ANNOTATION

Dissertation for the degree of Doctor of Philosophy PhD in the educational program 8D07201 - "Geology and exploration of mineral deposits"

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STUDY OF DISTRIBUTION PATTERNS OF IMPURITIES-ELEMENTS IN COALS AND CLAY ROCKS DEPOSITS OF THE JURASSIC PERIOD OF KAZAKHSTAN

The relevance of the work. The coal industry is one of the most important resource sectors of the Republic of Kazakhstan. In terms of coal reserves, Kazakhstan is among the top ten leading countries. According to the Concept of the development of the fuel and energy complex of the Republic of Kazakhstan until 2030 and the transition to a "green economy", the expansion of the use of coal should give a powerful impetus to the research and development of environmentally friendly technologies for the extraction and combustion of coal, as well as its processing. In recent years, due to the constant increase in oil prices, the reduction of its reserves, high costs for the exploration of new fields in many countries of the world, intensive work continues to be carried out to advance and improve the indicators of individual stages of the deep coal processing. This involves considering coal as a potential source of rare, valuable and precious metals.

Currently, coal deposits in the world are already considered as sources of a large group of rare elements and precious metals (SeredinShpirt, 1995; Hower, 1999; Arbuzov, Ershov 2007; Arbuzov, 2006; Dai et al. 2006, 2008, 2010a, 2010b, 2012, 2016; Wang, 2008, 2009; Sun et al. 2010; Seredin-2004, 2012; Eskenazy, Stefanova, 2007, etc.). In some countries (USA, China, Russia, etc.), the rare metal potential of coal is partially estimated, these metals are contained in organic matter, where coal waste may contain increased concentrations of impurity elements, in some cases this indicator reaches theindustrial concentration.

Numerous works of foreign scientistspresent data on impurity elements contained in coal and coal ash that reach industrial values (Yurovskiy, 1968; Leonov et al., 1988; Yudovich, 2006; Arbuzov 2008, 2014, 2019, 2021, 2022; Dai et al. 2010, 2014, 2019, 2021; Hower 2015, 2016). This topic is especially relevant for countries with a high level of coal production and large coal resources, such as China, Russia, the USA, Australia and others. The germanium-bearing capacity of brown coal deposits has been most well studied, since currently only germanium is extracted from coals along the way. Deposits of this type are being developed in China and on the territory of Russia in the Primorsky Territory. In China, Li and Ga are also extracted on an industrial scale (Dai et al., 2015, Finkelman, 2018). Rare earth elements play an important role in the economy of various countries, in particular in rapidly developing innovative industries (SamsonovN.Yu., 2014;

Kondratiev V.B., 2017; Gasanov A.A., 2018; Fortier S.M., 2017; Wall S., 2017; Yushina T.I. et al., 2015).

For most coal deposits in Kazakhstan, there are no reliable estimates of the average content of impurity elements in them. Fundamental generalizing works of the last quarter of the last century (Kuznetsov et al., 1963; Timofeyev et al., 2000), a series of methodological recommendations on the evaluation of associated components are devoted to these objects. These works are the basis for an analytical review of the metallicity of coals.

Due to the growing demand and scale of coal mining, there is a need to assess the content of impurity elements in coal, coal ash and clay rocks of deposits of the Jurassic age of Kazakhstan, which is of great interest from the point of view of obtaining geological and genetic information about the accumulation of valuable and precious metals, the mechanisms of their concentration, the forms of their location.

Jurassic coal deposits in Kazakhstan are among the largest and most significant, having a low ash content and shallow occurrence. The genetic features of coals are related to their origin, composition and geological processes that occurred during their formation.

The idea of the work: to establish the conditions for the accumulation of coal-bearing deposits, to determine the geochemical features of coal deposits of the Jurassic period of Kazakhstan, in order to identify increased concentrations of impurity elements and determine the nature of their accumulation.

The purpose of the dissertation is to study the regularities of the distribution of impurity elements, to establish the conditions and nature of their accumulation in coal and clay rocks of deposits of the Jurassic period of Kazakhstan.

Research objectives:

1. To study the geodynamic situation of coal formation in the Jurassic deposits of Kazakhstan (Karazhyra, Shubarkol and Maikubecoal basin)

2. To study the biogeochemical situation of the Jurassic coal-bearing strata on the example of the Shubarkol deposit;

3. To assess the content of impurity elements in coal, to identify patterns of their distribution in coal seams and clay rocks;

4. To study the influence of the nanostructure of coals on the formation of anomalies of rare earth metals in them;

5. To substantiate the nature of the accumulation of rare, including rare-earth elements in coal and clay rocks of deposits and to study the forms of the presence of impurity elements in coal.

The objects of the study are the Jurassic coal-bearing deposits of the Karazhyra deposits (East Kazakhstan), Shubarkol and the Maikube basin (Shoptykol, Sarykol, Taldykol) - Central Kazakhstan.

The subject of the study is the elemental and mineral composition of coals and clay rocks included in the coals.

Factual material and research methods. The work is based on the results of studies of 107 samples of coal and carbon–containing rocks of the Shubarkol deposit, selected by the staff of the Geoecology and Geochemistry Department of

Tomsk Polytechnic University with the direct participation of the author of the work; 20 samples of coal and carbon-containing rocks selected by the author at the Karazhyra deposit; 20 samples of coal selected at the Maikube basin (Shoptykol); 5 samples of coal – Sarykol; 5 coal samples –Taldykol, as well as stock materials of geological reports.For quantitative analysis for rare earth, noble and other elements, a modern highly sensitive neutron activation analysis (INAA) with thermal neutron irradiation was used at the IRT-T research nuclear reactor of the Institute of Nuclear Physics in the Laboratory of Nuclear Geochemical Research Methods of Tomsk Polytechnic University. Analytical studies were performed for the coals of the Shubarkol deposit using the ICP AS and ICP MS method at the scientific and Analytical center of the Far Eastern Geological Institute of the Far Eastern Branch of the Russian Academy of Sciences, Vladivostok.

Scientific novelty:

1. It has been established that the coal-bearing sediments of the deposits (Karazhyra, Shubarkol and Maykube basin) belong to a single Jurassic coalbearing sedimentary formation, are characterized by a similar lithological composition, zoning of lake-type facies, continental outlook of coarse-grained sediments, formed in inherited depressions and sags of the Hercynian platform basement, represented by metamorphosed Paleozoic rocks.

2. The biogeochemical conditions of carbon formation at the Shubarkol deposit were studied for the first time and two types of coal reduction (lithofacial and floristic) were identified.

3. The regularities of enrichment with elements-impurities of coal deposits of Shubarkol (Sc, V, Co, Y, Zr, Hf, Mo, Ag and individual lanthanides), Karazhyra (Sc, Co, Sr, Au) and the Maykube basin (Sc, Co, Sr, REE) are established, in which rocks of the demolition areaof the basic and acidic compositions play an important role; increased concentrations in clay rocks, in part, are consistent with the geochemical specialization of the coals of the studied deposits; the mechanisms of REE formation in non–oxidized coals are their adsorption and replacement of vacancies in the surface nanolayer, as well as in oxidized coals - a hydrogenic mechanism of concentration, which is confirmed by the identified mineral forms of REE.

Protected scientific provisions.

1. The genetic features of the Jurassic coal-bearing deposits of the studied deposits are related to their origin, lithological composition, geological and geodynamic processes that arose at the stage of their formation.

2. The use of diffuse reflection infrared spectroscopy with Fourier transform (DRIFTS) with the processing of the IR spectrum by the SCAUF program for the determination of structural and genetic parameters in coal seams together with geochemical analysis made it possible for the first time to study the biogeochemical situation of carbon formation at the Shubarkol deposit.

3. The accumulation of abnormal concentrations of impurity elements is mainly due to the peculiarities of the rocks of the basic and acidic compositions of the field demolition area. Coals and clay rocks of deposits of Jurassic age are enriched with a large group of valuable, rare and noble elements-impurities (Sc, Co, Zr, Hf, Au, Sr and REE). Comparative analysis of the formation of the thickness of the surface layer and the surface energy of the Jurassic coal deposits, indicating that the mechanism of accumulation of increased concentrations of REE and uranium is their adsorption and replacement of vacancies in the surface nanolsyer formed during relaxation and reconstruction of coal monolayers.

Practical significance.

Knowledge of the genetic and geochemical specialization of Jurassic age coals is the basis for the organization of predictive prospecting work, both within the coal-bearing deposits and in the structures of their framing.

The assessment of the accumulation of impurity elements is due to the possibility of using coal not only as an energy fuel, but also as a source of alternative production of semi-cokes and medium-temperature cokes.

The research results were implemented in "Azimut Geology" LLP and "Shubarkol Premium" JSC, and in the educational process, during lectures and practical classes, at the Department of Geology and Exploration of Mineral Deposits, Abylkas Saginov Karaganda Technical University NPJSC.

The final result of the research is the established biogeochemical situation of the coal-bearing deposits of the Shubarkol deposit, which shows the change of paleoclimatic conditions at the stage of sedimentation; patterns of distribution of impurity elements in coal and clay rocks of the Jurassic deposits of the Eastern (Karazhyra) and Central (Shubarkol and Maykube basin) of Kazakhstan; the nature of the accumulation of increased concentrations of impurity elements in coal and the form of REE in coals.

The author's personal contribution consisted in collecting, processing, systematization, generalization and interpretation of actual and stock materials; conducting field work with sampling for analytical studies of impurity elements; conducting laboratory studies on a scanning electron microscope to identify mineral forms of REE; substantiating the relevance of research work; studying the geochemical features of the distribution of rare and precious metals; establishing regularities of distribution of impurity elements in coal and clay rocks and substantiating the nature of their accumulation.

Approbation of work and publications. The main provisions of the dissertation work were reported at:

- seminars of the "Geology and Exploration of Mineral Deposits" Department of the Abylkas Saginov Karaganda Technical University;

- at the "Geoecology and Geochemistry" Department in the IISEC "Uranium Geology" of Tomsk Polytechnic University;

- at international conferences: Scientific Collection with the Proceedings of the 3rd International Scientific and Practical Conference "Recent Scientific Investigation", Oslo, 2021;

- at the 25-th International Scientific Symposium of Students and Young Scientists named after Academician M.A.Ussov "Problems of geology and subsoil development", Tomsk, 2021;

- 17-th International Forum-Contest of Students and Young Researchers "Topical Issues of Rational Use of Natural Resources", Saint Petersburg, 2021; - at the 8-th International Scientific and Practical Conference "SCIENCE AND EDUCATION IN the MODERN WORLD: CHALLENGES OF THE XXI century", Nur-Sultan, 2020;

- in the proceedings of the international scientific and practical conference "Integration of science, education and production – the basis for the implementation of the National Plan" (Saginovsky Readings No. 13), dedicated to the 30^{th} anniversary of independence of the Republic of Kazakhstan, Karaganda, 2022.

A scientific internship was completed in the period from May 22 to June 06, 2022 at the of "Geoecology and Geochemistry "Department at the IISEC "Uranium Geology" of Tomsk Polytechnic University, during which analyses of the study of impurity elements in coal were carried out, mineral forms of finding were studied and advice on the topic of the dissertation was provided by the Doctor of Medical Sciences, Professor Arbuzov S.I.

The main provisions of the dissertation work have been published in 14 scientific papers, 2 of which are in publications recommended by the Committee for Quality Assurance in Science and Higher Education of the Republic of Kazakhstan; 5 – in the proceedings of national and international conferences; 4 – articles included in the Scopus database, 2 Eurasian invention patents and 1 invention patent of the Republic of Kazakhstan.

Structure and scope of the dissertation: The dissertation is presented on 122 pages and consists of an introduction, three chapters, a conclusion and a list of sources used, including 146 titles. The dissertation work is illustrated with 37 figures and 23 tables.

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