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A multi-instrumental geochemical study of anomalous uranium enrichment in coal

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ABSTRACT

Contents of uranium in coals from Odeř in the northernmost part of the Sokolov Basin, Czech Republic, in the vicinity of the well known St. Joachimsthal uranium ore deposits, reach extremely high values. In the present work, coal samples with contents of uranium ranging from 0.02 to 6 wt.% were studied. The study employing a whole complex of analytical techniques has been aimed at identification of changes in the structure of coal organic matter, which are associated with the high contents of uranium in coal. The study includes proximate and ultimate analyses, multielement analysis by instrumental neutron and photon activation analyses, micropetrographic analysis by optical microscopy, ESEM/EDX analysis of mineral matter, infrared and Raman spectroscopies, solvent extraction followed by gas chromatography with mass spectroscopy (GC/MS), and analytical pyrolysis (Py-GC/MS). The study has confirmed previously proposed explanation of uraniferous mineralization in sedimentary carboniferous substances by the mechanism of reduction and fixation of soluble U(VI) (uranyl, UO_2^{2+}) species (e.g., humic, carbonate/hydroxo/phosphate complexes) by sedimentary organic matter under diagenetic or hydrothermal conditions, and formation of insoluble U(IV) species as phosphate minerals and uraninite. The process is accompanied with alteration and destruction of the coal organic matter. The changes in the structure of coal organic matter involve dehydrogenation and oxidation mainly in the aliphatic, aromatic and hydroxyl structures, and an increase in aromaticity, content of ether bonds, and the degree of coalification.

1. Introduction

1.1. Role of organic matter in uranium mineralization

Coal organic matter plays an important role in the transport, accumulation and hydrothermal mineralization of uranium in sediments. It is a very sensitive marker allowing characterization of the paleoenvironment, geochemistry and diagenetic history of sediments, including alteration processes. The main alteration processes of organic matter occurring in the presence of uranium comprise oxidation, biodegradation, radiolysis, and thermal degradation. A comprehensive review of the organic geochemistry of sedimentary uranium ore deposits has been elaborated by Landais (1996).

As described in numerous papers (Meunier et al., 1990; Nakashima et al., 1984; Nakashima, 1991) and summarized by Landais (1996), from a chemical standpoint, “complexation” and reduction–oxidation reactions are two main processes that can be identified in interactions between uranium and organic matter.

During contact of coal with solutions containing the uranyl cation, UO_2^{2+}, adsorption of the cation onto the coal surface via physisorption or ion exchange occurs, followed by its subsequent chemisorption or complexation by functional (mainly carboxyl) groups of the coal organic matter, both on the surface and in the bulk of the coal matrix:

$$2R{-}COOH + UO_2^{2+} = RCOO{-}(UO_2){-}OOCR + 2H^+$$

Although the uranium complexation by coal organic matter from aqueous solutions containing trace levels of uranium is

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already a process with a high enrichment factor, a subsequent process, consisting of reduction of U^{6+} to U^{4+}, accompanied by dehydrogenation of organic matter, contributes to high concentrations of uranium in organic-rich facies:

$$2(RH) + UO_2^{2+} = 2R^0 + 2H^+ + UO_2$$

The degree of dehydrogenation of organic matter depends on its initial composition (the number of available active sites), and on temperature. It has been found by infrared spectroscopy that the reduction of lignin by uranium decreases the relative abundance of aliphatic CH bonds by their dehydrogenation, with simultaneous dehydrogenation of hydroxyl groups. Cleavage of aliphatic substituents occurs, as well as an increase in aromaticity. Dehydrogenation of organic matter is indicated by a decrease in the H/C atomic ratio, which is usually accompanied by an increase in the O/C atomic ratio, because oxidative degradation of organic carbon structures, leading to formation of oxygenated functional groups, often occurs in addition to their dehydrogenation (Landais, 1996). On the contrary, in the Příbram uranium deposits, Kříbek et al. (1999) did not observe oxidation of the mineralized organic matter, but both H/C and O/C atomic ratios decreasing with increasing uranium content. Oxidation can also occur during biodegradation, thermal alteration, and radiolysis. The degradation of organic matter by radiolysis is limited by distance, occurring only within 50–100 μm of the uranium mineral. Savary and Pagel (1997) suggested that radiolysis of both water and organic products may also be responsible for the oxidation of organic matter. In general, the radiolytic process is associated with polymerization by free radicals. Changes in the distribution of hydrocarbons, generated during pyrolysis, were also found, compared with mineralized and non-radiolyzed organic material from the same coal deposit (Landais, 1996). Lewan et al. (1991) suggested that elemental, isotopic and pyrolysate compositions of kerogen are not significantly affected by radiolysis, unlike bitumen. The content of bitumen decreases, as well as the content of acyclic isoprenoids and carboxylic acids.

According to Taylor et al. (1998), radioactivity can lead to changes in the composition and properties of coal, similar to thermal alteration or tectonic and hydrothermal activities. An increase in light reflectance is usually observed with increasing uranium content, which reflects an increase in the degree of coalification of the organic matter (coal rank). For example, Smieja-Król et al. (2009) found a direct correlation between an increase in the maximum reflectance of carbonaceous materials and the concentration of uranium in a Proterozoic basin in South Africa. An increase in uranium content, from 2.5 wt.% to 15 wt.%, was accompanied by an increase in the maximum reflectance from 2% to 7%, corresponding to an increase in the degree of coalification from anthracite to graphite.

The above facts show that changes in the structure of the coal organic matter is a very complex process, assessment of which requires detailed information on the structure of organic material associated with uranium in a particular coal deposit. Investigations of changes in the structure of uranium-enriched coal samples has been an interesting topic, mainly in geological research, from the standpoint of coal utilization for production of electrical energy and heat, gasification, and in the chemical industry (Roubíček et al., 2006), but also in nuclear research and its industry, in connection with the effects of radioactive materials and wastes in the environment (Havlová et al., 2006).

The present study was aimed at identifying changes in the structure of coal organic matter that has been exposed to medium to extremely high levels of uranium. The study was focused primarily on coal samples from the Odeř Tertiary deposit in western Bohemia, Czech Republic, and a uranium-enriched sample from the Uhelná coal deposits in northern Moravia was used for comparison. Elemental compositions of these coals, and their dependence on uranium content, was compared with the composition of a large representative set of Czech and Moravian coals characterized previously. The study included proximate and ultimate analyses, multielement analysis by activation analysis methods, optical and electron microscopy, infrared and Raman spectroscopy, sample solvent extraction followed by gas chromatography with mass spectroscopy (GC/MS), and analytical pyrolysis, i.e., thermal disintegration of samples combined with GC/MS (Py-GC/MS).

2. Methodology

2.1. Study area and the environmental data

The Odeř coal deposit belongs to stratiform uranium/coal bearing deposits. It is a small isolated basin situated in the foothills of the Krušné hory mountains (“Ore Mountains”, Erzgebirge in German), on the north-northwestern side, bounded by the Erzgebirge fault zone (Eger Rift) and separated from the Hroznětín Basin by the Erzgebirge granites, which emerge in the direction of the Erzgebirge fault zone and form bedrock of the basin. The coal seam is situated in close vicinity to the well known St. Joachimsthal uranium ore deposits (see Fig. 1).

The basin filling in the overburden direction is formed by granitic diluvium, lacustrine sediments of layered clays, and volcanic material. Coal layers start with sapropelite and sapropelitic shales, and terminate in a seam of brown coal. Volcanogenic sediments are deposited in the overburden of the coal seam. Quaternary soil slopes and a thick layer of peat are the last members (Obr, 1978; Veselý, 1984).

Conditions for formation of exogenous uranium deposits in the coal matrix have been summarized by Klemenc (1967) as: *i)* proximity of U source minerals/rocks and the possibility of migration and concentration of U in rocks of different compositions and mechanical properties, *ii)* suitable paleoclimatic conditions, *iii)* correlations between various types of rocks. The Odeř locality meets such conditions. Granites in the neighborhood, and in the bedrock, have high uranium contents, and relief ratios of granite bodies are suitable for migration of uranium enriched solutions. The warm Miocene climate that prevailed during the formation of the coal seam was also suitable, and along with humidity, was an important factor in the strong kaolinization of the granites. Dissolution of granite may also have been promoted by humic acids arising from decaying plant materials. Uranium could migrate in the acidic groundwater environment of this weathered, and often tectonically disturbed layer, in the form of sulphates or organic (humic) colloids. The composition of individual lithological horizons, and their location on the edge of the basin, where the influence of uranium enriched solutions could be most pronounced, was also suitable. Syngenetic uranium mineralization has been found in the bedrock of the isolated basin filling, in the coal seam, and in other stratigraphic horizons including the uppermost peat position, and always bound to organic matter. The mineralization is very finely dispersed and cannot be observed macroscopically. Klemenc (1967) reports restriction of industrially exploitable mineralization to the peat horizon, several positions in the coal seam, and in the granitic diluvium horizon. He points to the existence of zoning in the main uranium-bearing position – the coal seam, which is characterized by the formation of zones of leaching, secondary enrichment, as well as zones of primary ores and unchanged coal. In addition to uranium, there are also economically interesting levels of germanium, beryllium and gallium in the deposit, bound to the coal seam and other underlying and overlying rocks.