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Coal inclusions in sedimentary rocks: a geochemical phenomenon. A review

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Abstract

In many coal-bearing basins, there are numerous coalified fragments of ancient plants (coal-precursors) enclosed in host rocks. Such fragments occur in isolated positions out of the coal beds. In the Russian literature, these coal fragments are named *coal inclusions*. Coal inclusions are mostly the remains of stems, trunks, and branches, as well as the roots of trees.

The review presented covers: (a) definition and classification of fossil woods; (b) relations between coalification and mineralization of fossil woods; (c) some special topics dealing with different and even zonal coalification degree of coal inclusions embedded different host rocks; (d) some historical data on geochemistry of coal inclusions; (e) basic empirical regularities in geochemistry, observed world-wide; (f) some data about chemical nature of humin substance—a precursor of lignite and vitrain matter in coalified wood; (g) results of calculations modelling the Ge enrichment in coal inclusions; (h) economic importance of Ge in coal inclusions; and (j) use of coal inclusion geochemistry for indication of some diagenetic and catagenetic processes, and as a tool for stratigraphic correlation.

The most part of the above studies performed during 1934–1972 were outlined in the monograph “Geochemistry of coal inclusions in sedimentary rocks” [Yudovich, Ya.E., 1972. *Geochemistry of coal inclusions in sedimentary rocks*. L.: Nauka [Leningrad: “Science” Pub. House], 84 pp.]. These materials are added to some recent work by Bulgarian and Russian geologists, performed with use of modern analytical methods. It has been shown that: (a) coalified wood may contain very exotic micro-mineral phases, sometimes far unexpected; (b) apart from Ge, coalified wood may contain high concentrations of some other trace elements, which were earlier not detected because of analytical limitations (REE, As, etc.). These special peculiarities can be partly contributed by epigenetic hydrothermal processes.

As a summary, the review shows that coal inclusions are unique geochemical phenomenon, sharply different from even neighboring coal beds in trace element content. Among the most extreme elements is germanium, its mean concentration in the ash of coal inclusions being up to 220 times higher than in the ash of coal beds. The most important peculiarity of the coalified wood is the good preservation of the original lignin structures, which may effectively scavenge Ge from solutions, whereas peat-born coals (in beds) contained such structures in far fewer amounts. In addition, a reservoir of dissolved germanium in peat bog waters was of lower concentration than in sediments, which buried the coal inclusions. Finally, the peat bog acidic environment may act as an unfavorable factor.

Ge-enrichment can be completed in a time ranging from a few thousand years up to tens of million years. However, if the waters are enriched in Ge, the process can proceed more rapidly and would be completed even under the most unfavorable

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parameters (compared to the model conditions). This implies that enrichment can take place during the early diagenetic stage. Such a scenario was supported by geologic considerations.

Some Canadian and Soviet works performed from 1950 to 1960 along with some recent Russian studies show that Ge in coal inclusions can be of economic interest.

Geochemistry and mineralogy of coal inclusions are of great interest and need further detailed study.

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Keywords: Germanium; Coal; Sediments; Coal inclusions; Geochemistry

1. Introduction

In many coal-bearing basins, there are numerous coalified fragments of ancient plants (coal-precursors) enclosed in host rocks. Such fragments occur in isolated locations outside of the coal beds. In the Russian literature, these coal fragments are referred to as *coal inclusions* (Yudovich, 1972a). Coal inclusions are mostly the remains of stems, trunks, and branches as well as the roots of trees.

Commonly, the coal inclusions are enclosed in roof rocks, directly above coal bed, for example, in some British coalfields (Jones and Miller, 1939; Reynolds,

1948). However, in cyclic coal-bearing sequences, the coal inclusions may be present in the middle sandy parts of the cyclothem, nearly equal distance from the upper and lower coal seams. Sometimes, entire trees are preserved in horizontal and vertical (as living) position (Yudovich, 1972a, 1989). As was demonstrated in the Lower Cretaceous Yakutian coal-bearing section (Lena coal basin), such a position means the buried *fossil soils* are represented, with the “growing” and fallen trees as well as parts of these trees (Yudovich, 1972a, 1989) (Fig. 1).

The coal inclusions are present mostly in terrigenous coal-bearing strata, but they can also be found in

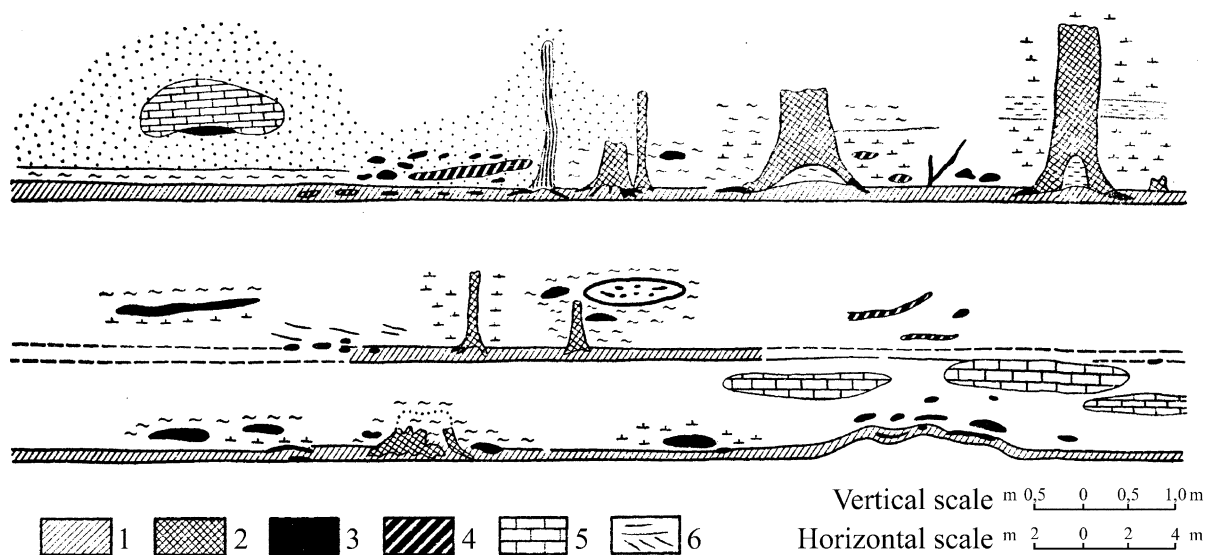


Fig. 1. Three fossil soils with “growing” and fallen trees. Lena coal basin, Lower Cretaceous, Kagalassy coalfield. Clearings of the outcrops over the left Lena River shore (after Yudovich, 1989, p. 101). 1—fossil soils; 2–3—lignite-like coal inclusions (logs, branches, stems, a bark, roots): brown soft (2) and black more solid, half-matt or semi-bright gagate-like, composed of conchoidal vitrain (3); 4—redeposited “peatborn” coal of non-lignitic nature (matt, earthy, thin-banded, etc.); 5—calcareous concretions in the cross bedded deltaic sands; 6—bedding in sands (they are shown as light background on the figure). Note that the vertical scale is exaggerated.

Table 1
A classification of coal inclusions

Relative age of the inclusions	Initial plant matter	
	A	B
(1) Coal inclusions are syngenetic with host sediments	<p><i>Coaly detritus</i> or “peatborn” inclusions. The debris of coal-forming plants (not necessarily arboreal!) passed decay stage in the peat bog that result in banded-structure (or layer, etc.) coal formation</p> <p>The inclusions were formed by erosion and re-deposition of peat during accumulation of coal-bearing sequence</p>	<p>“Non-peatborn” woody inclusions. The remains of the trees were buried in host sediments out of swamp facies, resulting in formation of unbanded, vitrain-like coals with woody structures: coal inclusions in <i>s.str.</i></p> <p>The inclusions were formed from the trunk, stem, branch, root fragments as well as from entire trees and stumps, both in allochthonous and indigenous positions (including living positions)</p>
(2) Coal inclusions are older than host rocks	<p>Coaly detritus (“coal particles”, “coal fragments”) was formed by means of later erosion of the coal (not the peat!) beds. For instance: the particles of coking coal in the alluvial Quaternary sediments, Pechora coal basin (Russia)</p>	<p>The coalified wood is redeposited from the older into the younger strata, by means of erosion of the older host rocks. For instance: redeposited (from underlying Lower Cretaceous) woody coal in Pliocene pebbles, Kangalassy coal field (see Fig. 2)</p>

After Yudovich (1972a, p. 5), with moderate changes.

non-coal-bearing sequences, for example, in Lower Jurassic marls of Dorset, England (Hallam and Payne, 1958) or in the Upper Devonian Chattanooga oil shale, Tennessee and Ohio, USA (Breger and Schopf, 1955).

Apart from the above mentioned coal inclusions, there is also *coaly detritus* resulting from syngenetic or epigenetic erosion of the buried peat or coal beds. Such detritus is distinct from coal inclusions *sensu stricto*, in that the precursors of the coaly detritus were once in a peat. On the contrary, the precursors of coal inclusions *sensu stricto* were *never* in a peat bog. They are buried in host sediments, *out* of the peat bogs. Such a difference in origin results in great geochemical differences. Coal inclusions, *sensu stricto*, have to be clearly distinguished from coaly detritus, as shown in Table 1 and Fig. 2.

Coal inclusions of the 1A and 1B types are the primary subject of oil geologists, who constructed the *catagenesis scale* based on the vitrinite reflectance of such inclusions. It is well known that vitrinite reflectance is a more sensitive tool for indication of catagenesis than authigenic minerals (Lebedev, 1992). Coal inclusions of the 2A type (“coal fragments”) can be used as a tool for many applications in paleogeography, neotectonics, and new coalfield prospecting based on the remarkable studies of Yu.V.

Stepanov (geologist and former Vorkuta prisoner; see Yudovich, 1972a for references). Lastly, coal inclusions of the 1B type are of geochemical interest because of their large concentration of trace elements (Ge, U, V, Ti, Cr, etc.).¹

Some Bulgarian data (Table 2) provides a good illustration of the great geochemical difference between woody coal inclusions (type 1B) and “peatborn” coal inclusion (type 1A). As is seen in Table 2, the woody inclusions (vitrains) are far more enriched in vanadium than non-woody, “peat-born” inclusions (clarains and other banded coals).

The highest known Ge concentration in the ash of a coal inclusion, 8.2%, is from a lignite inclusion in Lower Jurassic marine marls of Dorset, England (Hallam and Payne, 1958). The mean content of Ge in these inclusions (our calculation of over 29 samples) is 1.48% on an ash basis, or 1880 ppm on a whole coal basis. For comparison, the global mean Ge content (“Clarke value”) in sedimentary rocks is 1.4

¹ On 22 February 1961, the author presented a report “On the independent genetic type of the trace element concentrations” (Yakutsk: a session of the Yakutian Territorial Geol. Survey). This report was published later (Yudovich, 1963). After this, the concept was accepted in the Russian literature, but unfortunately, not in the Western literature.

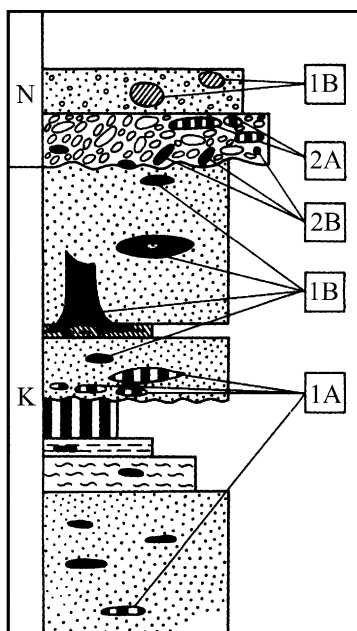


Fig. 2. A sketch of the coal inclusion characterization (Yudovich, 1972a, p. 6). The Pliocene pebbles discordantly cover coal-bearing sands of the Lower Cretaceous, which contain horizons of fossil soils (with “growing” stumps—1B). Woody syngenetic coal inclusions of the 1B type are represented with bright black lignites (in Lower Cretaceous) and soft brown lignites (in Pliocene). Redeposited woody inclusions represent the 2B type. Peatborn inclusions formed at intraformational erosional boundaries are represented now as banded semi-bright coals; they are 1A type. The same inclusions, but redeposited in Pliocene strata, represent the 2A type. The “zebra” sign—a coal bed. See Table 1 for further explanation.

ppm. Therefore, for the Lower Jurassic inclusions, the mean Ge content in ash is about 10,000 times more than the Clarke value, and the “record” content—around 59,000 times.

2. Fossil wood: mineralization versus coalification

Both mineralization and coalification occur hand-in-hand in coal basins. However, mineralization of the woody tissues generally occurs before coalification. As a rule, highly decayed wood may be mineralized, preserving some of the wood structure; but total decay leaves nothing to be preserved. In contrast, coalified wood is better-preserved (Fig. 3). Of course, coal

spans a wide range of coalification, although at any one place, a narrow range, essentially iso-rank, of coalification is present.

Mineralized wood, as well as coalified wood, occurs more often outside of coal beds. Of course, there are numerous small lens-like vitrain and fusain inclusions in coals. It is well known that they are very often mineralized with sulphides and carbonates. The minerals may infill empty cellular cavities or (more rarely) substitute the cell walls. Many good illustrations in the literature can be cited (as example, see Renton's, 1982 excellent outline). In such cases, mineralization and coalification may occur near simultaneously, alternating during diagenesis. Nevertheless, rare finds of mineralization are also known within coal beds. For instance, a large accumulation of mineralized stumps and fallen wood fragments was described in the Upper Permian Vorkuta coalfield (Pechora Basin, Russia), within the upper bench of the i4 coal seam. Within a fossil soil horizon (thin, dark-brown siltstone layer), the stumps “grew” in situ on the soil substratum, and were later mineralized with carbonates; some carbonized wood fragments, perhaps fallen from the stumps, are found near the stumps. This remarkable “stony forest” stretched 200–250 m; the stumps are generally 0.2–0.3 m in diameter, and as much as 0.4 m high. They were “cut off” by the overlying bright coal bench, and do not reach the additional 0.1–0.2 m to the coaly argillite roof. As geologic reconstruction has shown, these were Cordaitales trees (Yudovich, 1972b). A combined model of

Table 2
A comparison of V concentrations in three varieties of coal inclusions

Characteristics	Coal inclusions		
	Vitains (woody coals, non-peat-born)	Clarains (banded peat-born bright coals)	Ash-rich coals (banded peat- born mat coals)
Sample number	60	8	4
Mean ash content, %	3.73	7.37	42.02
Mean V content, ppm	559	187	109

Modified figures of Uzunov and Kotorova (1972), the Pernik deposit, Bulgaria (Yudovich, 1989, p. 113).

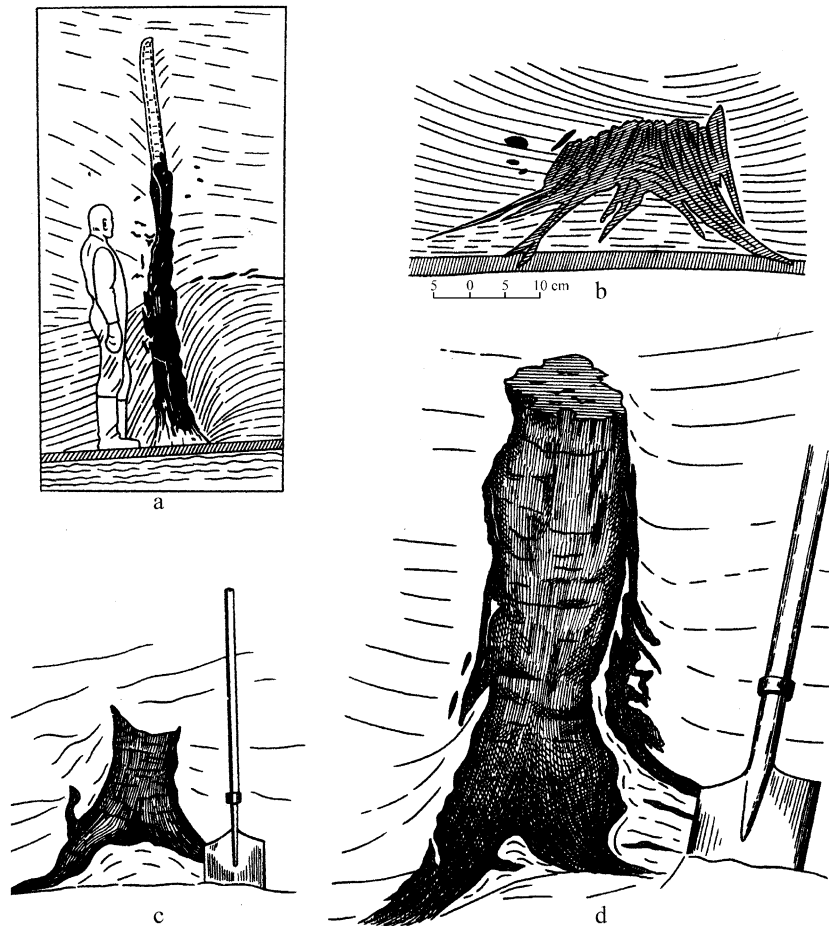


Fig. 3. Four lignite stumps on the fossil soils: completely coalified (b–d) and partly mineralized (a). In the latter case, the top part of the tree was decayed before burial, and the rest was mineralized with carbonate. See Fig. 1 for further explanation. Lena Basin, Kangelassy coal field (Yudovich, 1989, p. 100).

mineralized and coalified woods may be constructed on three bases: burial place, position, and composition (Table 3).

3. Influence of host rock composition and zonal coalification

Chernousov (1959) described a strange phenomenon in Mesozoic measures on the east slope of the Urals: coal inclusions in argillites appeared more coalified (more black, hard, and bright) than ones in sandstones! Later, Uzbek geologists (Sofiev et al., 1962) and oil geologists reported similar observa-

tions in oil-prospecting cores. Finally, Yudovich noted the same phenomenon in the Lower Cretaceous Kangelassy coal deposit (near Yakutsk, Lena coal basin) (Yudovich, 1968, 1972a,b, 1989). Thus, different degrees of woody fragment coalification are found in different host rocks, which had different permeability for water and gas.

However, an even more remarkable phenomenon was detected: a zonal coalification of the same vertical stumps in situ, if they were buried by alternating different lithologies (for example: silt–sand–silt, or sand–silt–clay). In such stumps, the parts surrounded by more clayey rock are more coalified. Zones surrounded by sand consist of soft, friable, brown and

Table 3
Characteristics of woody remains in coal-bearing strata

Burial place	Composition	Position	
		Standing (in situ)	Lying (fallen on the place and/or allocthonous)
Within coal seam	Mineralized	“Stony Forest” in the i ₄ seam. Vorkuta coal field—very rare case	Numerous vitrains and fusains mineralized in the early (pyrite) and late (pyrite, carbonate) stages of diagenesis
	Coalified	Lignite seams of East Germany and Hungary	Very often: all the large vitrain lenses in bituminous coals, lignite and xylite in soft brown coals
In the host rock	Mineralized	Fairly often; in the roof of coal beds	Very often: in all coal basins of the World
	Coalified	“Coaly Forests”: Mesozoic coals of the Middle Asia and Lena basin, Meso- and Cenozoic coals of the USA, Neogene coals of the Slovakia, Paleogene Latrobe Valley (Australia), Carboniferous “cauldrons” (“kettle-bottoms”) of England, etc.	Fairly often: metalliferous “coal inclusions” <i>s. str.</i> , usually appeared in deltaic facies and above fossil soil horizons

After Yudovich (1972b, p. 100) with moderate changes.

dull lignite. Zones surrounded by silt or clay consist of dense, hard, black, and semi-bright lignito-gagate (Fig. 4). The chemical differences were not so large as the visible differences, but were also quite noticeable: 1% for C, 0.5% for H, and 1.5% for O contents in the coal.

It is possible that the phenomenon of different coalification may be the result of a *catalytic effect* of clay matter. The clay creates an alkali environment during the fossil wood diagenesis. In such environment, the polymerization of coal macromolecules followed the splitting off CO₂, H₂O, and CH₄ from the phenyl-propane framework were performed, probably, more readily.

4. Trace metal content: early studies

In 1935, V.A. Zilbermints (Russian geochemist and mineralogist, killed during Stalin’s regime in 1938) carried out a systematic geochemical study of the coal basins of the USSR. More than 500 samples from the Donetsk, Caucasus, Urals, Minusa, Middle Asian, Kazakhstan, and Far East basins and coalfields were studied. The study showed that the mean vanadium content in the coal ash was in the 0.03–0.06% range (Zilbermints and Kostrykin, 1936). As was shown later, these figures were too high because of the method of sampling (Yudovich et al., 1985, p. 91). Unexpectedly, the highest V concentrations were found in the coalified wood (coal

inclusions *s.str.*), originated from the Jurassic and probably Lower Cretaceous sections of the Fore-Urals: as much as 8.75% V₂O₅ (or 4.92% V) in the ash. Included in the study were the samples from A.A.Chernov and V.A.Varsanof’eva’s (Komi Republic), P.L. Bezrukov’s, and A.L. Yanshin’s (Baskiriya Republic) collections.

Zilbermints attached high significance to his windfall and in 1936 he conducted additional sampling of the Jurassic coals in the Southern Urals. The results obtained were the same: all the extremely high V-contents (up to 4.19% V₂O₅) were found only in the coalified wood. These were isolated woody fragments buried in fluvial or deltaic measures. On the contrary, the vanadium content in the coal beds was no more than 0.5% V₂O₅. Even so, all these elevated contents were found in thin beds (thinner than 0.5 m) or very thin riders (nearly 5–10 cm) (Zilbermints and Bezrukov, 1936). As our analysis of the above data show, the ash of the coal inclusions was enriched in V on average of one order of magnitude (Table 4).

In 1939, Jones and Miller (1939) described two types of coal inclusions in the Carboniferous of Northumberland and Durham, England: *cauldron* and *horse backs*, as the English miners named them. A cauldron (or “kettle-bottom”) is a conical argillite body in the coal roof, sometimes framed by the coalified roots, but root prints alone usually remained. On the top of the cone, vitrain (anthraxylon) coal is seen—the remainder of the near-root lowermost part

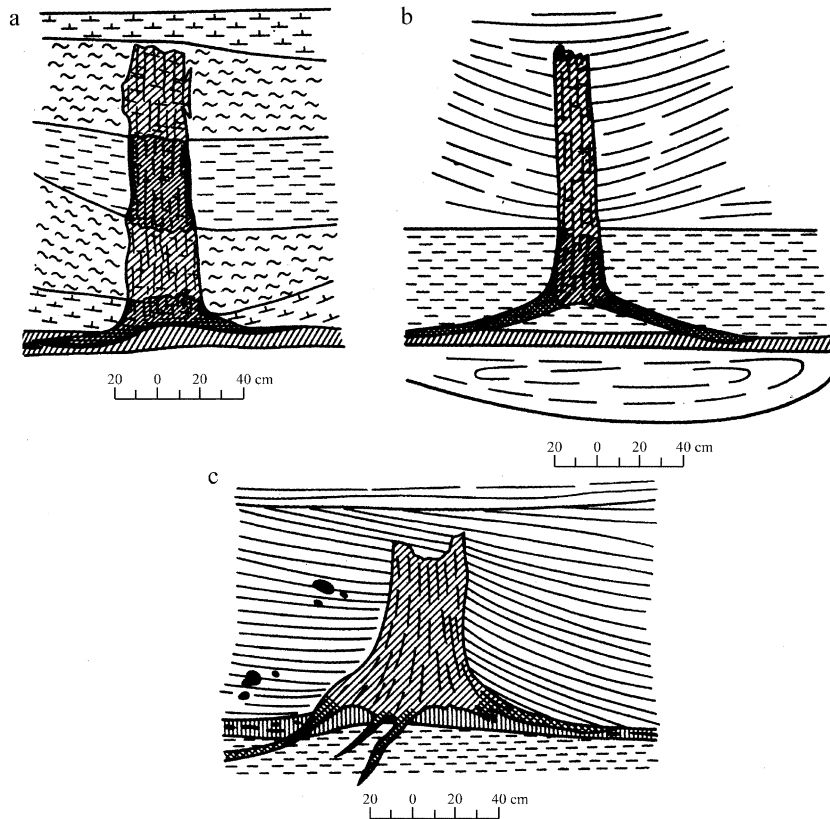


Fig. 4. Zonal coalification of the in situ buried stumps (Yudovich, 1989, p. 104). Note that parts of the stumps surrounded with finer sediment (silty clay and siltstone) appear to be darker (also roots, (c)). On (b), a carbonate concretion lies beneath fossil soil. Cross-bedded sands are also shown (see Fig. 1 for comparison). On (a) and (b), one can see some hillock at the stump base, resembling “kettle-bottoms”.

of the ancient tree, in situ. Most of the cauldron-coals appear to be pressed cellular structures, which were identified as *Sigillaria* bark. A *Horseback* is a coalified

branch within the roof, with lens-like cross-section, often with central part filled up with shale. Fifteen analyses of the float fractions of above coals ($< 1.35 \text{ g/cm}^3$) showed an extraordinarily large TiO_2 content in the ash, in the 7.0–24.3% range (Jones and Miller, 1939).

Later, Reynolds (1948) studied inclusions of the vitrified wood, including bark tissues of *Sigillaria*, in the floor and roof of Pennsylvanian coal beds in North Staffordshire and North Wales. The V_2O_5 content in the ash of the float fraction was as high as 14.1% (or $\sim 7\%$ V, and 5400 ppm on a whole coal basis) (Yudovich et al., 1985, p. 92).

Because of massive coal sampling, with particular interest in Ge and U after World War II, there emerged many new studies on the geochemistry of coal inclusions.

Table 4
Mean V contents in the ash of the Jurassic coals, Southern Urals

Material	Number of samples	Ash, %	V in the ash, %
Coalified wood (coal inclusions)	15	6.96	1.0
Thin coal beds and riders with ash content less 10%	5	4.49	0.11
Thicker coal beds with ash content more than 10%, usually weathered	16	25.37	0.08

Modified from Zilbermintz and Bezrukov (1936) (see in: Yudovich et al., 1985, p. 92).

The data concerned coalified woods from:

- England (Briggs, 1934; Davidson and Ponsford, 1954; Hallam and Payne, 1958),
- Belgium (Jedwab, 1960),
- Bulgaria (Eskenazy, 1965; Minčev and Eskenazy, 1963, 1966, 1969; Uzunov, 1965; Uzunov and Kotorova, 1972),
- Canada (Hawley, 1955; Buckland, 1959; Boyle, 1968; Kronberg et al., 1987),
- Chile (Mueller, 1960),
- Czechoslovakia (Bouška and Honek, 1962; Čadek et al., 1961; Mrázek and Vlasek, 1958),
- Germany (Leutwein and Rösler, 1956),
- Poland (Gawel, 1962),
- Spitsbergen (Svalboard) (Pavlov, 1966),
- United States (Breger and Chandler, 1960; Breger and Schopf, 1955; Ergun et al., 1960; Stadnichenko et al., 1950, 1953; Zubovic et al., 1961, 1964, 1966),
- Japan (Oka et al., 1956).

In the former USSR, such data were obtained for the coals from:

- Russia (Bol'shakov, 1964; Kochetkov, 1966; Lomashov, 1961; Pavlov, 1967; Ratynsky, 1946; Travin, 1960; Yudovich, 1963, 1968; Yudovich et al., 1971, 1972, 1973, 1987),
- Ukraine (Nikitin, 1964),
- Belorussia (Kovalev and Narodetskaya, 1981),
- Kazakhstan (Azizov, 1965),
- Uzbekistan (Savel'ev, 1964; Sofiev et al., 1962; Ziltsov et al., 1965; Ismailov et al., 1964),
- Kirgizia (Tkachev et al., 1965).

All the studies performed during 1934–1972 were outlined in the small monograph “Geochemistry of coal inclusions in sedimentary rocks” (Yudovich, 1972a). The outline has shown that coal inclusions represent a *unique geochemical material*, distinctly different from coal beds. Therefore, a mechanical data compilation (of the inclusions with that of the coal beds) can be misleading. If this condition is violated, results can be confusing (Table 5). One can see that combining 15 samples of the coal inclusions (7% of the whole sample number) for the mean calculation resulted in overstating of the V

Table 5

Two variants of calculated trace elements mean content, for the Northern Great Plains coal ashes (North and South Dakota, Wyoming, and Montana)

Elements	Mean contents, ppm in the ash		a/b
	a	b	
Vanadium	650	150	4.3
Chromium	200	70	2.8
Gallium	100	47	2.0
Germanium	740	22	33.6

Modified from Zubovic et al. (1961).

a—the arithmetic mean, for all 221 samples, including coal beds and coalified woods.

b—the weighed mean (weighing on the bench thickness), for the 206 samples of the coal beds only.

content nearly four times and Ge contents—nearly 34 times.

Unfortunately, in some publications this procedural requirement was ignored. Even in Swaine's (1990) excellent monograph, the extraordinary Ge enrichments in coal inclusions were not understood. He interpreted them only as an indication of the early incorporation of Ge into the coal:

The presence of large amounts of Ge in coalified wood (Breger and Schopf, 1955) and in lignitic inclusions (Stadnichenko et al., 1953; Hallam and Payne, 1958) establishes that there can be marked enrichment of Ge during the early stages of coalification [Swaine, 1990, p.119].

Bouška (1977) is even more problematical. There are 55 Ge values in Table 22 (pp. 126–128),² with more than 30 references. Probably, the author wished to provide information about *global Ge-distribution*. Unfortunately, he achieved quite the opposite result. From this table, the reader may imagine that Ge content in coals changes quite chaotically, in the four order-of-magnitude range. In this compilation, the Ge contents in raw coal samples are mixed with ones in clean coal concentrates; whole-bed samples—with Ge-enriched marginal bench samples; ordinary ash samples—with fly ash (!) samples sharply enriched in Ge, etc. However, the main chaos in this compilation is introduced by coal inclusions. In fact, no less

² Corresponds to Table 36 in the English version of Bouška's book (Bouška, 1977).

than 35 of the 55 values presented are not from coal beds, but coal inclusions.

The second interesting result in Yudovich's (1972a) monograph was the suggestion of two geochemical types of coal inclusions: "Vanadium type" and "Germanium type". The former is well exemplified by English Carboniferous coalified woods (V, Ti, Cr, Ni, Co, Cu) and some others, for instance with the Pernik, Bulgaria, deposits. Ge-type inclusions (Ge, Ga, As, Be, Zr, Y, Ce, La) are well exemplified by Cretaceous coalified wood derived from many deposits in USA (Atlantic Coast Plain and Northern Great Plains), Russia, Uzbekistan, England (Dorset), as well as from the Neogene of British Columbia (Canada). It is likely that such differences resulted from initial botanic differences; the V-type inclusions derived from bituminous bark tissue and the Ge-type inclusions derived from non-bituminous stem (or trunk) woody tissue. This explanation is consistent with the "hard-soft acid–base theory" (HSAB) of Pearson (1963a,b), a method of explaining the behavior of Lewis acids and bases. *Acids* (i.e. metal ions) have an affinity for similar *bases* (i.e. organic acids): for example, a soft acid combines mainly with a soft base, and a hard acid with a hard base. For example, Ge^{4+} is a hard acid, and humic acid is the hard base. This results in strong bonding of Ge with humic acid. On the contrary, sapropel-like bituminous organics are soft bases, and they combine with the soft acids, such as VO^{2+} , etc.

5. Trace metal content: observed regularities

At the beginning of the 1960s, it became clear that coal inclusions contain extraordinary concentrations of trace elements (Yudovich, 1963). In reality, average contents of many trace elements in coal inclusions are noticeably higher versus coal beds (Table 6).³ For example, exceptionally high concentrations are found for Ge, with Ge content in the coal inclusions ash being 220 times the concentration in coal bed ash!

³ The global average concentrations of trace elements in coal ("Coal Clarke figures") were firstly calculated by Yudovich et al. in 1972, and later—on the far larger data base—in 1985 (Yudovich et al., 1985).

On examining the concentration ratios of inclusions versus coal beds, we find the following:

- Enrichment of 1.5–2 times: Sr, Ba, Be, Sc, Yb, Zr, Mn;
- Enrichment of 2–5 times: Y, Ce, Ti, Sn, V, Mo, Cu, Ag, Zn, As, Sb, Co, Ni;
- Enrichment of more than five times: La, Ga, Ge, Nb, and Cr.

The highest Ge enrichment is quite extreme. Coal inclusions are deficient in boron and lead(?). However, some exceptions are not yet clear. For example, coal inclusions in Famennian oil shale-bearing measures over the Pripyat' depression (Belorussia) are enriched in boron, in addition to germanium (Kovalev and Narodetskaya, 1981, p. 1035).

Analysis of trace element data resulted in five empirical regularities for Ge (and some other "coal-ophile" elements⁴ (Yudovich, 1972a, 1989)).

1. *The phenomenon is global in nature.* The enrichment in trace elements (Ge; as well as Ga, Cr, V, Ni, and many others) of coal inclusions in is a worldwide occurrence. It was observed in coal-bearing and coal-free measures in Europe, Asia, and the Americas.
2. *Coal inclusions are much more highly enriched in trace elements than vitrains within neighboring coal beds.* This difference is especially displayed when coal inclusions lie only a few centimeters from the roof or floor of the coal beds. In such cases, geological age, coal rank, and, to a lesser extent, coal-forming plants are similar.
3. *Enrichment of trace elements in coal inclusions appears independently of geologic age of the host rock.* In fact, the high concentrations of trace elements in coal inclusions are known in Devonian (Timan Ridge, Russia; Chattanooga Shale, USA) and as well as in Pleistocene (Japan) measures. However, because of the biological evolution of coal-forming flora, coal inclusions occur much more often in Mesozoic and Cenozoic strata than in the Paleozoic. Such historical geological evolution

⁴ The term "coalophile" means: *the element, which are enriched in coal ash versus host rocks.* It is of note that such elements were named earlier as "typomorph elements" (Yudovich, 1968).

Table 6

Median trace element contents in the ash of coal inclusions and coals from the beds (Yudovich, 1989, p. 106)

Element	Number of random samples	Number of analyses	Contents of elements, ppm (median \pm S.D.)		Concentration ratio (4:5)
			Ash from the coal inclusions	Ash from the bed coals	
1	2	3	4	5	
Sr	7	1140	1200 \pm 150	780	1.5
Ba	7	1140	1800 \pm 340	910	2.0
Be	11	1150	26 \pm 13	16	1.6
Sc	9	860	32 \pm 8	17	1.9
Y	12	1170	160 \pm 87	42	3.8
Yb	7	560	9 \pm 8	6	1.5
La	5	610	150 \pm 96	3–80	2–50
Ce	7	340	500 \pm 130	100–200 (?)	2.5–5
Ga	10	1160	220 \pm 82	43	5.1
Ge	27	1780	3100 \pm 2200	14	220
Ti	12	1170	8600 \pm 3200	3600	2.4
Zr	7	1110	380 \pm 300	210	1.8
Sn	10	1150	28 \pm 17	6	4.7
V	30	1680	640 \pm 600	150	4.3
Nb	4	540	50 \pm 23	8	6.3
Mo	10	1150	39 \pm 24	19	2.1
B	5	1060	430 \pm 200	620	0.7
Cu	11	1170	160 \pm 110	64	2.5
Ag	11	560	5.6 \pm 3.8	1.7	3.3
Zn	8.4	1000	310 \pm 300	125	2.5
Pb	9	1140	51 \pm 16	110	0.5
As	8	610	290 \pm 240	75	3.9
Sb	5	80	31 \pm 91	5–10	3–6
Cr	16	1160	1400 \pm 950	78	18
Mn	7	1130	630 \pm 280	485	1.3
Co	12	1170	110 \pm 36	27	4.1
Ni	16	1180	290 \pm 200	10	4.1

resulted from the shift of coal-accumulation from seacoast to central regions of the continents, from Paleozoic to Mesozoic and Cenozoic (according to N.M. Strakhov, a prominent Russian lithologist).⁵

4. *All coal inclusions enriched in trace elements have a woody nature, but represent vitrains (xylains) exclusively.* In fact, a fusinized wood (unless it is mineralized later), or non-woody (“peat-born”) inclusions are usually not enriched in trace elements.
5. *Enrichment of trace elements in coal inclusions is observed in a wide range of host rocks.* In fact, one can see enrichment in conglomerate, coarse sandstone, sandstone, siltstone, shale, marl, and tuff or

tuff-like rocks. The initial sediments were deposited in quite different facies: alluvial (as well as channel and flood-lands), deltaic, lacustrine, swamp, and shallow- and deep-water marine. At the same time, the nature of the host rock imprints the geochemistry of coal inclusions. Such relations were studied in detail for the Lower Cretaceous strata of the Near-Yakutsk region, Lena coal basin (Yudovich et al., 1971; Yudovich, 1972a).

Yudovich (1989, p. 108–121) concluded that *any interpretation of the geochemical nature of coal inclusions might be plausible only if there are no conflicts with all of the previous empirical regularities.* Thus, enrichment mechanisms offered in previous studies may be possible, but have only restricted (particular) significance because they do not account for all the observed relationships.

⁵ For example, see Strakhov’s “Principles of Lithology”, translated into English.

For example, Goldschmidt's (1935) idea of growth uptake of elements by the coal-forming plants, followed by residual concentration of trace elements by means of leaching of ash-forming elements (Jones and Miller, 1939) appears to conflict with empirical regularities 1–3. Similarly, the mechanism of anomalous growth enrichment that was advanced for the coal inclusions from the Ruhr coal basin (Meisch and Reinle, 1981) conflicts with empirical regularities 1–3.

Some epigenetic enrichment by means of hydrothermal “metalliferous” solutions is quite possible (Boyle, 1968; Leutwein and Rösler, 1956; Seredin and Magazina, 1999); however, such enrichment may not be universal because it conflicts with the second regularity.

The concept of a specific sedimentary facies is not consistent with empirical regularity 5.

Finally, the concept of vitrain as main factor in the enrichment process conflicts with the 2nd empirical regularity. This is demonstrated in Tables 7 and 8 (after Yudovich, 1989, pp. 114–115). Thus, vitrains from Peacock bed are richer in V, Cr, and Ti than the adjacent non-vitrain lithologies. However, this difference is much less than the difference for coal inclusions in the roof of the coal; the inclusions being enriched in V₂O₅—138 times, Cr₂O₃—26 times, TiO₂—75 times, and NiO—at a minimum 30 times.

As a result, as far back as 1972 (Yudovich, 1972a, p. 56), the most probable conclusion was made: *geochemical uniqueness of coal inclusions resulted from their isolated position—isolated from peat bog*. It was proposed that some peculiarities of the buried woody transformation (high specific surface area, an alkali milieu, a large volume of solutions extracted) resulted in an exclusively high capacity of the fossil wood to the metal sorption from dilute solutions.

Table 7
A comparison of V concentrations in two varieties of vitrains

Characteristics	Vitrains		
	Inclusions in host rocks	In the coal beds	
		Near the bed margins	Distant from bed margins
Sample number	60	33	27
Mean V content, ppm	559	193	125

Recalculated from Uzunov and Kotorova (1972), the Pernik deposit, Bulgaria (Yudovich, 1989, p. 114).

Table 8

A comparison of V, Cr, Ti, and Ni concentrations in coal, intra-coal-vitrains and coal inclusions

The matter	A ^d , %	Content, ppm			
		V ₂ O ₅	Cr ₂ O ₃	TiO ₂	NiO
Vitrain inclusions in the roof of bed, light fraction (<1.35 g/cm ³)	1.8	2500	180	2700	270
Coal bench, 58 inch (147 cm) thickness	5.5	16	11	33	Not detected
Vitrains from the bench	3.6	18	70	36	Not detected

Recalculated from Reynolds (1948), the Peacock bed, N. Wales, England (Yudovich, 1989, p. 115).

Some years later, this somewhat qualitative conclusion was confirmed, at least for germanium, from a chemical approach (Yudovich, 1989, pp. 117–120).

6. Germanium enrichment: nature of humin and related lignite

The chemical character of fossil wood is related to the nature of the *humins* that composed the main part of the soil and peat humus. It is known that humin is high-molecular weight geopolymer, comprising humic acids and related humic substances that are not soluble in dilute alkalies. For many years, humin was interpreted to be a product of humic acid condensation. However, some recent studies have shown that the latter is not the case (Hatcher et al., 1985). It was found by means of ¹³C NMR that the following types of structures dominate peat humus: (a) aromatic derivatives of lignin (=COOH–), (b) polysaccharide derivatives, and (c) paraffin derivatives (–OCH₃), the latter being mostly from algal or bacterial biomass. As peat was buried, polysaccharide structures disappeared and the other two remained. Because of this process, it was claimed that humic acids are not precursors for the humin and that: “It is likely, that humic acids are products of the degradation of humin rather than precursors” (Hatcher et al., 1985, p. 301). In turn, such a conclusion requires a revision of the lignite-origin concept. As was accepted, lignites originated from vascular plant by the following series of processes: *wood (lignin plus cellulose) ⇒ (loss of polysaccharides, i.e. of the cellulose) ⇒ selective preservation of the lignin*. In this process, lignite-stage

organic matter is depleted in H because of the loss, probably, of methoxyl groups and chains joined to the C-3 atom of the aromatic framework. This transformation likely occurs in the solid-phase, without the formation of intermediate humic acids. As a result, Hatcher et al. (1985, p. 298) concluded: “Thus, the lignite is essentially humin that is further modified by coalification. Eventually, the lignite is transformed to higher rank coal via loss of oxygen functionality”. In support of such a mechanism, they noted that:

1. there are few humic acids in the fossil wood at any stage of coalification;
2. ^{13}C NMR spectra also shows that carboxyl groups are apparently absent in lignites; and
3. if humic acids originated by means of monomers resynthesis (polymerization), this must have resulted in the destruction of cellular structure (whereas it is well preserved in lignites).

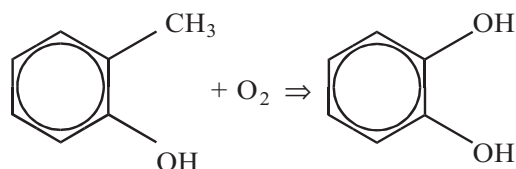
It is proposed here that the most important peculiarity of the coalified wood is the good preservation of the original lignin structures, which may effectively scavenge Ge from solutions. It is obvious that peat-born coals contained such structures in far fewer amounts. In such coals, one may observe only small lenses of vitrain or xylain. In addition, a reservoir of dissolved germanium in peat bog waters was of lower concentration than in sediments, which buried the coal inclusions. Finally, the peat bog acidic environment acted as an unfavorable factor, as noted below.

The origin of Ge enrichment in coalified (or lignified only) wood has been understood from experiments of Russian geochemists S. Manskaya, T. Drozdova, L. Kodina and M. Shpirt (Manskaya and Drozdova, 1964 or 1968; Manskaya et al., 1972; Manskaya and Kodina, 1975; Shpirt, 1977). Results of these studies proved that the main factor controlling Ge extraction from solution was an appearance of lignin derivatives. Such derivatives may rapidly bind up Ge by means of a stable complex formation.

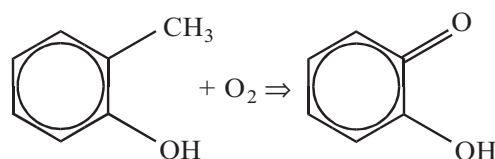
As is generally known, the main factors controlling biochemical decay of wood are fungi and bacteria. However, the acid environment of a peat bog is unfavorable for their activity. Therefore, the microbial transformation of the wood in peat bog is strongly hindered. On the contrary, the wood buried in sediments may be effectively decayed and transformed,

resulting in many small lignin fragments, such as phenyl-propane monomers. Such monomers are built from aromatic methoxylated and hydroxylated nuclei with a side propane chain. Subsequently, lignin derivatives lose the methoxyl group ($-\text{CH}_3$) that may be substituted with both hydroxyl and oxygen (Manskaya and Drozdova, 1964 or 1968).

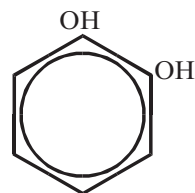
In the neutral and alkali milieu, the orthodiphenol group is formed:



In the acid milieu, the *ortho*-oxychinon group is formed:



Therefore, the type of methoxyl group substitution is strongly controlled by the pH of the environment. Thus, the formation of orthodiphenol groups appears to be a decisive factor for Ge extraction and binding from solutions. Experiments by Shpirt (1977) demonstrated that only 7% of functionality might react with germanium in common peat humic acids. Therefore, with large Ge concentrations in the solution (500 mg/l GeO_2), the maximum Ge absorption by peat humic acids would be no more than 0.725%. At the same time, the lignin extracted from natural wood attacked by the fungi contains as much as 30% pyrocatechol (i.e. benzol ring with two phenol groups):



Although pyrocatechol is a strong chelating agent, synthetic “humic acid” obtained by means of pyrocatechol oxidation has been shown to extract large amounts of Ge from solution—up to 8.4% (Manskaya and Kodina, 1975)! The difference between natural versus synthetic humic acids accounts for Ge reaction *only with ortho-positioned functionality* bonded with carbon of the benzol ring by means of π -linkage (Shpirt, 1977).

It is astonishing that a global geochemical phenomenon—Ge-enrichment in coal inclusions—was explained in term of the finest, quantum chemistry (Yudovich, 1989, pp. 120–121).

7. Germanium enrichment: process and model

Experiments have been conducted to model sorption with different sorbent-chelators (peat, lignite, vitrain, xylain, humic acids) (Manskaya and Drozdova, 1968; Manskaya et al., 1972; Manskaya and Kodina, 1975; Shpirt, 1977; Eskenazy, 1994). In these time-limited experiments Ge concentrations were 5–7 orders of magnitude higher than natural concentrations. This difference justifies an attempt to mathematically model the sorption process, as was done by Rysanov and Yudovich (Yudovich, 1972a; Rysanov and Yudovich, 1975).

In these studies, the modeling employed the following initial conditions.

(1) Changes with time, both of sorbent (coal inclusion) as well as of environment (pH, Eh, porosity, T, etc.), were not considered.

(2) Three mechanisms of the Ge transport were examined: infiltration; diffusion (the metal ions move in the still solution); and combined, convective diffusion (infiltration supplies some metal to the “sphere of influence” surrounding the coal inclusion and metal subsequently comes to the reacting surface by means of diffusion). For an estimation of the diffusion/infiltration ratio, a non-dimensional *Pecle criterion* (Pe) was used:

$$Pe = u \sqrt{k/D}, \quad (1)$$

where u is the velocity of infiltration in cm per year; k is sediment permeability in millidarcy (md); D is the diffusion coefficient in cm^2/s . $Pe > 1$ values indicate

that infiltration is dominant, values in the 1–0.01 range characterize a convective diffusion, and $Pe < 0.01$ indicates pure diffusion.

Fig. 5 shows that infiltration is nearly excluded in clays with k in the 10–100 md⁶ range. Infiltration probably occurs in permeable sands with k of 10^4 – 10^5 md, but at very high flow velocity; convective diffusion is more probable. However, the most likely scenario for clays and sands is diffusion. Diffusion coefficients ranging from 10^{-5} to 10^{-9} cm^2/s were used for calculations.

(3) Coal inclusions were modeled as a sphere with a radius 1.06 cm and a volume 5 cm^3 . Instead of permeability, corresponding values of porosity were used: 30% (corresponding to depths up to 1000 m), 20%, and 5%.

(4) Four Ge contents (expressed as wt.%) in coal inclusions were modeled: 0.01 (“background”, near the mean value), 0.005 (as a low value), 0.03 (as enriched), and 0.3 (as extremely high, or “hurricane” in the Russian literature).

(5) Two values of Ge content in ground water were considered: 6×10^{-8} g/l (as in seawater) and 6×10^{-6} g/l (as in some connate waters).

(6) Two values of temperature ($^{\circ}\text{C}$) at the depths were used: 20 and 70 $^{\circ}\text{C}$. It is known that a 50 $^{\circ}\text{C}$ increase in T results in a doubling of D .

Table 9 shows estimates of the time, τ (in years), necessary to attain a given metal quantity, Q , in a coal inclusion with radius $r = 1.06$ cm, volume $V = 5$ cm^3 , and specific gravity ρ , from the solution with specific gravity ρ_0 . Values for τ in Table 9 were calculated from the expression:

$$\tau = (Q/\eta C_0)(\rho/\rho_0)(V/4\pi D r), \quad (2)$$

where C_0 is a metal concentration in the solution, and, η is a porosity.

As is seen from Table 9, diffusion is capable of producing high Ge contents in coal inclusions, with concentrations up 10–100 times more than in the host rock. These concentrations can be produced from the background Ge content in the ground water and at quite plausible environmental parameters: a porosity range of 30–5%, T° range of 20–70 $^{\circ}\text{C}$ (equivalent to the initial catagenesis stage, i.e. soft brown coal stage) and

⁶ Permeability unit Darcy (D) is equal to ~ 1 μm^2 .

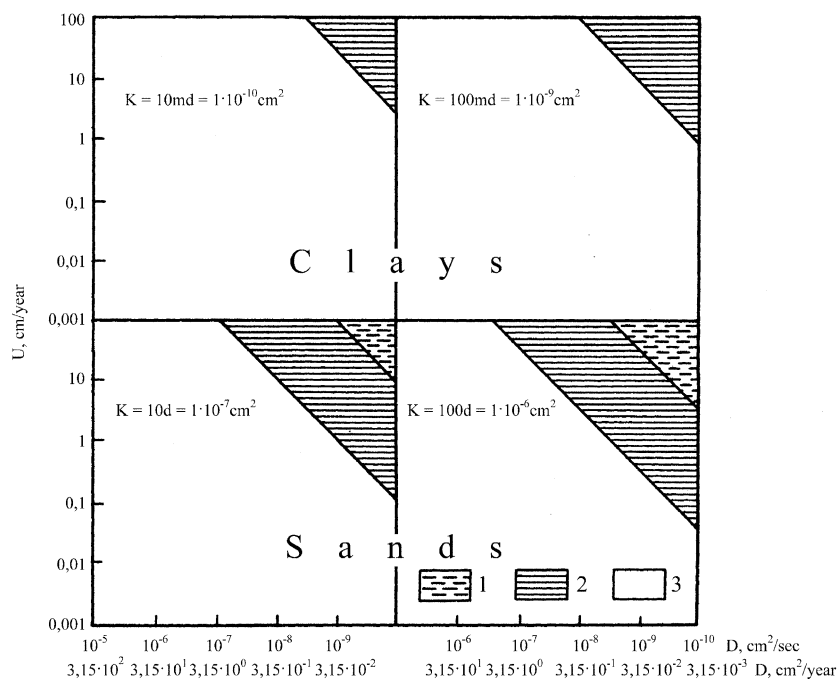


Fig. 5. Relation of mass-flow from sediment permeability (k), diffusion coefficient (D), and infiltration velocity (u). Compiled by I.V. Rysanov (Yudovich, 1972a, p. 65). 1—Area of infiltration, $Pe > 1$; 2—area of convective diffusion, $0.01 < Pe < 1$; 3—area of pure diffusion, $Pe < 0.01$.

diffusion coefficients ranging from 10^{-7} to 10^{-9} cm^2/s . At these conditions, Ge-enrichment can be completed in a time ranging from a few thousand years up to tens of million years. However, if the waters are enriched in Ge, the process can proceed more rapidly and would be completed even under the most unfavorable parameters (compared to the model conditions). This implies that enrichment can take place during early diagenetic stage. Such a scenario was supported by geologic considerations (Yudovich, 1972a).

8. Trace metal content and mineralogy: recent study

More recently, coal inclusions have been studied using highly sensitive analytical equipment (SEM-EDS, ICP-MS, etc.) to analyze trace elements that were previously below the limit of detection (Vassilev et al., 1995). In addition, some extremely exotic authigenic minerals were quite unexpectedly found in coal inclusions (Seredin and Magazina, 1999).

Vassilev et al. (1995) studied a vitrain lens (20 to 30 cm by 2 to 3 cm), with an ash content of 7.8%, from Eocene conglomerates in the Vulche Pole (Bulgaria) lignite deposits. Extremely high concentrations of trace elements were found in the ash (all in ppm):⁷ 77500 Ge, 11900 U, 1750 Sb, 1310 As, 2220 Ce, 865 Sm, 1100 Y, 115 Yb, 25 Tb, 5000 V, 500 Mo, 2300 Zr, 40 Hf, and 1730 Zn. Pyrite, sphalerite, galena, gypsum, jarosite, and anglesite were described among the authigenic minerals. It is obvious that sulfates resulted from the sulphide oxidation. Among the minerals of uncertain origin (the authors were not certain that the minerals are authigenic, but it is more possible that they are authigenic)—opal, cristobalite, kaolinite, gamagarite [$\text{Ba}_2(\text{Fe}, \text{Mn})(\text{VO}_4)_2 \cdot 2\text{H}_2\text{O}$], fine-grained apatite, delafossite [CuFeO_2], stolzite [PbWO_4], monazite, xenotime, and native gold were detected. Some trace elements determined are major constituents of min-

⁷ Rounded from original figures.

Table 9

Calculated duration (τ , million years) of Ge-enriching event for coal inclusions with volume 5 cm^3 , by means of diffusion at different process parameters

D , cm^2/s	Ge content in water (g/l) and in inclusion (%)							
	6×10^{-8} g/l				6×10^{-6} g/l			
	0.005	0.010	0.03	0.3	0.005	0.010	0.03	0.3
<i>Room temperature</i>								
<i>Porosity 30%</i>								
10^{-7}	0.155	0.310	0.925	9.5	0.002	0.003	0.009	0.093
10^{-8}	1.55	3.10	9.25	(92.5)	0.016	0.031	0.093	0.925
10^{-9}	15.5	31.0	(92.5)	(925)	0.155	0.310	0.925	9.25
<i>Porosity 20%</i>								
10^{-7}	0.230	0.460	1.39	13.9	0.002	0.005	0.014	0.139
10^{-8}	2.30	4.60	13.9	(139)	0.023	0.046	0.139	1.39
10^{-9}	23.0	46.0	(139.0)	(1390)	0.23	0.460	1.39	13.9
<i>Porosity 5%</i>								
10^{-7}	0.925	1.85	5.55	(55.5)	0.009	0.019	0.055	0.555
10^{-8}	9.25	18.5	(55.5)	(555)	0.093	0.185	0.555	5.55
10^{-9}	(92.5)	(185)	(555)	(5550)	0.925	1.85	5.55	(55.5)
<i>Temperature 50–70 °C</i>								
<i>Porosity 20%</i>								
10^{-7}	0.077	0.155	0.460	4.60	0.001	0.002	0.005	0.046
10^{-8}	0.77	1.55	4.60	(46.0)	0.008	0.016	0.046	0.46
10^{-9}	7.7	15.5	(46.0)	(460)	0.077	0.155	0.460	4.6
<i>Porosity 5%</i>								
10^{-7}	0.31	0.615	1.85	18.5	0.003	0.006	0.019	0.185
10^{-8}	3.10	6.15	18.5	(185)	0.031	0.062	0.185	1.85
10^{-9}	31.0	(61.5)	(185)	(1850)	0.310	0.615	1.85	18.5

Comment: figures in brackets present doubtful or geologically unattainable values.

Compiled from Yudovich (1972a).

erals, such as Zn (sphalerite), Zr and Hf (zircon), and REE (monazite, xenotime); or are the impurities in other minerals (Zn, As, V, Ge, Hf, U in monazite and zircon). However, the mineral contribution to total amount of trace elements is small; the dominant part of trace elements is organically bound.

Seredin and Magazina (1999) studied weakly lignified wood fragments in Pliocene alluvial sediments in the overburden of the Miocene Pavlovsk lignite deposits, Russian Far East. Twelve wood fragments with the mean size of 2 to 4 cm by 10 cm and a mean ash content of 5.6% were examined. Extremely high contents of some trace elements (the high figures are in bold)⁸ were determined in the ash (all in ppm): 6.5 Cs, 300 Sr, 1060 Ba, 17.5 Be, **110 Sc**, **340 Y**, **280 La**, **900 Ce**, **400 Nd**, **100 Sm**, **23 Eu**, **110 Gd**, **18 Tb**, **47**

Yb, **7 Lu**, 15 Ga, 175 Ge, 5000 Ti, 390 Zr, 10 Hf, 70 Th, 11 Sn, **1000 V**, 9 Nb, 1.5 Ta, **430 Mo**, 95 U, 46 B, 1120 P, **560 Cu**, 13 Ag, 0.75 Au, **1030 Zn**, **170 Pb**, **6260 As**, 660 Cr, **3400 Mn**, **2480 Co**, **1830 Ni**, 0.4 Pd, and 0.7 Pt.

An SEM-EDS study by Seredin and Magazina (1999) displayed a striking diversity of minerals (Table 10). The particles ranged in size from 1 to 2 mm down to a few microns. Some of them are considered to be clastic (quartz, alkali feldspars, zircon) and the remaining to be authigenic (kaolinite, smectite, gypsum, zeolites, opal, framboidal pyrite, and a great number of rare minerals). The latter (5–10% of all minerals) are of special interest. Extremely exotic phases are detected among them, including native elements, intermetallic compounds, halogenides, and unusual oxides. Because of their very small size, some phases were only tentatively detected (see Table 10 for details).

⁸ Rounded from original figures.

Table 10

List of rare minerals and mineral phases in fossil wood from Pliocene sands and pebbles, in the overburden Pavlov's lignite deposit

Mineral class	Minerals and their formulas
Native metals	Aluminum (Al), iron (Fe), nickel (Ni), cobalt (Co), copper (Cu), tin (Sn), lead (Pb), silver (Ag), gold (Au), platinum (Pt), antimony (Sb), selenium (Se), bismuth (Bi), tungsten (W), thallium (Tl), cadmium (Cd)
Solid solutions, intermetallides	Nickel–iron (Fe ₃ Ni, Fe ₄ Ni), chromium–ferreed (Fe ₈ Cr), nickel–chromium–ferreed (Fe ₆ Cr ₂ Ni), zinc-bearing copper (Cu ₂ Zn), tin-bearing copper (Cu ₃ Sn), cupriferous gold (Au ₃ Cu), electrum (AuAg), kustelite (Ag ₃ Au)
Sulphides and sulphates	Pyrite (FeS ₂), Ni–Co pyrite [(Ni, Co, Fe)S ₂], chalcocopyrite (CuFeS ₂), bornite (Cu ₅ FeS ₄), covellite (CuS), sphalerite (ZnS), galena (PbS), akantite (Ag ₂ S), antimonite (Sb ₂ S ₃), stannite (SnCu ₂ FeS ₄), tin-bearing cooperite? [(Pt, Sn)S], hawleyite? (CdS); sulphates of the Pb, Zn, Cu
Cl-bearing halogenides (oxihalogenides, hydroxihalogenides, halogen-carbonates)	Halite (NaCl), sylvite (KCl), chlorine-calcite (K, Ca, Cl), tachyhydrite? (Ca, Mg, Cl), chlorine-aluminate? (Al, Cl), atacamite? [(Fe, O, Cl), (Cu, O, Cl)], cerargyrite (AgCl), bastnesite [TR _{Ce} (CO ₃)F, Cl], daubreicite? [(Sn, Cl), (Co, O, Cl), (Bi, O, Cl)], niobium chloride? (Nb, W, Cr, Cl), samarium chloride? (Sm, O, Cl)
Br-bearing halogenides	Bromine–argyrite (AgBr), thallium bromide (Tl, Br), tungsten bromide (W, Br)
I-bearing halogenides	Iodine–argyrite (AgI), thallium iodide (Tl, I)
Carbonates	Carbonates of Al, Fe, Mg, Ni, Co, Cu, Zn
Phosphates	Phosphates of Ca, Al, Fe, TR _{Ce}
Oxides	Perovskite (CaTiO ₃), tausonite (SrTiO ₃), barium titanate (BaTiO ₃), hongquuite (TiO), cassiterite (SnO ₂), baddeleyite (ZrO ₂)

After Seredin and Magazina (1999).

Based on the exotic nature of many mineral phases and very unusual morphology of many of them, Seredin and Magazina (1999, p. 14) came to the following conclusions:

... Anomalous enrichment in precious metals and other elements resulted from reaction of organic matter with brines and reduced gases. The latter... may be of diagenetic as well as juvenile nature... The presence of precious metals in the coal inclusions distant from source areas, the abundance of halogenides and presence of thallium and antimony minerals that are very characteristic of near-surface hydrothermal deposits, testify to hydrothermal contribution to ground waters.

Thus, the unique geochemical peculiarities of the wood studied resulted from a special geological environment, ascending volcanic brines affecting the wood fragments, that is quite atypical of most known coal inclusions. Besides, the above data force to some revision of the enriching mechanisms. It is likely that some other (not diffusion-influenced sorption) mechanism may operate: *the reduction of metal*

from solutions. Further study of coal inclusions by means of modern analytical methods will bring new understanding of the origin of the reduced mineral phases.

9. Economic importance

In May 1951, in a park area of the University of Maryland, Prince Georges County, MD, USA, Stadnichenko and her colleagues fortuitously found a coalified vertical *Cupressinoxylon* stump in situ, in Cretaceous clay, with well-preserved roots (Stadnichenko et al., 1953, p. 5). The ash content was 2.85% and Ge content in the ash—as much as 7.5%! A number other coalified logs, stumps, and roots, all extremely enriched in Ge, were found in the Cretaceous formations of the Atlantic Coastal Plain. Thirty-two analyses (of 62 tabulated) had a Ge content more than 1% in the ash, a mean content about 2.52% (our calculation). The authors noted:

The logs represent a possible commercial source of germanium, but their sporadic distribution over

an area generally densely populated makes their recovery difficult. However, the clays that contain the logs are mined in several places for manufacturing bricks; so there is a possibility that the logs could be gathered as a byproduct from such clay pits.

Likely, the first serious exploration for Ge in coal inclusions was conducted in 1948 in the Powell River basin, British Columbia, Canada (Buckland, 1959). In this area there is an Eocene conglomerate–sand–shale formation, which covers weathered granite substratum. Sands and silty shales contain numerous coal inclusions enriched in Ge. The most interesting horizon, the basal “brown-bed”, was explored (1957–1958) by means of 161 drill holes followed by grubbing up with shovels and bulldozers. The “brown bed”, enriched in coal lenses and fragments, has a thickness up to 6 m and probably stretches out over the entire basin area. The mean GeO₂ content in coal ash is nearly 2% (or ~ 1.4% Ge), with a maximum of 9.5% GeO₂ (6.59% Ge). As one might suspect, the exploration prospects were regarded as very good.

Later, in the Near-Yakutsk region, Yudovich (1972a) performed some exploration by means of ditch and trench cutting. It was found that most of coal inclusions lay near the unconformable Lower Cretaceous/Neogene contact. The contact zone stretches out many hundred meters with a thickness of only 0.1–0.5 m, but contains up to 20 vol.% woody coal inclusions. Among them, the largest black coalified “logs”, in the range of 0.5–5-m long and 0.05–0.20-m thick, were most enriched in Ge, Ga, and V. Another type of coal inclusion accumulation represents fossil soil horizons in the middle parts of coal-bearing cyclothems. There are the fossil “forests”, with many standing and recumbent coalified woods (see above, Fig. 2). However, the economic significance of both of the above accumulations has never been fully assessed.

Recently, Ge-resource of some West Siberian lignite accumulations have been evaluated (Evdokimov et al., 2002). They described two “lignite-bearing horizons”⁹ that stretched out over 587 and 135 m,

with thickness of 1.1 and 1.0 m, containing 16.0 and 19.7 vol.% of Ge-enriched lignite inclusions. The economic importance of the deposit was estimated as very high.

10. Conclusion

The discussions above show that coal inclusions (isolated coalified or lignitized woody fragments in host rocks—out of the coal beds) are unique geochemical phenomenon, sharply different from even neighboring coal beds in trace element content. The most different content has germanium: its mean concentration in the ash of coal inclusions is 220 times higher than in the ash of coal beds.

Although many details of enriching mechanism are still not clear, main conclusion is evident: the most important peculiarity of the coalified wood is the good preservation of the original lignin structures, which may effectively scavenge Ge from solutions, whereas peat-born coals (in beds) contain such structures in far lesser abundance. In addition, a reservoir of dissolved germanium in peat bog waters was of lower concentration than in sediments, which buried the coal inclusions. Finally, the peat bog acidic environment may act as an unfavorable factor.

Some Canadian and Soviet works performed from 1950 to 1960, along with some recent Russian studies, show that Ge in coal inclusions can be of some economic interest.

As far as 1963–1972 it was demonstrated that coal inclusions may be used as a very interesting geochemical indicator at the studying of coal-bearing strata (Yudovich, 1972a).

1. A comparison of coalification degree between coal inclusions embedded different host rock (as example: argillite and sand) can give some information about delicate peculiarities of the coalification process (catalysis, etc.).
2. A comparison of difference in trace element concentration between coal inclusions embedded different host rocks can give valuable information about diagenetic (and early catagenetic?) processes, transporting trace element in the solutions.
3. A comparison of difference in trace element concentration between coal inclusions embedded

⁹ I think that there are some horizons with abundant inclusions of lignitized wood—and not peat-born lignitic beds.

host rocks of different geologic age may serve as a tool for stratigraphic correlation.

4. A comparison of difference in trace element concentration between coal inclusions embedded host rocks of different maturity stage (of “degree of metamorphism”) may help in the understanding of geochemistry of coal metamorphism (catagenesis).

Some recent studies performed by Bulgarian and Russian geologists that used modern analytical procedures (Vassilev et al., 1995; Seredin and Magazina, 1999) show that:

- (a) coalified wood may contain very exotic micro-mineral phases, sometimes far unexpected;
- (b) apart from Ge, coalified wood may contain very high concentrations of some other trace elements, which were earlier not detected because of analytical limitations (REE, As, etc.).

These and some other facts indicate that processes of enrichment in trace elements of coal inclusions may have not only pure diagenetic nature, but may be partly contributed by epigenetic hydrothermal solutions, as exemplified by Pb and Zn in Jurassic and Cretaceous inclusions, the former East Germany (Leutwein and Rösler, 1956—see Yudovich, 1972a, p. 59); REE in Pliocene inclusions, the Russian Far East (Seredin and Magazina, 1999); and Ag in Carboniferous inclusions, Canada (Boyle, 1968). However, such processes would be more rare than global extended “background cold-water” enrichment by Ge (and some other trace elements).

Thus, geochemistry and mineralogy of coal inclusions are of great interest and need further detailed study.

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