



# Vibrational spectroscopy with chromatographic methods in molecular analyses of Moravian amber samples (Czech Republic)



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## ABSTRACT

New information on the molecular composition of valchovite (from Boskovice Furrow, Czech Republic) and studlovite (Študlov, near Valašské Klobouky, South-east Moravia, Czech Republic) were obtained using gas chromatography, attenuated total reflection Fourier transformed infrared spectroscopy (ATR-FTIR), and Fourier transformed Raman spectroscopy. ATR-FTIR was coupled to principal component analysis and used for the classification of ambers according to their composition. The archaeological amber originating from a Lusatian Urnfield settlement of the Hallstatt period (Kralice na Hané, near Prostějov, Czech Republic), together with Baltic amber (Denmark), were used to demonstrate that two principal components suffice to classify the samples into distinct groups. Valchovite (Upper Cretaceous) and studlovite (Eocene) did not show compounds and features typical for Baltic amber, but only nonspecific or non-identifiable compounds that are remnants of the original terpenoids. However, although the results of the analytical records did not indicate a more specific plant source, studlovite was classified as belonging to amber classification Class 2, and valchovite, to Class 1b. The results confirmed the higher degree of maturation of studlovite in comparison with older valchovite and the close spectral resemblance between ambers of different ages emphasises the importance of alterations and post-depositional conditions on the character of the resulting amber. Succinic acid, determined as its dimethyl ester, and the 'Baltic shoulder', the well-known markers in ambers of Baltic origin, as well as softening point, or the ratio 11645/11450 in the FT-Raman spectra, showed that the archaeological samples were derived from Baltic amber, confirming the view that the territory of Moravia was a trading or market center for this material on its way to southern and southeastern Europe.

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## 1. Introduction

The term amber refers mainly to brittle and hard fossil resins with a high content of succinic acid, originating usually in the Upper Eocene deposits as outcrops on the Baltic Sea shore. However, amber is generally synonymous with all fossil resins that differ geographically in age and chemical composition [1]. Amber has been documented from the late Carboniferous to late Pleistocene sediments throughout the world, predominantly derived from gymnosperm trees.

Rare amber deposits occur in Bohemia and Moravia of the Czech Republic. They are mainly of Cretaceous (Cenomanian) and Tertiary (Eocene, Oligocene, and Miocene) ages, and some of them are known by their mineralogical names duxite, valchovite, neudorfite, muckite [2–3]. In Moravia, the most substantial deposit is of the Eocene amber studlovite, from the Carpathian Flysch Belt (the village of Študlov, near

Valašské Klobouky, South-east Moravia). Amber of such quality and variety of colours suitable for grinding, has not been found anywhere else in the Czech Republic. Additionally, fossil insects (wasps, spiders, ants) were discovered in some pieces of this amber. The basic description was reported in [2] and [4]. The other amber found in Moravia is valchovite (valchovite, walchowite; from Valchov east of Boskovice, central Moravia) of the Upper Cretaceous age, basic investigation about which was reported in [5] and [3]. Baltic amber has also been found in Moravia, although rarely, in glacial deposits of Pleistocene continental ice sheets in the surroundings of Vidnava (Czech Silesia).

Different analytical techniques have been applied to the characterization of amber. Infrared spectroscopy has been most often employed because it was the first technique capable of readily identifying Baltic amber through the presence of a succinic acid peak (so called 'Baltic shoulder') in the infrared spectrum, and was used to simply identify fakes in jewellery. Today, attenuated total reflection (ATR), a sampling technique used in conjunction with infrared spectroscopy with no

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sample preparation and requiring small samples is mainly used for the discrimination of various types of amber [6]. Raman spectroscopy is also a useful and non-destructive method to differentiate between amber specimens of various geological, geographical, and archaeological origins [7–9]. However, although these spectroscopic techniques have advantages, the spectral data may not always give sufficient information for chemical classification of the amber and discrimination of non-Baltic ambers. This is because where discrimination relies only on the presence of the ‘Baltic shoulder’ there are other varieties of European ambers such as gedanite [10], romanite [11], goitschite [12], and American ambers [13,14] that also containing traces or larger amounts of succinic acid. Gas chromatography/mass spectrometry (GC/MS) or pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) are other methods capable of separating a broad range of functional groups or compounds that comprise amber, and the Py-GC/MS method was primarily used to differentiate and classify fossil resins [15]. In fact, the combination of more analytical techniques is a valuable tool in studying amber-related topics in an attempt to better understand amber chemistry, origins, and fossilization processes.

The aim of this study was to provide detailed information on the molecular composition of studlovite and valchovite using GC/MS of resins extracts, Py-GC/MS using *in situ* sample derivatisation with tetramethylammonium hydroxide (TMAH-Py-GC/MS), ATR-FTIR analysis, and FT-Raman spectroscopy analysis. For the preliminary stage of the study, elemental analysis was carried out in order to confirm the type and authenticity of the samples.

The next aim of this study was to find typical representative features of studlovite and valchovite in order to permit correct identification of geological and archaeological amber finds. Reflections on utilisation of the local Moravian fossil resins from Valchov and Študlov for jewellery in prehistoric times can be found in archaeological and mineralogical papers [16–17]. Small decorations e.g. from the Študlov raw material were prepared in recent times. For this reason, typical representative features were sought after to provide evidence that the excavated amber jewellery dated to the Hallstatt Age from Kralice na Hané not only for Baltic amber but also for both Moravian sources. Baltic amber from Burg on Fehmarn was chosen as a reference amber sample for the comparative analyses.

## 2. Materials and methods

### 2.1. Samples

Nine samples were analysed: two samples of studlovite (I, II) from the village Študlov (near Valašské Klobouky, South-east Moravia), two valchovites (I, II) from Boskovice Furrow (Czech Republic), two Baltic ambers (I, II) from Burg on Fehmarn (Germany), and three archaeological samples (A, B, C) of unknown provenience from Kralice na Hané (near Prostějov, central Moravia).

The samples of studlovite were found in Eocene deep-sea sediments. The amber-carrying position was formed by dark grey to black sandy claystone or clay sandstone. The analysed amber samples were brown in colour, and were partly transparent. Valchovite accumulated in Cenomanian dark grey claystones of fluvio-lacustrine origin. It formed waxy butterscotch, with opaque grains. Two pieces of brown-yellow, partly transparent amber of known Baltic origin were analysed for comparison of the samples.

### 2.2. Archaeological background

The territory of Moravia is rich in archaeological finds of amber because it was crossed by the Amber Road, connecting sources on the Baltic Sea shore with lands along the Danube and with Italy. The earliest known archaeological finds were derived from the end of Palaeolithic, connected with the Magdalenian settlement in caves of the Moravian Karst. Amber decorations from the Neolithic in Moravia are not known, which is curious. For the first time relatively abundant amber

artefacts have been found in graves of the Bell Beaker culture (Late Eneolithic). Mass occurrences effectively appeared in the Bronze Age, and especially in the Hallstatt and La Tène periods.

One of the most important archaeological findings is represented by a Lusatian Urnfield settlement from the Hallstatt period, at Kralice na Hané near Prostějov, central Moravia [18]. Two settlement pits were extremely rich in amber – a few thousands small pieces with a total weight of 202.64 g, including finished beds, their rough-outs, waste, small chips and raw material as well. The archaeological features were evidence of local production of amber beds and were unique in the Hallstatt period of the Lusatian Urnfield culture in Moravia. Small amber beds had diameters from 3.6 to 13.5 mm and they were 1.5 to 9 mm high. The most prevalent were symmetrical or asymmetrical two-conical beds. The large amount of production waste and chips allowed us to apply destructive analyses for the determination of amber provenience.

### 2.3. Methods

The elemental organic composition was determined using a CHNS/O microanalyser Flash FA 1112 (ThermoFinnigan). Softening point was determined using the Vicat method (Laget).

Powdered samples (<0.2 mm) were dissolved in dichloromethane (DCM) and analyses were performed using a Trace GC Ultra-DSQ II (ThermoElectron) instrument equipped with a TR-5MS column (30 m × 0.25 mm × 0.25 μm). The oven temperature was programmed from 36 °C (3 min) to 120 °C (12 °C/min), to 250 °C (6 °C/min), to 300 °C (3 min) (12 °C/min). Samples were injected in splitless mode, the injector temperature was set at 200 °C and helium was the carrier gas. Mass spectra were obtained by scanning from *m/z* 45 to 500 in full scan mode. α(H)-androstane in isooctane was used as an internal calibration standard. TMAH-Py-GC/MS analyses were performed using a Pyroprobe 5150 (CDS Analytical) pyrolysis unit connected to the GC/MS instrument described above. Samples of powdered amber, together with 10 μL of a 25% aqueous solution of TMAH for methylation trials were heated at 610 °C for 20 s. The TR-5MS column was used and the temperature programme of the columns was set from 40 °C (3 min) to 210 °C at 8 °C/min, and continued to 300 °C (2 min) at 20 °C/min. For data processing, the Xcalibur software (ThermoElectron) was used. Components were assigned from retention times and comparison with mass spectra from the National Institute of Standards and Technology spectral library.

Fourier transformed infrared (FTIR) spectra of the bulk samples were collected on a Nicolet 6700 FTIR spectrometer (Thermo Nicolet Instruments Co.) with a N<sub>2</sub> purging system. Spectra were acquired using a single reflection ATR GladiATR accessory equipped with a single bounce diamond crystal (angle of incidence 45°). Each sample spectrum averaged 64 scans and the resolution was 2 cm<sup>-1</sup>. The spectra were plotted against a single-beam spectrum of the clean ATR crystal and converted into absorbance units by ATR correction. Data were collected over a wavenumber range 4000–400 cm<sup>-1</sup>.

FT-Raman spectra were obtained using a Nicolet 6700 instrument with the NXR 9650 FT-Raman module attached and Nd<sup>3+</sup>/YVO<sub>4</sub> near-infrared excitation at 1064 nm. Spectra were recorded at 4 cm<sup>-1</sup> resolution from 1024 accumulated scans. A nominal laser power of about 0.1 W was used with a spot size of 50 μm.

The discriminant analysis was carried out using TQ Analyst software ver 9.3.107 (Thermo Fisher Scientific Inc.). The infrared spectroscopic data for discriminant analysis were fitted by mean-centering. Two-point baseline (1870, 1505 cm<sup>-1</sup>) was used for the wavenumber region of 1870–1505 cm<sup>-1</sup>. A constant pathlength was used for calculations. The Mahalanobis distance was used to formulate the distance between clusters. The number of principal components used for calculation was 10.

## 3. Results and discussion

The composition of fossil resins can vary depending on their botanical source, and usually is: carbon, 67–87%; hydrogen, 8.5–11%; oxygen,

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