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THE ROLE OF ORGANIC SUBSTANCES IN THE PROCESSES OF HYDROTHERMAL MINERALIZATION

(Figs. 3, Tab. 2)

Abstract: The carbonaceous substances are associated with the stratiform deposits of Cu-ores, hydrothermal deposits of fluorite and uranium in the area of the Bohemian Massif.

The occurrence of isoprenoid hydrocarbons, fatty acids, amino-acids and $\delta\ ^{13}C$ values (from —16.8 to —58.4 ‰) indicates, that the origin of carbonaceous substances may be derived from the organic compounds extracted by hydrothermal solutions from the host rocks.

The oxidation of organic substances during a hydrothermal process may have participated in the lowering of redox potential of the hydrothermal solutions, and may lead to the reduction of sulphate or UVI ions.

Резюме: Вещества битуминозного характера сопровождают в области Чешского массива стратиформные местонахождения сульфидов и сплошь и рядом встречаются в гидротермальных местонахождениях флюорита и урана.

Наличие изопреновидных углеводородов, карбоксильных кислот и аминокислот, а также данные $\delta\ ^{13}C$ (—16,8 до —58,4 ‰) свидетельствуют о том, что мы имеем дело с органическими веществами, экстрагированными действием гидротермальных растворов из окружающих горных пород.

Результаты работы указывают на то, что органические соединения углерода могут играть важную роль при восстановлении соединений уранила и сульфатной серы.

The carbonaceous substances designated as anthraxolites or thucholites were described for the first time by H. V. Ellsworth (1928) from the uranium-bearing pegmatites of the Parry Sound area in Ontario. With the development of analytical techniques and the investigation of organic compounds during the last twenty years, it became clear that their occurrence in hydrothermal deposits is not a mere mineralogical rarity.

In contrast, the presence of carbonaceous substances (bitumens) has been proved by many authors in deposits of mercury (V. S. Balickij, 1966; A. I. Germanov and L. A. Bennikova, 1972), V. S. Sobolev (1975), lead and zinc (G. Mueller, 1954; W. S. Updergrove et al., 1973), Ag-Co-Ni ores (R. Kranz, 1971), copper (S. N. Ivanov et al., 1961, I. R. Jonasson et al., 1977), gold (N. S. Beskrovnyj, 1967; V. A. Amuzinskij et al., 1975) and fluorite and barite (G. Mueller, 1954; V. V. Mogarovskij and A. V. Markov, 1966; N. S. Beskrovnyj, 1967).

Gaseous, liquid and solid carbonaceous substances often occur in hydrothermal uranium deposits (S. Davidson and S. H. Bowie, 1951; V. M. Sobolev and I. A. Pudovkina, 1975; E. M. Galimov et al., 1975, and G. B. Naumov et al, 1976).

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The origin of bitumens in hydrothermal veins has been the subject of a fairly large number of papers, the authors of which have very often drawn contrary conclusions.

N. S. Beskrovnyj (1967, 1975); E. E. Voronoj (1967), and V. N. Florovskaja and V. G. Melkov (1976) are of the opinion that the bitumens of ore veins arise by abiogenic synthesis from gases (H_2, CH_4, CO) which are released during degassing of the Upper Mantle.

The argument for this is based on numerous finds of carbonaceous substances in the deposits which are spatially associated with deep structural lines, and on the presence of abiogenic hydrocarbons in volcanic gases and gaseous-liquid inclusions of nephelinite syenite and pegmatite (H. V. Ellsworth, 1928; S. V. Ikorskij, 1967).

But V. A. Uspenskij et al. (1961), A. I. Zubov and V. V. Kazancev (1970), N. T. Sokolova et al. (1972) and V. N. Florovskaja and V. G. Melkov (1975) are inclined to believe that vein bitumens represent products of the distillation or pyrolysis of organic matter of the host rocks provoked by hydrothermal solutions.

Investigations carried out by the working group of the Department of Mineral Deposits of the Faculty of Science, Charles University in Prague (Z. Pertold et al., 1975; V. Oružinský, 1978; P. Burdová et al., 1979; B. Kříbek et al., 1978 and 1980; V. Oružinský and B. Kříbek, 1981) have proved that in the area of the Bohemian Massif carbonaceous substances are associated with the stratiform deposits of Cu-ores, hydrothermal deposits of fluorite and a number of hydrothermal uranium deposits. This paper presents the results obtained from these investigations. The methods used in studying the carbonaceous substances under consideration are described in detail in the above-cited papers.

The carbonaceous substances in the rocks of the Tisová deposit near Kraslice

The stratiform Cu-sulphidic deposit Tisová near Kraslice lies in sericite-chlorite phyllites with layers of metabasic rocks of Ordovician (?) or Cambrian to Upper Proterozoic age. The ore layers of the deposit and their host rocks contain increased amounts of carbonaceous substances (O. X — X % C_{org}). This primary geochemical aureole is 50—100 m thick. The rocks outside the aureole contain 0.0X ½ C_{org}. The 92 to 99 % of the carbonaceous substances consist of insoluble matter, the infrared spectra of which have the character close to those of the substances of the anthraxolite type or to the type of „graphitized organic substance" (P. Burdová et al., 1979). However, graphite is never involved. In addition to the above-mentioned type, small amounts of substances are present in the Tisová deposit, which are soluble in organic solvents. In the soluble extract, aliphatic hydrocarbons (n-alkanes) within a range of n-C_{15} — n-C_{30}, isoprenoid hydrocarbons and fatty acids ranging between n-C_9 — n-C_{20} have been identified. The character of the isolated substances, for instance the owerwhelming predominance of fatty acids with an even number of carbons in a molecule or the presence of isoprenoid hydrocarbons of provably biogenic origin are a convincing proof of the organic origin of the carbonaceous matter in the deposit (V. Oružinský, 1978).

The ascertainment that the increased C_{org} contents are not bound to the ore layers themselves but also occur in some fault zones and zones of crushing in the vicinity of the deposit is important for an elucidation of the origin of the carbonaceous aureole. This fact furnishes evidence of a remobilization due to hydrothermal solutions of the organic substances contained in the host rock.

With regard to the otherwise petrologically and geochemically uniform character of the rocks of the ore-bearing series, it may be assumed that these remobilized organic sunstances may have participated in the processes of precipitation of iron- and copper sulphides by reduction of sulphate ions to sulphides

$$SO_4^{2-} + 2\left[H - C\begin{matrix}O\\H\end{matrix}\right]_{org} \longrightarrow S^{2-} + 2\,CO_2 + H_2O\,,$$

this corresponding to the increased amount of carbonates in the deposit.

The Křižany deposit of fluorite and barite

The deposit Křižany lies at the margin of the crystalline Ještěd area close to the Lusatian fault which separates the epizonally metamorphosed Ordovician and Silurian rocks from the sediments of the Bohemian Cretaceous Table. The fluorite mineralization of the deposit has been described in detail by F. Reichmann (1970), and the uranium mineralization by J. Horáček et al. (1979).

A bituminological analysis provided the proof that the fluorite-barite gangue contains 0.004—0.014 % of the extractable bitumens. Aliphatic hydrocarbons were isolated from the bitumens. Their amount, similarly as the total amount of the extract, rises with increasing fineness of grinding of the extracted samples (Fig. 1).

This means that the bitumens do not represent a recent or subrecent surface contamination, but they are enclosed in the intergranulars of the gangue or directly in the fluorite crystals.

As the composition of the hydrocarbons resembles that of the hydrocarbons of the metasediments of the surrounding crystalline rocks (Fig. 1), it may be assumed that the bitumens of the Křižany deposit represent the organic substances extracted from the host rocks.

For the sake of comparison, the same figure also presents a chromatogram of the aliphatic hydrocarbons of the Cenomanian rocks of the Bohemian Cretaceous Table, whose composition is quite different.

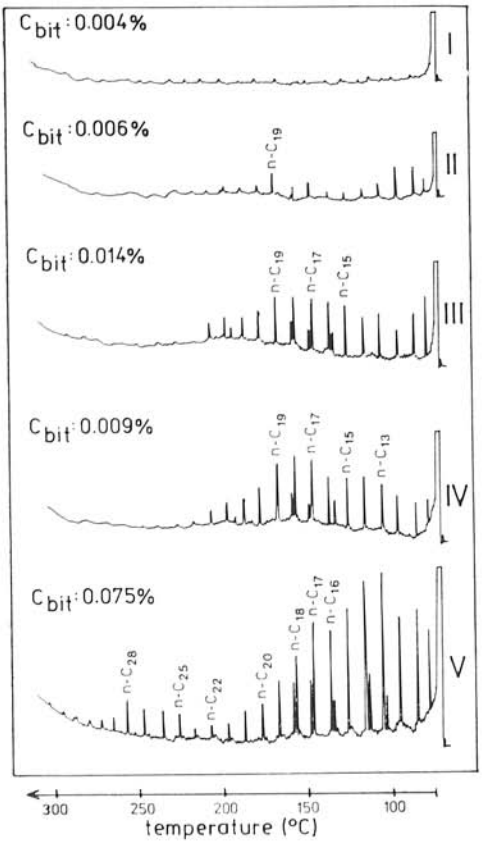
Hydrothermal uranium deposits

The occurrence of anthraxolites in uranium deposits has been described by many authors. Bitumens are present in the Licoměřice deposit (O. Pluskal, 1971), Rožná (V. E. Bojcov and Ju. M. Dymkov, 1970), Olší (A. Sojka, 1980), Jáchymov (N. T. Sokolova et al., 1972), Dyleň (K. Ro-

manidis, 1974) and Příbram deposit (V. S. Brodin and Ju. M. Dymkov, 1964; J. Komínek and S. Prokeš, 1969 and 1970; A. V. Zavarzin et al., 1970 and S. Prokeš, 1974).

In studying the Příbram deposit it has been found that the anthraxolites contain varying amounts of extractable substances of which some have been specified in greater detail (B. Kříbek et al., 1978).

In the extracts, n-alkanes have been found which range from n-C_{11} to n-C_{24} (Fig. 2), as well as fatty acids ranging between n-C_8 and n-C_{22}, and a number of amino acids. In addition to these substances, the anthraxolites also contain isoprenoid hydrocarbons — phytane ($C_{20}H_{42}$) and pristane ($C_{19}H_{40}$) —



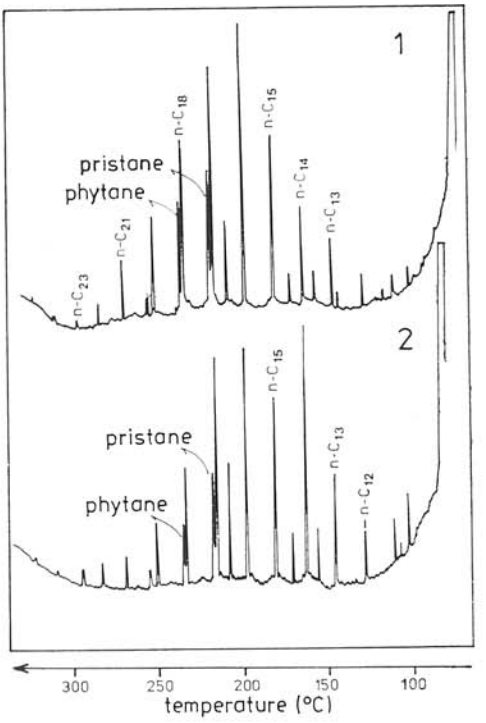


Fig. 1. Gas chromatogram of aliphatic hydrocarbons isolated from the fluorite of the Křižany deposit (I—III), from the chlorite-sericite schists of the Ještěd crystalline area (IV) and the Cenomanian rocks of the Bohemian Cretaceous Table (V).
I — fluorite, size fraction > 2 mm; II — fluorite, size fraction 2 — 0.2 mm, III — fluorite, size fraction < 0.074 mm.

Fig. 2. Gas chromatogram of aliphatic hydrocarbons isolated from the anthraxolites of the Příbram deposit (1) and the Precambrian country rocks (the Lečice Member) (2).

Table 1

Fatty acid	n-C_8	n-C_9	n-C_{10}	n-C_{11}	n-C_{12}	n-C_{13}	n-C_{14}	n-C_{15}	n-C_{16}	n-C_{17}	n-C_{18}	n-C_{19}	n-C_{20}	n-C_{21}	n-C_{22}
Sample no.															
1	0.679 (Q)	<LD	0.195 (Q)	0.029 (Q)	0.012	0.066	0.071	0.037	0.132	0.094	0.145	0.140	0.143	<LD	<LD
2	0.013 (Q)	<LD	0.096 (Q)	<LD	<LD	<LD	<LD	0.004	0.048	0.005	0.040	0.006	0.028	0.029	0.031
3	<LD	<LD	<LD	<LD	<LD	0.012	0.015	0.006	0.048	0.004	0.033	0.005	0.009	0.007	0.014
4	0.850 (D)	0.139 (Q)	<LD	0.201	0.103	<LD	0.113	0.042	0.045	<LD	0.057	0.068	0.110	0.120	0.140

Analysts: J. Toul, I. Borkovcová, Central geol. surv., Brno

Fatty acids isolated from the anthraxolites of the Příbram deposit (1 and 2) and from the Preterozoic surrounding rocks (Lečice Member) (3). (4) Fatty acids isolated from the marble of the graphite deposit Bližná (the varied series of the Moldanubicum). Q — semiquantitative assessment; LD — limit of detection (0.002 $\mu g.g^{-1}$). Concentration in $\mu g.g^{-1}$.

whose origin may be derived from the phytol chain of a chlorophyll molecule (E. J. Gallegos, 1976).

This means that the origin of the bitumens of the Příbram deposit may be sought in the organic substances of the surrounding Precambrian rocks from which these substances have been extracted (pyrolyzed) by the effect of hydrothermal solutions, and deposited in ore veins. This has also been confirmed by the analysis of the same groups of organic substances from the country rocks of the deposit (Lečice Member), the composition of which is close to that of the substances isolated from the ore veins (Tables 1 and 2).

Of the deposits lying in metamorphic rocks, the bitumens of the Zadní Chodov deposit were studied in detail. Similarly as in the preceding case, n-alkanes, isoprenoid hydrocarbons and fatty acids were isolated from anthraxolites.

Table 2

Sample no.	1	2	3	4
Aspartic acid	0.96	0.22	1.07	0.72
Threonine	0.72	0.15	0.98	0.68
Serine	1.07	0.34	0.85	0.72
Proline	1.30	0.19	1.15	0.98
Glutamic acid	1.97	0.41	2.20	1.80
Glycine	1.06	0.39	0.62	0.74
Alanine	0.93	0.22	0.93	0.86
Valine	1.07	0.40	1.32	1.12
Isoleucine	0.50	0.22	0.12	0.21
Leucine	tr.	tr.	tr.	tr.
Phenylalanine	tr.	tr.	tr.	tr.
Lysine	1.00	0.15	0.48	0.32

Amino acids isolated from the anthraxolites of the Příbram deposit (1 anl 2) and from the surrounding Proterozoic rocks (Lečice Member) (3 and 4). Concentration in $\mu g.g^{-1}$.

It is probable that the epigenetic (post-metamorphic) organic substances of the host rocks are the source of the above-mentioned organic substances. This is attested e.g. by the relatively high concentration of fatty acids in the graphitic marble of the Moldanubicum (Table 1).

In studying the isotopic composition of the anthraxolites, a significant difference between the values $\delta^{13}C$ (PDB) of the anthraxolites from the deposits in metamorphic rocks, and the anthraxolites from the Příbram deposit (Fig. 3) was found. In the first case these values practically do not differ from the isotopic composition of the carbonaceous compounds derived from a biological source. In contrast, the anthraxolites from the Příbram deposit are extremely enriched in the light isotope of carbon and considerably differ from the isotopic composition of the kerogen of the surrounding Precambrian and Cambrian rocks. These results suggest that in the first group of deposits, during the origin of anthraxolites, no fairly conspicuous isotopic differentiation took place. In contrast, in the case of the anthraxolites of the Příbram

deposit, the extreme enrichment in the light isotope testifies to a pronounced isotopic differentiation of the primary material.

In relation to the uranium mineralization, the bitumens of all the deposits studied (together with calcite, quartz and sulphides) form part of the post-ore supply periods. Their absence in higher-temperature stages of mineralization may be explained either by a change of the source of hydrothermal waters or, more probably, by their complete oxidation while CO_2 originated. In the latter case, e.g. U^{VI} ions could be the oxidation agents:

$$OU_2(CO_3)_2^{2-} + \left[H-C \begin{matrix} O \\ OH \end{matrix} \right]_{org} \rightarrow UO_2 + CO_3^{2-} + 2CO_2 + H_2O,$$

as is the common case in epigenetic uranium deposits in sediments.

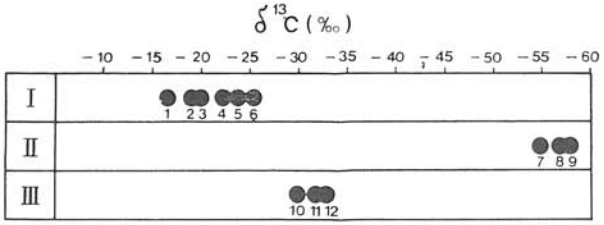


Fig. 3. Isotopic composition of the carbon of the anthraxolites from the uranium deposits in metamorphic rocks (I), the anthraxolites of the Příbram deposit (II), and of the kerogen of the Proterozoic and Cambrium rocks in the surroundings of the Příbram deposit (III).

1 — Licoměřice, 2—3 — Západní chodov, 4 and 6 — Dyleň, 5 — Jáchymov, 7—9 — Příbram, 10 and 11 — Proterozoic, the Příbram area (Lečice Member), 12 — Cambrian.

Conclusion

Results of the investigations carried out have shown that the compounds of the reduced form of carbon represente the common part of hydrothermal solutions. Their presence is to be considered in interpreting the causes leading to the origin of a mineralization or in modelling hydrothermal processes.

In all the cases studied it has been proved that the carbonaceous substances in hydrothermal deposits originate by remobilization of organic material of the host rocks. With regard to the minimal solubility of bitumens in aqueous solutions, their presence in ore veins furnishes evidence of considerable volumes of the waters by which these substances had to be extracted from the host rocks; this agrees with the results of the isotopic study of oxygen in a number of hydrothermal deposits (H. P. Taylor, 1974). The oxidation of organic substances during a hydrothermal process may then be one of the causes of the lowering of the redox potential of the hydrothermal solution, and may lead to accumulation of the ore component. The production of CO_2 derived from organic sources may then be responsible for the considerable scatter of the values $\delta^{13}C$ of the carbonates of the gangue.

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