Organic Geochemistry 124 (2018) 190–204

Contents lists available at ScienceDirect

Organic Geochemistry

journal homepage: www.elsevier.com/locate/orggeochem

Duxite – Fossil resin of Miocene age

Martina Havelcová [a,*], Vladimír Machovič [a,b], Ivana Sýkorová [a], Ladislav Lapčák [b], Alexandra Špaldoňová [a], Karel Mach [c], Zdeněk Dvořák [c]

[a] Institute of Rock Structure and Mechanics AS CR, V Holešovičkách 41, 182 09 Praha 8, Czech Republic
[b] University of Chemistry and Technology, Prague, Technická 5, 166 28 Praha 6, Czech Republic
[c] Severočeské doly, a.s., Doly Bílina (North Bohemian Mines, Bílina Mines), 5. května 213, 418 29 Bílina, Czech Republic

ARTICLE INFO

Article history:
Received 27 February 2018
Received in revised form 18 July 2018
Accepted 26 July 2018
Available online 4 August 2018

Keywords:
Fossil resin
Amber
Resinite
Terpenoids
Py-GC/MS
FTIR

ABSTRACT

A series of Miocene fossil resin from the northwest part of the Czech Republic, called duxite, has been analyzed by elemental, microscopic, gas chromatography (GC/MS), pyrolysis-gas chromatography, Fourier Transform infrared (FTIR), and Raman techniques. The set of samples consisted of museum, contemporary and artificially altered samples. The results of GC/MS revealed fine variances in chemical structure among the samples, which could be attributed to the geologic paleosituation during resin deposition, as was verified by alteration of a sample under different conditions. Sesquiterpenes, including α-cedrene and cuparene, were identified in sample extracts and sample pyrolysates together with diterpenoid members abietanes, pimaranes, and dehydroabietanes. The distribution and intensity of functional groups of FTIR spectra also confirmed that the duxite samples were fossilised exudates from a member of the Cupressaceae conifer family. Raman spectra supported this record indicating aromatic character of duxite and higher maturity of the samples. The chemical composition indicated that duxite is a member of Class IV resins of the fossil resin classification system. Members of this group do not have a polymeric structure. This nonpolymerizable behaviour was confirmed by their excellent solubility in an organic solvent and the low softening point of the material. Our results therefore provide a valuable insight into the duxite-producing process and its potential for evaluating the geological environment and diagenetic conditions.

1. Introduction

In 1874, the first details of the discovery of a fossilized resin from a Miocene coal seam in the former Emeran Mine of Duchcov in the North Bohemian Basin were published. The substance was named duxite after the German name of the town Dux (Doelter, 1874). The fossilised resin, 2–8 cm thick, was directly connected to coal on each side. The resin was described as an indigenous deposit, dark brown, wax-shiny, brittle with a conchoidal fracture.

Bittner (1913) first described duxite in a mine and later Jurasky (1940) described duxite in the Elly Mine which closed in 1941, in the same region of the North Bohemian Basin, forming fillings of vertical fractures in layers of xylitic coal. Jurasky also published the first concepts about the genesis of duxite, followed by Kuhlwein (1951), both describing the transformation of the resin under the influence of volcanic heat. The resin becomes mobilized by superheated steam at approximately 350 °C (or at a lower temperature under a high pressure), migrates, and impregnates the surrounding coal material. The geological systems of the Doupovské Mountains and České Středohoří Mountains are connected with an intrusive body that can provide volcanic underground heating over a large area. According to Kuhlwein (1951), other localities where duxite had been found include, the Pluto Mine at Osek and Mariánské Radčice (North Bohemian Basin), the Josef and Anežka Mine (Sokolov Basin), and in a Slovakian bed at Handlová.

Stach (1966), during his coalification studies, also researched duxite. Based on its solubility, melting point, and degree of polymerization, he referred to duxite as black amber. The black colour of the resin was attributed to the presence of humic substances in the coal, and he also assumed that duxite was a product of volcanic and thermal processes. However, this view of duxite genesis was refuted by Havlena (1964) and later by Zelenka (1972): the formation of fossil resins was described as being the sum of pressure and temperature, but only a local temperature increase during coalification was responsible for resin fossilisation, as induced by the composition of the original plant resins. Murchison (Murchison

* Corresponding author.
E-mail address: havelcova@irsm.cas.cz (M. Havelcová).

https://doi.org/10.1016/j.orggeochem.2018.07.014
0146-6380/

and Jones, 1964; Murchison, 1966) studied samples containing resinites, including duxite, using infrared spectroscopy. Showing aliphatic structures and carbonyl absorption with developing aromatic clusters, duxite was described as thermally metamorphosed resinite created during natural pyrolysis. With regard to duxite, Millais and Murchinson (1969) stated that the duxite's infrared spectrum was very similar to that of alginite present in Scottish boghead coals.

Since the 1970s, duxite discoveries have been reported in botanical structures; cavities of fossilised and coalified trees, stumps and roots; or in pelocarbonate concretions (Zelenka, 1972, 1982; Bouška and Dvořák, 1997; Dvořák and Řehoř, 1997; Dvořák, 1999). The fossil resin substances had a red-brown or brown-black color, a waxy and resinous luster, conchoidal fractures, a melting point of 94–246 °C, a carbon content of 61–84%, and a hydrogen content of 8–17%. Fossil resin discoveries in the area of the Vršany mine, located in another region of the North-Bohemian coal Basin, were published in 1998 with a summary of the physical-chemical properties of samples (Bartoš et al., 1998). These samples differed from the previously discovered duxites in color and carbon content. The authors also mentioned the unusual location of this discovery: inside a charred tree trunk.

Bouška and Dořák then summarised the acquired knowledge and localities of duxite discoveries (Bouška and Dvořák, 1997; Dvořák and Řehoř, 1997; Bouška et al., 1999; Dvořák, 1999) and described new locations in the Medard-Libík coal mine of the Sokolov Basin, confirming reports about findings of such materials in the past in this area (Kuhlwein, 1951). This duxite was located in the cracks of sideritized coalified trees, and the roots and trunks of trees that had traces of fire with coalified and fusinized bark on their surfaces. Physical properties and chemical analyses of the samples confirmed their similarities to those samples from the North Bohemian Basin. The authors concluded that according to variations in melting points, the samples were mixtures of several solid hydrocarbons as a result of diagenetic processes that had occurred in the original resins.

Vávra summarized previous work (Vávra et al., 1997; Vávra, 2009) and added the results of the analyses of new samples from two sites: the Bílina and the Vršany open cast mines. These duxite samples were concentrated in preserved parts of coalified roots and trunks. These samples are highly soluble in organic solvents and are therefore suitable for analysis by GC/MS. Six hydrocarbon compounds were identified as products of the diagenesis of plant terpenes: drimane, C_{16}-bicyclic sesquiterpane, labdane, simonellite, retene, and C_{18}-tricyclic diterpane. As the compositions of the samples varied extensively, Vávra (2009) concluded that duxite was a mixture of resins and waxes. This author, along with Paclt (1953), therefore included duxite among resinous bitumens. Krumbiegel (2002) also classified duxite as a mixture of bitumen, resins and waxes. Nevertheless, due to its high resin content, duxite can be characterized as an accessory fossil resin, and the basic conditions for duxite formation are the presence of resin in the original plant material and its specific transformation. Information about duxite was most recently summarized by Juríková (2011).

Duxite is not just of local interest because a similar type of Tertiary fossil resin has been documented in Devon (England) and the Ione Valley (California) (Grantham and Douglas, 1980). However, no other detailed investigations of these substances have been carried out. Generally, fossil resin is distinctive for its extraordinary preservation, and the uniqueness of duxite lies in the fact that it is most likely the only fossil resin that can be found directly in trees, i.e. *in situ*. From previously published information about duxite, it is obvious that there are differences in its descriptions and many questions are still unanswered. These include, Can all fossil resins found in the area of the North Bohemian and Sokolov basins be called duxite? Are there any differences between duxites, and if so, what are they and why? Can duxite have a specified botanical origin? Is it possible to further characterise duxite and speculate on how it was created? Can this information help to evaluate sedimentary or diagenetic conditions?

To answer these questions, a set of duxite samples was collected, including samples from museums. These were analysed by several methods. Because thermal maturation can modify the chemical structure of resins heating experiments were performed to determine the influence of temperature on sample structure and to explain differences in chemical structures among duxites.

2. Materials and methods

2.1. Samples

Twenty samples of fossil resins, collected from the northwest part of the Czech Republic in the North Bohemian and Sokolov basins, were processed. The set included four samples from museum collections (marked H) from the Emeran mine (samples H01 and H02 - probably originally defined by Doelter in 1874) and other historic samples from a museum in Ústí nad Labem (H03-H04). Fifteen fossil resins (marked D) were of modern findings (since 1988) from the Vršany, Bílina and Nástup Tušimice mines (Most Basin) (D01-D15), and one sample (marked S) from the Medard-Libík mine (Sokolov Basin) (S01). Samples D13, D14, and D15 were the deepest deposits and were collected from the Bílina Mine. All samples were divided into two groups: resins found and collected from trees whose trunks were standing in an upright position, i.e. *in situ*; and resins from trunks stored in sandstones or secondarily deposited material that was transported by water to the site of discovery. The list of the samples with their known descriptions and year of collection is shown in Table 1.

A highly pure duxite sample D08 available in abundance was used for experiments involving carbonisation in air and in inert atmosphere of nitrogen at various temperatures (100–400 °C) for 48 h, to observe changes in sample composition and to help explain chemical differences among samples.

2.2. Geological setting

The majority of historical samples described and presented in this paper are Miocene. Their origin is the sedimentary fill of two sub-basins of the Ohře Rift (or Eger Graben) structure – the Most Basin and the Sokolov Basin (Fig. 1). The Most Basin is the largest and deepest of sedimentary basins within the Ohře Rift system. Its volcanic and sedimentary fill was formed from the Oligocene to middle Miocene. The oldest filling (Oligocene) is called the Střezov Formation and is mainly of volcanic origin. The Miocene filling of the basin is called the Most Formation and is divided (Matys Grygar et al., 2014) into the Duchcov Member unit (generally under the main coal seam), the Holešice Member (coal seam and equivalent deltaic to alluvial sediments), the Libkovice Member (monotonous lacustrine clays with illite – smectite above coal seam), the Lom Member (lacustrine clays to coal) and the Osek Member (monotonous lacustrine clays). All newly described samples were found within sediments of the Holešice Member, in clastic sediments in the vicinity of the main coal seam. Samples from the Vršany Mine originate from alluvial conditions of the Žatec Delta system and are slightly older than samples from the lacustrine Bílina Delta – the main coal seam overburden at the Bílina Mine (Mach et al., 2014). The position of the Libík Mine sample from the Sokolov Basin can be defined as Oligocene in age. Usually, duxites from the Vršany and Bílina mines were found within wood permineralised by carbonates (dolomite or siderite) and quartz, often in the form of droplets or other formations indicating flow