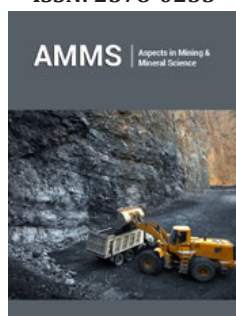


# Anthraxolite-Uranium Mineral: Composition, Structural Features and Genesis

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## Abstract

The most common uranium minerals are uraninite, coffinite and ningyote. From a mineralogical point of view, anthraxolite is particularly interesting because it is a mixture of bitumen, uraninite and a small amount of coffinite while its composition has been significantly influenced by radiation metamorphism. As a mineral, it is light, hard, crumble, black in color with a brownish cut, matte sheen and a conchoidal fracture. Anthraxolite is always bound to the accumulation of uraninite, often metasomatically replacing uraninite. In the case of uranium deposit in Příbram, Czech Republic, the anthraxolite formation is the result of the transformation of organic matter into bitumens in the sediments of the Upper Proterozoic and Lower Cambrian, mobilization and transport of these bitumens by hydrothermal fluids into uranium deposit, and - after incorporation of uraninite particles / fragments - the radiation effect of uranium radionuclides causing the polycondensation of aromatic hydrocarbons in the bituminous mass and a change in its properties.

**Keywords:** Minerals; Uranium; Chemical composition; Coal

## Basic Description

**Table 1:** Composition of anthraxolites from Central Europe with different uranium content (wt.%).

U	Proximate Analysis (Dry Basis)			Ultimate Analysis of Organic Matter (daf Basis)				
	UO <sub>2</sub>	Organic Matter	Ash	C	H	O	N	S
0	0	99.8	0.2	83.2	6.8	8.3	0.1	1.6
11.3	12.8	79.4	7.8	86.9	5.8	7	0.1	0.2
18.4	20.9	70.3	8.8	85.7	4.8	9.1	0.1	0.3
24.9	28.3	65.5	6.2	84.9	3.9	10	0.1	1.1
33.1	37.5	46.2	16.3	91.4	3.2	4.8	0.1	0.5
55.8	63.3	14.1	22.6	92.2	2.8	4.5	0	0.5

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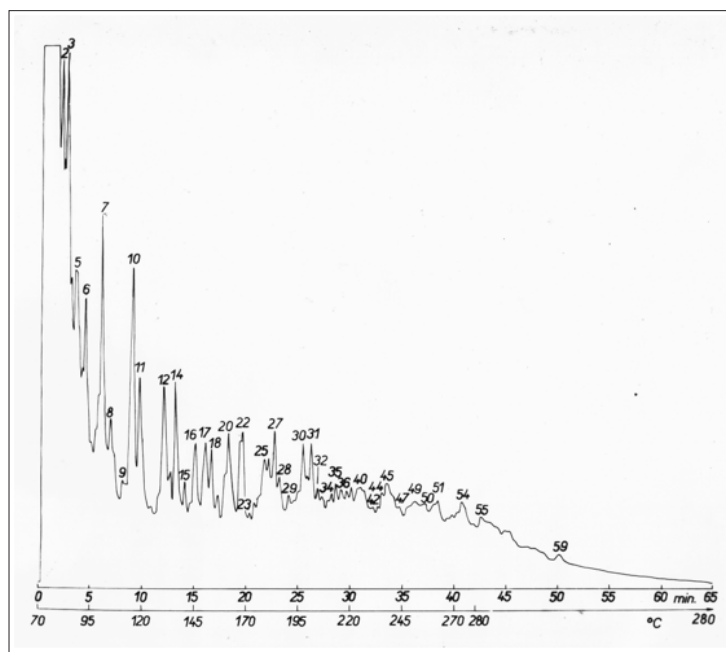
Anthraxolite is a solid bitumen with incorporated uraninite (UO<sub>2</sub>) particles or fragments of tenths of mm to several mm in size and admixtures, most commonly coffinite (U(SiO<sub>4</sub>)<sub>1-x</sub>(OH)<sub>4x</sub>) and calcite, but also but also other, such as pyrite, chalcopyrite and gersdorffite, found e.g. in locality Vrchlabí, Czech Rep. However, the uranium-free form of anthraxolite is also known, but it always occurs in close proximity to uraninite or uraniferous anthraxolite accumulations. The chemical composition of anthraxolite is quite variable, but it can contain up to 80% of bitumen. On average, anthraxolite may contain 70% bitumen, 20% uraninite and 10% ore minerals (iron pyrite, galenite, sphalerite, silica, calcite and siderite). The composition of uranium and uranium-free anthraxolite is given in Table 1. Significant anthraxolite deposits are in Central Europe, especially in the Czech Republic. One of the largest known accumulations of anthraxolite in hydrothermal veins is the Late Variscan uranium deposit (275-278Ma) in Příbram, Czech Rep. Geological setting of the Příbram uranium deposit is given in the work [1]. It is located along the northwestern border of the Central Bohemian pluton (345-335Ma) with low-grade metamorphic Late Proterozoic and non-metamorphic Cambrian rocks. The amount of anthraxolite in the ore veins increases in the direction roughly perpendicular to the contact line with the plutonic body and increases with depth. The bituminous mass of anthraxolite is either amorphous (less common texture)

or microporous. Morphologically, the solid bitumen can be globular (uranium-free), asphalt-like (uraniferous, low-grade) and coke-like (uraniferous, high-grade). Thus, the yield of extraction with organic solvents is always very low. The following analyzes and conclusions are devoted to the Příbram anthraxolite as a typical case. Data on the chemical composition of uranium minerals from Czech deposits are quite limited [1]. However, two studies [2,3] have recently been published on the nature and chemical composition of uraninite and coffinite. This work summarizes little known knowledge about the composition and structural features of anthraxolite.

### Instrumental Analysis of Anthraxolite Bitumens

The key to characterizing anthraxolites is the analysis of their bituminous component. Pyrolysis-gas chromatography: Using on-line pyrolysis, bitumens in the globular uranium-free and coke-like uraniferous anthraxolites were analyzed. In the former case, aliphatic ( $C_{1-6}$ ) and alicyclic hydrocarbons; benzene, methylbenzenes, and cymene; styrene, methylstyrene and divinylbenzene; indane and

indene; diphenyl, naphthalene and methyl naphthalenes; acenaphthene, methylacenaphthene and acenaphthylene; fluorene; anthracene, methylanthracene and phenanthrene; and chrysene were identified (Figure 1). In the latter case, the composition of the identified compounds was similar, but the yield of aliphatic hydrocarbons was significantly lower, some methylated benzenes and aromates such as methyl naphthalenes, methylacenaphthene and methylanthracene were not identified. From these results it can be deduced that in bitumen of uraniferous anthraxolite the aliphaticity decreased, contrary, its aromaticity increased compared to uranium-free bitumen. This finding was confirmed by the work [4], which reports the amount of aliphatic and aromatic hydrocarbons in globular uranium-free and uraniferous coke-like bitumens obtained using off-line pyrolysis. From their data it follows that-if we define the aromaticity  $f_{ar}$  as the ratio of aromatic and total hydrocarbons-while the  $f_{ar}$  of globular uranium-free bitumens is only 0.39 or 0.35, the  $f_{ar}$  of uraniferous coke-like bitumens is 0.64 or 0.58 or 0.55. It is clear that the aromaticity of the latter is significantly higher.



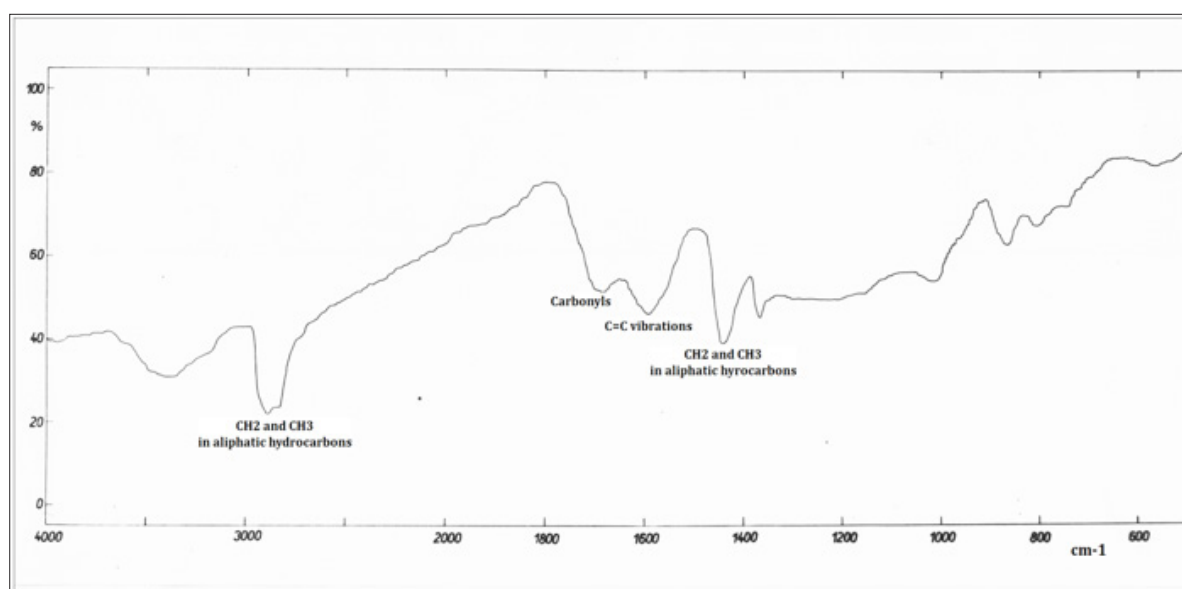
**Figure 1:** Pyrolysis chromatogram of globular bitumen of uranium-free anthraxolite. Identified hydrocarbons: 1,2 aliphatic hydrocarbons C1-6, 3 benzene, 4-6 alicyclic hydrocarbons, 7 toluene, 10,11 xylenes, 11 styrene, 12 phenol, 14 methylstyrene, 16 indane, 17 indene, 18 cymene, 20 divinylbenzene, 22 naphthalene, 23,24 tetramethylbenzenes, 25 quinoline, 27 2-methylnaphthalene, 28 1-methylnaphthalene, 30 biphenyl, 34,35 dimethylnaphthalenes, 36 acenaphthylene, 40 acenaphthene, 42,44 methylacenaphthene, 45 fluorene, 49 anthracene, 51 methylanthracene, 59 chrysene.

FTIR spectroscopy. Two beneficial results were revealed from FTIR spectra, (a) the presence of both aromatic and aliphatic ketones, (b) while the FTIR spectra of the uranium-free anthraxolite bitumen show aliphatic groups  $CH_2$  and  $CH_3$ , these groups were practically not recorded in uraniferous anthraxolite. The presence of ketones is important to explain the association between uraninite and bitumen. Due to its electron configuration, uranium atom can bound four or more ligands around it, consequently, it forms many

complexes, particularly with ligands that have oxygen donor atoms. The affinity of uraninite for bitumen, and thus the formation of anthraxolite, is most likely based on this property of the uranium atom. Another finding concerning the aliphatic groups  $CH_2$  and  $CH_3$  supports the mentioned result of pyrolysis-gas chromatography, because if these groups do not occur in uraniferous anthraxolite, then the aromaticity of its bitumen is higher compared to uranium-free anthraxolite bitumen. Thus, generally the FTIR spectra

of anthraxolite bitumens include five important bands, 2950-2850 $\text{cm}^{-1}$  (stretching vibrations in  $\text{CH}_2$  and  $\text{CH}_3$  groups, aliphatic hydrocarbons), 1730-1685 $\text{cm}^{-1}$  ( $\text{C}=\text{O}$  stretching vibrations in carbonyls), 1600 $\text{cm}^{-1}$  ( $\text{C}=\text{C}$  stretching), 1448 $\text{cm}^{-1}$  (bending vibrations in  $\text{CH}_2$  and  $\text{CH}_3$  groups, aliphatic hydrocarbons) and 800-625 $\text{cm}^{-1}$  (the out-of-plane C-H bending vibrations in polyaromatic rings). Spectra of the asphalt-like bitumens contain all five bands; those of globular uranium-free bitumens lack the band of polyaromatic C-H vibrations, and the spectra of uraniumiferous coke-like bitumens show a significant polyaromatic band while the bands of  $\text{CH}_3$  and  $\text{CH}_2$  groups in aliphatics are strongly suppressed. Spectrum of the globular uranium-free bitumen shows (Figure 2) (KBr pellet technique). Representative spectra of uraniumiferous coke-like bitumen and comparison of them with globular uranium-free bitumen are demonstrated in the work [4, Figure 12].  $^{13}\text{C}$  MAS NMR spectroscopy:  $^{13}\text{C}$  MAS NMR spectra showed that the aromaticity of uraniumiferous anthraxolites was  $f_{\text{ar}}=0.60$  and higher, but that of

the uranium-free anthraxolite was  $f_{\text{ar}}=0.50$  only. Thus, aromaticity of bitumen in uraniumiferous anthraxolite is higher compared to bitumen in uranium-free anthraxolite. This result is consistent with the above findings of pyrolysis-gas chromatography and FTIR and shows that the  $\alpha$ ,  $\beta$  and  $\gamma$  radiations from radionuclides  $\text{U}^{238}$  and  $\text{U}^{235}$  aromatize the bituminous mass of anthraxolite, in other words, cleave bonds of aliphatic groups in alkyl-aromatics and other bonds and, subsequently, by radicals, the polycondensed hydrocarbons are formed. The increase in aromaticity and degree of polycondensation with increasing uranium content in the case of coal is reported also by Havelcová et al. [5]. Another study demonstrates a radiolytic alteration in the organic matter of amber [6]. Uranium radionuclide radiation has led to structural changes that have included (a) increased aromatics, (b) loss of oxygen functional groups, (c) increased degree of polymerization, (d) cross-linking and other changes.



**Figure 2:** Infrared spectrum of the globular uranium-free bitumen. No significant absorbance in the region 800-625 $\text{cm}^{-1}$  was recorded.

Isotopic ratio  $^{12}\text{C}/^{13}\text{C}$ . For anthraxolites, Dubanský [7] states the high values of  $^{12}\text{C}/^{13}\text{C}$  ratio: 93.86 for uranium-free anthraxolite, 94.38 for uraniumiferous anthraxolite from the depth 800 m and 94.24 for that from the depth 600m. This means that during the transport of highly viscous bitumens by hydrothermal fluids from depths of several km to depths of several hundred meters, isotopic fractionation took place, and, further, that the bitumens of current anthraxolites are isotopically light. However, this also means that the source of anthraxolite bitumens were the bitumens in sediments of Upper Proterozoic and Cambrium age. Anthraxolites at the Příbram are younger than the main uranium mineralization. Their age can be estimated at 270Ma, while the age of the uranium deposit is 275-278Ma and the Central Bohemian pluton 345-335Ma, as mentioned above.

### Other occurrences of anthraxolite

Anthraxolite is not common but can be found all over the planet. Dubanský [7] reports globular uranium-free bitumens from the eastern part of Germany with high  $^{12}\text{C}/^{13}\text{C}$  ratio (91.9-92.9), Erokhin et al. [8] described anthraxolites from the border of the Ural and western Siberia, other authors report anthraxolites from South China [9] and northern Minnesota [10]. Anthraxolite is sometimes compared to shungite [11].

### Outline of anthraxolite genesis

With respect to the works from Křibek [4] and Dubanský [7] it may be suggested that the source of anthraxolite bitumen were bitumens contained in the Upper Proterozoic and Lower, possibly Middle, Cambrian host rocks. During intrusion of the Central

Bohemian pluton into sediments, these highly viscous bitumens were mobilized from the contact-metamorphic aureole (possibly they were also partially, but weakly pyrolyzed), then accumulated in structural traps in less heat-affected parts of the sedimentary complex and subsequently extracted and transported with hydrothermal fluids into a uranium deposit. Here, particles and fragments of uraninite penetrated into the highly viscous bitumens, and the bituminous mass was gradually changed by radiation from uranium radionuclides. In other words, bitumens have been metamorphosed by radiation  $\alpha$ ,  $\beta$  and  $\gamma$  to polyaromatics coke-like structures. Radiation metamorphosis is also confirmed by methane blow outs from anthraxolite accumulations.

## Conclusion

Anthraxolite is the solid bitumen with incorporated uraninite particles and/or fragments and admixtures (coffinite and ore minerals). Three types were distinguished: globular (uranium-free), asphalt-like (uraniferous, low-grade), and coke-like (uraniferous, high-grade). Based on analyzes of these three types by advanced instrumental methods, description of Upper Proterozoic and Cambrian sediments, assessment of uranium ore composition and anthraxolite accumulations in hydrothermal veins, the anthraxolite genesis has been outlined. The source of bitumen were the mentioned sediments, whose original biological material was gradually transformed into more homogeneous organic matter, which subsequently polymerized to kerogen as a thermodynamically more stable form. By long-term exposure to temperature and pressure, the kerogen was changed to highly viscous bitumens. After magmatic activity between 345 and 335Ma, these viscous bitumens were transported by hot (250-350 °C) hydrothermal fluids from depths of several km to depths of several hundred meters into a uranium deposit aged 275-278Ma. Here, with uraninite fragments and particles, the uraniferous anthraxolites aged ~270Ma were formed, and - always in close proximity to uraninite accumulations - also globular uranium-free anthraxolite originated. Then, the anthraxolite bitumens have been metamorphosed by radiation  $\alpha$ ,  $\beta$  and  $\gamma$  to polyaromatics asphalt-like and coke-like structures as low- and high-grade types.

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