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Determination of the Nature of Carriers of Ash-Forming Elements in Coal from the Kaa-Khem Deposit

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Abstract

Statistical analysis of the material according to the composition of ash-forming elements in coal from the Kaa-Khem deposit (n = 43) including the data previously obtained by other researchers was carried out. The study samples of coal have a low ash content on average (ash content A^d is 11.8 %), with a relatively high content of CaO (17.4 mass %) and Fe_2O_3 (16.6 mass %). Regression analysis of the data by means of the least-squares allowed us to reveal correlations between ash content and the content of elements. The dependences of the element's contents in coal $[E_i]$ and ash $[E_i]^A$ were estimated over a broad range of ash content values A^d (3–51 %). The types of diagrams for Si, Al, Ti, K, Na differ from those for Fe, Ca, Mg, S. It is demonstrated that the main carriers for Si, Al, Ti, K, Na in the studied coals are mineral inclusions of allothigenic origin. The authigenic mineral formations of coals contain mainly the carriers of Fe, Ca, Mg, S.

Keywords: coal, coal ash, ash carrier, ash-forming element

INTRODUCTION

Black coal from the Kaa-Khem deposit belongs to marks G (GZh_{ok}), GZh and Zh. According to the data reported in [1], the main coal bed 2.2-Ulug of the deposit is low-ash on average (ash content A^d 12.0 %), low-sulphur (total sulphur content S_t^d 0.3 %), low-phosphorus (phosphorus content P^d <0.01 %). Technical parameters: the yield of volatile substances V^{daf} 45 %, plastometric shrinkage x = 38 mm, plastic layer thickness y = 15 mm, upper heating value per dry ash-free state Q_s^{daf} 34–36 MJ/kg. Petrographic composition: vitrinite Vt 95 %, semivitrinite Sv 0 %, liptinite L 3 %, inertinite I 2 %. The average composition of coal ash, mass %: SiO_2 27.8, CaO 22.4, Fe_2O_3 18.0, Al_2O_3 16.3, MgO 3.1, K_2O 0.8, Na_2O 1.6, TiO_2 0.7, SO_3 8.2 [1].

According to the data reported in [2–4], coal ash is represented by allothigenic and authigenic mineral inclusions. The former are brought in paleo peat lands by water streams from feeding regions and by winds, the latter are formed from peat-forming plants and soluble compounds at the stages of syn- and diagenesis of peat and coal. It is known that authigenic minerals in black coal play an essential part as the major carriers and concentrators of rare earth elements [5]. At present, in addition to the known methods of sequential coal demineralization, petrography, also modern methods of analysis are widely used, including X-ray fluorescence analysis, mass spectrometry with inductively coupled plasma, and scanning electron microscopy [5, 6].

Published sources contain no data on the genetic nature of the carriers of ash-forming elements in coal under study. To establish the regularities of microelement distribution in coal from the Kaa-Khem deposit, in the present work we describe the results of statistical treatment of the data on element content in the samples of coal ash and coal with different ash content. Results of the studies allowed us to determine the genetic type of fixed ash of coal.

EXPERIMENTAL

Procedures

Analysis of the chemical composition of the samples of ashed coal was carried out. The ash content (A^d) of coal was determined using a standard procedure at 815±10 °C [7]. The content of the oxides of ash-forming elements (SiO, CaO, Fe_2O_3, Al_2O_3, MgO, Na_2O, K_2O, TiO_2, MnO, SO_3, P_2O_5) in the ash of coal samples collected by researchers during exploration works (1964, 1985) was determined according to the general requirements to the methods of chemical analysis of ash [8]. The content of the listed oxides and the oxides of geochemical satellites of calcium (SrO, BaO, ZrO_2) in the ash of coal sampled by us was determined in the analytical division of the A. P. Vinogradov Institute of Geochemistry (Irkutsk) by means of X-ray fluorescence analysis with the help of SRM-25 spectrometer (Russia) using a standard sample ZUK-1 (ash of coal from the Irsha-Borodino deposit of the Kans-Achinsk fuel and energy complex, distinguished by high CaO content); sample preparation was carried out by fusing the ash with lithium tetraborate; total sulphur content (S_t^d) was determined by means of semi-quantitative analysis using an S4 Pioneer spectrometer (Bruker, Germany).

Materials and methods

The data on ash content (A^d) in 68 coal samples were used; among these samples, two were collected by us in 2014 at the operating Kaa-Khem coal open-pit, other samples were collected by geologists during exploration works (the territorial foundation of geological information over the Republic of Tuva, Pichugin N. A., 1964, Ussar R. T. 1985).

The content of ash-forming elements in coal ash (Si, Ca, Fe, Al, Mg, Ti, Na, K, S) was determined through calculation from the oxide composition of ash using the coefficient of recalculation of element and oxide content of the rock [9]. Element content in coal $[E_i]$ was recalculated from element content in ash $[E_i]^A$ taking into account the ash parameter $[E_i] = ([E_i]^A \cdot A^d)/100$. Correlation analysis of interconnections of $[E_i]$ and $[E_i]^A$ with ash content A^d was carried out relying on the data of chemical analysis of ash composition in a set of 43 coal samples.

The data on element content were used to calculate regression equations, the dependences were plotted as element content in coal $[E_i]$ *versus* ash content A^d and element content in coal ash $[E_i]^A$ *versus* ash content A^d for ash content A^d range 3–51 %. Mathematical processing of the correlations of experimental data was carried out in Microsoft Excel software. Test of the significance of linear regression equation, in general, was carried out using determination coefficient (R^2). To estimate the statistical significance of the regression model, Fischer's ratio was calculated using equation

$$F = \frac{R^2/(k-1)}{(1-R^2)/(n-k)}$$

where k is the number of factors of dual regression ($k = 2$); n is the number of observations of parameter ($n = 43$). The critical (tabulated) value of F-statistics ($F_{0.1;1;41}$) was determined in Excel for the given significance value $\alpha = 0.1$, taking into account the fact that the number of degrees of freedom for the total sum of squares (the largest variance) $(k-1) = 1$, and the number of degrees of freedom of the residual sum of squares (the smallest variance) $(n - k) = 41$.

RESULTS AND DISCUSSION

The chemical composition of ash for coal from the coal bed 2.2-Ulug in the Kaa-Khem deposit is shown in Table 1. Coal is low-ash on average (A^d 11.8 %), but ash content increases to 51.5 % in the marginal parts of the coal-bearing area (oxidation zone). Coal under study is characterized by a relatively high content of calcium and iron. The average composition of ash in 68 coal samples, mass %: SiO_2 36.2, CaO 17.4, Fe_2O_3 16.6, Al_2O_3 14.9, MgO 5.1, Na_2O 1.1, K_2O 1.1, TiO_2 0.5, SO_3 5.2. In low- and medium-ash coal samples, the ash is ferrous(15–31 %)-calcium(16–28 %)-silicic(13–40 %), in high-ash (oxidized) coal it is alumina(21 %)-silicic(56 %).

According to the data of petrographic studies carried out by I. Yu. Yakovlev (the foundation of geological information in the Republic of Tuva, 1987), the content of the mineral forms of carbonates (calcite, ankerite, dolomite) in heavy fractions of coal with the density >1.6 g/cm^3 reaches 69 % of the total amount of mineral admixtures, pyrite – 3 %.

The law of the distribution of each of nine ash-forming elements in 43 coal samples is visualized in pair plots in $[E_i] - A^d$ and $[E_i]^A - A^d$ coordinates (Fig. 1). Relying on the differences in the general view of the diagrams, two groups of elements were distinguished; the first one includes Si, Al, Ti, K, Na, and the second one includes Fe, Ca, Mg, and S. The distribution of data on element content will be discussed taking into account a statement known in coal chemistry, that the diverse forms of element occurrence in coal are divided into two large groups, *aquagene* and *clastogene*. Aquagene group includes carrier ash (mineral and non-mineral substance), authigenic, sedimentation-diagenetic and partially epigenetic. Clastogene carrier ash is formed from the substance of allothigene, sedimentation minerals and mineraloids [4].

The distribution of Si, Al, Ti, K, Na

In coal, the content of Si increases linearly with an increase in ash content (see Fig. 1), and there is a significant positive correlation between [Si] and A^d variables; the determination coefficient is R^2 = 0.95, the angular line coefficient (slope) is k_{Si} = 0.29. In the sets of all studied elements, the significant correlation coefficient is r_s = 0.25, the correcting Student's t-test introduced into the standard error of approximation is $t_{0.10;42}$ = 1.68. It may be stated that 95 % of the variations of [Si] values are explained by changes in ash content A^d. Since element content in coal is determined by the amount of its carrier ash making the largest contribution to the overall content of this element in coal, it may be assumed that the amount of Si carrier ash increases according to the linear law, too.

For coal ash, the plot of the dependence of Si content on ash content looks like a parabola with downward branches. Two regions are distinguished: 1) in the ash of low- and medium-ash coal (A^d 3–35 %), silicon content increases with the deceleration of increment; 2) in the ash of high-ash coal, it decreases. In general, a trend to increase $[Si]^A$ values is noticeable. The maximal amount of silicon is determined in the ash of medium-ash coal (A^d 20–35 %). The obtained correlation may be explained if we admit that silicon in coal from the Kaa-Khem deposit is bound with carrier ash with different Si content; carrier ash with high Si content may be concentrator ash. According to [4], concentrator ash is a genetic class of the inorganic substance of coal in which the content of this element maximal. It may be admitted that an increase in silicon content in the ash of coal from the Kaa-Khem deposit with an increase in ash content is provided by an increase in the amount of carrier ash and concentrator ash; the contribution of the latter is likely to decrease gradually. Of course, this assumption is to be tested in further studies.

The functions of the correlations of Al, Ti, K, Na with ash content A^d in coal have a positive linear trend (similar to the plot for silicon), the content of Al, Ti, K increases significantly in proportion to ash content, determination coefficient R^2 is equal to 0.97, 0.86, 0.86, respectively. Variations of scattering of the experimental values of [Ti], [K] from the regression line are increased to 14 %. The scattering of [Na] values on the plot is substantial, and determination is low (R^2 = 0.23).

The content of Al, Ti, K in coal ash also increases significantly and in proportion with ash content; the slopes of paired lines in coal and in ash are almost the same: k_{Al} = 0.12 and 0.13, k_{Ti} = 0.005 and 0.0048, k_K = 0.02 and 0.03, respectively. Correlation coefficients for $[E_i]$ with A^d are significant: r^A_{Al} = 0.70; r^A_{Ti} = 0.53; r^A_K = 0.71. The largest scattering of the points with respect to regression line is observed for Ti. The plot of the distribution of $[Na]^A$ looks similar to that for $[Si]^A$ (a parabola), but the correlation is low: r^A_{Na} = 0.26 (r_s = 0.25).

All the ten equations of linear regression for the correlations of Si, Al, Ti, K, Na with A^d in coal and in coal ash (see Fig. 1) meet the hypothesis concerning their statistical significance in general. This conclusion follows from the fact that in each model the actual value of Fisher F-test is more than the tabulated value ($F_{0.1;1;41}$ = 2.83, $F_{act} > F_{tab}$), determined for the given degrees of freedom: k_1 = 1 (paired regression) and k_2 = 41 (the number of samples in the set n = 43) with 90 % reliability level (Table 2).

Simultaneous increase of Si, Al, Ti, K and possibly Na content in coal and in ash with an increase in ash content points to the connection of these elements with allothigenic mineral particles. Naturally, authigenic (aquagene) ash carriers are also present in coal, and the content of these elements in them is low, so their contribution to the overall Si, Al, Ti, K, Na content in total ash is generally insignificant. It may be concluded on the basis of the presented data that the major contribution to the overall Si, Al, Ti, K, Na content in coal from the Kaa-Khem deposit is made by terrigene (clastogene) ash carriers.

The distribution of Fe, Ca, Mg, S

The content of [Fe], [Ca], [Mg] in coal slightly increases according to the linear type with an increase in ash content, the slopes of the straight lines are small: k = 0.01; k_{Ca} = 0.03; k_{Mg} = 0.02 (for comparison, k_{Si} = 0.29; k_{Al} = 0.12), correlation coefficients are significant: r_{Fe} = 0.32; r_{Ca} = 0.41;

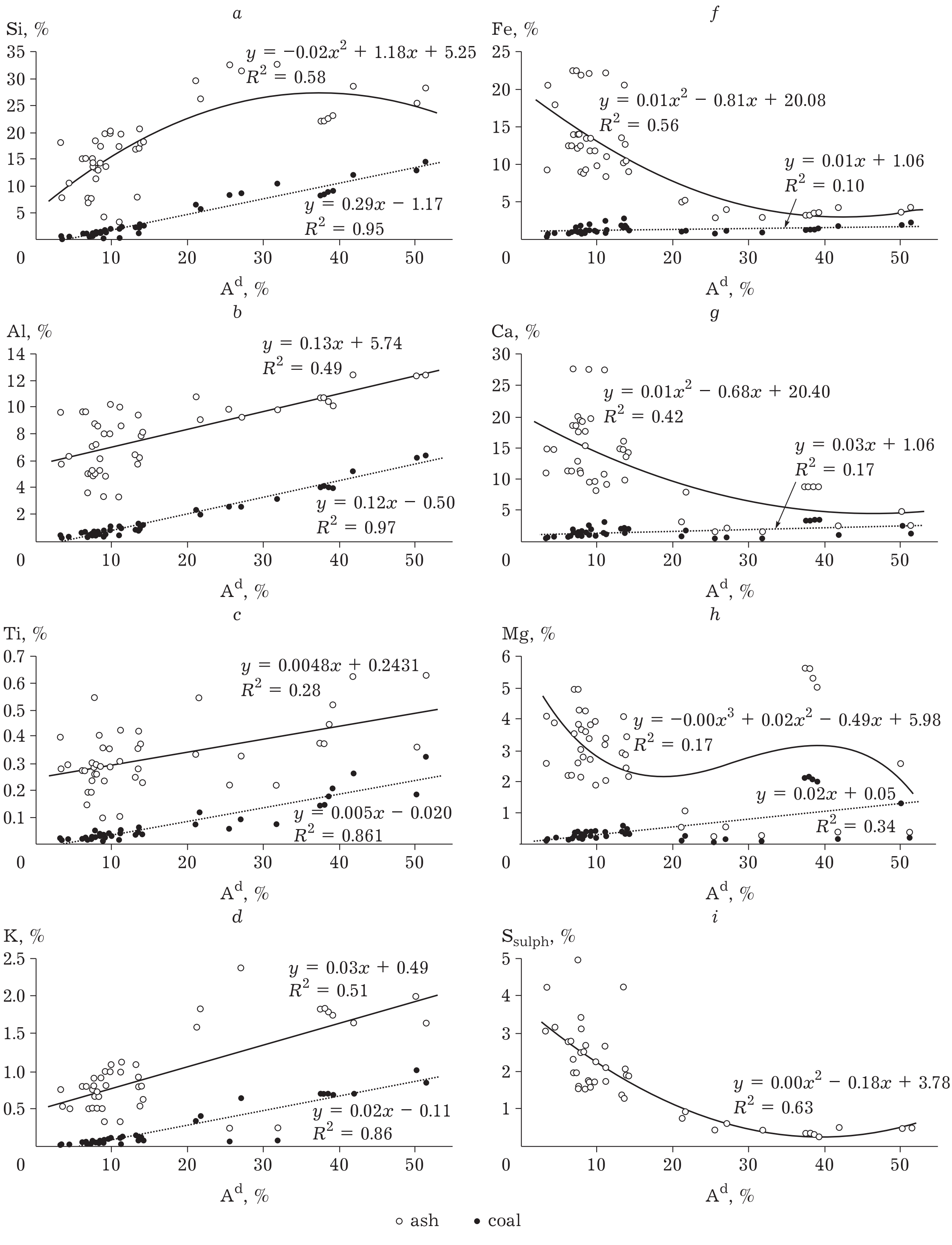

Fig. 1. (start).

$r_{Mg} = 0.58$. The distribution of S (sulphate form) in coal is non-uniform, the content of sulphur and/or its ash carrier increases in low-ash coal, decreases in medium-ash coal and again increases in high-ash coal; the coefficient of sulphur correlation with ash content is $r_S = 0.52$.

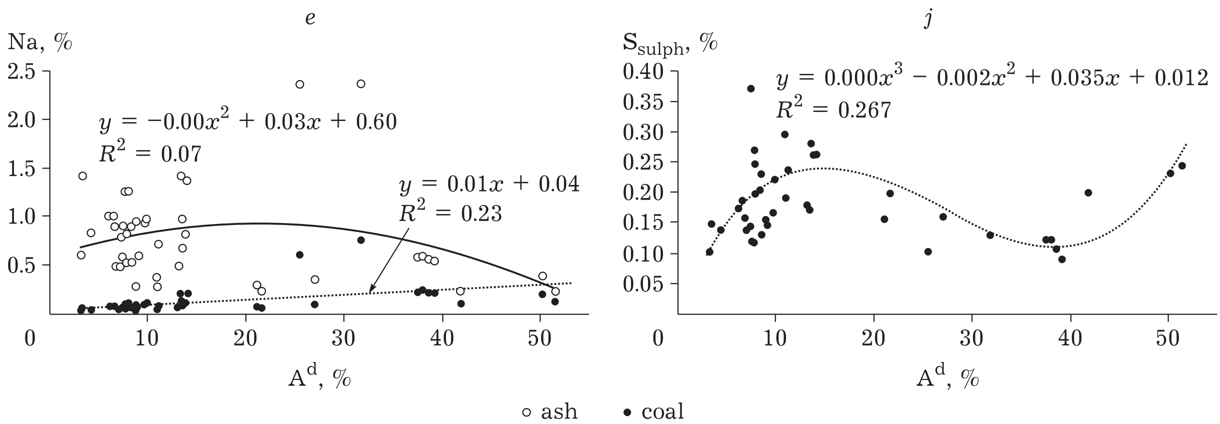

Fig. 1. (finish). Dependence of the content of Si (*a*), Al (*b*), Ti (*c*), K (*d*), Na (*e*), Fe (*f*), Ca (*g*), Mg (*h*), S_{sulph} (*i*, *j*) on ash content in coal from the Kaa-Khem deposit and its ash.

For coal ash, the plots of $[Fe]^A$, $[Ca]^A$, $[S]^A$ dependences on A^d in general are of parabolic type; the branches are directed upward, and correlations are significant: $r^A_{Fe} = 0.74$; $r^A_{Ca} = 0.65$; $r^A_{S_{sulph}} = 0.79$. With an increase in ash content, the content of Fe, Ca, S in ash decreases within the A^d range 3–40 % (low- and medium-ash coal) and after passing the minimum starts to increase slightly in the A^d region 40–52 % (high-ash coal). Magnesium content ($[Mg]^A$) decreases in low-ash coal, slightly increases in medium-ash coal, and again continues to decrease in high-ash coal.

The models of dual regression found for the distributions of Fe, Ca, Mg, S in coal and in coal ash are statistically reliable because for each model the value of the statistics of the actual F-test for the given significance level ($\alpha = 0.1$) and degrees of freedom ($k_1 = 1$; $k_2 = 41$) is larger than the critical or tabulated value, $F_{act} > F_{tab}$ (see Fig. 1 and Table 2). In this connection, it may be concluded for coal from the Kaa-Khem deposit that the content of Fe, Ca, Mg, S in coal increases with an increase in ash content and decreases in ash. These variations and a number of other regularities were revealed according to the results of processing and generalization of a large number of pair plots of the distribution of rate elements (microelements) in coal from different deposits, measured in 1970–1972 [4]. It is known that the amount of any element in total ash $[E]^A$ is equal to the sum of its content in terrigene and aquagene ash carriers: $[E]^A = [E]^A_{ter} + [Э]^A_{aq}$ [4]. If an element is mainly present, say, in the aquagene carrier, while its content is low in the terrigene carrier, and the fraction of this terrigene carrier is low, then the distribution of this element in ash will be determined practically completely by the fraction of the aquagene carrier.

Regression analysis shows that this case is realized for Fe, Ca, Mg, S in the ash of coal from the Kaa-Khem deposit: these elements are present mainly in aquagene ash carriers, both mineral and non-mineral. Evidently, incomes of Fe, Ca, Mg, S from terrigene ash carriers are insignificant, so they do not alter the negative de-

TABLE 1

Chemical composition of ash of coal from 2.2-Ulug bed of the Kaa-Khem deposit

Sampling period, years; number of samples	Average ash content of coal, A^d, %	Averaged content of ash-forming elements, mass %														
		SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	TiO_2	MnO	Na_2O	K_2O	SO_3	P_2O_5	SrO	BaO	ZrO_2	L.A.
2014; $n = 2$	6.1	23.4	10.6	28.4	18.0	6.2	0.5	0.3	0.9	0.6	8.2	0.05	0.3	0.2	0.02	1.9
1960–1985[a]; $n = 41$	16.5	37.4	15.4	15.5	17.4	5.0	0.5	–	1.1	1.1	4.9	–	–	–	–	1.0

Note. 1. L.A. – losses during annealing. 2. Dash means the absence of data.

[a]Materials of the Territorial Foundation of Geological Information for the Republic of Tuva (N. A. Pichugin, 1964 г., R. T. Ussar, 1985).

TABLE 2

Statistical parameters of dual linear regression for correlations between element content and ash content for coal and coal ash (the Kaa-Khem coal deposit)

Element	Determination coefficient, R^2		Fisher F-test		
	Coal	Ash	Actual value		Tabulated value ($F_{0.1; 1; 41}$)
			Coal	Ash	Coal, ash
Si	0.95	0.58	799.00	56.625	2.83
Al	0.97	0.49	1325.67	39.39	2.83
Ti	0.86	0.28	251.86	15.94	2.83
K	0.86	0.51	251.86	42.67	2.83
Na	0.23	0.07	12.25	3.09	2.83
Fe	0.10	0.56	4.56	52.18	2.83
Ca	0.17	0.42	8.40	29.69	2.83
Mg	0.34	0.17	21.12	8.40	2.83
S_{sulph}	0.27	0.63	15.16	69.81	2.83

pendence (a decrease) of element content in the ash of low- and medium-ash coal. A small increase in Fe, Ca, Mg, S, observed in the ash of high-ash coal, may be connected with the development of epigenetic mineralization: carbonate, sulphate, and sulphide.

CONCLUSION

Regression analysis of the distributions of Si, Ca, Fe, Al, Mg, Ti, Na, K, S in coal and in coal ash as a function of ash content was carried out. Interrelations between ash content A^d and the content of microelements in coal $[E_i]$ and in coal ash $[E_i]^A$ were revealed, which allowed us to determine the nature of ash carrier for elements in 2.2-Ulug coal bed of the Kaa-Khem deposit.

Coal from the Kaa-Khem deposit contains Si, Al, Ti, K, Na mainly in clastogene carriers of ash, while Fe, Ca, Mg and S are present in aquagene ash carriers of authigenic, sedimentation and partially epigenetic genesis.

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