Sources and Forms of Metals Accumulation in Coal-Bearing Deposits of the Southern Primorye: Validation of the “Granite-Water” Model

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Abstract. The work deals with the role of Paleozoic granites as possible sources of metals in coals. The process of dissolution and transfer of metals in the system "granite-water" was modeled. It is shown that the scale of accumulation of ore matter in water depends on the duration of interaction between water and rock. As a result of physical and chemical modeling, the probable set of migration forms of components and their transformations were calculated. The results of modeling indicate in favor of the assumption that the studied leucocratic granites of the pre-Cenozoic basement could be a source of metals concentrated in the coals of the Rakovka depression.

1. Introduction

The role of framing granites as possible sources of metals in coals is studied in the example of the Rakovka depression. The Rakovka coal depression with an area of 70 km² is located on the southern edge of the Khanka Lowland in Primorsky Krai. In addition to the lignite deposit itself, high concentrations of uranium, germanium, rare earth elements, tungsten, beryllium, gallium, arsenic, and several other rare metals were noted in the sediments of the depression [1-4].

The Eocene-Oligocene is considered to be the time when coal-bearing sediments of the depression were formed [5]. The foundation of the depression is composed of magmatic formations of mainly acid composition and, to a lesser extent, intensely dislocated metamorphic rocks with a thick weathering crust. Coal-bearing formations belong to the platform type (coal-bearing sediments were formed during the period of platform activation) and bear all its features [1, 2]. In geological and tectonic terms, the Rakovka depression is confined to the Ussuri fault within the Ussuri-Voznesensk rare-metal-fluorite and manganese-iron-ore mineralization zone of the Khanka-Bureinsk mineralization province. The tectonics of the depression is characterized by weak folded deformations (dip angles of rocks and coal seams rarely exceed 20°) and active manifestation of fault dislocations of the fault and fault-slip types with vertical amplitudes from tens to first hundred meters and horizontal ones from first meters to first kilometers.

Many researchers [6, 7, etc.] noted the ore-controlling role of faults. However, there is an alternative recent hypothesis on hydrogenous and clastogene genesis of coal mineralization in coals of the Rakovka...
depression associated with granites of the Pre-Cenozoic basement and framing of the depression which is receiving more and more evidence [8, 9].

Paleozoic granites framing the Rakovka depression are characterized by a low CaO content (0.14%), increased K₂O (4.38%), and also high concentrations of Be, Zn, Ga, Ge, As, Se, Rb, Y, Nb, Sn, Sb, Cs, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Sm, Yb, Lu, Hf, Tl, Pb, Th, and U, relative to the average composition of the upper continental crust.

The mechanism behind the formation of metalliferous coals in the Rakovka depression is not completely clear. However, a similar pattern of REE distribution in coal ash and granites of the Rakovka depression framing suggests that the metals, increased concentrations of which were observed in the coals, came from the studied granites that were exposed to weathering for a long period of time.

This work deals with the possibility of the hypothesis of ore mineralization in coals as a result of the destruction of rock-forming and accessory minerals of granites in the hypergenesis zone and extraction of elements by meteoric waters from the position of physical and chemical modeling, which has been previously used by the authors in studying the formation patterns of groundwater in the abandoned coal mine areas [10, 11].

2. Materials and methods
The efficiency of physicochemical simulation experiments is determined by a combination of interrelated problems solved for complex heterogeneous multi-systems involving water solutions, solid mineral phases, and a gas mixture, and by the capabilities of the software package “Selector” (Windows) [12], which implements the convex programming approach to calculating equilibrium in heterogeneous systems by minimizing the isobaric-isothermal potential (Gibbs potential).

During modeling of the “water-granite” system, the natural chemical composition of leucocratic granite of pre-Cenozoic basement was introduced, recalculated for the number of moles of each component. Pure rainwater, thermodynamically equilibrium with the atmosphere, at T = 25 °C was introduced into the reaction with the rock.

The “water-granite” system is characterized by a matrix of 59 independent components (C, N, Al, Fe, Si, Be, Cd, Sc, As, Ga, Ge, Rb, Sr, Hf, Pb, W, Ag, Sn, Eu, Gd, Nd, Sm, K, Li, Lu, P, Y, Yb, Ca, Na, Mg, Mn, Co, Cr, Ni, V, Ba, Cu, Pr, Zn, Cs, Mo, Nb, Zr, Sb, Ce, La, Th, U, Dy, Er, Ho, Se, Ti, Tb, Sm, H, and O). The list of substances potentially in equilibrium consisted of 503 dependent components, including 27 mineral phases and 15 gas phase components. Thermodynamic properties of minerals, gases, and aqueous solution components presented in the following databases adapted to the software package “Selector” (Windows) were used: a_Shock [13-15], g_Reid [16], s_dump, s_Robie Hemingway [17], s_Yokokawa [18].

In determining the probable flow composition, the assumption was that the water composition is in thermodynamic equilibrium with the host rocks, and the rock/water mass ratio (R/W) takes the meaning of the time of interaction (conditionally, water exchange time) between the rock and water solution [19].

3. Results and discussion
Minerals are unstable in the hypergenesis zone, therefore they intensively dissolve from the very beginning of interaction with water. Due to the simulation of dissolution of increasingly large portions of the initial rocks, there was a clear trend in the simulated “granite-water” system toward increasing salinity of the water solution (131.76 mg/kg H₂O → 47548.5 mg/kgH₂O), as well as a consistent change in pH from 6.3 to 8.8, which is a natural and directional transformation of the water phase composition. In the process, hydrocarbonate potassium-sodium waters were formed with a minimum amount of calcium. With each step (an increase of mass ratio R/W) simulating the infiltration meteoric water flow, there was a consistent increase in the content of elements and variations of their migration forms.

According to the results of the “granite-water” system modeling analysis, there is a very wide range of rare and other elements in the water caused by the chemical composition of granite. Based on their physical and chemical parameters (ionic potential and electronegativity [20]), we selected elements that form mainly simple free cations (ionic potential < 2, electronegativity < 600 kJ/mol): Na⁺, K⁺, Rb⁺, Cs⁺.
Ca$^{2+}$, Sr$^{2+}$, Ba$^{2+}$, and Pb$^{2+}$, which can intensively accumulate in liquid phase when the solution is concentrated. They can migrate readily and selectively form well-soluble compounds with water anions. In the absence of sufficient concentrations of addends in the water, these elements, being typical hydrolysates, can form hydroxyl compounds, and with increasing concentrations of addends – displace OH$^-$ ions from the coordination sphere of elements.

The complexing elements were determined (ionic potential of 2–10, electronegativity of 600–1100 kJ/mol), which are present in significant quantities in the simulated system: Mg$^{2+}$, Y$^{3+}$, Zn$^{2+}$, Th$^{4+}$, Co$^{3+}$, Nd$^{3+}$, Ni$^{2+}$, BeOH$^+$, TIOH, YOH$^-$, ZnOH$^-$, NiOH$^-$, Pb(OH)$^-$, PbOH$^-$, LaCO$_3^-$, CeCO$_3^-$, Cu(CO$_3$)$_2$$^{2-}$, DyCO$_3^-$, ErCO$_3^-$, EuCO$_3^-$, GdCO$_3^-$, HoCO$_3^-$, LuCO$_3^-$, NdCO$_3^-$, PrCO$_3^-$, SmCO$_3^-$, SrCO$_3^-$, TbCO$_3^-$, TmCO$_3^-$, and YbCO$_3^-$.

These are characterized by the low solubility of hydroxyl compounds but are capable of forming highly soluble complexes. For example, rare-earth elements (REE) in simulated water are mainly connected with the formation of fairly stable carbonate complexes. Since the concentrations of CO$_3^{2-}$-ions in the system gradually increase with increasing pH, an increase in simple carbonate complexes is observed in the water under study. Nevertheless, in the example of thorium, which is characterized by a close correlation with REE due to both hypogenic paragenesis of REE-Th and the close forms of occurrence of these elements in natural water, it is clear that thorium migration is in Th$^{4+}$ form, which may indicate a lack of sufficient concentrations of addends in the studied system.

Anionic elements with the ability to form anions with oxygen in water solutions (ionic potential $>$10, electronegativity $>$ 1100 kJ/mol) were identified: ScO$_2^-$, GaO$_2^-$, Ga$^+$, CrO$_2^-$, HCrO$_4^-$, YO$_2^-$, ZrO$_2^-$, CO$_3^{2-}$, UO$_2^{2+}$, MnO$_2^-$, SeO$_4^{2-}$, WO$_4^{2-}$, NbO$_5^-$, HBeO$_2^-$, H$_2$VO$_4^-$, HVO$_4^-$, HZrO$_4^-$, HHF$^-$, HAsO$_4^{2-}$, H$_2$AsO$_4^-$, HSO$_3^-$, SnO, HSnO$_2^-$, H$_2$SiO$_4^-$, and HSiO$_3^-$ – oxyanions. It is noteworthy that in the modeled "granite-water" system SbO$_3^-$ is not formed in significant quantities and is transformed into antimony acid HSbO$_3^-$ according to the equation of potential-charging reaction SbO$_3^-$ → H$^+$ + SbO$_4^{2-}$. But with increasing water alkalinity (Eh = 0.843–0.697; pH = 6.32–8.80) SbO$_3^-$ can acquire significant amounts in them. Also, tungsten, a typical anionic substance, forms the compound WO$_2^{2-}$, which has low solubility. In the presence of other elements (Mn, Pb, Cu, etc.) WO$_2^{2-}$ can precipitate as tungstate. But, the degree of dissociation of tungstic acid increases with increasing water alkalinity, so with increasing pH, there is a rise in tungsten content in the solution. Uranium forms a complex cation UO$_2^{2+}$ with strong covalent bonding in the modeled system too, which also indicates the possibility of uranium accumulation in the studied water and its strong migration ability.

Such elements as Fe, Al, and Mg are immobile in slightly alkaline solution, so there is no sharp accumulation of them, but these components create new mineral phases. Almost immediately, at minimum R/W mass ratios, the studied water is in equilibrium with montmorillonite, which indicates the development of montmorillonite group clays in the weathering zone of granites. Montmorillonites have a maximum sorption capacity and control the content of chemical elements in the water.

4. Conclusions
Based on physical and chemical modeling of the dissolution process of rock-forming minerals in the "granite-water" system, calculation of equilibrium forms of element migration, and analysis of their physical and chemical parameters, it was shown that the transfer and accumulation of metals in coals and the weathering crust of granites in the framing of the Rakovka depression depend on hydrogeochemical conditions and the duration of water-rock interaction and are defined by migration abilities of elements. Although the analysis of modeling results raised new questions related to the hypergenic transformations of rocks and water in the "water-granite" system, which require further study, the obtained data may indicate in favor of the assumption that the studied leucocratic granites of the pre-Cenozoic basement could be a source of metals concentrated in the coals of the Rakovka depression.

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Acknowledgments
The reported study was funded by RFBR and NSFC, project number 21-55-53013.