS spectra provided a first appraisal of the chemical composition of the samples, focusing on silica-rich zones, which were abundant not only in geode-like structures (Figure 1), but also in white, black and green-coloured parts of the fossil plants. While some textural features were evident by ESEM-EDS, the determination of the exact types of silica polymorphs was managed by employing XRD, Raman spectroscopy and CL-SEM methods.

Quartz, opal, cristobalite and tridymite were determined by XRD technique (Figure 2). Opal is a micro to non-crystalline form of hydrated silica with high degree of structural disorder. Cristobalite and tridymite are both more common as components of opal than as individual minerals and may form metastable phases in silica-rich volcanic and sedimentary environments (Pe-Piper et al., 2019).

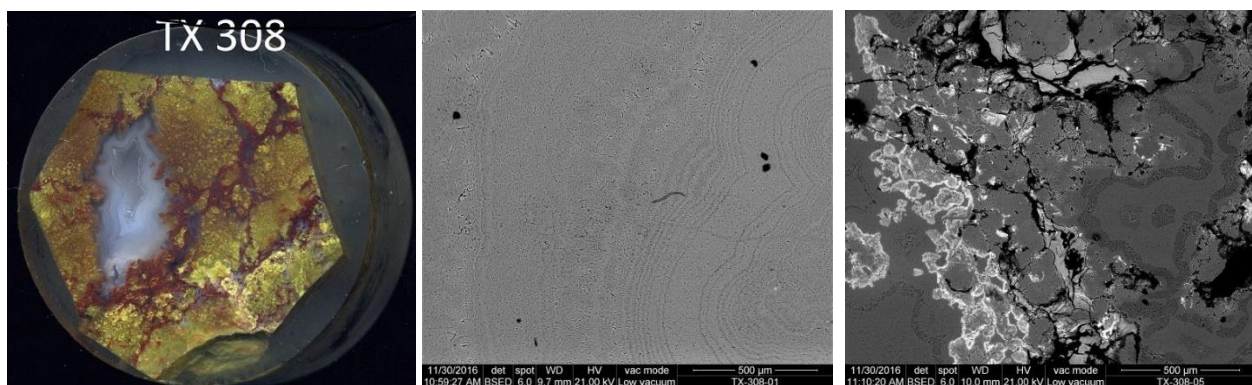


Figure 1. Polished block section of the TX308 fossil plant sample [left] and characteristic SEM images of the same sample showing different silica-rich zones [middle] and geode-like, Si-rich microstructure (various hues of grey colour) and Fe-rich parts (white colour hues) [right].

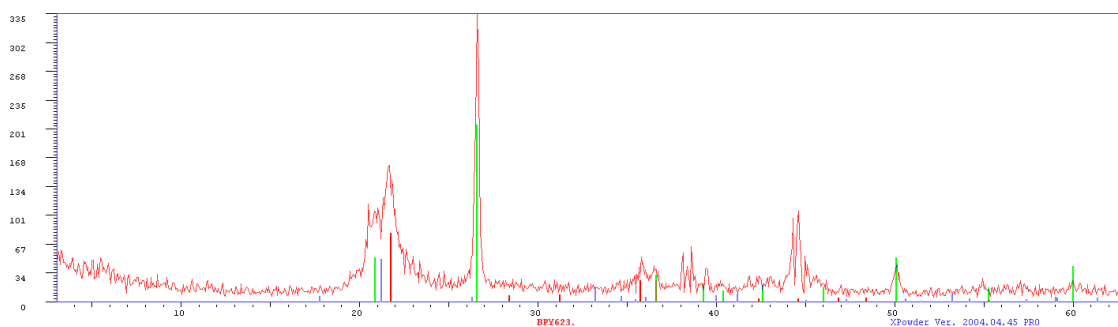


Figure 2. XRD pattern of a fossil plant sample, showing the mineral phases of quartz (green bars) and opal (red bars).

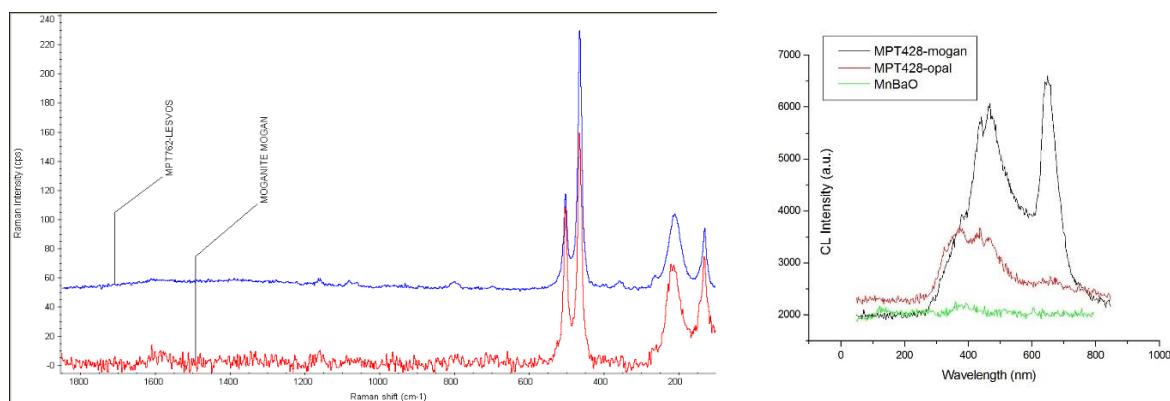


Figure 3. Raman spectra of a standard moganite mineral (red) and the moganite mineral phase found in a fossil plant sample (blue) [left] and CL spectra of moganite, opal and a Mn and Ba-rich phase found in another fossil plant sample [right].

Raman spectroscopy confirmed the presence of opal and quartz. Thus, quartz was revealed with its intensive band at 465 cm^{-1} and the secondary bands at 123 , 203 and 497 cm^{-1} , while opal showed a characteristic hump between 200 and 500 cm^{-1} , with distinct, strong peaks at 350 , 784 and 1590 cm^{-1} (Jordanidis et al., 2014). Furthermore, moganite, which is a meta-stable silica polymorph typically intergrown with cryptocrystalline quartz, was also determined by Raman spectroscopy, revealing its characteristic peak at 502 cm^{-1} and the three other shifts at 464 , 206 and 123 cm^{-1} . Figure 3 shows the assignment of moganite mineral phase compared to the Raman spectrum of an original, standard moganite sample, collected from Mogan, Gran Canaria, Spain.

The cathodoluminescence (CL) technique was employed as a complementary method to all the aforementioned techniques (ESEM-EDS, XRD, Raman) to investigate the fossil wood samples. Quartz, opal and moganite showed distinctive CL spectra. An intensive peak at 650 nm (aprx. 12000 a.u.) and two lower, broader peaks at 430 and 460 nm are determined for quartz (Aparicio and Bustillo, 2012). Opal revealed a CL spectrum with a broad hump between 300 and 500 nm , showing a rather low intensity (aprx. 3500 a.u.), while moganite presented a characteristic double peak at 440 and 470 nm and another at 650 nm with equal intensity (aprx. 6500 a.u.). Additionally, the CL spectrum of a manganese and barium rich phase with very low luminescence is also shown in Figure 3.

In conclusion, the utilization of complementary techniques (ESEM-EDS, Raman, CL-SEM and XRD) provided substantial information for the identification of the silica polymorphs comprising the Lesvos petrified wood samples.

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