

Concentration of Trace Elements in Coal

L. A. Admakin

Koks i Khimiya, ul. 2d Baumanskaya 9/23, Moscow, Russia

e-mail: koks1931@mail.ru

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Abstract—Trace elements are standard indicators of coal quality. Their distribution in coal is determined by means of the petrographic composition and ash content. However, despite extensive research, the dependence of the trace-element concentrations on these parameters has not been established. Physicochemical functions that relate the trace-element concentrations to the petrographic composition and ash content are introduced in the present work. The analysis is based on redox reactions in the organic system. The basic relations of the trace elements with physicochemical parameters are considered. The physicochemical parameters are regarded here as independent characteristics of the state of the coal, specified by its surroundings. Trace elements may be concentrated in coal in anaerobic conditions, outside of the peat-forming level—that is, in diagenesis.

Keywords: petrographic composition, vitrain, fusain, ash content, redox reactions, trace elements, germanium, peat-forming level, aerobic and anaerobic conditions, organic systems, diagenesis

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The most important indicators of coal quality are the petrographic composition and ash content. They are also of great geochemical significance, since they determine the accumulation and distribution of trace elements in the coal.

The petrographic composition is produced by transformation of biochemical organic matter into the organic component of coal. By contrast, the ash content is associated with the mineral components present in solid or dissolved form in the organic system. Since trace elements may be present in the organic system in the same phase states, we may expect that their concentrations will be related to the petrographic composition and ash content of the coal.

In practice, however, those relations are very complex. Therefore, the relation between the trace-element concentrations and the coal's petrographic composition and ash content is an ongoing preoccupation in research on coal quality.

GEOCHEMICAL RELATIONS

The petrographic composition and ash content were traditionally used as indicators of coal quality, before coal was identified as a potential source of germanium and other elements. Requirements on coal quality are more complex now that industrial Ge, Ga, and U concentrations have been established in coal and the presence of toxic trace elements (such as Be, Co, Ni, V, and Se) is known. At present, coal deposits cannot be adequately assessed without estimating their

content and distribution of trace elements; the content of trace elements is an indicator of coal quality.

Petrographic Composition and Trace-Element Content of Coal

Special research on trace elements in coal began with Goldschmidt [1]. Some data were obtained earlier. In 1887, for example, Jensch identified ZnO (0.09–1.12%), PbO (0.008–0.02%), CdO (0.001–0.008%), and MnO (0.20–2.84%) in the ash of coal from the Upper Silesian Basin; in 1915, Fersman established the presence of sphalerite, galenite, and Ag in Borowicz coal. However, only Goldschmidt provided a firm foundation for the systematic quantitative study of the trace elements in coal. Without special petrographic research, he showed that the GeO₂ content in vitrain and clarain (0.1%) is an order magnitude greater than in durain (0.01%) and emphasized the possibility of extracting rare elements from coal.

Attention first focused on germanium. The germanium content in vitrain is always considerably higher than in coal, as shown in [2, 3]. This was attributed to the capture of Fe by gel in humic acids. Coal petrography quickly expanded to include other relatively uniform components of coal: durain and spores [4, 5]. It was established that the Ge content is 18 times greater in vitrain than in durain and confirmed that germanium is concentrated by a gelled mass containing vitrain and other petrographic components. However, spores do not concentrate germanium.

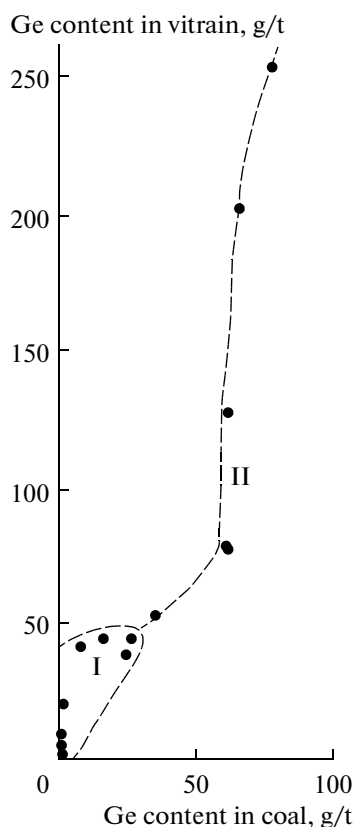


Fig. 1. Distribution of the Ge content in vitrain as a function of its content in the surrounding coal without germanium (I) and surrounding germanium-bearing coal (II).

The Ge content is always higher in structured vitrain, as noted in [5]. The highest Ge content is associated with structured vitrain (90–4000 g/t) from uniform coal (3–43 g/t); a smaller content (up to 920 g/t) is associated with structured vitrain from banded coal (2–5 g/t); and the smallest content (79 g/t) is associated with structured vitrain among large fusinized columns (4–28 g/t). By separating coal samples into fractions on the basis of their density, it was shown that the basic carriers of germanium are nonoxidized components of the organic mass (vitrain, xylain, xylovitrain, primary gelified mass) [6]. In this case, the maximum content is associated with the fraction that has the highest vitrain content. Exinite microcomponents (cuticle, tar, spores) do not concentrate germanium.

Subsequently, the direct relation between the Ge content and the degree of humification was repeatedly confirmed [7–10]. An anomalously high Ge content (>6%) was recorded in lignite ash from cretaceous rock in the District of Colombia [11]. Such lignite ash also has high concentrations of V (0.7–5.0%), Cr (0.1–0.8%), and Ga (0.03–2.0%). A number of samples exhibit high Cu content.

Higher Ge content (8.4%) is observed in lignite ash from the Lower Lias in Dorset [12]. The Ge content in the coal itself is equally high (9.5% for the ash). An

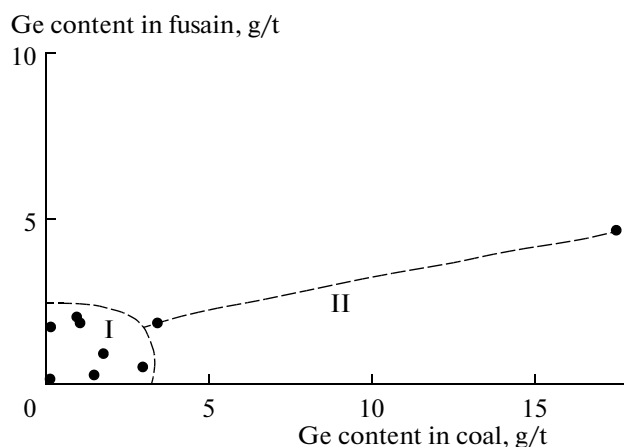


Fig. 2. Distribution of the Ge content in fusain as a function of its content in the surrounding coal without germanium (I) and surrounding germanium-bearing coal (II).

incomplete compilation of empirical data regarding the germanium distribution in some coal components may be found in [13].

Recently, relatively high trace-element concentrations were found in dopplerites of the Nazarovsk field within Kansk-Achinsk Basin [14]. For several Zabaikal fields, it has been shown that the Ge content is concentrated by vitrain, in which the Ge content increases sharply as the coal's Ge content rises (Fig. 1). Conversely, fusain plays no role as a germanium concentrator (Fig. 2). The Ge content rises in the sequence telinite, posttelinite, precollinite, collinite [15–17]. That reflects the influence of redox reactions in the organic system [18].

The same behavior is observed for other trace elements [19, 20]. It is obvious that germanium and other trace elements are concentrated selectively in coal; the enrichment is greatest in uniform humified components—especially lignites. However, no explicit functional relation is established between the trace-element concentrations and the petrographic composition, since the conversion of the petrographic composition to a quantitative parameter remains baffling.

Ash Content and Trace-Element Concentrations in Coal

In Goldschmidt's era, when the determination of elementary concentrations in rock was the focus of a new specialization, geochemistry, trace elements were investigated by spectroscopy of the ash, by analogy with rock. The high levels of germanium in coal directed particular attention to that element; other elements were regarded as secondary. Little attention was paid to the influence of the ash content on the trace-element concentrations.

At present, only a small proportion (~17%) of the many (>60) trace elements in coal are known. These

include valuable elements extracted from the ash (Ge, Ga, U); potentially valuable elements, for which extraction technology has been proposed (V, Sc, Li, B); and secondary elements (Hg, Ga, Mo, W, Pb, Zn, Cu, Ag, Au, Ti), which are taken into account together with germanium. As a result, finding the dependence of the trace-element concentrations on the ash content is a priority in assessing the potential rare-metal content in coal.

Vistelius adopted a different approach, by statistical assessment of the relation between the Ge content and the ash content, on the basis of the corresponding correlation coefficient [21]. A significant negative correlation coefficient ($r = -0.7$) indicated a relation of germanium with the organic component of the coal. On the basis of the correlation coefficient, the form of the element may be assessed: mineral for a positive correlation and organic for a negative correlation.

This method indicates that vanadium is in the mineral component, while beryllium is in the organic component of the coal [22]. For a large group of elements in English coal, V is associated with mixed laminar minerals; Zr with fragmented material; and Mn with complex carbonates [23]. Affinity with the coal's inorganic component was noted for Co, Eu, Ce, La, Sc, Ti, and Y.

However, no negative correlation of germanium with the ash content was noted in [24]; on that basis, their relation is only apparent. A positive correlation was found between the germanium content in Donbass Basin coal and the ash content [25]. A positive correlation was found in [13]. To resolve these inconsistencies, differentiation of the ash into genetic types was proposed in [26].

These complications were characterized as the paradox of the ash content in [26]. However, the genetic types of the ash are simply virtual components and are not susceptible to analytic definition.

Many attempts have been made to describe the concentration of germanium by means of functional relations. The simplest function was obtained in [27]

$$K = Rt/V\rho. \quad (1)$$

Here K is the Ge content in plant residues; t is the time for which the solution acts; R is its concentration; V is the volume of the organic system; ρ is the density of the surrounding rock, which affects the infiltration of the solution. Equation (1) fails to take account of the organic component's affinity for the ash content and can only be regarded as a mechanical set of parameters.

A better formula was proposed in [28]

$$E_{wf} = E_0 + 0.01f_m(E_a - E_0)A_{wf}. \quad (2)$$

Here E_{wf} is the total content of the element in ash-free coal, %; E_a is the total content of the element in the mineral component, %; E_0 is the total content of the element in the pure organic component of the coal, %; f_m is the mineral coefficient ($f_m = M/A_{wf}$); M is the min-

eral content in the ash-free coal, %; A_{wf} is the ash content of dry coal, %.

The parameters in Eq. (2) may be calculated with high precision. The function itself may be plotted as a graph of the content of the element (g/t) against the ash content (%), as demonstrated in [28]. The following possible correlations of the content of the element and the ash content were noted:

- a positive correlation, $E_a > E_0$;
- no correlation, $E_a = E_0$;
- a negative correlation, $E_a < E_0$.

In Eq. (2), however, no account is taken of the element's affinity for the ash content. Therefore, the same correlations are obtained for different trace elements; that is unrealistic. In addition, no distinction is made between the clastogenic and diagenetic components of the ash.

A very simple function was proposed in [26]

$$C_A = [(1 - A^d)C_{org} + A^d C_{min}]/A^d. \quad (3)$$

Here C_A is the content of the element in the ash; C_{org} is the content of the element in the organic component of the coal; C_{min} is the content of the element in the mineral component; A^d is the ash content of the coal.

This formula is less informative than Eq. (2). It contains the same assumptions as Eq. (2); in particular, it fails to take account of different elements.

Thus, like the petrographic composition, the ash content cannot be identified as a simple factor in the concentration of trace elements within coal. Its role in their accumulation is complex, and the dependence of the trace-element concentrations on the ash content is problematic.

FUNCTIONAL RELATIONS

Coal may be regarded as a complex mixture of organic matter and mineral impurities. The organic component of the coal, which, in petrographic terms, consists of newly formed microcomponents (the vitrinite and fusinite groups) and inherited microcomponents (the liptinite group). The conversion of the biochemical organic matter into the organic component of the coal depends on the redox reactions in the organic system [18].

The reactive component of the coal, expressing the ratio of the organic system to the dissolved microelements, is determined by the newly formed microcomponents, the most important of which are in the vitrinite group. The newly formed microcomponents in the fusinite group are geochemically inert. Thus, the concentration of the organic system is maintained by a single group of microcomponents—the vitrinite group.

The mineral impurity is formed by two pathways: as clastogenic mineral component supplied to the organic system in solid form; and as dissolved mate-

rial, with humic compounds and various mineral–diagenetic phases. Note that the supply of the first component is limited by the peat-forming level. The infiltration of the solution may be maintained in diagenesis and catagenesis—in other words, with no access of free oxygen to the organic system.

Dependence of the Trace-Element Concentrations on the Coal's Petrographic Composition

The relation between the trace-element concentrations and the petrographic composition of the coal is either derived by direct comparison for the specific coal or is established from the distribution of trace elements among density fractions. Such data cannot be converted to functional relations that correspond to the reactions of the trace elements with the organic component of the coal, as is customary in mineral systems. In contrast to mineral systems, there are no structurally uniform phases in the organic system.

However, coal is represented by a limited set of chemical elements—the organogenic elements. The compounds that they form react with the trace elements only through specific structural units. In particular, these reactive structures include the peripheral functional groups: carboxyl groups –COOH; phenolic hydroxyl groups –OH; carbonyl groups C=O; and methoxyl groups –CHO₃. The carboxyl groups are the most important components reacting with dissolved trace elements.

The functional groups are coordinated relative to the aromatic ring. The reactive complex may be written in the form RCOOH, where R is the aromatic ring. Then, the reaction of metal cations (Me^{z+}) with humic acid, corresponding to cleavage by the alkyl-group method, may be written in the form



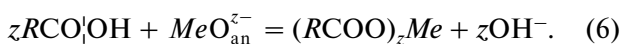
Here (RCOO)_zMe is a stable compound of the metal with humic acid; RCOOH denotes a reactive complex corresponding to cleavage of the carboxyl group by the alkyl-group method.

Assuming that [RCOO_zH] = 1, we obtain

$$(\text{RCOO})_z\text{Me} = K'_{alc} \frac{[\text{Me}^{z+}]}{[\text{H}^+]^z}, \quad (5)$$

where K'_{alc} is the reaction constant.

The reaction of anionic forms of the metal with humic acid, corresponding to cleavage by the acyl-group method, may be written in the form



Correspondingly, when [RCO_zOH] = 1, we obtain

$$(\text{RCOO})_z\text{Me} = K'_{acl} \frac{[\text{MeO}_{an}^{z-}]}{[\text{OH}^-]^z}. \quad (7)$$

The activity of oxygen in an acidic medium is

$$[\text{O}_2] = \frac{K_{ac}}{[\text{H}^+]^4 [\text{e}^-]^4}, \quad (8)$$

where K_{ac} is the equilibrium constant of acidic reaction in an aqueous medium.

Substituting Eq. (8) into the relation F/Vt = f[O₂], we obtain [20]

$$F/Vt = \varphi_{ac} \frac{K_{ac}}{[\text{H}^+]^4 [\text{e}^-]^4}, \quad (9)$$

where φ_{ac} is a constant of proportionality.

The activity of oxygen in alkaline medium is

$$[\text{O}_2] = \frac{[\text{OH}^-]^4}{K_{al}[\text{e}^-]^4}, \quad (10)$$

where K_{al} is the equilibrium constant of alkaline reaction in an aqueous medium; [e⁻] is the electron activity; [OH⁻] is the activity of the hydroxyl group.

Using Eq. (10), by analogy, we obtain

$$F/Vt = \varphi_{al} \frac{[\text{OH}^-]^4}{K_{al}[\text{e}^-]^4}, \quad (11)$$

where φ_{al} is a constant of proportionality.

In Eq. (11), the degree of transformation of the coal's organic component is expressed as a function of the basicity (alkalinity) of the solution supplied to the organic system. Substituting Eqs. (9) and (11) into Eqs. (5) and (7), we obtain the following:

—for cations

$$(\text{R}'\text{COO})_z\text{Me}_{ct} = K'_{alc} [\text{e}^-]^{z \left(\sqrt[4]{\frac{F/Vt}{K_{ac} \varphi_{ac}}} \right)^z} [\text{Me}^{z+}]; \quad (12)$$

—for anions

$$(\text{R}'\text{COO})_z\text{Me}_{an} = \frac{K'_{acl}}{[\text{e}^-]^z} \left(\sqrt[4]{\frac{\varphi_{al}}{K_{al} F/Vt}} \right)^z [\text{MeO}_{an}^{z-}]. \quad (13)$$

In Eqs. (12) and (13), the trace-element concentration is related to the petrographic composition of the coal—expressed as the ratio of the newly formed microcomponents F/Vt, which are produced in redox reactions within the organic system. We also see that the trace-element concentrations in the organic system are functions of several independent variables.

If the reaction constants K'_{alc}, K'_{acl}, K_{ac}, K_{al} and constants of proportionality φ_{ac}, φ_{al} are assumed to be invariant, the independent variables will be F/Vt, [e⁻]^z, [Me^{z+}] in Eq. (12); and F/Vt, [e⁻]^z, [MeO_{an}^{z-}] in Eq. (13). The activities of the cations, anions, and electron are specified by the external medium; in other words, they are independent variables. The ratio F/Vt

is an expression of the redox conditions in the organic system.

The three variables may vary independently, reflecting the redox conditions, the humification of the organic component, and the concentration of the dissolved trace elements in the organic system. On the basis of Eqs. (12) and (13), we may assess how the degree of oxidation of the organic mass affects the trace-element concentrations, with equal or different concentrations in the solution.

At the same time, these functions do not include exinite-group macerals as parameters. That is consistent with the fact that they are not involved in boosting the trace-element concentrations in the coal.

The functions

$$(RCOO)_z Me_{kt} = f[e^-]^z, [Me^{z+}] \text{ and}$$

$$(RCOO)_z Me_{an} = f[e^-]^z, [MeO_{an}^{z-}]$$

correspond to complex surfaces reflecting the parameter variation. At each point of those surfaces, the relations between the independent variables will be different. Hence, the ratio F/Vt will be different and, likewise, the petrographic composition of the organic component and the activity of the dissolved trace elements will be different. Correspondingly, the ratio of the independent variables will ultimately determine the trace-element content in the coal, and this, in turn, determines the coal's potential as a valuable metal source.

There is no need to analyze different relations between the independent variables and the trace-element concentrations, since there will be innumerable such combinations.

Note, however, that the independent variables in Eqs. (12) and (13) are raised to the power 1/4. That considerably slows the concentration of the trace elements within the organic system, but this effect is somewhat compensated by the charges of the cations and anions. The compensation is greater for higher charges. This is consistent with the known empirical rankings of the rare elements in terms of affinity for the organic mass and their concentrations in lignite [11, 12, 22].

It also follows from Eqs. (12) and (13) that the actual content of trace elements in the coal is a linear function of their concentration in aqueous solution, regardless of their soluble form. Thus, in each case, the concentration of the trace elements within the organic system will depend on the permeability of the organic system. Consequently, the trace-element content over the coal bed will be very variable.

Finally, note that, for different methods of carboxyl-group cleavage, the petrographic parameter F/Vt has a different position within the equations. This corresponds to distinctive locations of the cations and anions within the organic matrix and the formation of particular stable compounds.

Dependence of the Trace-Element Concentrations on the Coal's Ash Content

As shown earlier, no clear dependence of the trace-element content on the ash content of the coal has been established. The correlation method, which seemed promising at first, has not led to a clear conclusion regarding the relationship of microelements—primarily germanium—with the organic or mineral component of the coal. Other methods—the division of coal into fractions on the basis of its density, the extraction of pure organic compounds from coal, the isolation of ingredients—are either inconclusive or do not apply to the coal as a whole. They offer no guidance as to the inadequacy of the correlation method.

There is a single function relating the trace-element content C_c in coal with its ash content A^d

$$C_c = C_a A^d. \quad (14)$$

Here C_a is the trace-element content in the ash.

We may rewrite Eq. (14) in the form

$$C_a = C_c / A^d. \quad (15)$$

This function is continuous. The independent variables are C_c and A^d . It follows from the continuity condition that

$$dC_a = \frac{dC_c}{A^d} - \frac{C_c}{(A^d)^2} dA^d. \quad (16)$$

If we set $C_c \approx \text{const}$, then $C_a = C_c / A^d$. In that case, the trace-element content in the ash is inversely proportional to the ash content. However, this is the case only with a low trace-element content in the coal, as shown in [29].

With considerable variation in C_c , which is typical of anomalous concentrations, the relation between the trace-element content and the ash content is broken, since not only the ash content but also the trace-element content varies, and their variation will be incoherent.

If the ash content fluctuates within a narrow range, we may set $A^d = \text{const}$. Then $C_a = C_c / A_{\text{const}}^d$. In that case, we cannot say anything definite about the relation between C_a and A^d , since C_c may be different. Only the ratio C_a / C_c remains constant.

If C_c is variable, the necessary and sufficient condition for a positive correlation between the trace-element content and the ash content is

$$\frac{dC_c}{A^d} > \frac{C_c}{(A^d)^2} dA^d. \quad (17)$$

Solution of Eq. (17) gives a result that seems odd at first glance

$$C_c > A^d. \quad (18)$$

Hence, a positive correlation between the trace-element content and the ash content arises when Eq. (18) is valid. Obviously, this condition may only be satisfied in anaerobic conditions, where clastogenic material is not supplied to the organic system, while the trace element is supplied in dissolved form.

Hence, we conclude that *the trace elements are concentrated in anaerobic conditions, outside of the peat-forming level—that is, in diagenesis.*

At the same time, dissolved petrogenic elements (Ca, Mg, Fe, Na, K) may be supplied to the organic system in this case, and their humates will create an elevated ash content, as shown by dopplerites [14]. In that case, Eq. (18) will not be satisfied, since the humate ash content is high and its variation will disrupt the correlation.

A different situation arises when the organic system is supplied with dissolved Na and K, as in the silicon module. These petrogenic elements have low affinity for the organic mass; they are hardly captured there. In these conditions, Eq. (18) will be satisfied. Coal with such ash is usually enriched with trace elements. In many cases, anomalous concentrations are seen, reaching industrial values.

Obviously, the clastogenic component of the ash accumulating in the peat-forming level always complicates the diagenetic ash content and thereby disguises the true correlation. Therefore, attempts to find some genetic optimum of the ash content for coal enriched with germanium are generally unsuccessful [26]. The tendency of the Ge content to approach the modal value of the ash content simply reflects the statistical properties of the coal and provides no information about the trace elements.

If we adopt C_c and C_a as coordinates, we find from Eq. (14) that

$$A^d = \tan \alpha. \tag{19}$$

On the basis of Eq. (19), we may represent the complex surface $C_c C_a A^d$ on the $C_c - C_a$ plane, where A^d is represented by $\tan \alpha = \Delta C_c / \Delta C_a$ (Fig. 3, inset). Since A^d may vary from 0 to 1, α will vary correspondingly from 0 to 45°.

With the given configuration of the axes (Fig. 3), the concentration field is bounded by the C_a axis and a line leaving the coordinate origin at 45°. Within this concentration sector, a system of rays A_i^d may be created for different values of C_c / C_a . (Several such rays are shown in Fig. 3.) Each ray corresponds to a particular value $A_i^d = \text{const}$ ($i = 0, 1, 2, \dots$). That allows the concentration field to be divided into smaller sectors with different ash content and thus subfields of low-ash coal, carbonaceous shale, and finally carbonaceous rock, bounded by a pure-rock ray with $A^d = 1$.

Note that A^d is constant over the length of each ray. If the ash content of the samples is mineralogically and

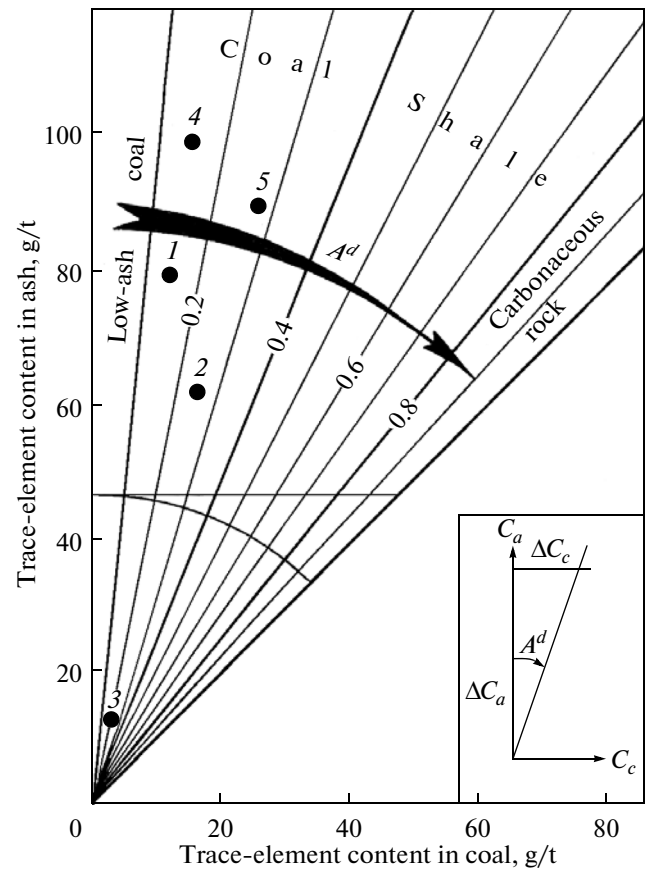


Fig. 3. Relation between the trace-element content and ash content for Altai (1), Mordoi (2), Kharanor (3), Khumarinsk [3] (4), and Podmoskovnyi [3] (5) coal.

geochemically uniform, movement along the ray reflects different content of the trace element, depending on its concentration in the coal's organic component. Obviously, with a given trace-element content in the ash, the ash content in the coal's organic component will increase with increase in the total ash content in the coal.

On the basis of Fig. 3, we may compare the germanium content of coal from different beds and fields. To that end, we drop a perpendicular from the point corresponding to the content in one field to the ash-content line for the other field and note the content at this point. The difference between the two values corresponds to the difference in germanium concentration.

As an example, we show the germanium content in coal from several fields with different ash content in Fig. 3. We see that the germanium content in Khumarinsk coal (recalculated for ash content $A^d = 0.14$) is 20 g/t greater than for Altai coal.

In Podmoskovnyi coal, the content of organically bound germanium (recalculated for ash content $A^d = 0.26$) is 25 g/t greater than for Mordoi coal. For Kharanor coal, the content of organically bound germanium (recalculated for ash content $A^d = 0.20$) is 50 g/t

less than for Mordoi coal ($A^d = 0.25$). By this method, the relative content of trace elements bound with organic matter may conveniently be compared.

The basic functional relationship between the trace-element content and the parameters of the organic system takes the form [29]

$$C = e^{-\Delta G/RT} \frac{[Me^{z+}]}{[H^+]} \frac{\nu t}{M} + 0.01 f_m A^d (C_{\min} - C_{\text{org}}). \quad (20)$$

Here ΔG is the increment in free Gibbs energy in the reaction of the trace element with humic acid; R is the gas constant; T is the absolute reaction temperature; $[Me^{z+}]$ and $[H^+]$ are the concentrations of the trace element and protons in aqueous solution; ν is the infiltration rate of the solution; t is the infiltration time; M is the mass of the organic matter; f_m is the mineral coefficient of the ash ($f_m = m/A^d$); A^d is the ash content of the coal; C_{org} and C_{\min} are the trace-element contents in the coal's organic and mineral components, respectively.

In Eq. (20), the first term on the right side reflects the dynamics of the interaction between the trace element and the organic system, while $e^{-\Delta G/RT}$ is the affinity of the trace element for the organic mass. The second term is some value of the trace-element content in the coal, varying over time.

If the trace-element content in the mineral component $C_{\min} = 0$, then

$$C_c = e^{-\Delta G/RT} \frac{[Me^{z+}]}{[H^+]} \frac{\nu t}{M} - 0.01 f_m A^d C_{\text{org}}. \quad (21)$$

Thus, the trace element accumulates in the organic component; increase in ash content reduces its concentration.

If the trace element is organophobic, the first term and C_{org} disappear. In that case

$$C_c = 0.01 f_m A^d C_{\min} = 0.01 m C_{\min}. \quad (22)$$

The trace-element content in the coal must then be proportional to the ash content and its content in the mineral component. From Eq. (21), we obtain the trace-element content in the ash

$$C_{\text{ash}} = e^{-\Delta G/RT} \frac{[Me^{z+}]}{[H^+]} \frac{\nu t}{A^d M} + 0.01 f_m (C_{\min} - C_{\text{org}}). \quad (23)$$

With intense diagenetic transformation, autogenous materials develop; they will form a significant and sometimes dominant component of the ash. The most typical diagenetic minerals are pyrite, melnikovite, and marcasite; less common minerals include galenite, sphalerite, chalcopyrite, and millerite. In contrast to clastogenic components, they form a

diagenetic ash. If we regard them as ash-forming components that contain trace elements, we may write

$$C_c = e^{-\Delta G/RT} \frac{[Me^{z+}]}{[H^+]} \frac{\nu t}{M} \quad (24)$$

$$+ 0.01 f_m A^d (C_{tr} + C_{at} - C_{\text{org}}),$$

where subscripts tr and at denote the terrigenous and autogenous components of the ash, respectively.

Hence, if the trace element is bound with the organic component and autogenous minerals, then $C_{tr} = 0$. Accordingly

$$C_c = e^{-\Delta G/RT} \frac{[Me^{z+}]}{[H^+]} \frac{\nu t}{M} + 0.01 f_m A^d (C_{at} - C_{\text{org}}). \quad (25)$$

If the microelement is carried by the autogenous minerals, then

$$C_c = 0.01 f_m A^d C_{at}. \quad (26)$$

Consequently, the content of this trace element is proportional to the ash content and to the content of the trace element in the autogenous component.

Each of the relations obtained corresponds to specific conditions in the organic system. It is clear from these relations that the trace-element content in coal is not determined solely by the petrographic composition and ash content. If the multifactorial process is reduced to an elementary two-dimensional model, without regard for the other parameters, no clear correlation can be obtained. Therefore, any conclusions regarding the behavior of trace elements in coal that are based on such analysis must be regarded with skepticism.

REFERENCES

1. Goldshmidt, V.M., *Sbornik statei po geokhimii redkikh elementov* (Papers on the Geochemistry of Trace Elements), Moscow-Leningrad: GONTI, 1938.
2. Ratynskii, V.M., Accumulation of germanium in coal, *Dokl. Akad. Nauk SSSR*, 1943, vol. 40, no. 5, pp. 183-185.
3. Ratynskii, V.M., Germanium in coal, *Tr. Biogeokhim. Lab. AN SSSR*, 1946, vol. 8, pp. 183-223.
4. Gordon, S.A. and Saprykin, F.Ya., Distribution of germanium and gallium in lignite, *Nauch. Tr. MGI*, 1959, no. 27, pp. 13-24.
5. Sofiev, I.S. and Semasheva, I.N., Distribution of germanium in components of coal, *Geokhimiya*, 1960, no. 6, pp. 541-543.
6. Ratynskii, V.M. and Shterenberg, L.E., Relation between germanium and the petrographic components of coal, *Dokl. Akad. Nauk SSSR*, 1960, vol. 130, no. 1, pp. 180-182.
7. Ershov, V.M., Relation between germanium and organic matter, *Geokhimiya*, 1958, no. 6, pp. 605-606.
8. Volkov, K.Yu., Distribution of germanium in Podmoskovnyi coal, in *Materialy po geologii i poleznym iskopaem*

- tsentral'nykh regionov evr. chasti SSSR* (Geology and Minerals in the Central European Regions of the Soviet Union), 1958, Issue 2, pp. 228–242.
9. Travin, A.B., Means of germanium accumulation in coal, *Izv. Vost. Fil. AN SSSR*, 1957, no. 1, pp. 44–48.
 10. Travin, A.B., Distribution of germanium in Western Siberian coal, *Geol. Geofiz.*, 1960, no. 2, pp. 57–73.
 11. Stadnichenco, N., Murata, K.Y., and Axelrod, I.M., Germaniferous lignite from District of Columbia and vicinity, *Science*, 1950, vol. 112, p. 109.
 12. Hallam, A. and Payne, K.V., Germanium enrichment in lignite from the Lower Lias of Dorset, *Nature*, 1958, vol. 181, pp. 1008–1009.
 13. Yudovich, Ya.E., *Geokhimiya iskopaemykh uglei* (Coal Geochemistry), Leningrad: Nauka, 1978.
 14. Admakin, L.A., Impurity elements in dopplerite, *Dokl. Akad. Nauk SSSR*, 1994, vol. 337, no. 3, pp. 352–354.
 15. Admakin, L.A., Facial analysis of some germanium-bearing coal beds, *Litol. Polez. Iskop.*, 1973, no. 5, pp. 82–90.
 16. Admakin, L.A., Germanium content of genetic types of coal, *Dokl. Akad. Nauk SSSR*, 1974, vol. 214, no. 6, pp. 127–130.
 17. Admakin, L.A., Two types of germanium accumulation in coal, *Dokl. Akad. Nauk SSSR*, 1975, vol. 224, no. 1, pp. 194–197.
 18. Admakin, L.A., State of organic systems and coal petrogenesis, *Coke Chem.*, 2010, vol. 53, no. 8, pp. 281–289.
 19. Admakin, L.A., Metal content of genetic types of coal, *Dokl. Akad. Nauk SSSR*, 1974, vol. 217, no. 4, pp. 919–922.
 20. Admakin, L.A., Redox conditions in the organic system and trace elements in coal, *Coke Chem.*, 2010, vol. 53, no. 10, pp. 365–372.
 21. Vistelius, A.B., Confirmation of Goldshmidt's observations regarding the distribution of germanium in coal, *Dokl. Akad. Nauk SSSR*, 1947, vol. 58, no. 7, pp. 1455–1457.
 22. Razdorozhnyi, V.F., Correlation of beryllium and uranium with the mineral component of coal, *Geokhimiya*, 1967, no. 4, pp. 472–475.
 23. Asuen, C.C., Die Konzentration der chemischen Elemente und ihrer Beziehungen, *Chem. Erde*, 1968, vol. 4, pp. 321–332.
 24. Sharkov, A.Z. and Dolgoplov, V.M., Statistical analysis of the geological and geochemical characteristics of rare metals in coal, *Geol. Zh.*, 1968, vol. 28, no. 5.
 25. Pogrebitskii, E.O., Distribution of germanium in Donetsk Basin coal, *Zap. Leningr. Gorn. Inst.*, 1969, vol. 35, no. 2, pp. 87–103.
 26. Yudovich, E.Ya. and Kemris, M.P., *Neorganicheskoe veshchestvo uglei* (Inorganic Component of Coal), Yekaterinburg: UrO RAN, 2002.
 27. Travin, A.B., Germanium accumulation in coal, *Geol. Geofiz.*, 1961, no. 5.
 28. Scholz, A., Das Vorkommen von Spurenelementen in Steinkohlen, *Glückauf-Forschungshefte*, 1988, vol. 48, no. 2, pp. 99–103.
 29. Admakin, L.A., Relation between the trace-element content and ash content of coal, *Koks Khim.*, 2004, no. 9, pp. 8–11.

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