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Dependence of the Microelement Concentrations in Coal on the Petrographic Composition

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Abstract—The redox conditions of an organic system, the cleavage of carboxyl groups, and the reaction of aqueous solutions of cationic and anionic states of microelements are considered. Two types of functional relationships of the microelement content are obtained: with the petrographic composition; and with the concentration of cations and anions in the aqueous solution. These relationships are analyzed.

Keywords: redox conditions, oxygen partial pressure, oxygen activity, humification, humic acids, microcomponents, vitrinite, fusinite, carboxyl-group cleavage, cations, anions

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In research today on the rare-metal content of coal, insufficient attention is paid to its petrographic composition. General studies on the relation between the microelements and the petrographic composition have been replaced by formal acknowledgment of their distribution in the basic lithotypes. A broader approach would be to identify the physicochemical conditions of the organic system in which coal of different petrographic composition is formed and to analyze its geochemical characteristics. A fundamental role is played here by the redox conditions of the organic system, which affect its evolution, as shown in [1, 2]. Active reactions are seen between the microelements and the organic matter. Accordingly, it is important to establish the relation between the content of the microelements and the petrographic composition of coal.

PETROGENESIS OF COAL

Coal is composed of relatively stable organic structures consisting of inherited and newly formed microcomponents and mineral impurities. We may distinguish between three groups of microcomponents (macerals) [3, 4]: vitrinite, inertinite, and exinite. These groups are composed of a limited number of individual macerals (no more than 14). This distinguishes an organic system from a mineral system, where the number of minerals in groups and classes of rock is incomparably large. This difference may be attributed primarily to the very limited set of organogenic elements (C, H, O, N) present in coal and secondarily to the very narrow range of physicochemical conditions in which the macerals are stable.

Beyond that range, the state of the organic material changes: the organic matter is converted to mineral form (graphite, diamond). Within the specified narrow range, biochemical organic compounds are irreversibly converted to organic compounds of the coal (humic) series, with subsequent gelification.

However, in the evolution of organic compounds of the coal series, the events determining the petrographic composition of the coal occur in the early stages, corresponding to diagenesis. At this stage, the biopolymers of the plant tissue are converted to monomers, which subsequently form heteropolycondensates of the coal series with a colloidal state (humic materials).

New microcomponents are formed and retained throughout gelification; they are present in metaanthracites. These microcomponents belong to the vitrinite (Vt) and fusinite (F) groups. Vitrinites are irreversibly converted to fusinites: $Vt \rightarrow F$.

Petrographically, this corresponds to loss of transparency of the vitrinite, its change in coloration, and its reflectivity; analytically, it is identified from the decrease in O^{daf} and increase in C^{daf} and the calorific value. Since vitrinite and fusinite are the primary coal-forming microcomponents of humic coal and their proportions may vary widely, their petrogenetic importance is evident [4, 5]. The complete series of inherited microcomponents takes the form

$$\text{telinite} \rightarrow \text{posttelinite} \rightarrow \text{precollinite} \rightarrow \text{collinite} \\ \rightarrow \text{semivitrinite} \rightarrow \text{semifusinite} \rightarrow \text{fusinite}$$

In this series, the independent factors are the partial pressure and activity of oxygen, which are specified by the external surroundings and determine the redox conditions of the organic system. The condition of the oxygen may be assessed on the basis of the ratio

F/Vt, which petrographically reflects the redox state of the organic system [6, 7]. Hence

$$F/Vt = f[O_2]. \tag{1}$$

With development of the redox state of the organic system, the ratio F/Vt increases, and there is more transformation of the organic matter. The limiting state of the organic system is the formation of a soil layer (a black layer). On the basis of F/Vt, we may establish a relation between the petrographic composition and the physicochemical conditions of the organic system and thus investigate its development.

The organic system may be in an aerobic or anaerobic state or facies, with corresponding change in its redox state and the associated processes in the organic system.

In an aerobic state, the organic system is in direct contact with the atmosphere, so that oxygen has free access. The plant debris and its conversion products form a complex of different degrees of decomposition, in which macromolecules of plant tissues forming the biochemical series coexist with their monomer decomposition products, which are converted to heteropolycondensates of the coal series [8, 9].

Complex redox conditions are maintained in the organic system; they are specified by the oxygen partial pressure in the atmosphere (p_{O_2}). In these conditions, the organic matter is rapidly colonized by microorganisms and plant tissue is enzymatically split by bacteria and fungi. Hydrocarbons, amino compounds, and heterocyclic compounds are the least stable; aromatic compounds (phenols) corresponding to lignin and tannin are relatively stable.

On account of vigorous oxidation, the free-oxygen budget declines rapidly with depth. The oxygen partial pressure p_{O_2} declines to zero at the bottom of the aerated peat-forming level. This boundary may be at a depth of 0.4–1.0 m and sometimes 10 m. Nevertheless, splitting of the plant matter (especially lignin), is not complete but amounts to 50–60% of the gross organic mass, as a rule. For the peat-forming level

$$F/Vt = \omega_0 p_{O_2}, \tag{2}$$

where ω_0 is a constant of proportionality.

The microcomponents of the exinite group are stable in the oxygenated conditions of the peat-forming level. They form inherited macerals in the coal.

In physical terms, the organic matter in the peat-forming level is very hydrophilic. Therefore, its volume increases on flooding and, conversely, declines on drying. This may result in fragmentation of the plant residues, to the point of mixtinite formation. In paralic basins, such conditions are created by tidal behavior; in limnic basins, it is associated with peat accumulation in delta facies [10].

Below the peat-forming level, anaerobic conditions develop. Free oxygen has no access. Low-entropic mineral phases are unstable and are replaced by more entropic phases. For example, goethite (18.1 cal/mol deg) is replaced by hematite (21.5 cal/mol deg); and hematite by magnetite (35.0 cal/mol deg). If sulfuric-acid solutions are present, iron sulfides (melnikovite, marcasite) begin to be formed in the organic system from iron present in the humates. The copious deposition of sulfides results in pyrite content in the coal.

The presence of carbonic-acid solutions leads to the deposition of carbonates: ankerite and calcite. Once again, the calcium is taken from the humates. The redistribution of cations from humates to mineral phases is a consequence of the greater stability of the mineral compounds relative to humates.

Thus, the selective accumulation of chemical elements in organic matter favors those metals whose cations are stable in the given geochemical conditions—in other words, metals whose cations are less reactive with inorganic ligands than with organic matter.

The oxidative potential in anaerobic conditions is lower, as a rule, and is maintained by the presence of infiltrating solution. The oxygen activity in these solutions is determined by their basicity (alkalinity) [11]

$$[O_2] = \frac{[OH^-]^4}{K_{al}[e^-]^4}, \tag{3}$$

where K_{al} is the equilibrium constant of the alkaline reaction in aqueous medium; $[e^-]$ is the electron activity; $[OH^-]$ is the activity (basicity, alkalinity) of the hydroxyl group.

Substituting Eq. (3) into Eq. (1), we find that

$$F/Vt = \varphi_{\alpha l}\frac{[OH^-]^4}{K_{al}[e^-]^4}. \tag{4}$$

Here $\varphi_{\alpha l}$ is a constant of proportionality.

Equation (4) reflects the dependence of the degree of transformation of the organic matter on the basicity (alkalinity) of the solution supplied to the organic system. Note that the composition of this solution is specified by the surroundings and is an important characteristic of the organic system. In anaerobic conditions, fusinite develops with respect to the components of the vitrinite group and humic matter; aspects of superposition are present.

In an acidic medium, the oxygen activity is

$$[O_2] = \frac{K_{ac}}{[H^+]^4[e^-]^4}, \tag{5}$$

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

Substituting Eq. (5) into Eq. (1), we find that

$$F/Vt = \varphi_{\alpha c}\frac{K_{ac}}{[H^+]^4[e^-]^4}. \qquad (6)$$

Here $\varphi_{\alpha c}$ is a constant of proportionality.

In Eq. (6), we see that the degree of transformation of the organic matter depends on the acidity. Two factors may be responsible for acidity of the organic system.

1. The supply of acidic solutions. Sulfuric, chloride, carbonic, sulfate, and fluoride solutions are acidic. As a rule, they are associated with the activity of acrothermal and thermal sources. In this case, the activity $[H^+]$ is specified by the surroundings and is an important characteristic of the organic system.

2. Humification of the organic matter: the acidity in the organic system may vary widely, depending on how open the system is to the infiltration of water [12]. In an organic system with vigorous exchange of water, the acidity is reduced; neutral or alkaline conditions are possible. In closed conditions, reduction to pH = 2–3 is possible.

In anaerobic conditions, the mineral impurity is diagenetic and is associated with the solidification of minerals from solution. Such minerals reflect the chemical composition of the infiltrating solutions and the aqueous medium in the organic system.

MICROELEMENT CONCENTRATION AND PETROGRAPHIC COMPOSITION OF COAL

Most microelements in coal (Ge, Ga, Be, Mo, V, U, etc.) are bound in organic matter and are said to be *organophilic*. A very broad range of rare elements has been identified as inclined to accumulate in coal [13]; in organic systems, in contrast to mineral systems, the specific properties of their atoms and ions are related to the concentration processes. However, these microelements are present in coal in different forms. Many may also be present in mineral phases, although the relations between the organic and mineral components in the coal depend on the local geochemistry.

Many researchers have analyzed the dependence of the microelement concentrations and distribution in the coal on the petrographic composition. Note that the initial extensive research on this problem produced contradictory results. Some researchers asserted that the microelement concentrations are related to the lithotype and petrographic composition of the coal [14–22]. Others accepted the relationship with the lithotype but rejected that with the petrographic composition [23–26]. However, it is clear that lignites concentrate germanium and other microelements [11, 27, 28].

Consequently, in research on the microelements in coal, attention to the petrographic composition has sharply declined. For example, only four pages (with tables) were devoted to the petrography of coal in a substantial (more than 400 pages) recent text on rare elements in coal [29]. It is easy to get the impression that the petrographic composition of coal is unrelated to its content of microelements.

Obviously, in order to understand the relationship between the content of microelements and the petrographic composition, the first step is to establish a functional physicochemical dependence.

The content of microelements is different in different microcomponents of coal; the difference is greatest between newly formed and inherited microcomponents. Inherited microcomponents (in the exinite group) do not concentrate microelements. They are also present in humic coal in small quantities, as accessories. In general, plant tissues of different structure do not actively concentrate microelements in anomalous quantities, although elevated concentrations are noted. If such anomalous concentrations are created, the resulting imbalance has pathological consequences in living tissue.

Conversely, newly formed microcomponents (in the vitrinite group) are not only concentrators but carriers of rare elements in coal, although their content is considerably different in coal from different fields and coal beds. For example, for Ge, the difference may amount to 10^2 or 10^3. Special tests have produced analytical data regarding the Ge content in vitrains from the Tarbagataisk, Mordoisk, Kharanorsk, and Chernovsk fields in the Zabaikal region. The Tarbagataisk field is rich in germanium.

The germanium content in the vitrains is plotted as a function of its content in the corresponding coal in Fig. 1. The Ge content in the Mordoisk, Kharanorsk, and Chernovsk vitrains corresponds to region *I* (low Ge content) and is largely independent of the total Ge content in the coal. Conversely, very wide variation in Ge is seen for the Tarbagataisk vitrains (distribution *II*). In regions of the bed with low Ge content, the vitrains also exhibit low Ge content, approaching the values in region *I*. Since the vitrinite microcomponents are produced in the conversion of plant matter, humification is the most important stage in the concentration of microelements, as confirmed repeatedly in petrographic and geochemical research.

The newly formed fusinite has consistent Ge content, regardless of the total Ge content in the coal (Fig. 2): specifically, the Ge content in the fusinite is low (fields *I* and *II*). As we know, this is because fusinite is a highly carbonized maceral, with no reactive groups. However, that is not true of the other macerals in the fusinite group, such as semifusinite, micrinite, and mixtinite: they contain functional groups and are often involved in concentration of the microelements.

The interaction and concentration of microelements in coal is determined by the reactivity of the newly formed microcomponents, which are derivatives of humic materials and humic acids—that is,

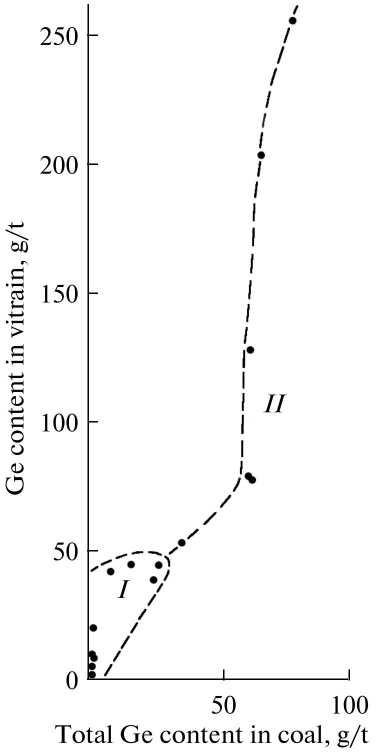

Fig. 1. Germanium content in vitrains as a function of the total germanium content in the coal: (*I*) low-germanium coal (Mordoisk, Kharanorsk, and Chernovsk fields); (*II*) germanium-bearing coal (Tarbagataisk field).

macerals of the vitrinite (*Vt*) and fusinite (*F*) groups. The *F*/*Vt* ratio is controlled by the oxygen activity and partial pressure (which, in turn, are specified by the external medium) and serves as a characteristic of the redox system. Therefore, we may investigate the relation between the concentration of microelements and the petrographic composition of the coal.

We know that humic acids are more acidic than other organic acids but less acidic than mineral acids. Structurally, they consist of aromatic rings and peripheral functional groups: carboxyl (–COOH), phenolic hydroxyl (–OH), carbonyl (C=O), and methoxyl ($-\mathrm{COH_2}$) groups. The carboxyl group is susceptible to cleavage and plays a determining role in the microelement concentration.

The corresponding reactions may be classified on the basis of the point of cleavage of the carboxyl group [30]. In hydrolysis, cleavage of the alkyl–oxygen bond

$$R'\mathrm{COO}{\mid}R + \mathrm{HO}{\mid}\mathrm{H} \tag{7}$$

and cleavage of the acyl–oxygen bond

$$R'\mathrm{CO}{\mid}\mathrm{O}R + \mathrm{H}{\mid}\mathrm{OH} \tag{8}$$

are possible.

In alkyl–oxygen cleavage, $\mathrm{H^+}$ may be neutralized by the hydroxyl group; the alkyl group $R'\mathrm{COO^-}$ remains free. In acyl–oxygen cleavage, $\mathrm{OH^-}$ may be neutralized by a proton; the acyl group $R'\mathrm{CO^+}$ remains free. (Here R' is an aromatic ring.)

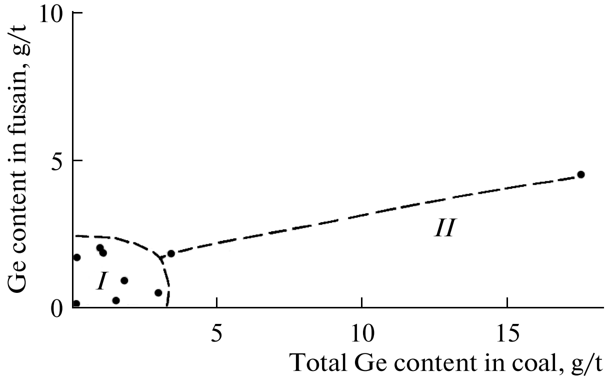

Fig. 2. Germanium content in fusains as a function of the total germanium content in the coal: (*I*) low-germanium coal (Mordoisk, Kharanorsk, and Chernovsk fields); (*II*) germanium-bearing coal (Tarbagataisk field).

The reaction of metal cations (Me^{z+}) with humic acid through the alkyl group may be written in the form

$$zR'\mathrm{COO}{\mid}\mathrm{H} + Me^{z+} = (R'\mathrm{COO})_z Me + z\mathrm{H^+}. \tag{9}$$

Here $(R'\mathrm{COO})_z Me$ is a compound between the metal and humic acid or the concentration of metal in the humic component, which may also be regarded as an acidic humic material. On the basis of Eq. (9) and the condition $[R'\mathrm{COO}{\mid}\mathrm{H}] = 1$, we may write the following expression for the concentration of metal

$$(R'\mathrm{COO})_z Me = K'_{\mathrm{alc}}\frac{[Me^{z+}]}{[\mathrm{H^+}]^z}. \tag{10}$$

The reaction of anionic forms of metal with humic acid by acyl–oxygen cleavage takes the form

$$zR'\mathrm{CO}{\mid}\mathrm{OH} + Me\mathrm{O}_k^{z-} = (R'\mathrm{COO})_z Me + z\mathrm{OH^-}. \tag{11}$$

Correspondingly, on the basis of Eq. (11) and the condition $[R'\mathrm{COO}{\mid}\mathrm{H}] = 1$, we may write the following expression for the metal concentration in the humic component

$$(R'\mathrm{COO})_z Me = K'_{\mathrm{acl}}\frac{[Me\mathrm{O}_k^{z-}]}{[\mathrm{OH^-}]^z}. \tag{12}$$

Substituting Eq. (6) into Eq. (10) and Eq. (4) into Eq. (12), we obtain formulas for the metal concentrations in the humic component of the organic system:

—for cations

$$(R'\mathrm{COO})_z Me_{\mathrm{kt}} = \frac{K'_{\mathrm{alc}}}{[e^-]^z}\left[\sqrt[4]{\frac{F/Vt}{K_{\mathrm{ac}}\varphi_{\alpha\mathrm{c}}}}\right]^z [Me^{z+}]; \tag{13}$$

—for anions

$$(R'\text{COO})_z Me_{\text{an}} = \frac{K'_{\text{acl}}}{[e^-]^z}\left[\sqrt[4]{\frac{\varphi_{\alpha\text{l}}}{K_{\text{al}}F/Vt}}\right]^z[Me\text{O}_k^{z-}]. \quad (14)$$

Equations (13) and (14) relate the microelement concentrations to the petrographic composition of the coal, expressed as the ratio of the primary microcomponents arising in the organic system on humification of plant tissue. In coal geochemistry, as we know, attention has focused on analytic solution of this problem, by comparison of the microelement concentrations in the primary lithotypes (vitrain and fusain). By this means, as well as research on the composition of peat and soil, it has been established that the microelements are primarily bound by humic acids, associated with macerals of vitrinite and fusinite type. However, the existence of an explicit relation between the microelement concentrations and these macerals does not specify a unique dependence on the petrographic composition, which has disheartened researchers.

It follows from Eqs. (13) and (14) that the microelement concentrations in organic matter depend on several independent variables. If the reaction constants (K'_{alc}, K'_{acl}, K_{ac}, K_{al}) and constants of proportionality ($\varphi_{\alpha\text{c}}$, $\varphi_{\alpha\text{l}}$) are assumed to be invariant, the independent variables will be F/Vt, $[e^-]^z$, $[Me^{z+})$ in Eq. (13) and F/Vt, $[e^-]^z$, $[Me\text{O}_k^{z-})$ in Eq. (14). The activities of the cations, the anions, and the electron are specified by the external surroundings. In other words, they do not depend on the organic system. The ratio F/Vt, which reflects the redox conditions in the organic system, depends on those conditions.

Three independent variables determine the redox conditions, the humification of the organic matter, and the budget of microelements that may be captured and concentrated by this organic matter. The functions

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

and

$$(R'\text{COO})_z Me_{an} = f([e^-]^z, [Me\text{O}_k^{z-}])$$

correspond to complex surfaces expressing the parameter variation. At each point of these surfaces, the relation between the independent variables will be different, and hence the ratio F/Vt will be different. In other words, the petrographic composition of the organic matter and the activity of the dissolved microelements will be different. Correspondingly, the relation established between the independent variables will determine the microelement concentrations in the coal, which, in turn, determine the potential metal content of the coal.

There is no need to analyze the relations between the independent variables and the microelement concentrations here, because so many combinations exist. Note, however, that the fourth root of the independent variables appears in Eqs. (13) and (14), and so the rate of microelement concentration will be relatively slow. However, the charges on the cations and anions sometimes compensate this effect; the compensation is greater for higher charge. This is consistent with the empirical rankings for the affinity of rare elements with organic matter [31, 32], as well as their concentrations in lignites [33] and in active coal [34].

It is also evident from Eqs. (13) and (14) that, regardless of their soluble forms, the actual microelement content in coal is a linear function of the microelement concentrations in aqueous solution within the organic system. Hence, in each case, the concentration of microelements in coal will depend on the permeability of the organic mass. Accordingly, the distribution of microelement concentrations over the area and depth of the coal bed will necessarily be very variable, as tests consistently show. Note also the different position of the petrographic ratio F/Vt in these equations. This is due to the different conditions of carboxyl-group cleavage and the different soluble forms of the microelements.

We have established formulas expressing the microelement accumulation in coal as a function of its petrographic composition and the water-soluble forms of the microelements in the organic system. We also know that the microelements differ in their affinity for organic matter and are therefore inadequately concentrated in coal. For several metals, it has been shown that the formation and stability of organometallic compounds increases with increase in the ionization potential [35]. That is commonly the case for organic complex formation.

In fact, the second ionization potential of Fe^{2+} in many heavy metals in the second period of Mendeleev's table is relatively low (16, 18) and consequently iron is primarily deposited in sulfides (creating pyrite coal) rather than in organic matter. The ionization potential of each microelement must be taken into account, as well as the functional dependence of its concentration on the petrographic composition.

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