



## Structural changes in amber due to uranium mineralization



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### ABSTRACT

The presence of uranium, with a bulk mass fraction of about 1.5 wt% and radiolytic alterations are a feature of Cenomanian amber from Křížany, at the northeastern edge of the North Bohemian Cretaceous uranium ore district. Pores and microcracks in the amber were filled with a mineral admixture, mainly in the form of Zr-Y-REE enriched uraninite. As a result of radiolytic alterations due to the presence of uranium, structural changes were observed in the Křížany amber in comparison with a reference amber from Nové Strašecí in central Bohemia; this was of similar age and botanical origin but did not contain elevated levels of uranium. Structural changes involved an increase in aromaticity due to dehydroaromatization of aliphatic cyclic hydrocarbons, loss of oxygen functional groups, an increase in the degree of polymerization, crosslinking of C–C bonds, formation of a three-dimensional hydrocarbon network in the bulk organic matrix, and carbonization of the organic matrix around the uraninite infill.

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## 1. Introduction

In organic geochemistry, the interaction of ionizing radiation with natural organic matter is an interesting phenomenon that should be studied for several reasons, and can be viewed from various standpoints. The energy transferred by ionizing radiation to organic matter can induce a complex series of reactions generating and altering organic matter in various environments. Vice versa, the organic matter plays an important role in the transport, accumulation and hydrothermal mineralization of uranium and thorium in sediments, and it is also a sensitive marker allowing characterization of the paleoenvironmental, geochemical, and diagenetic history of sediments. Processing of organic matter also takes place in extraterrestrial environments such as cometary and interstellar ices and planetary atmospheres, and must have represented an important process of prebiotic organic evolution on the early Earth (Court et al., 2006; Landais, 1996).

The radiolytic alteration of organic assemblages has been studied by analysis of organic matter present in various forms (usually as bitumens and kerogens) and amounts in uranium and thorium sedimentary deposits (e.g., Court et al., 2006; Kříbek et al., 1999; Landais, 1996; McCready et al., 2003; Sangély et al., 2007). Fixation of uranium by coal, and the influence of uranium on the structural transformation of coal organic matter, has also been studied (e.g., Havelcová et al., 2014b; Meunier et al., 1990; Nakashima et al., 1984). The main alterations in organic matter, which take place in the presence of uranium, are oxidation, biodegradation, radiolysis, and thermal degradation. Complexation and redox reactions are two main processes involved in uranium ore formation, promoted by the presence of organic matter. During thermal treatment, soluble U(VI) species, including organic uranyl complexes, can be reduced to insoluble U(IV) species (Landais, 1996).

Court et al. (2006) summarized the effects of radiolytic alteration of organic matter, as reported previously in the literature: *i*) enrichment in <sup>13</sup>C; *ii*) greater aromaticity; *iii*) decreased degree of alkylation of polyaromatic hydrocarbons; *iv*) decreased pyrolysis and yields of solvent extracts; *v*) greater structural disorganisation;

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vi) lower H/C and higher O/C ratios; vii) increased hardness and reflectance; viii) increased thermal maturity, as indicated by an elevated Rock-Eval peak pyrolysis temperature. Based on experimental data obtained on a set of naturally occurring organic assemblages, the authors further concluded that the radiolytic modification of hydrocarbon complex mixtures proceeds via cleavage, aromatization and oxidation, and by transforming aliphatic hydrocarbons into aromatic hydrocarbons. In the pyrolysis products of the complex hydrocarbon mixture, a decrease in the average size and degree of alkylation of polycyclic aromatic hydrocarbons caused by irradiation, as well as enrichment in  $^{13}\text{C}$ , was observed. Radiolysis of water produces hydroxyl radicals, whose reactions increase the degree of oxidation due to the formation of phenols, aromatic ketones, aldehydes, and carboxylic acids (Court et al., 2006).

Radiolysis is a spatially localized process and thus the interpretation of analytical data obtained in a larger or even bulk rock sample is difficult. The radiation dose absorbed by organic matter is imparted only to the mass of material within reach of the emitted particles, i.e., mainly alpha particles in the case of uranium and thorium decay. Their effective range in organic matter, within which the particles have sufficient energy to alter the material, has been estimated to be 50  $\mu\text{m}$  (Sangély et al., 2007). In coal, e.g., a local increase in the degree of coalification and iso- or anisotropic haloes around mineral grains and along cracks filled with minerals is typical for radiolytic alteration (Taylor et al., 1998).

Decay of uranium and thorium can induce radiolytic polymerization of light hydrocarbons such as methane, and the formation of complex polyaromatic hydrocarbons (Court et al., 2006). Through radiation-induced polymerization of liquid and/or gaseous pyrolysates, thoriferous and uraniferous bitumen nodules in Phanerozoic sandstones were formed. In these, alpha particles caused the rupture of bonds and formation of free radicals by removing hydrogen, and subsequent crosslinking as new C–C bonds formed a three-dimensional network of hydrocarbons. The molecular weight increased and the materials quickly became insoluble (McCready et al., 2003).

The present work is, to our knowledge, the first report of uranium mineralization in a fossil plant (tree) resin - amber. The ability of some resins to fossilize and to be preserved in the geological record is a fascinating aspect. The main process in fossilisation of resins and formation of amber is polymerization of terpenoid compounds that form the general polymeric structure. Because resin is a mixture of compounds, fossil resins are not completely consistent heteropolymers. Moreover, some terpenoids are non-polymerisable, and they stay protected in the fossilized polymer structure. Polymerizability depends on the molecular structure of terpenoids. Mainly the conjugated diene in terpenoid acids (labdane skeletal type) enables polymerization and, hence, formation of amber. Other terpenes, for example, abietic and pimaric acids, the most abundant components in resins of Pinaceae, remain due to their skeleton being unpolymerized. High pressure, heat, bacterial processes, and the strength of mineral crystallization cause oxygen deprivation and displacement of resinous substances into cracks in the fossilized wood matter and beyond. Individual tree species produce different types of resins; however, not all types of resins can fossilize. The fresh natural resin must be resistant to decay. The resin, sealed and preserved in rocks, changes its structure over time with the formation of complex compounds of higher molecular weight and conversion of volatile and reactive components into stable compounds. This leads to curing of the resin. This process is slow and depends on complex geological conditions, including composition of the original resin. Resin can fossilize as either a precipitated product of tree bark, or in a non-excluded form inside the tree. "Amber" is a term that refers to materials derived from

biological matter that is incorporated into sediments. In anaerobic environments, e.g., during formation of a peat swamp and particularly during coal formation, the resin is concentrated and its mass can increase. Despite chemical alteration during diagenesis, biomarkers still have the characteristic basic skeletal structures of their precursors in natural resins, and can thus be used as chemosystematic markers (Langenheim, 2003; Otto et al., 2002).

In the present work, the structure of a sample of uranium-rich Cretaceous (Cenomanian) amber from Křizany, at the north-eastern edge of the North Bohemian Cretaceous uranium ore district, was studied using various techniques: elemental, micropetrographic, and thermal analyses, optical and electron microscopy, infrared spectroscopy and microspectroscopy, gas chromatography with mass spectroscopy detection (GC/MS), and analytical pyrolysis (Py-GC/MS). An amber sample of Cenomanian age from Nové Strašecí, with a low uranium content, was analysed as a reference sample.

The study was aimed at identifying and interpreting changes in the polymeric structure of fossil resins due to radiolytic and chemical alterations that probably occurred in the presence of local uranium mineralization.

## 2. Experimental

### 2.1. Samples and geological setting

A sample of uranium-rich amber of Cretaceous (Cenomanian) age (94–100 Ma) from the Křizany locality in the Czech Republic was studied. The Křizany uranium deposit is located at the north-eastern edge of the North Bohemian Cretaceous uranium ore district (NBCUOD, Fig. 1). The deposit was mined from 1982 to 1990 and was ranked among smaller uranium deposits in the North Bohemian uranium district. The total mine production of low-grade uranium ore (0.07–0.1 wt% U) was 1108 t of U; for comparison, the total uranium production in NBCUOD mined from 1967 to 1996 was 28 046 t (Kafka, 2003).

Two formations - lower freshwater continental and upper marine sediments - form the fully developed Cenomanian sequence. The basement is formed by low metamorphosed metasediments (phyllites and quartzites) and small bodies of Upper Proterozoic and Upper Devonian granitic rocks. Freshwater sediments are developed in depressions of the paleorelief and consist of conglomerates, pebbly to fine-grained sandstones, and lacustrine siltstones. All of these rocks are often rich in organic matter (coalified plant detritus). The sediments of marine Cenomanian cover the whole area of NBCUOD. The basal part of the marine Cenomanian sediments is formed by washout non-graded, wave-cut and beach sediments, and their upper part by shallow marine sandstones. Uranium mineralization developed in the basal part of the Cenomanian formation, and is divided into four ore horizons according to their stratigraphical positions: The A horizon occurs in the freshwater stream and lacustrine sandstones, the main B horizon occurs at the base of marine Cenomanian in wash-out, fine-grained sandstones and siltstones, and C and D horizons are found in friable sandstones and the uppermost Cenomanian fucoidal sandstones. The main shapes of the ore bodies are plates and lenses, mostly horizontal. The area of the ore bodies exceeded their thickness, varying from decimetres to several metres, by many fold. The mineral assemblage and geochemical composition in the sandstone-hosted infiltration-type uranium mineralization occurring in NBCUOD is diversiform and unique (Čadek et al., 1975; Scharm et al., 1980; Smetana et al., 2002; Sulovský, 2005). Uraninite, complex U-containing gels, hydrozircon, baddeleyite, and U–Th–Ca phosphates (ningyoite, brockite) are the main carriers of uranium. In the whole NBCUOD, four main mineral types have been

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