

## Analysis of the Microelement Content in Coal

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Received July 22, 2017

**Abstract**—Microelements are present in coal in its organic matter, mineral impurities, and biochemical material. The microelement content in these components will be different, on account of the different forms of migration and access to the organic system. Estimation of the microelement content in the basic components of the coal is of interest in terms of assessing the rare-metal content in coal fields and extracting those metals. Statistical analysis of the microelement contents in different components of the coal is proposed.

**Keywords:** microelements, gross content, abundance ratio, distribution function, basic microelement carriers, organic content, infiltration, biogeochemical component

**DOI:** 10.3103/S1068364X17080026

The microelements in coal come from different sources, by different means. This is not fully appreciated in coal geochemistry, where the analysis of microelements is based on their gross content. No methods exist for direct determination of the microelement content in the basic coal components. Existing estimates of the microelement content in coal fractions of different density only identify trends associated with preferential concentration in the organic material and mineral impurities.

The concept of the *basic microelement carriers* in coal was introduced in [1]. Carriers are components of the coal with independent microelement distributions. They appear in the organic system in different states, which are not closely interrelated. Analysis is based on a statistical method that permits the gross microelement concentrations in the coal to be broken down into the contents in the basic carriers. As yet, however, we only have preliminary estimates of the microelement content in the organic matter of the biogeochemical series (in the paleophytomass). In the present work, we take the next step.

### MICROELEMENT CARRIERS AND ACCUMULATION IN COAL

Coal is a heterogeneous system, as established visually in coal beds and samples. Under the microscope, heterogeneity is even more evident, since the fine structure determining the petrographic composition and transformations of the organic matter may be distinguished.

Coal is an organic system that evolves differently from inorganic systems. Therefore, it has its own physicochemical features. Despite the heterogeneity of the

organic matter, the system does not include phases, in the usual sense of the term, since its components are chemically heterogeneous, lack short- and long-range order, and are colloidal. This is the case up to the highest stage of coalification, the formation of a mineral phase (graphite).

As a result of the transformation of the organic matter in the biogeochemical series (phytomass) into organic matter in the coal series (humic acids, humus), coal is formed in specific redox conditions and in different geochemical conditions, and its components are predominantly secondary structures. Macerals of the vitrinite and fusinite groups that appear in the course of humification are redox structures of the organic system. They may readily be identified under the microscope, and their petrographic composition may be determined. The ratio of the components is a function of the oxygen content and characterizes the redox conditions [2]

$$F/Vt = f(O_2). \quad (1)$$

The organic system, which is physically open, may be in different redox conditions specified by the external medium, which will affect the transformations of the organic matter and determine the geochemical state of the coal [3]. In this situation, the organic matter expresses its chemical activity exclusively through the newly formed macerals.

Coal also contains the exinite group, whose components are relatively stable in humification and are retained even in anthracites. In the redox conditions of the organic system, they are neutral. They are inherited throughout most of coal development, maintaining their composition and structure. Thus, the organic system is heterogeneous not only in maceral composi-

tion but in the relative reactivity of the organic components. Nevertheless, the organic matter must be regarded overall as an independent microelement carrier, corresponding to humic acids and humus with reactive properties [4–8].

The inorganic impurity consists of minerals of two different genetic types: clastic material and authigenic (diagenetic and catagenetic) minerals. The radical difference in these phases in the coal results in their specific geochemical features and creates independent microelement carriers. Clastic minerals are relatively uniform and correspond to regional sources of lithoclastic materials present as a solid sink in the organic system. Since the equalization of the landscape conditions and the formation of erosion cores in the terrace regions are correlated with the stages of coal accumulation, the clastic minerals are relatively homogeneous in different regions and constitute the aleuropelite fraction of the coal.

Clay minerals and quartz grains, which are sometimes lithoclastic, represent the dominant clastic material of the mineral impurity in the coal and inherit the composition of products of different age in the erosion core. Various silicates, including those that are very resistant to auxiliary erosion, are rare in coal [9]. Even with the prevalence of granitoids in sink regions of the Baikal region, with relatively high content of auxiliary erosion products, their concentration in the nearby coal beds is not observed. The clastogenic impurity in coal is close to mineral composition to the rock layers in the coal beds.

The organic matter and mineral impurity in coal are independent microelement carriers. In geochemical research and for technological purposes, it is important to estimate the microelement content in these carriers. Traditionally, coal is separated into fractions in terms of the density, which characterize the ratio of the microelement content in the organic and mineral components of the coal. The correlation between the microelement content and the maturity of the coal is also calculated. As already noted, however, these methods do not give clear results [10–12]. They only reveal trends regarding the preferable microelement concentrations in these components. We lack direct estimates of the true contributions of the different carriers to the gross microelement contents in the coal.

Two other independent microelement carriers should be noted. One is the organic matter of the biogeochemical series, in which the content of microelements is due to their accumulation in the growth period [13]. They enter the organic system in the phytomass, undergo humification, and are represented by humic acids and humus in the coal [14]. Since the organic matter of the biogeochemical series is converted to organic matter of the coal series, the biogeochemical content of the microelements is lost. Geochemical pathways of biogeochemical concentration cannot be assessed. Usually, the corresponding values are limited in current plant cover. In other words, the

problem cannot be solved by analogy across time (on the principle that the present is the key to understanding the past).

Another carrier is the authigenic mineral that solidifies within the organic system. In fact minerals of different groups are present: sulfides (usually melnikovite, marcasite, and pyrite; sometimes galenite, sphalerite, chalcopyrite, cinnabar, and linnaeite); carbonates (calcite, ankerite, dolomite, siderite); oxides and hydroxides (quartz, limonite, goethite, lepidocrocite, hematite, magnetite; silicates (kaolinite replacing particles of volcanic cinder; its pseudomorphoses with respect to biotite and plagioclase); phosphates (apatite), chlorides, sulfates, and nitrates. Especially significant are deposits of iron sulfides (pyrite), which run through the coal in some beds in the form of impregnations or layers of pyrite, carbonates, and sometimes chlorides [9]. The development of authigenic minerals is assessed by mineralogical methods. Their contribution as carriers is not considered here but must be taken into account in the analysis of the microelement parageneses in the coal [1].

Thus, the basic microelement carriers contributing the gross content in coal are as follows:

- the organic matter;
- clastogenic mineral impurity;
- paleophytomass.

#### CONTRIBUTIONS OF THE BASIC CARRIERS TO THE GROSS CONTENT OF MICROELEMENTS

The main microelement carriers in coal are substances that are characterized by specific chemistry and structure and that behave as independent microelement concentrators. As already noted, there are three main microelement carriers: organic matter of the biogeochemical series (paleophytomass); organic matter of the coal series; and clastogenic mineral impurity. It is of great interest to assess the microelement content in these carriers for geochemical, predictive, and technological purposes.

The gross microelement content  $C_c$  in the coal is the sum of the content in the basic carriers

$$C_c = C_{\text{org}} + C_{\text{min}} + C_{\text{bio}} - C_s, \quad (2)$$

where  $C_{\text{org}}$  is the microelement content in the organic matter accumulated during humification;  $C_{\text{min}}$  is the microelement content in the clastic material;  $C_{\text{bio}}$  is the microelement content introduced by the paleophytomass; and  $C_s$  is the microelement content lost on account of solubility and entrainment from the organic system.

Equation (2) expresses the material balance of the microelement content introduced by independent substances; it is closed. However,  $C_s$  is unknown. It is obvious that this component is mainly due to soluble organic compounds of the coal series such as fulvic acid [7]. In other words, these compounds are drawn

from  $C_{\text{org}}$ . Therefore, this factor may be disregarded. We then have the equation

$$C_c = C_{\text{org}} + C_{\text{min}} + C_{\text{bio}} \quad (3)$$

Equation (3) includes the microelement content in the basic carriers, which may be estimated analytically or by calculation. That provides the basis for analysis of the contributions of the main microelement carriers to the gross microelement content. Statistical principles are employed [1]. We now consider that analysis in detail.

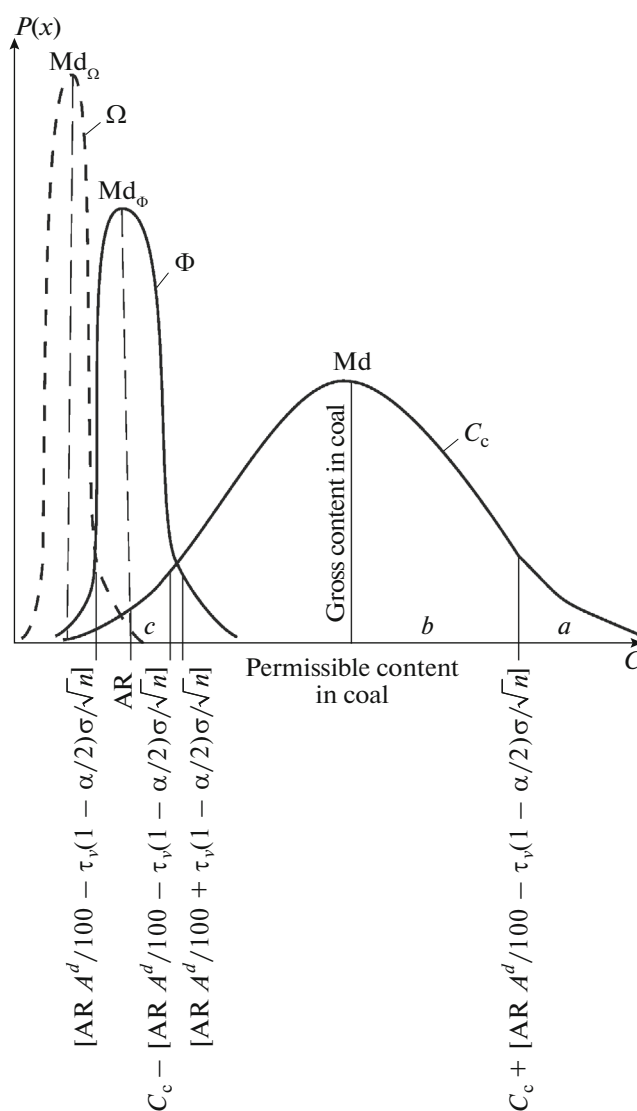
It is important to emphasize that the contributions of the different microelement carriers are independent. The microelements corresponding to the mineral impurity and paleophytomass are introduced mechanically in the organic systems. The microelements in the organic matter are introduced in solution, by infiltration.

Since the contents  $C_{\text{min}}$ ,  $C_{\text{bio}}$ , and  $C_{\text{org}}$  are independent quantities, they must be characterized by different statistical distributions, which have different central points. This is a statistical law, since independent parameters of different samples cannot have identical distributions and central points, although some degree of partial superposition is permitted. Note that, in terms of probability theory, the agreement of the central points of independent random quantities is practically impossible, since natural conditions and processes are unimaginably different in all respects.

The gross microelement content may vary widely: from low (background) levels to anomalously high levels due to the infiltration time and the solutions involved. Geochemical data regarding the microelement content in coal clearly illustrate this finding. Few coal fields contain high levels of rare metals or complexes of rare metals and trace elements (for example, germanium coal, uranium coal [15], and germanium-gallium coal. Conversely, most fields are characterized by low microelement content. In the continuous geochemical series of coal fields ranging from background to anomalous fields, background fields predominate.

That series of coal fields demonstrates the geochemical principle that the microelement content is determined by the corresponding concentration in the organic matter of the coal series. These concentrations correspond to the microelement parageneses in the coal, whereas the gross microelement content reflects their associations, as shown in [1].

Since they are independent, the central points of the gross microelement content and the contributions of each carrier may be assessed in terms of representative samples. Large samples ( $n \geq 30$ ) are regarded as representative [16]. The central points determined from such samples will be of sufficient statistical validity. We assume that, with large samples, the distribution of the microelement contents are close to normal and may be assessed on the basis of the normal law [17]. Such transformation of the distributions was considered in [18].



**Fig. 1.** Statistical functions of the microelement distributions in the coal ( $C_c$ ), in the clastogenic mineral impurity ( $\Phi$ ), and in the phytomass ( $\Omega$ ):  $Md$ , mean (modal) microelement content corresponding to the distributions in the carriers;  $a$  and  $c$  denote the upper and lower confidence limits;  $b$  is the confidence interval for the gross microelement content and the microelement contents in the mineral impurity. The functions correspond to the permissible limits of the gross microelement content and the contents in the mineral impurity.

The greatest deviations from the normal distribution are observed in the gross microelement content  $C_c$  and the content  $C_{\text{org}}$  in the organic matter, especially in coal with anomalous concentrations.

The microelement concentrations in the mineral impurity and the paleophytomass may be assumed to have normal distributions, since they vary within narrow limits. In Fig. 1, we show the distribution of the gross microelement content and the content in each carrier.

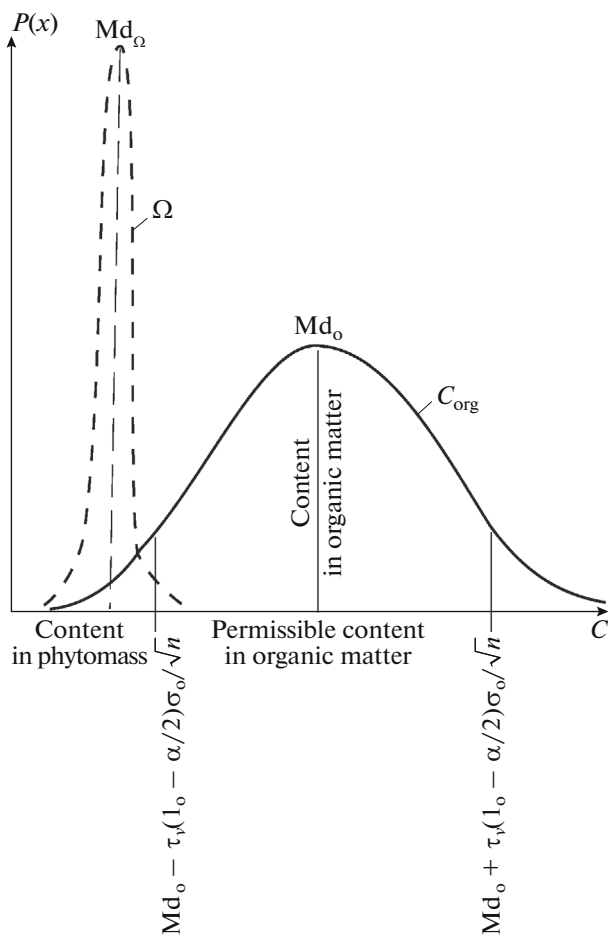


Fig. 2. Statistical functions of the microelement distributions in the coal's organic matter ( $C_{\text{org}}$ ) and in the phytomass ( $\Omega$ ). The functions correspond to the permissible limits of the microelement content in the organic matter.

The microelement content  $C_{\text{min}}$  in the mineral impurity is characterized by upper and lower limits. The corresponding confidence intervals may be determined at a confidence level  $1 - \alpha/2$

$$C_{\text{min}} = AR A^d / 100 + \tau'_v(1 - \alpha/2)\sigma' / \sqrt{n}. \quad (4)$$

Here AR is the abundance ratio of the element in the clay and shale [19];  $A^d$  is the ash content of the coal, %;

$\alpha$  is the significance level;  $\tau'_v$  is the Student statistic with  $v = n - 1$  degrees of freedom;  $\sigma'$  is the standard deviation of the microelement content in the sample.

In accordance with the sample size,  $\tau'_v(1 - \alpha/2)\sigma' / \sqrt{n}$  is taken from a nomogram [20].

With 95% probability, we may say that the content of each microelement associated with the mineral impurity falls within the specified confidence interval. We may also assume with the same probability that the content values falling outside the confidence interval do not belong to the confidence interval; they may be regarded as random surges.

The microelement content  $C_{\Sigma\text{org}}$  in the organic matter is characterized by particular central points and distribution densities (Fig. 2). This component is determined by the equation

$$C_{\Sigma\text{org}} = C_c - [AR A^d / 100 + \tau'_v(1 - \alpha)\sigma' / \sqrt{n}]. \quad (5)$$

These contents correspond to a sample of the same size. Since they are independent, they may be broken down into independent components. In practice these components correspond to two subtypes. One subtype is associated with organic matter of the coal series and arises in the humified organic matter during infiltration of the solution. This is the *infiltrational organic component*  $C_{\text{i.o}}$ . The other subtype enters the organic system with the paleophytomass. This is the biogeochemical *component*  $C_{\text{bio}}$  in the coal.

The confidence limits of the distribution for the content in the coal's organic matter are assessed on the basis of the condition

$$C_{\Sigma\text{org}} = C_{\text{mod}} \pm \tau'_v(1 - \alpha/2)\sigma' / \sqrt{n}, \quad (6)$$

where  $C_{\text{mod}}$  is the mean (modal) content of the microelement in the organic matter of the coal series;  $\sigma$  is the corresponding mean square deviation; and  $\tau'_v$  is the Student statistic for the microelement content in the coal's organic matter.

Within the confidence interval, the microelement content in the coal's organic matter is nonuniform. It consists of samples of genetically different components: the infiltrational organic component and biogeochemical component. These are uniform and cannot be further resolved. Hence

$$C_{\Sigma\text{org}} = C_{\text{i.o}} + C_{\text{bio}}. \quad (7)$$

The infiltrational organic component is independent of the biogeochemical component and is associated with the infiltration of the solution in the organic system. Because this system is open, different geochemical environments may be created. That not only affects the transformation of the organic matter but determines the set of microelements and their concentrations. The geochemical environments are characterized by the anionogenic components ( $\text{O}_2$ ,  $\text{H}_2\text{CO}_3$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{HCl}$ ,  $\text{Cl}^-$ ,  $\text{H}_2\text{S}$ ,  $\text{S}_2^{2-}$ ,  $\text{HSO}_4^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{HF}$ , and  $\text{F}^-$ ), are specified by the surroundings, and determine the state of the organic system [2, 21]. They are determined by the solidification of authigenic minerals and the formation of microelement parageneses in the coal [1].

By analogy with the gross content, we may say with 95% probability that the content of each microelement that falls within the specified confidence interval belongs to the infiltrational organic component and is concentrated in the organic matter of the coal series. Although they vary, they fall within the specified confidence interval, they cannot be resolved into smaller components, and, within the established limits, they are typical of the coal's organic matter.

We may also assume with the same probability that the content values falling outside the confidence interval do not belong to the confidence interval and are statistically random. As already noted, we may distinguish between two types here.

(1) Values above the upper limit of the confidence interval may be due to samples with higher content of reactive macerals in the vitrinite group than for samples within the confidence interval.

(2) Values below the lower limit of the confidence interval correspond to concentrations that, with 95% probability, are not part of the infiltrational organic component and are not associated with infiltration.

The only source of such values of the microelement content is the organic matter of the biogeochemical series (the paleophytomass). In fact, in sections of the organic system that are closed or characterized by very limited mass transfer, the microelement content is low (often below the sensitivity of the analytical method) and of a single type. It is close to the biogeochemical concentration in contemporary plant cover.

The upper limit on the biogeochemical concentration is the lower boundary of the confidence interval. The only lower limit is the sensitivity of the analytical method.

Thus, the biogeochemical microelement concentration varies within the following interval

$$0 < C_{\text{bio}} < [C_{\text{mod}} - \tau_v(1 - \alpha/2)\sigma/\sqrt{n}]. \quad (8)$$

These concentration values are uniform and cannot be resolved into separate components. They accumulate during plant growth and are supplied to the organic system as paleophytomass. Note that the biogeochemical concentration in the coal depends on its ash content

$$C_{\text{bio}}^c = C_{\text{bio}}(1 - A^d/100). \quad (9)$$

The variation in biogeochemical concentration of the microelements in the coal is due to barrier accumulation, depending on the biogeochemical environments, the delivery medium, the plant populations, etc. [22]. For geochemical and predictive purposes, it is expedient to combine the microelement content in the clastic impurity and the biogeochemical concentration so as to obtain some aggregate background concentration:  $C_b = C_{\text{min}} + C_{\text{bio}}$ . By that means the infiltrational organic component may be isolated:  $C_{\text{i.o}} = C_c - C_b$ . That component is of most interest in predicting the coal's rare-metal content.

At this point, the development of the statistical method for resolving the gross microelement concentrations into components associated with specific carriers is complete.

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Translated by Bernard Gilbert