

Bitumens in the Late Variscan Hydrothermal Vein-Type Uranium Deposit of Příbram, Czech Republic: Sources, Radiation-Induced Alteration, and Relation to Mineralization

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Abstract

The late Variscan (275–278 Ma) Příbram uranium deposit is one of the largest known accumulations of uraniumiferous bitumens in hydrothermal veins. The deposit extends along the northwestern boundary of the Central Bohemian pluton (345–335 Ma) with low-grade metamorphosed Late Proterozoic and unmetamorphosed Cambrian rocks. From a net uranium production of 41,742 metric tons (t), more than 6,000 t were extracted from bitumen-uraninite ores during 43 years of exploration and mining. Three morphological varieties of solid bitumen are recognized: globular, asphaltlike, and cokelike. While the globular bitumen is uranium free, the other two types are uraniumiferous. The amount of bitumen in ore veins gradually decreases toward the contact with the plutonic body and increases with depth.

Two types of bitumen microtextures are recognized using high-resolution transmission electron microscopy: amorphous and microporous, the former being less common in uraniumiferous samples. A lower Raman peak area ratio (1,360/1,575 cm^{-1}) in mineralized bitumens (0.9) compared with uranium-free samples (2.0) indicates a lower degree of microtextural organization in the latter. The H/C and O/C atomic ratios in uranium-free bitumens (0.9–1.1 and 0.09, respectively) are higher than those in mineralized samples (H/C = 0.3–0.8, O/C = 0.03–0.09). The chloroform extractable matter yield is very low in uranium-free bitumens (0.30–0.35% of the total organic carbon, TOC) and decreases with uranium content increase. The extracted solid uraniumiferous bitumen infrared spectra show depletion in aliphatic CH_2 and CH_3 groups compared to uranium-free samples. The concentration of oxygen-bearing functional groups relative to aromatic bonds in the IR spectra of uranium-free and mineralized bitumen, however, do not differ significantly. ^{13}C NMR confirmed that the aromaticity of a uraniumiferous sample is higher ($F_{\text{ar}} = 0.61$) than in the uranium-free bitumen ($F_{\text{ar}} = 0.51$). Pyrolysates from uraniumiferous and nonuraniferous bitumens do not differ significantly, being predominantly cresol, alkylphenols, alkylbenzenes, and alkyl-naphthalenes. The liquid pyrolysate yield decreases significantly with increasing uranium content. The $\delta^{13}\text{C}$ values of bulk uranium-free bitumens and low-grade uraniumiferous, asphaltlike bitumens range from -43.6 to -52.3 per mil. High-grade, cokelike, uraniumiferous bitumens are more ^{13}C depleted (-54.5 to -58.4 ‰). In contrast to the very light isotopic ratios of the high-grade uraniumiferous cokelike bitumen bulk carbon, the individual n-alkanes and isoprenoids (pristane and phytane) extracted from the same sample are significantly ^{13}C enriched. The isotopic composition of the C_{13-24} -alkanes extracted from the high-grade uraniumiferous sample ($\delta^{13}\text{C} = -28.0$ to -32.6 ‰) are heavier compared with the same compounds in a uranium-free sample ($\delta^{13}\text{C} = -31.9$ to -33.8 ‰).

It is proposed that the bitumen source was the isotopically light ($\delta^{13}\text{C} = -35.8$ to -30.2 ‰) organic matter of the Upper Proterozoic host rocks that were pyrolyzed during intrusion of the Central Bohemian pluton. The ^{13}C -depleted pyrolysates were mobilized from the innermost part of the contact-metamorphic aureole, accumulated in structural traps in less thermally influenced parts of the sedimentary complex and were later extracted by hydrothermal fluids.

Bitumens at the Příbram deposit are younger than the main part of the uranium mineralization and were formed through water-washing and radiation-induced polymerization of both the gaseous and liquid pyrolysates. Direct evidence for pyrolysate reduction of uranium in the hydrothermal system is difficult to obtain as the chemical composition of the original organic fluid phase was modified during water-washing

and radiolytic alteration. However, indirect evidence—e.g., higher O/C atomic ratios in uranium-free bitumens (0.1) relative to the Upper Proterozoic source rocks (0.02–0.05), isotopically very light carbon in associated whewellite ($\delta^{13}\text{C} = -31.7$ to -28.4%), and the striking absence of bitumens in the pre-uranium, hematite stage of the mineralization—indicates that oxidation of organic fluids may have contributed to lowering of $a\text{O}_2$ and uraninite precipitation.