Analytical characterization of "Indonesian amber" deposits: evidence of formation from volcanic activity

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Abstract In this study the new mineralogical and geochemical evidence for the reason behind intensive resin production in trees and the formation of Indonesian resin deposits is presented. The analysed specimens of the "Indonesian amber" were subjected to the following comprehensive investigations: PAS, IR, RS XRD and SEM-EDS. It was found that the resins are originated due to intensive volcanic activity. Based on spectroscopic investigations, "Indonesian amber" was assigned to the glessite group. The investigations revealed that the traces of volcanic activity have survived in the studied specimens in their structure were the presence of tonstein and inorganic minerals are related to volcanic phenomena. "Floating" in opaque solid–foam resin indicated that resinous substance was strongly heated trough volcanic activity.

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INTRODUCTION

The fossil resin known in jewellery markets under a commercial name of Indonesian amber or "Borneo amber" (Fig. 1) is currently generating much interest due to its massive resources. It is mined, i.a., as an accessory material to the Miocene brown coal of the Nyalau Formation, at the Merit Pila Mine, Sarawak, Malaysia, with an annual output of 2 to 5 000 tonnes of raw amber. This mine yielded the world's largest piece of amber: a 3.5 x 1–2 m, which corresponds to ca. 5 m² (Hillmer *et al*.1992; Schlee *et al* 1992; Kosmowska-Ceranowicz *et al.* 1994). During the last decade the Indonesian resins found in the several number of outcrops located in the Miocene sediments (17 Ma) were intensively investigated. Lambert confirmed the origin of the resin from the trees of the large tropical family *Dipterocarpaceae*, genera: *Dip-*

terocarpus, *Hopea, Vateria* and *Vatica* (Lambert *et al.* 2013). Finaly he included Indonesian resins then in Group B of' Anderson's chemical classification (Langenheim 2003; Lambert *et al.* 2013).

It is believed that intense resin production in Cenozoic trees was induced by multiple causes. *Dipterocarp* forests were among the most important resin-producers and production of resin was caused by botanic factors, pathogenic factors and most of all by geological conditions, i. e. active volcanism. In the 1960s. the Polish botanist and amber researcher Hanna Czeczott suggested that the volcanism-related activity had intensified resin production. This hypothesis was not verified by unambiguous evidence since today.

Here the authors present new mineralogical and geochemical evidence for the reason behind intensive resin production in trees and the formation of Indo-

Fig. 1 Survey of the finding places of investigated glessite samples on the Malayan Archipelago. Compiled by M. Kazubski
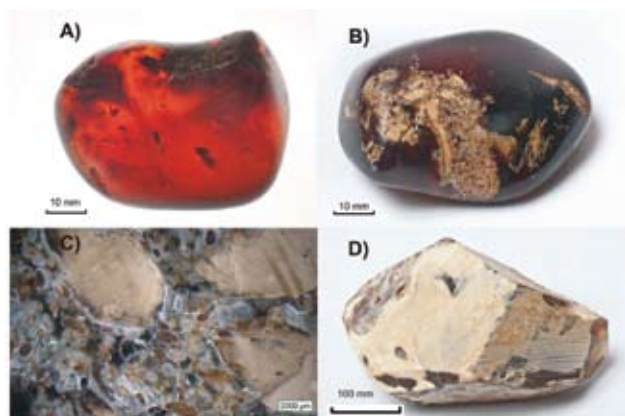
Fig. 2 Indonesian amber (glessite), samples from the collection of the PAN Museum of the Earth in Warsaw. **A.** Specimen No. 26648 in the transmission light (size, mm: 47.3 x 34.6 x 40.5); typical glessite, coal mine in Sumatra Island (Jambi mine). **B.** Specimen No. 26648 in the visible light; amber with creamy inclusions of tonstein, Sumatra Island (Jambi mine). **C.** Glessite No. 26647, structure as seen in 3D Hirox KH 8700 digital optical microscope, x 35. **D.** Specimen No. 26645, pseudomorphs of glessite after calcite, Sumatra. Compiled by B. Kosmowska-Ceranowicz

nesian resin deposits. Specimens of Indonesian fossil resins from the collection of the Polish Academy of Sciences Museum of the Earth in Warsaw were investigated by PAS, IR, RS XRD and SEM-EDS. It was found that the resins are originated due to intensive volcanic activity, as the nanopore structure was confirmed and traces of volcanic activity have survived in the studied Indonesian specimens. The investigated samples include micro-detached blocks of tonstein, chips of pyrogenic quartz, volcanic glass and various minerals related to volcanic phenomena, such as paramorphs of amber after calcite and the resinous microstructures previously not described in literature. The presence of accumulation of microdrops of transparent resin occurred in amorphous or "layered" forms, "floating" in opaque solid-foam resin indicates that resinous substance has been heated to

high temperature trough volcanic activity. Based on spectroscopic investigations, Indonesian amber (Fig. 2 A, B) was assigned to the glessite group

MATERIALS AND METHODS

The investigated specimens of Indonesian amber belong to the collection of the Museum of the Earth's Amber Department in Warsaw. This outstanding museum collection which was started in 1951 includes amber objects from Europe, Asia, South America and Oceania. The first analyzed specimen is originated from the Island Sumatra in the Indonesia, from the settlement Lampung in the province Jambi (Figs 2A, 2B and 2C; size: 47.3 mm long). The second investigated piece of amber was found in the mine Merit-Pila located on the island Borneo in the Malaysia (Fig. 2D; size: 100 mm long).

The macroscopic analysis of the investigated amber objects was followed by the comprehensive study which covered the various physicochemical methods of investigation: positron annihilation spectroscopy (PAS), infrared spectroscopy (IR) and Raman spectroscopy (RS), X-ray powder diffraction (XRD) and scanning electron microscopy with X-ray microanalysis (SEM-EDS). The research on the specimens made under a Nikon stereoscopic microscope at the Museum of the Earth, and the 3D Hirox KH 8700 optical digital microscope made at the Military University of Technology, Warsaw, did provide a more detailed description of the internal structure of the analysed objects.

Positron annihilation spectroscopy (PAS) was involved in the more detailed analysis of the internal structure of the Indonesian amber. The application of PAS has confirmed the presence and the size of empty spaces (nanopores) in the analysed specimens while the preliminary results have been presented (Chojcan *et al.* 2013).

The room temperature measurements of positron annihilation lifetime spectra (LS) were carried out for six samples of amber originating from Gdansk (Poland) and Sambian Peninsula (Kaliningrad Oblast, Russia), two samples from Valchov (Czech Republic) and two samples from Borneo. LS were collected by means of a conventional fast-timing apparatus with plastic scintillators, constant fraction differential discriminators (Ortec 583 Model), a time-to-pulse-height converter (Ortec 457 Model) and a multichannel analyser data buffer (Ortec 919 Model). The full width at half maximum (FWHM) of the time resolution function of the spectrometer is about 310 ps. As the source of positrons the ^{22}Na isotope of the activity of the order of 10^4 Bq was used. It was sandwiched between two pieces of the same studied material. Spectra were recorded in the time range 0–45 ns mak-

ing use of 860 channels of the multichannel analyser. The total number of counts for one LS was at least 4 x 10^6. The measured spectra are shown in Fig. 3.

The obtained positron lifetime data were analyzed with the LT computer program, in terms of two three-component models. The first one is a set of free discrete components with different mean lifetimes τ and intensities I. The second one assumes (1) the intensity of ratio of annihilating para- and ortho-positronium of 1:3, (2) lifetime of annihilating para-positronium, τ_1, of 125 ps, (3) the presence of the log-normal distribution for both, the mean lifetimes τ_2 corresponding to free annihilation of positrons and the mean lifetimes τ_3 related to annihilation of ortho-positrons by "pick off". In the analyzed spectrum this corresponds to components with mean value $<\tau_2>$ and dispersion value σ_2 as well as mean value $<\tau_3>$ and dispersion value σ_3, respectively. The fitted parameters of the models are presented in Table 1.

The identification of analyzed copal resins has been confirmed by Infrared and Raman spectroscopy. The FT-IR measurements were performed in the KBr pellet on the spectrometer Perkin Elmer Spectrum 2000. The infrared spectra of the analyzed sample and the reference sample were collected in the range 4000–500 cm^{-1} with the resolution 4 cm^{-1}.

Further, the amber specimens were investigated by Raman spectroscopy on the spectrometer Nicole Magna 860 FTIR/FT Raman equipped with In: Ga: Ar laser line at 1064 nm. For each sample, the Raman spectra were recorded at the room temperature in the range 100–3800 cm^{-1} with the spectral resolution 4 cm^{-1} and with the same number of scans (512 scans/measurement). The laser power at the exit was set below 0.8 W and was selected individually for each measurement. Since the measurements were recorded *in situ*, from archaeological features, without sampling or prior preparation.

The studied specimens of Indonesian amber contain the inorganic inclusions which were investigated by the XRD and SEM-EDS. The initiatory analysis of the inclusions was carried out using X-ray radiography, with a Siemens D5005 diffractometer. The detailed results of this investigations were previously reported (Kosmowska-Ceranowicz *et al.* 2008). Moreover, in this article is presented the more in-depth analysis of the inclusions which was performed with the application of the SEM- EDS. The SEM-EDS measurements were carried out on the microscope Hitachi S3400N Thermo Scientific with the EDS Noran System 7 (detector Thermo Scientific Ultra Dry Lithium Drifted Silicon with the resolution 129 eV). During the analysis it was applied the accelerating voltage of 30.0 kV and various magnification from 450x up to 1000x with the resolution 3 nm.

RESULTS

The wealth of Indonesian resin varieties, with varying degree of transparency and colour intensity, has been caused by non-homogenous microstructure and the presence of inorganic inclusions and organic residue. Depending on their forms, colour and internal structure they can be classified into varieties: (1) proper varieties – transparent, multicoloured Indonesian resins, and (2) – off white to light beige opaque varieties.

Accomplished IR (Fig.4) and Raman spectra (Fig. 5) allowed to identify Indonesian resins as
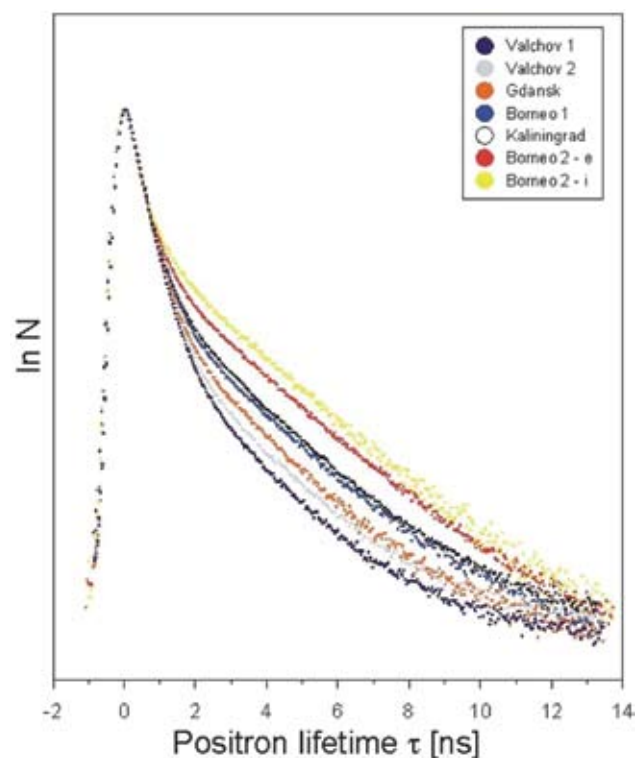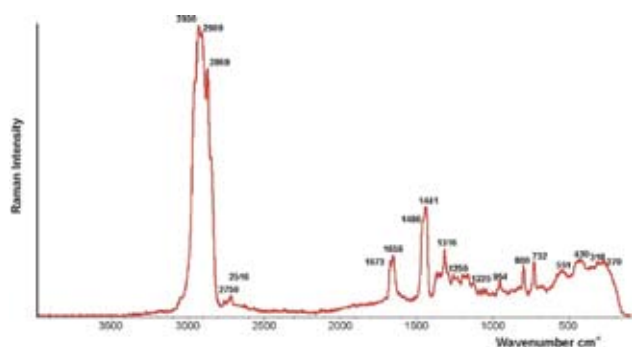

Fig. 3 Positron annihilation lifetime spectra for ambers. Compiled by M. Sachanbiński
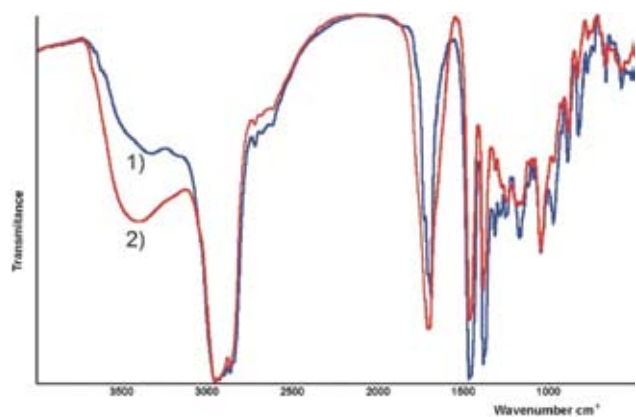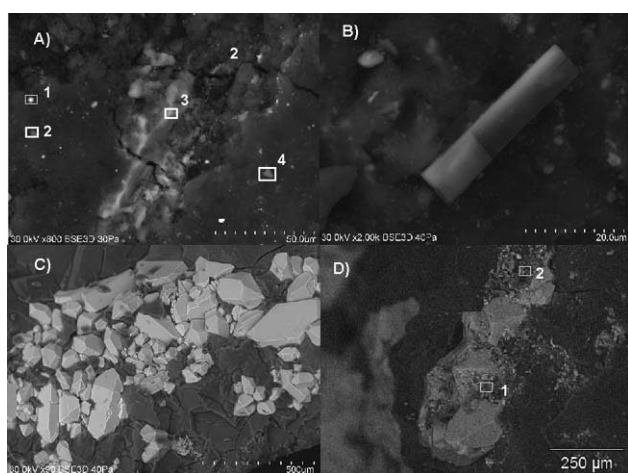

Fig. 4 Infrared spectra: 1 – glessite, Goitsche amber mine, Bitterfeld, Saxony; 2 – Anhalt, Germany; 3 – Indonesian amber (glessite). Compiled by B. Kosmowska-Ceranowicz

Fig. 5 Raman spectra of Indonesian amber (glessite). Compiled by B. Łydżba-Kopczyńska

Fig. 6 SEM-EDS images of Indonesian amber (glessite) from Sumatra. **A.** Inclusions in the typical glessit from Sumatra (presented in Fig. 1A): 1 – pyrite, 2, 3, 4 – pyrogenic quarz originating from volcanic ash. **B.** Halloysite in the tonstein inclusion. **C.** Euhedral quarz crystals placed in contact between tonstein inclusion and glessite. **D.** Sylvine with NaCl and KCl. Compiled by M. Sachanbiński

belonging to the glessite group. IR spectra typical of glessite have a low intensity of the ca. 1740 and 1710 cm-1 bands of the C=O group in esters and the C=O group in fossil carboxylic acids.

Additionally, the nanostructure of Indonesian amber was studied using the PAS method. The measurements have demonstrated that, much like in other resins, positronium is formed in the amber samples, which indicates the presence of nanopores with linear dimensions of from 0.1 nm up to 10 nm. An analysis of the test results allows us to conclude that the parameters of the ortho-positronium component of the positronium lifetime spectrum suggested that the nanoporous structure of fossil resins depends on their age and degree of weathering.

Based on the SEM-EDS analysis, the inclusions of the pyrogenic quartz and pyrite were identified in the typical glessite from Sumatra (Fig. 6A). The creamy inclusions in Indonesian amber appear as isolated grains or are arranged in layers. Our studies verified that these inclusions are fragments of clayey rock cap-

tured by the plastic mass of fossil resin. This type of the resin from Sumatra (Jambi mine) when roasted at 475°C, had a mass loss of 98,05 % and leaves 1,85 % of white residual substance.

The SEM-EDS investigations indicate the presence of kaolinite, quartz, and chlorite calcite and confirmed the identification of creamy inclusions as a tonstein. Moreover, according to SEM-EDS analysis further 11 minerals have been identified. The analysed inclusions contain large quantities of halloysite (Fig. 6 B), which forms thin plates rolled into tubes. Halloysite is known as a weathering product of pyroclastic rock minerals.

Tonstein inclusions also contain hydrous mica and chlorite in the form of fine, highly-weathered grains that was difficult to identify unambiguously. The presence of non-clayey materials including pyrogenic quartz in the form of idiomorphic crystals with reduced prism faces (Fig. 6 A) and chips of quartz crystals (Fig. 6 C) unequivocally confirmed occurence of tonstein.

Also there have been discovered several minerals which evidence tonstein's formation out of volcanic ash: calcite, dolomite, ankerite, pyrite, native nickel, a copper oxide (probably tenorite) with Zn, Pb, Ni and Fe impurities; typical of volcanic exhalation products, baddeleyite (?), gypsum, barite. halite, sometimes symphysis with sylvine (Fig. 6 D).

The crystallographic measurement and SEM-EDS analysis of the preserved faces additionally proved that previously it was a calcite crystal. The pseudomorph's extant faces are cream-coloured. In some places, small amber surfaces are visible under this creamy layer. All the faces of the scalenohedron display visible striation which developed as a deformation of the original calcite. The SEM-EDS elemental distribution map of scalenohedron face showed considerable quantities of Ca, Mg, C, and O, with traces of Al, Si, Na, K, S, and Cl. One of the pseudomorph's face has micron-sized mineral growths, identified as calcite, dolomite, ankerite and halite.

The petrographic composition of the tonsteins, which form the light-grey inclusions in Indonesia's fossil resins indicated that they formed when acidic volcanic material (tuff and tuffite) had been deposited in peat land. The impact of volcanic activity on the origin of Indonesian glessite is also exemplified by the directional ("flowing") microstructure of the white variety which interlays with the often coloured transparent resin, having formed due to increased temperatures.

The region's significant volcanic activity in the Miocene is proven by the accumulations of volcanic tuff transformed into tonstein. The dirty-white tonstein is described by us as the micro-detached blocks in the white variety of glessite and inclusions in

pseudomorphs of amber after calcite. They formed through the subaerial weathering of volcanic tuff in a palustrine environment, in which resin-producing trees had grown, and which was periodically flooded over by the sea. It is worth emphasising that chips of quartz crystal discovered in even macroscopically pure varieties of the Indonesian glessite were originated from the atmosphere.

DISCUSSION

The geological sites of Indonesian amber (glessite) has been toughly investigated in Teguh Sinar Abadi (TSA) coal deposit in the eastern province of Kalimantan in the River Mahakam basin. Amber specimens are found there in the Puluba-balang Formation, in Middle Miocene sediments of terrestrial and neritic environment.

Today, Borneo, Sumatra and other Indonesian Islands can be considered tectonically quiet, with no volcanic presence observed. However the situation has been different in the past. The geological structure of the Indonesian part of Borneo reveal multiple intrusions of volcanic rock and other manifestations of former volcanic activity. Intrusions had a great influence on the properties of the local coal and, in consequence, also the related resins. About 10–15 km north-west of the Melamyk Mine, Meragoh Formation, lava of diabase and tuff are found, related to the former volcanic activity, dated at the Early or Middle Miocene according to geological data.

The natural forms of amber found in the coal beds may indicate that this resinous substance of high plasticity was present when the sediments were formed as a result of the volcanic activity. This allowed voids and cavities in the sediments to be filled up and perhaps also to migrate relatively freely in the sediment. The completed macroscopic analysis did provide a more refined description of the analysed amber It was revealed that accumulations of micro drops of transparent resin occur in amorphous forms (they look like drops), with a diameter of 0.1 mm or larger, "floating" in opaque solid-foam resin. They create the white-coloured variety of resin (Kosmowska-Ceranowicz et al. 2014) which Schlee (1992) named "Eier–Tröpfchen"[2] while others call droplet inclusions (Leelawatanasuk et al. 2013).

The greatest concentration (17.2–37.37 %) of nanopores was (see Table 1) found in the youngest Borneo amber (ca. 17 Ma) (Czechowski et al. 1996; Łydżba-Kopczyńska et al. 2012; Chojcan, et al. 2013).

In the Late Eocene succinite aged 50–40 Ma, found in the Northern Port (Gdańsk, Poland) and the Sambian Peninsula (Russia), the nanopore concentrations are lower. The lowest number of nanopores was found in the oldest (90–80 Ma) Cretaceous Valchovite of Moravia (Czech Republic). As resins age, the radius (R) of the nanopores changes as well: the younger the resin, the bigger the voids.

The (τ_3) parameter, i. e. the average positron lifetime in fossil resin nanopores, also makes possible the determination of the substance which they are filled with. Results (Table 1, Fig. 3) indicate that the nanopores in the analysed resins are filled with various substances depending on the samples' age and origin site (Chojcan, et al. 2013).

The PAS method shows that nanopore structures undergo an age-related transformation process from the Miocene resins of Indonesia to the Cretaceous ones from Moravia. This probably results from the time-related process occurring in conducive conditions, whereby the structure is transformed towards greater cross-linkage and polymerisation. Such a process may also involve the unsaturated bonds in the skeletons structure of di- or triterpenoids forming many natural resins.

The performed XRD analysis of the white residual substance reaveals weak bands originating from kaolinite, chlorite and quartz, minerals that are the componets of tonstein (Kosmowska-Ceranowicz et al. 2014). According to Bohor (Bohor et al. 1993) tonstein is a rock developed through the transformation of the pyroclastic material ejected by volcanoes and formed through subaerial weathering in a palustrine (swampy) environment.

Table 1 Positron annihilation parameters. Compiled by M. Sachanbiński

Sample	τ_2 [ns]	I_2 [%]	τ_3 [ns]	I_3 [%]	R [nm]
Valchovit 1*	0.38310(87)	73.75(37)	1.7422(65)	8.238(70)	0.261(1)
Valchovit 2*	0.4052(32)	45.41(66)	1.7576(88)	9.08(14)	0.262(1)
Succinite* from Gdansk	0.3819(17)	65.62(62)	1.8267(45)	13.79(17)	0.268(1)
Succinite* from Kaliningrad	0.4313(44)	33.33(55)	1.8186(49)	18.39(21)	0.268(1)
Amber from Borneo1 (No. 24548)	0.3942(19)	62.93(57)	1.9956(60)	17.20(20)	0.284(1)
Amber from Borneo 2 – external (No. 22671)	0.4071(24)	47.18(43)	2.0793(34)	29.57(26)	0.292(1)
Amber from Borneo 2 – interior (No. 22671)	0.4338(86)	33.06(56)	2.0576(82)	37.75(53)	0.290(1)

*Specimens from M. Sachanbiński's personal collection.

Another original type of the Indonesian amber with polyhedron shape was photographed by Schlee *et al*. (1992). A similar looking 37.8 g specimen from Sumatra was identified by us as pseudomorphs of glessite after calcite (Kosmowska-Ceranowicz *et al*. 2014). It is a natural polyhedron which looks exactly like a calcite crystal, in both its edge-edge angles now filled with amber. Originally, it was an idiomorphic (idiomorphous) crystal with faces typical of calcite crystallographic form. The carbonates had been rinsed out of the original crystal, after which it was filled with amber. This is how a substitution pseudomorph (pleromorph) of amber after calcite was formed, a so-called "false crystal". As a result, the original $CaCO_3$ was displaced completely, to be replaced by liquid resin. It has an outline of a scalenohedron (see Fig. 2 D), typical of the high-magnesium calcite that grows in marine environments, as indicated by the pseudocrystal's intensive growth along the c-axis. Conversely, freshwater calcite crystals grow intensively perpendicular to the c-axis.

The Miocene volcanism had an large influence on the composition of Cenozoic's atmosphere. As a consequence it changed its composition and thus the permeability of sunlight and heat conduction of the air. Clouds of volcanic dust and ash, especially given the intense and frequent explosions which occurred in the region, may have cut off the access of light for extended periods, while volcanic deposits may have effectively disturbed the physiological processes in trees to change their vegetation. The intensive resin production might have been the effect of the trees' adjustment to the new climate conditions., with increased resin production as a defence mechanism to cope with adverse vegetation conditions caused by the changing climate.

CONCLUSIONS

A characteristic feature of Indonesia's fossil resins (from the glessite group) is that they are found in the region mainly in primary deposits, related to coal-bearing layers, probably in the peripheral parts of these layers. The formation of glessite was no doubt related to the volcanic processes which were destroying the resin-producing forests. The petrographic composition of the tonsteins which form the light-grey inclusions in Indonesia's fossil resins indicated that they formed when acidic volcanic material (tuff and tuffite) had been deposited in peat land. The impact of volcanic activity on the origin of Indonesian glessite is also exemplified by the directional ("flowing") microstructure of the white variety which interlays with the often coloured transparent resin, having formed due to increased temperatures.

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