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# **Geochemical and thermodynamic factors of high-dispersed mineral formation in the fluidization zones**

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## **Abstract**

The study aims to investigate geochemical and thermodynamic factors of high-dispersed mineral formation in the fluidization zones via comparative qualitative research methods. As a result, when local cavitation anomalies with very high thermodynamic differences occur, the appearance of diamond nanocrystals seems quite probable in the process of opening of the releasable sources. In conclusion, the development of the reverse explosion effect, nanocrystals of non-ferrous, rare and noble metals may be formed, which form previously unknown associations of industrially significant sources of ore and non-metallic mineral matter.

**Keywords:** Coal, Seams, Fluidization, Dispersed, Minerals.

# Factores geoquímicos y termodinámicos de la formación de minerales altamente dispersos en las zonas de fluidización

## Resumen

El estudio tiene como objetivo investigar los factores geoquímicos y termodinámicos de la formación de minerales altamente dispersos en las zonas de fluidización a través de métodos comparativos de investigación cualitativa. Como resultado, cuando se producen anomalías de cavitación local con diferencias termodinámicas muy altas, la aparición de nanocristales de diamantes parece bastante probable en el proceso de apertura de las fuentes liberables. En conclusión, el desarrollo del efecto de explosión inversa puede formar nanocristales de metales no ferrosos, raros y nobles, que forman asociaciones previamente desconocidas de fuentes industrialmente significativas de mineral y materia mineral no metálica.

**Palabras clave:** Carbón, Costuras, Fluidización, Dispersado, Minerales.

## 1. INTRODUCTION

In the modern system of Earth sciences, one of the promising directions in the development of applied geology is the study of the formation processes and the prospects for the practical use of highly dispersed associations of minerals of carbon, silica, non-ferrous, rare and noble metals formed in tectonically disturbed zones of coal seams under the influence of deep mineral-forming solutions. The relevance of these studies is determined, first of all, by the need for a

comprehensive development of geological resources of the subsoil of coal-bearing basins, containing not only multi-billion reserves of fossil coal but also a significant number of ore and non-metallic types of mineral raw materials, which are of both theoretical and practical interest from the point of view of revealing the nature and mechanism the formation of highly dispersed mineral associations, as well as with the aim of developing new methods of mining within coal deposits and with Creation of effective technologies for extracting various impurity elements from them (NEZHENSKY, 2013).

The need to address these issues is determined by the fact that in many cases highly dispersed mineral associations contain nano-dispersed crystalline formations, that is, two-dimensional aggregates of non-ferrous, rare and noble metals that are practically not diagnosed by conventional widespread optical research methods. There is an obvious discrepancy between the results of litho-geochemical spectral analyzes, which show high concentrations of such metals in the fluidization zones of coal seams, and the confirmation of their presence in conventional optical studies (BULATOV, 2011).

Preliminary results obtained in the process of autoclave research methods show that such a discrepancy can be eliminated by revealing the special conditions for the formation of these nanocrystals of ore elements. Since these issues are still insufficiently studied, we attempted to consider the relationship between tectonic disturbance of coal seams, thermobaric geochemistry parameters of fluidization zones and crystallization mechanisms of highly dispersed mineral individuals, to demonstrate the possibility of discovering new similar

non-traditional types of ore and non-metallic mineral raw materials (KISELSTEIN, 2006).

## **2. METHODOLOGY**

Physical and chemical conditions of formation of highly dispersed mineral associations in the zones of fluidization of coal seams at the first and second stages are confirmed by the results of our conducted thermobaric geochemistry studies based on the methods of vacuum decryptometry and gas chromatography with the use of original installations such as VD-5 and LHM-8MD. In particular, it has been established that these processes took place in a mode of complex change of thermodynamic parameters of mineral-forming fluid systems, as evidenced by the dynamics of gas separation processes, characterized by several decryption effects in the temperature ranges of 90-120, 180-220, 300-350, 375-425 and 500-6000 C, with changes in F-indicator of fluid activity from 200-250 to 500-600 conventional units (NASEDKINA, 2009).

According to gas chromatographic studies, in the composition of mineral and ore-forming fluids in the first stages, there are reduced gases, among which nitrogen, hydrogen, methane, and its homologs predominate. At subsequent stages, with a gradual decrease in thermodynamic parameters, an increase in the relative amount of oxidized fluids, such as H<sub>2</sub>O, CO<sub>2</sub>, SO<sub>2</sub>, and other oxidizing gases, is observed. In this case, the vertical temperature and baric zonality are

distinguished, which confirms the existence of the thermodynamic barriers noted above, which play a decisive role in the formation of highly dispersed mineral associations and are an additional search criterion for the discovery of deep sources of mineral raw materials.

Of particular interest is the consideration of the genetic features of the formation of highly dispersed associations of minerals of carbon, silica, non-ferrous, rare and noble metals directly in the outburst foci of coal seams. According to the results of previous studies, it was found that sudden emissions of coal, rocks, and gas, as a rule, occur in the zones of fluidization of fossil coals, while the outburst foci themselves have a rather complex internal structure (RYBIN, 2017).

In such foci, a peripheral reservation zone stands out, composed of quartz-carbon metasomatized and the central part, represented by the so-called sponge coal, which is intensely fragmented, dispersed, saturated with numerous fluid inclusions, which determines its porous and micro-globular structure.

In the peripheral zone, finely dispersed aggregates of silica and graphitized carbon are noted, which have a formation temperature of about 500-6000 C and a thickness of up to 1.5-2 m, which are practically impermeable to volatile components and actually determine the possibility of accumulation of a large number of mobile components in the central parts of outlying hazardous foci and elements of impurities. So, for example, the content of volatile components in sponge coal reaches 500-600 m<sup>3</sup> per ton of coal, and in

some cases exceeds these values. The content of non-ferrous, rare and noble metals can reach 16.0 g / t (YUDOVICH, 2006).

To simulate the processes of formation of finely dispersed associations of minerals at significant temperature and pressure differences, we performed experiments using the BAR-1 autoclave unit, which is a closed-type autoclave device consisting of a reaction chamber, a bar-gradient divider with Laval nozzles, a vacuum crystallization chamber, and vacuum systems, as well as a heating element and a complex of measuring equipment (TRUFANOV & HYDROCARBON, 2004).

In the course of the experiment, the initial substance under study in the amount of 25 g was crushed to the fraction of 0.5-1 mm, placed in the reaction chamber and filled with 2/3 of distilled water, then the chamber was closed by a locking copper membrane. Baro gradient divider and crystallization chamber were evacuated with the help of a vacuum system up to the value of  $2 \cdot 10^{-2}$  mm Hg, after which the autoclave was heated up to the temperature of 5000 C for 2 hours (TRUFANOV, 2008).

Subsequently, the locking membrane was automatically opened and the reaction mixture formed was released into the next chamber, where, when passing through the Laval nozzles, high temperature and pressure differences occurred, simulating the natural processes of instant destruction of coal seams and host rocks. The reaction mixture was thrown into a vacuum crystallization chamber equipped with trapping membranes, on which crystallization products of finely dispersed minerals were deposited. The resulting material was

subsequently studied using optical, x-ray structural, spectral, electrophysical and other research methods (KHRUSTALEVA, 2007).

### **3. RESULTS AND DISCUSSIONS**

Analysis of the experimental results showed that on the surface of the membranes, as well as along the opening cracks, there are silver-gray crystalline neoplasms of the columnar, spear-like and tabular appearance. Numerous crystals of a rhombic and tetragonal shape with well-defined faces and brilliant luster were also found here, translucent from dark cherry to black. Further studies using a Camebax scanning electron microscope showed that the crystalline phase corresponds to rutile or anatase in chemical composition.

The study of crystallographic forms of separation of carbon, silica and ore minerals in emission-hazardous foci shows that coal substance here is characterized by the almost complete absence of aliphatic structures and predominant development of block six-carbon nuclei with separate graphitized areas.

When such foci are opened by underground mine workings and the rock pressure is relieved, the mechanism of fluid inclusions destruction is started according to the scheme of microexplosive processes development, which additionally destroy the structure of both organic matter and inorganic mineral substrate, sharply change the physical and mechanical properties of the matrix, increase the content of volatile components and transfer the whole system of coal-

rock-fluid to a metastable state. In the future, such a system begins to disintegrate into atomic-molecular compounds in the conditions of reverse explosion with the formation of nanocrystals of gold, lead, zinc, copper and other metals, which indicates the possibility of developing a new, fundamentally different from the traditional, method of extraction of these elements.

Studies of the processes of the formation of highly dispersed minerals in the centers of sudden emissions of coal, rocks, and gases reveal several poorly studied processes and phenomena that accompany these dangerous gas-dynamic phenomena. One such mystery is the formation of so-called grey coal. This is a sign of the approaching emission-hazardous situation, which is well known to miners, consisting in the fact that the surface of the coal fragments becomes matte-silver as if covered by the thinnest film of unknown origin. Our studies have shown that according to a number of features such a film can be a two-dimensional carbon - graphene, which is formed in the local zones of fluidized coal seams in the formation of a situation of reverse explosion, when a short-term state of deep vacuum occurs in the source of release, which leads to partial evaporation of carbon from the surface of coal fragments, changes in its molecular structure and subsequent deposition in the form of a silver-matt deposit.

Another, as yet poorly studied, phenomenon is the formation of the so-called sugar-like quartz, which is a finely dispersed aggregate consisting of micron-sized quartz grains, whale and coesite, polymorphic modifications of silica, which from above temperatures  $\alpha$

$\beta$  transformations of SiO<sub>2</sub> and which may occur during the sudden release of coal, rocks, and gas, if the coal seam or host rocks contained free silica. Significantly, such sugar-like quartz is dumb about the effects of gas evolution recorded during vacuum-decryptometric studies. In other words, its formation occurs at very high energy parameters, eliminating the possibility of trapping conventional gas-liquid inclusions.

In contrast to the usual autoclave modeling of the processes of transformation of matter, the results of our autoclave modeling show that the occurrence of such high temperatures and pressures is possible only in the case of the development of the effect of reverse explosion because this process is accompanied by the formation of the so-called shock waves with very high velocities of fluid movement.

According to the calculations, it was found that in some cases, with a flow velocity of 3-4 Move, the pressure can increase to 10-15 thousand atmospheres, and the temperature can reach 800-10000 C.

Finally, another mysterious phenomenon is the so-called rabid flour, which is an ejection of highly dispersed mass, consisting mainly of microcrystals of carbon, as well as the formation of a completely unusual fibrous carbon, which by its nature is actually not even two-dimensional, but one-dimensional nuclear carbon formation. This emission occurs already with the development of sudden destruction of the coal seam and it is not possible to explain it by simple mechanical destruction. It is quite obvious that the emergence of such a finely dispersed mass, the amount of which sometimes reaches impressive volumes and which clogs many-meter underground workings (which,

in fact, is one of the main reasons for the death of miners), is possible only on the basis of the decay of the initial coal-rock-fluid system into atomic -molecular groups. In this case, complex fluctuations of the thermodynamic parameters of the system occur, accompanied by thermobaric drops and cavitation effects, causing corresponding changes in the structure of the formed minerals.

It is quite likely that these processes are related to the recently discovered nanocrystals of diamond in coal deposits, the origin of which remains highly controversial at present. Concerning the mechanism of formation of highly dispersed mineral associations under conditions of a reverse explosion, considered by us, when local cavitation anomalies with very high thermodynamic differences occur, the appearance of diamond nanocrystals seems quite probable in the process of opening of the releasable sources.

#### **4. CONCLUSION**

Thus, the results of the researches testify to the wide development of geochemical processes of formation of highly dispersed mineral associations in the zones of coal bed fluidization under the influence of deep mineral-forming solutions penetrating the zones of tectonic disturbances. These processes can significantly differ depending on the specific stages of formation of coal deposits, the degree of their coalification and the geological and structural features of localization of areas of development processes of hydrothermal

metasomatic transformation of fossil coals and host rocks, which are characterized by abnormally high concentrations of ore elements.

Three most real cases of development of such processes are considered: at the stage of formation of tectonic cracks and occurrence of a system of high temperature and pressure differences up to deep vacuum, at the subsequent penetration of deep mineral and ore-forming fluids through tectonic zones with clearly expressed processes of hydrothermal-metasomatic formation of the containing rocks, and finally in the conditions of formation and unraveling of sudden emissions of coal, rocks and gas in relatively local emission-hazardous zones of coal beds.

Based on the results of thermo-baro-geochemical studies specific temperature and basic conditions of the processes of discrete highly dispersive mineral formation, which differ in a wide range of temperatures - from 90-120 to 500-6000 C and pressures from 200-300 to 800-1000 atm, with wide variations in the aggregate state and composition of deep mineral-forming fluids. It is shown that under certain conditions, namely, the development of the reverse explosion effect, nanocrystals of non-ferrous, rare and noble metals may be formed, which form previously unknown associations of industrially significant sources of ore and non-metallic mineral matter. Vertical and horizontal zoning of formation of such highly dispersed associations of ore and nonmetallic minerals, connected with the existence of thermodynamic barriers to their optimal crystallization, has been established, which predetermines the possibility of detecting

unknown sources of new types of minerals and complex development of resources of the subsoil of coal-bearing basins.

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