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BRIEF COMMUNICATIONS

The Geochemical Patterns of Rocks of the Bazhenov and Abalak Formations (Western Siberia)

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Abstract—The composition of rocks of the Bazhenov and Abalak formations in Western Siberia is described. Correlations of the concentrations of the major and minor components in rocks with the concentrations of minor elements and organic material are shown. Study of the concentration of minor elements allows us to determine the conditions of sedimentation: redox potential, hydrogen sulfide contamination, and the source of sedimentary material. The results show that rocks of the Bazhenov Formation were formed under the conditions of low fluxes of clastic material, a reduced environment, and a periodically occurring hydrogen sulfide mode.

Keywords: Bazhenov Formation, chemical composition, trace elements

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INTRODUCTION

Exhaustion of resources in traditional deposits of hydrocarbons leads to the search for methods of their extraction from new sources. One such source includes hydrocarbons generated by shale but not released to the traditional collector due to low permeability (Stupakova et al., 2015). In addition, development of new technologies of oil generation in a layer is possible (Bychkov et al., 2015). The rocks of the Bazhenov Formation with the highest concentration of organic material are the most promising.

We studied core of the holes from the Frolov–Tambei structural–facies region in the Ob–Lena facies area that occurs in the meridional direction for more than 1000 km. The western border of the Shitotnoe Priob'e separates the Priobsk and Krasloleninsk deposits to the west of Khanty-Mansiysk; the eastern border lies between the Vostochny Surgut and the Yuzhny Surgut deposits (the Surgut region).

There are three horizons in this area: Vasyugan, Georgievsk, and Bazhenov. The first two of these are related to the Abalak Formation; the third horizon totally corresponds to the Bazhenov Formation. The Bazhenov Formation overlies the Abalak Formation ubiquitously and is covered by the Neokom clinomorph complex (Khamidullin et al., 2013; Korobova et al., 2015).

The Abalak Formation is composed of different rocks including shale, carbonate, often clastic, and predominant mixed rocks. Rocks of the Abalak Formation are characterized by the presence of glauconite.

The Bazhenov Formation in this area is composed of siliceous rocks (silicite), mixed carbonate–siliceous and siliceous–carbonate, siliceous–argillaceous and argillo-siliceous including those with a high concentration of kerogen, carbonate rocks including lumpy, bacterial–algal limestones and those with relict radiolarian texture, crystalline and recrystallized limestones (Yurchenko et al., 2015), as well as dolomite with a relict radiolarian texture. Argillo-siliceous rocks with a high concentration of kerogen are the most abundant in deposits of the Bazhenov Formation. These rocks often are rhythmites composed of fine (from 0.5 to 2–3 mm) interbeds of argillo-siliceous and argillo-siliceous–carbonate, siliceous, and carbonate–siliceous rocks saturated with kerogen to various degrees. Such rocks are characterized by a banded or fine-banded structure.

METHODS OF THE STUDY

The concentrations of major oxides and minor elements in the samples were analyzed by the X-ray spectral fluorescent method using the methodologies established by the Science Council on Analytical Methods of the Russian Research Institute of Mineral Resources. An Axios mAX Advanced vacuum X-ray fluorescent spectrometer with a wavelength dispersion (PANalytical) was used at the Laboratory of Mineral

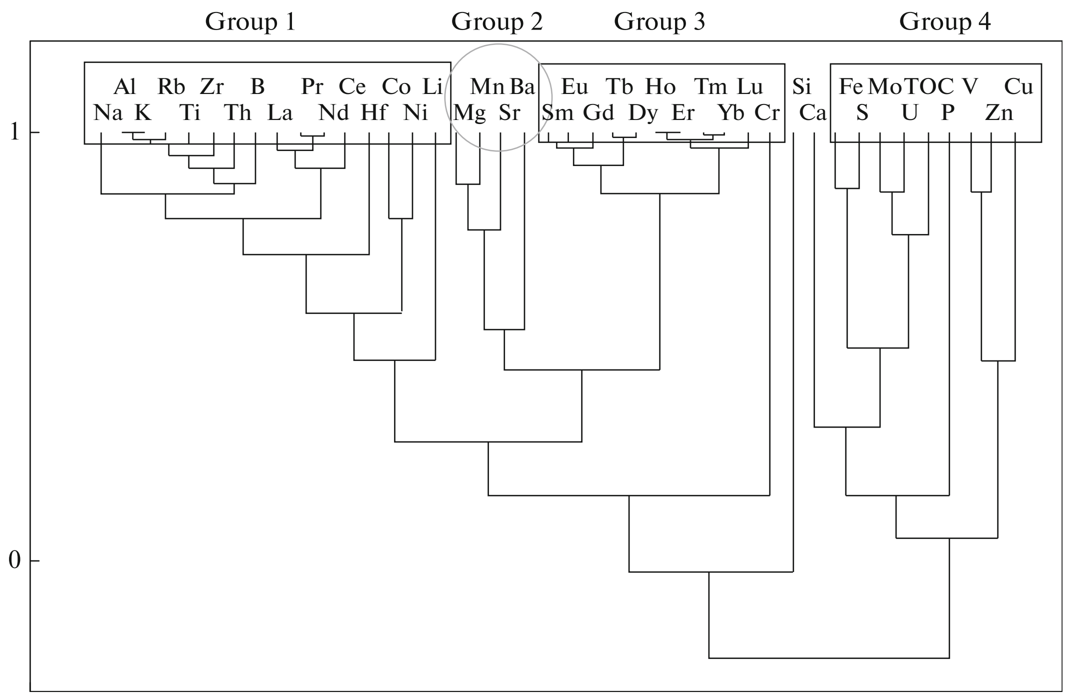

Fig. 1. A correlation dendrogram of the concentration of elements in rocks of the Bazhenov Formation.

Matter Analysis at the Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry of the Russian Academy of Sciences.

The ICP-MS method was used to study the element composition. Analysis was carried out on an ELEMENT2 (Thermo Finnigan) high-resolution mass spectrometer with ionization in inductively coupled plasma at the Laboratory of Experimental Geochemistry of the Department of Geology at Moscow State University. The methodology of sample preparation for analysis was described in detail in (Bychkov et al., 2016).

X-ray phase analysis was carried out on a Dron-3m X-ray diffractometer with an operating current of 20 mA, an operating voltage of 30 kV, and an X-ray tube with a Co anticathode. According to the data from the X-ray structural analysis, the samples contain the following phases: minerals of the silica group (chalcedony and quartz with the basic reflexes at 4.24 and 3.34 Å), clay minerals (hydromica, 10 Å; mixed-layer phases with alternating packets of hydromica and montmorillonite, more than 10 Å; kaolinite, more than 7.14 and more than 3.56 Å; chlorite, 14.1–14.4, 4.72, and less than 3.55 Å), carbonate minerals (calcite, 3.02–3.03; dolomite, 2.89; siderite, and 2.798–2.8 Å), pyrite (2.69–2.71 Å), albite (3.17–3.20 Å), potassium feldspar (3.23–3.25 Å), goethite (4.18 Å), and magnesite (3.53 Å).

Organic materials were studied on a RockEval-6 pyrolysis reactor with an independent two-stage sample treatment (in a flame–ionization detector and oxidation furnace) (Kozlova et al., 2015). In the course of pyrolysis, the flame–ionization detector registers three peaks of organic compounds upon programmable heating of rock samples from 30 to 650°C. Within the temperature range up to 300°C (S_1 peak ($S_0 + S_1$)), we observe desorption of free (C_1–C_7) and sorbed (C_8–C_{33}) hydrocarbons (HC) in the composition of associated gases and oils (hydrocarbons of the methane series, aromatic hydrocarbons, etc.). Pyrolysis proceeds within the range of thermal decomposition of kerogen at 300–650°C (S_2 peak), which results in transformation of organic matter into gaseous hydrocarbons (the total of pitchy–asphaltene components of free bitumen and HC formed during high-temperature cracking). The third peak (S_3) measured by the detector of heat conductivity at 300–390°C indicates the content of carbon dioxide. The products of pyrolysis that correspond to the described peaks are measured in units of mg/g of rock. The programmable rock heating (300–850°C) in oxygen proceeds in an oxidation furnace. The total organic carbon (TOC) is calculated with account for the fact that 83% of the S_1 and S_2 peaks in the element composition of HCs are related to carbon.

RESULTS OF THE STUDY

Sedimentary rocks of the Bazhenov and Abalak formations contain several groups of major minerals with different geneses and chemical compositions. X-ray phase analysis allowed us to study quantitative

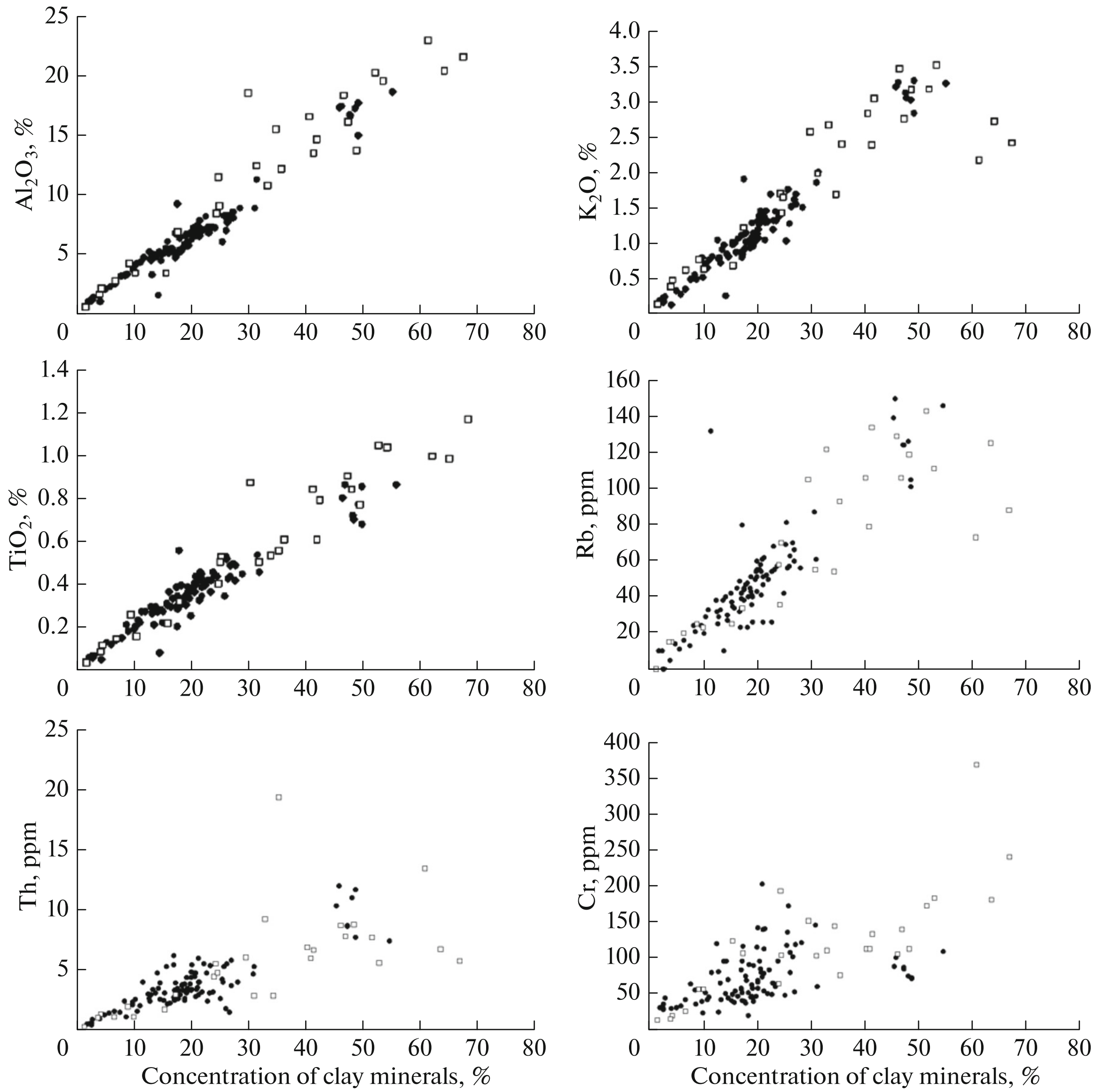

Fig. 2. Correlations of the concentrations of major and minor components with the content of clay minerals. (*1*) Bazhenov Formation; (*2*) Abalak Formation.

relationships between the clay, carbonate minerals, quartz, and pyrite. The high concentration of kerogen that may be estimated from the total concentration of organic carbon is an important feature of rocks. The distribution of the mineral components in rock is controlled by the conditions of sedimentation, gradational separation, bioturbation, and diagenetic alterations. As a rule, rocks are characterized by rhythmic layering, which results in a great dispersion in the concentration of minerals of different groups. This allows us to determine the predominant accumulation of a certain element in the mineral components by plotting correlation diagrams.

The dendrogram of the concentrations of the minor and major elements is given in Fig. 1, on which the components form four groups with similar geochemical behavior. The first group with the highest correlation with potassium and aluminum includes the elements related to the clay minerals, namely Rb, Ti, Zr, Th, B, Ni, Co, and LREEs. The second group includes the elements that enter carbonates, such as Mg, Mn, Sr, and Ba (except for Ca). The third group includes HREEs, Sm, and Eu, which are characterized by sorption from seawater. The forth group of elements (U, Mo, Fe, and S) shows correlation with OM. The correlation of P, V, Zn, and Cu with organic matter is below the significance level; Si and Ca do not correlate with other elements.

The distribution of minor elements in rocks is controlled by their mineral composition; however, in rocks

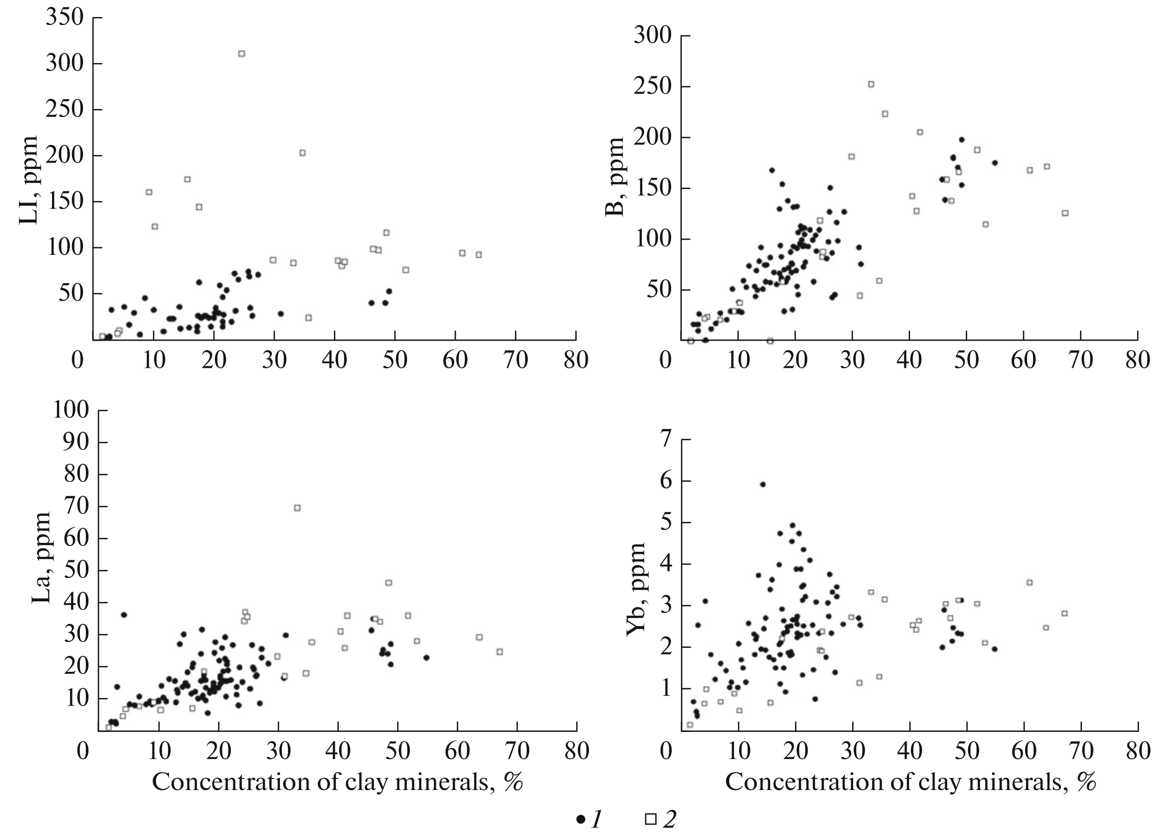

Fig. 2. (Contd.).

with a high concentration of organic matter, kerogen should be considered as a phase as well. Thus, the geochemical model of rock is a combination of the phase components, but not minerals. We may distinguish the following phase components of rock: siliceous, argillaceous, carbonate, sulfide, and organic matter.

Clay minerals. Clay minerals include mixed-layer minerals of the illite–smectite series with a packet proportion of 85 : 15–65 : 35, hydromicas, kaolinite, and chlorite. As a whole, these minerals correspond to the terrigenous component, but their composition underwent changes as a result of bioconcentration and adsorption from seawater. In addition to SiO_2, the major components of these minerals are Al_2O_3, K_2O, and Na_2O. Figure 2 shows the correlations of the concentrations of clay minerals with the concentration of these oxides in rock. Correlation with the concentration of Al_2O_3 is an unambiguous function of the total concentration of clay minerals, which may be applied for quantitative calculation of the mineral composition of rock on the basis of the data of X-ray fluorescent analysis with a high accuracy. However, correlations with alkaline metals (K_2O and Na_2O) are not as unambiguous, since they depend on proportions between the different clay minerals. In addition, some Na may form albite during diagenetic alterations. Titanium is traditionally considered as an indicator of the terrigenous component and has a significant correlation with the concentration of clay minerals (Fig. 2).

The correlations of the concentrations of clay minerals with the concentrations of minor elements are shown in Fig. 2. Rb, Th, Cr, Li, B, and REEs are among the components whose geochemistry is controlled by clay minerals in sedimentary rocks.

Rubidium is the geochemical analog of potassium; therefore, we could expect a correlation of the same level as that for potassium. However, Fig. 2 shows a wide dispersion, which requires an explanation. The wide dispersion for the Abalak Formation most likely results from the more complex composition of clay minerals in comparison with rocks of the Bazhenov Formation. In addition, such a dispersion indicates variability in the source of the material and conditions of sedimentation for rocks of the Abalak Formation.

Thorium is characterized by poor aqueous migration; its behavior is mostly controlled by capture of suspension. A wide dispersion in rocks of the Abalak Formation supports the conclusion on the variability in the conditions of sedimentation and material sources at that time.

Chromium migrates poorly in seawater as well. Deposition of a suspension is impacted by granulo-

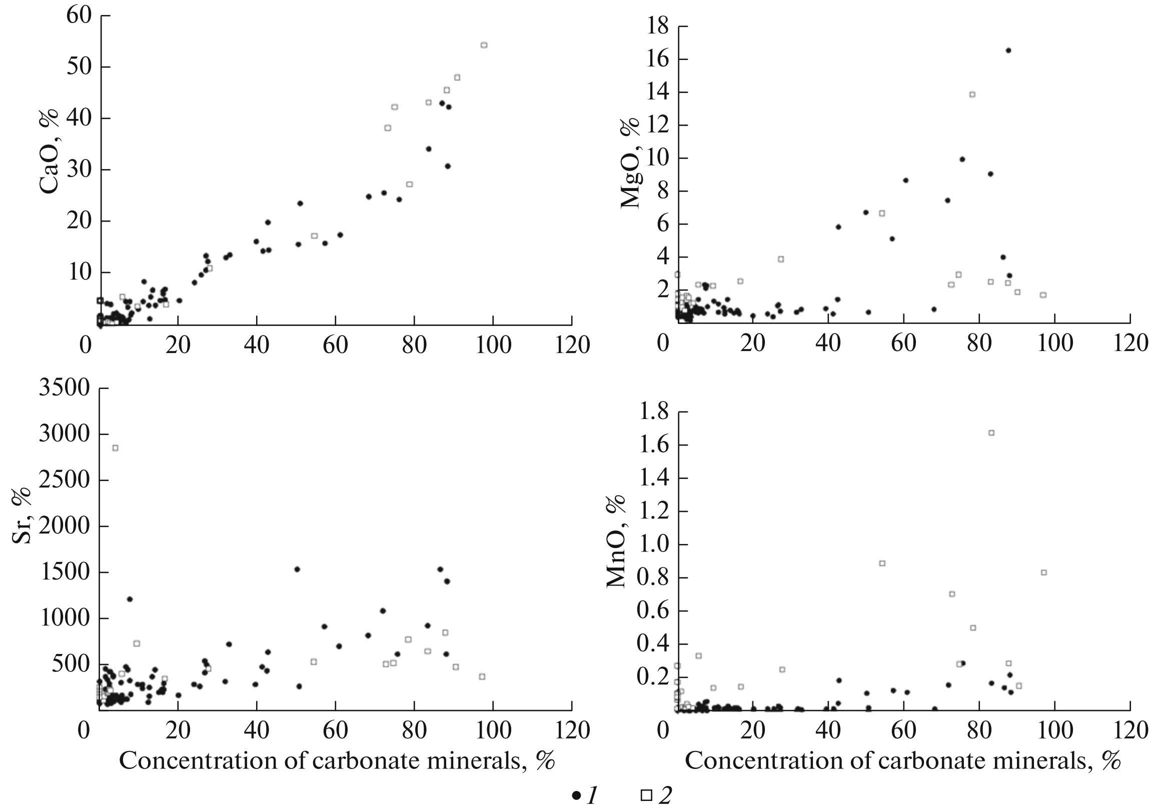

Fig. 3. Correlations of the concentrations of components with the content of carbonate minerals in rocks. (*1*) Bazhenov Formation; (*2*) Abalak Formation.

metric separation, during which the heavy fraction that contains chromium-bearing minerals may enrich individual interlayers without a positive correlation with the concentration of clay minerals. Such a process is observed for rocks of the Abalak, as well as Bazhenov formations (Fig. 2).

Although lithium is accumulated in clay minerals (Fig. 2), some samples of the Abalak Formation are extremely enriched in this element. This may be explained by the input of material with a low degree of weathering (volcanic ash) or by the conditions of specific sorption of lithium from seawater.

The geochemistry of boron is controlled by the adsorption from seawater on the surface of clay minerals. Boron may be partly released during diagenesis. The process of adsorption–desorption depends on the pH of seawater and porous waters during the formation of rock. Complex transformations of clay minerals in silt may result in redistribution of boron. This results in a wide dispersion depending on the concentration of clay minerals.

Correlation between REEs and clay minerals is significant for elements of the cerium group. This is demonstrated for lanthanum and is very different from the situation for elements of yttrium group, e.g., ytterbium (Fig. 2).

Carbonate minerals. The main carbonates determined by the X-ray phase analysis (calcite, dolomite, and siderite) demonstrate clear correlation between the concentration of calcium and carbonate minerals (Fig. 3). This allows us to calculate the quantitative mineral composition of rock using the data of X-ray fluorescent analysis. Comparison of the MgO concentration with the content of carbonate minerals demonstrates two trends of accumulation related to dolomitization (Fig. 3). The concentration of MgO in rock allows us to estimate the relative content of dolomite. Strontium is accumulated together with carbonate minerals (Fig. 3); one sample with an anomalous strontium content is most likely related to the horizon of the fish kill.

The concentration of MnO shows a poor correlation with the content of carbonate minerals. Rocks of the Abalak Formation are significantly enriched in this component in comparison with rocks of the Bazhenov Formation (Fig. 3).

Sulfide minerals. Pyrite is a typical mineral in rocks of the Bazhenov and Abalak formations. It is formed during the processes of bacterial sulfate reduction. This is usually accompanied by redistribution of sulfur and iron, as well as by accumulation of chalcophile elements. The concentrations of iron and sulfur in rocks of the Bazhenov Formation are fully controlled

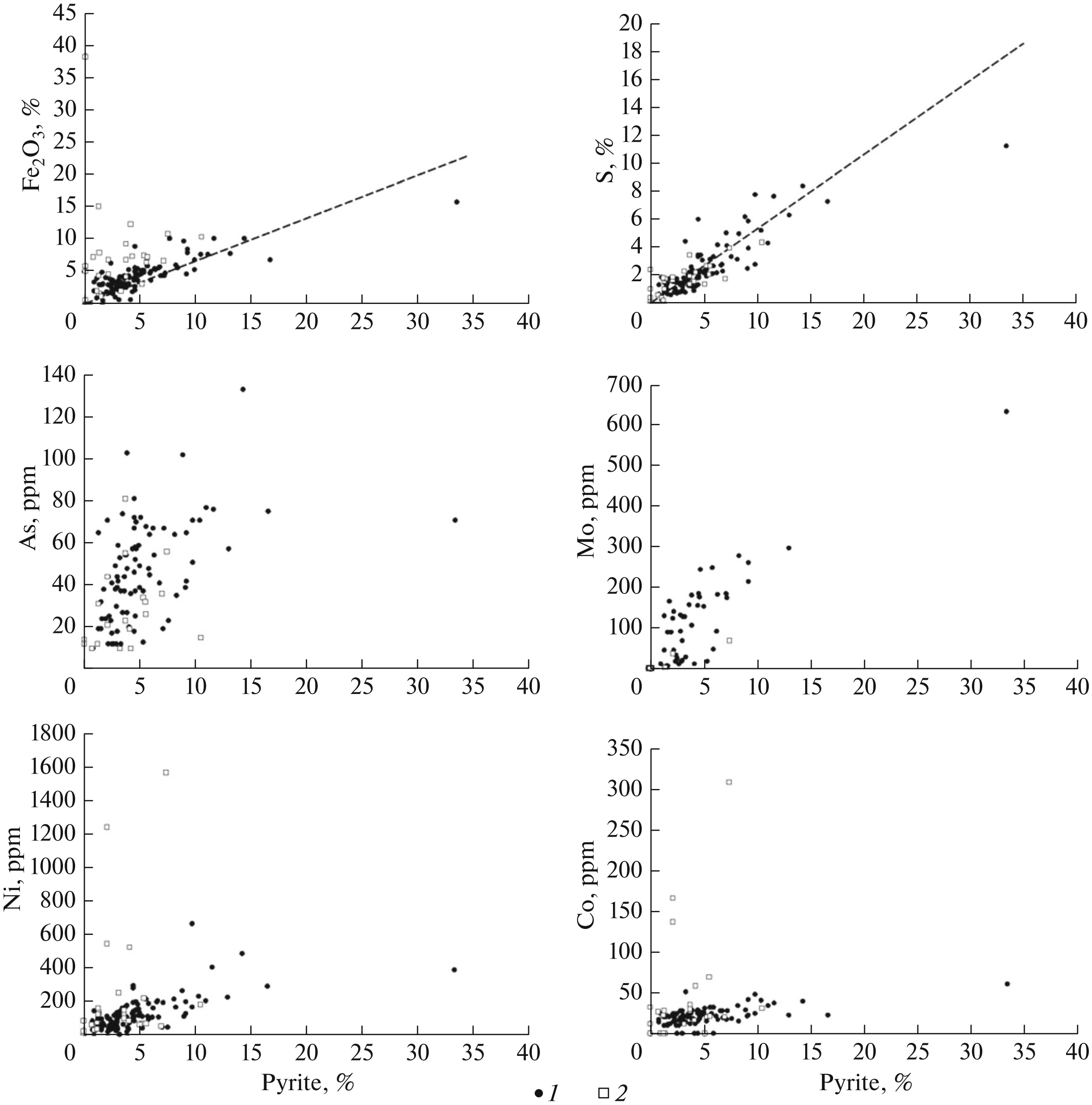

Fig. 4. Correlations of the concentrations of components with the content of pyrite in rocks. (*1*) Bazhenov Formation; (*2*) Abalak Formation.

by pyrite (Fig. 4). The concentration of iron in rocks of the Abalak Formation is much higher than that calculated from the pyrite content, which is explained by the presence of siderite and glauconite. As a whole, the concentration of sulfur in rocks of the Bazhenov Formation corresponds to the pyrite content. This may be used for calculation of mineral proportions on the basis of the X-ray fluorescent analysis.

As a whole, the concentrations of arsenic and molybdenum increase with increasing pyrite content (Fig. 4). In contrast to rocks of the Abalak Formation, rocks of the Bazhenov Formation are characterized by accumulation of nickel and copper with an increasing pyrite content. Such a correlation is not observed for copper and zinc.

Organic matter. The concentration of organic matter may be estimated by the TOC value. Correlations of the concentrations of minor elements with the content of organic matter have a wide dispersion, but allow us to distinguish the geochemical features of rocks of the Bazhenov and Abalak formations.

In general, the concentration of uranium in rocks of the Bazhenov Formation increases with increasing concentration of organic matter (Fig. 5). This effect is the most clear for the core material from some holes; plotting of all data results in an increase in dispersion. This provides evidence for compositional changes in

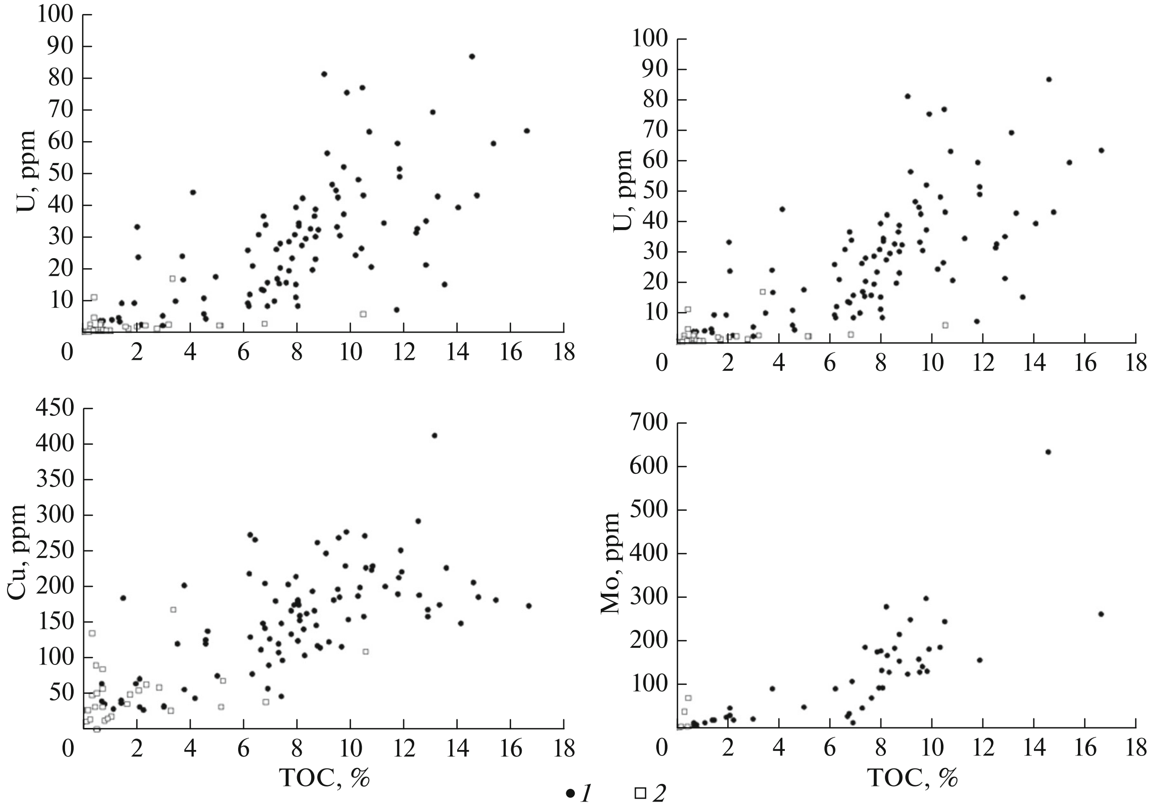

Fig. 5. Correlations of the concentrations of components with the content of organic material in rocks. (*1*) Bazhenov Formation; (*2*) Abalak Formation.

organic matter during diagenetic transformations. The increase in the uranium concentrations with increasing organic matter content is much smaller for rocks of the Abalak Formation; the behavior of vanadium is the same (Fig. 5). There is no remarkable correlation between the concentrations of vanadium and organic matter in rocks of the Abalak Formation. Therefore, we may suggest that significant accumulation of uranium and vanadium in organic matter is typical of the Bazhenov Formation and characterizes the conditions of sedimentation, in contrast to underlying rocks. The relationship between uranium and total C_{org} may be applied as a geochemical indicator for estimation of the degree of kerogen transformation.

Copper was accumulated in the organic matter of the Bazhenov and Abalak formations in a similar way (Fig. 5). The wide range of values does not allow us to distinguish significant differences. With an increase in the organic-matter content, the concentration of molybdenum increases in rocks of the Bazhenov Formation. The high molybdenum and low manganese concentrations in sedimentary rocks indicate hydrogen sulfide contamination, which provides reduction of molybdenum from seawater and its co-precipitation with iron sulfides. The processes of reduction stimulate accumulation of uranium and vanadium at the geochemical barrier as well. The problem of primary or secondary enrichment of organic matter in these elements cannot be solved unambiguously only on the basis of the correlations.

The concentration of REEs in rocks does not have clear correlation with the concentration of organic matter. Their behavior is most likely controlled by some factors that require additional study.

Other minerals in sedimentary rocks. Phosphorus and barium are distinguished among the elements that do not show remarkable correlations with major minerals. Phosphorus may form apatite, which can have a biogenic (buried parts of bones), as well as chemogenic (phosphorite concretions) origin. Since phosphorus does not show significant correlation with the mineral composition of the rock, it is evident that accumulation of phosphorite does not have much influence on the concentration of other elements.

Barium does not have a clear correlation with the major rock-forming components and minor elements. The high concentration of barium is most likely explained by contamination of the samples with drilling fluid, in which barite is used as a weighting agent. This is due to necessity; therefore, the geochemistry of barium should be discussed carefully until it is refined.

CONCLUSIONS

Our study showed the relationships between the concentrations of several elements and major minerals of the Bazhenov and Abalak formations, which allows us to calculate the component (mineral) composition of rocks from the data on the concentrations of elements and oxides obtained by the X-ray spectral fluorescent method and ICP-MS. This information is necessary for evaluation of the causes for the formation of collectors and signs of oil and gas potential, which may exceed the accuracy of the prediction of the resources in these formations.

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