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Earth sciences

Mathematical model of the formation of barite-lead mineralization of the Ushkatyn III deposit (Central Kazakhstan)

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ABSTRACT

The genesis of stratiform deposits of lead and barite in sedimentary rocks is of great interest from the point of view of replenishing reserves of polymetallic ores. The aim of the work is to establish the regularity of the hydrogenic formation of ores in limestones, taking into account the influence of the nanosurface of pores and cracks based on a mathematical model of the movement and characteristics of ore-bearing solutions in the pores. The thicknesses of the surface layer of limestones and minerals included in the ore-containing strata and sulfide minerals are calculated. The results indicate that they are nanostructures with special physical properties different from the rest of the substance, which is confirmed by the regularity of the formation of a heavy sulfur isotope in ores of various textural types. The influence of hydrotherms with different densities, kinematic viscosity, and velocity on the intensity of mineralization formation in cracks and pores of limestone, as well as the occurrence of new feathering cracks around the fractures of dismemberment, is estimated. The dependence of the hydrothermal flow density on the diffusion of the liquid is established. The equation of kinematic viscosity is derived from the pressure in the solution flow, the velocity of its movement, the mass of particles of ore-forming elements, and sulfur isotopes under thermodynamic conditions of determined Gibbs energies. The relationship of the viscosity of the solution with the surface tension of the nanolayer of limestone particles in cracks and pores is shown, indicating that the greater this energy, the greater the velocity of movement of ore-forming solutions, the fewer branches of newly formed cracks around the dissection crack. The mathematical model is applicable for the numerical analysis of the regularity of mineralization in cracks, taking into account the influence of the nanostructural layer of cracks and pores of limestone in the thermodynamic conditions of the occurrence of an ore-bearing formation.

Keywords: Ushkatyn III, stratiform deposits, Atasu type, isotopic composition, mathematical model

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Introduction

A large number of works have been dealing with the genesis of barite, lead, and zinc deposits in sedimentary complexes and areas, and the participation of generating hydrothermal systems in their formation (Kislyakov and Shchetochkin, 2000; Hanor, 2000; Robb, 2005; Hein et al., 2007; Wilkinson, 2014; Elswick and Maynard, 2014; Emsbo et al., 2016; Cansu and Ozturk, 2020; Smirnov, 1970; Baibatsha, 2012).

The main hypotheses regarding the genesis of barite lead-and-zinc deposits of the Atasu ore district and the Uspenskaya shear zone are described in a lot of works (Shcherba, 1964, 1967; Rozhnov, 1967, 1982; Kayupova, 1974; Buzmakov et al., 1975; Mitryaeva, 1979; Weimarn, 1982; Kalinin, 1982, 1985; Kalinin et al., 1984; Skripchenko, 1989; Varentsov et al., 1993).

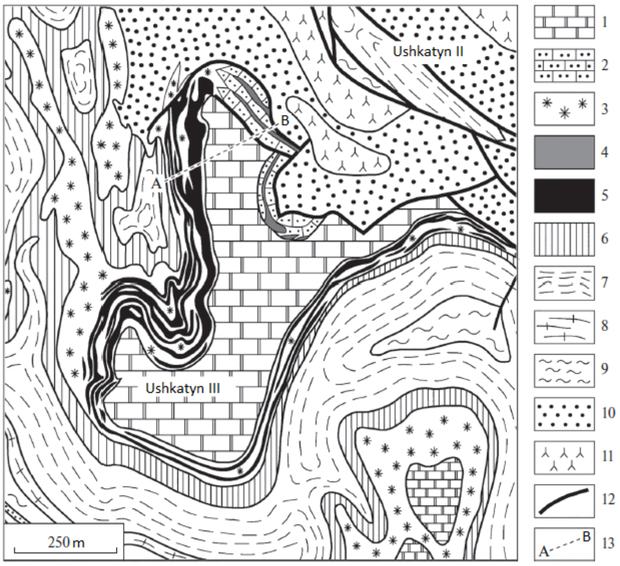

Figure 1 – Geological map of the Ushkatyn ore field (with simplifications).
1 – grey organogenic-detritus limestones, wavy-layered (C_1t_1); 2–5 – the pack is red-colored (D_3fm_2b):
2 – riphogenic organogenic-algal limestones,
3 – organogenic-detrital thin-layered limestones,
4 – barite-lead ores, 5 – ron and manganese ores;
6 – the pack is gray-colored (D_3fm_2a): organogenic-detrital lenticular-layered limestones;
7 – the pack is flishoid (D_3fm_1): rhythmic alternation of organogenic-detrital limestones, calcareous sandstones, and carbonaceous clay-siliceous-carbonate pelites;
8 – the pack is rhythmically layered (D_3fm_1): alternation of clay-siliceous-carbonate rocks with massive and ribbon-layered texture;
9 – the pack is intemperately layered (D_3fm_1): siliceous limestones, clay-carbonate rocks, shell rocks;
10 – The Darya formation (D_3fr): polymictic siltstones and sandstones;
11 – trachyriolites; 12 – faults.

The aim of this work is to study the regularities of the surface nanolayer of cracks and pores of ore-bearing limestones' effect on the formation of mineralization, taking into account textural factors and physical characteristics of aqueous solutions of hydrotherms.

The Ushkatyn III deposit was discovered in 1963 by V.Ya. Sereda when checking gravity anomalies identified by the Agadyr GRE.

Stratiform ore deposits are complex: iron-manganese and barite-lead bodies located on the wings of brachyform and box-like synclines lie in the section together with the enclosing deep-sea deposits of the Lower and Middle Famenian, participating in complex folding (Figure 1) [1].

They were formed in the active zone of seabed extension of the paleoriftogenic basin, along stepped normal faults and flexure-like bends, in the area of transition of deep-water Famennian facies to shallow-water facies.

A.N. Brusnitsyn [2] proposed a model of the formation of the Ushkatyn III deposit, in which barite-galena, iron, and manganese ores are the products of the development of a single hydrothermal system that developed in a thick sedimentary stratum. Barite-galena ores were formed near the surface of the seabed during the discharge of hydrothermal solutions in the inner zones of the still-forming reef. The ore matter deposited in the mixing area of hydrothermal solutions bearing Ba, Pb, Zn, Fe, Mn, and other elements filled the porous and fissure space of the reef, where the bacterial reduction of the sulfate ion of seawater to hydrogen sulfide took place. When hydrothermal fluid seeped through the reef, Ba and Pb deposited in it in the form of barite and galena, while Zn, Fe, and Mn remained in solution, which subsequently precipitated in the oxide form: Fe on the surface of the reef or at some distance from it, and Mn at a considerable distance. Zinc dissipated in the surrounding space without forming ore accumulations [3].

Iron and manganese, barite-galena ores of the Ushkatyn III ore deposit were formed as hydrothermal, superimposed on sedimentary rocks, simultaneously but in different parts of the sea basin [[4], [5]]. Thus, barite-galena ores are identified inside the carbonate structures of the coastal reef, while iron and manganese ores are identified on the bottom surface at some distance from the coast [6].

The difference between barite-galena ores of the Ushkatyn III deposit and other deposits is their low zinc content (Zn: Pb from 1:50 to 1:3000). The enclosing rocks of the barite-galena deposit are reef organogenic-algal limestones with the pronounced rhythmically banded structure, the average size of ore minerals is 20–30 µm, less often 100–500 µm [3].

Gray limestones are composed of a homogeneous mass of microgranular calcite (micrite), in which rounded or elongated lumpy-clotty segregations 0.1-0.2 mm in size are observed.

The texture of these limestones is massive, indistinctly layered, and lenticular-layered, caused by layers of siltstone [6]. Red and greenish-gray limestones contain tiny inclusions of hematite and siltstone with a large number of micropores.

The microgranular structure of limestones and good preservation of relics of microorganisms indicate the absence of the metamorphism effect.

The texture of ores is as follows: layered-banded, nest-like-latticed and continuous spotty, less often brecciated, breccia and vein textures. Barite, galena, and other minerals in banded textures develop along silty layers in limestones, filling the pore space. In the silty layers, there is a partial dissolution of calcite with rare formation of flattened-elongated caverns filled with ore minerals [7]. In all the textural varieties of ores, fine-grained structures predominate, with complex, not always unambiguously interpreted age relationships between minerals.

In works [[3], [6]], there are given the values of $\delta^{34}S$ in sulfide concentrate, which consists mainly of galena, the concentration of the "heavy" isotope varies from –25.7 to –12.6‰, and in barite, from 10.9 to 15.3‰ (Table 1). According to these data there has been built a dependency (Figure 2). Ore minerals are characterized by a very different isotopic comsposition of sulfur: galena is enriched in the light isotope ^{32}S, and barite is enriched by the heavy isotope ^{34}S. In the modern ocean, the value of $\delta^{34}S$ averages 21‰ [6]; in the water of the Late Devonian ocean, this value was 25–30‰. This indicates the formation of barite with participation of isotopically heavy sulfur dissolved in seawater sulfate ions. Sulfides were formed with participation of hydrogen sulfide enriched in the light isotope ^{32}S, which was formed at the stage of early diagenesis of sediments in the course of bacterial sulfate reduction [[7], [8]]. The processes of separation of sulfur isotopes in sediments containing organic matter are described in the work [9].

In work [3], the main signs of barite-galena ores formation in near-surface conditions during the formation of reef deposits are defined: a narrow stratigraphic range and stratiform type of ore-bearing deposit (as well as confinement); connection of ore bodies with consed mentation faults, which is confirmed by the absence of veinlet and other mineralization in the areas of late tectonic faults; the formation of textures and structures of ores is characteristic of incompletely consolidated ore-bearing carbonates; the isotopic composition of sulfur, carbon, and oxygen is characteristic of the joint participation in the formation of barite, sulfides, and carbonates.

A feature of the sedimentary stratum structure of the Ushkatyn III deposit is the transition of coastal facies to shelf facies, with lateral zonality of deposits of the same age with the replacement of the reef complex enclosing barite-galena ores with a bed of layered limestones containing layers of iron and manganese ores [[5], [6]].

The uniform distribution of trace elements (and accordingly a lot of accessory minerals) in the groundmass of the rocks indicates their simultaneous accumulation with the formation of ore-bearing deposits [3].

As a result of these processes, the newly formed hydrogen sulfide concentrates predominantly the light ^{32}S isotope, while the residual sulfate ion concentrates the heavy ^{34}S one. In a closed system with respect to the marine sulfate ion (that is, the access of SO_4^{2-} to the sediment is limited), as it is exhausted in the pore solution, the $\delta^{34}S$ values of both residual sulfate and hydrogen sulfide increase. If the system is open, then the concentration of $\delta^{34}S$ sulfate changes little compared to seawater and the concentration of hydrogen sulfide decreases markedly. The difference δ^{34} – δ^{34} SHS can reach more than 40 ‰ [[9], [10], [11], [12]].

Experimental part

The results of determining the isotopic composition of sulfur in sulfides of ores, together with the isotope-geochemical characteristics of carbon and oxygen, made it possible for A.I. Brusnitsyn to develop models of the Ushkatyn III barite-galena deposit formation in the carbonate-reef structure [6]. Deposits of ore minerals occurred as a result of decreasing the temperature of hydrothermal solutions that entered the near-surface zones; increasing pH (due to oxygen dissolved in seawater); the appearance of SO^{2-} (in the composition of seawater); changes in the H_2S/HS^- ratio in pore water (during bacterial sulfate reduction). Barium and lead precipitated immediately upon the appearance of a sulfate ion in solutions and at very acidic concentrations of hydrogen sulfide and oxygen [[13], [14], [15]].

One of the additional reasons for the formation of mineralization in porous limestones, in the authors' opinion, is the nanostructure of the enclosing rock surface layer effect.

To study this, the results of studies are used that are reflected in the correlation field linking the concentration of $\delta^{34}S_{sulfide}$ with the ore textures of the Ushkatyn III deposit (Figure 2, Table 1), (the concentrations are given relative to the meteorite standard).

Table 1 – $\delta^{34}S_{sulfide}$ composition, %, in the galena of the Ushkatyn III deposit ores [2]

No.	layered-banded		nest-like-latticed		continuous spotty
	Ush 3-2	Ush 3-17	Ush 3-12	Ush 318-153	Ush 319-514
1	-16.7	-13.7	-22.5	-17.1	-25.7
2	-	-12.7	-16.1	-21.3	
3	-	-12.8	-17.4	-22.2	
4	-		-19.9	-20.8	
5			-19.0		

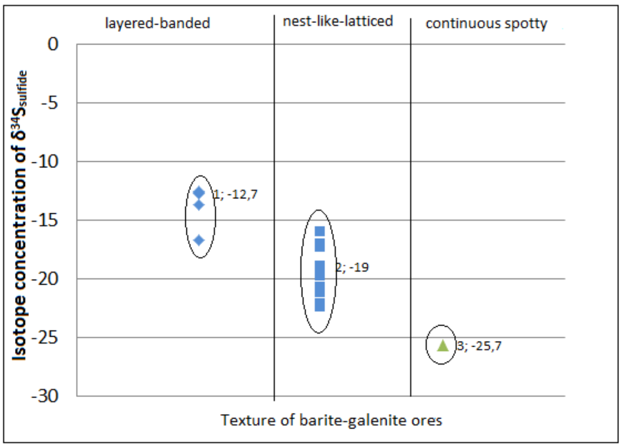

Figure 2 – Correlation fields of the $\delta^{34}S_{sulfide}$ concentration the texture of barite-galena ores of the Ushkatyn III deposit.

It can be seen in Table 1 that for the layered-banded texture, the values of $\delta^{34}S_{sulfide}$ range from -12.6 to -16.7; for nest-like-latticed texture from -16.2 to -22.2; and for continuous spotty it is -25.7.

Let us consider this pattern from the point of view of the nanostructured surface layer of porous and fractured limestones effect in which barite-lead mineralization is formed.

Classification of pores according to their radius is given in the work by M.N. Dubinin, 1980. These are macropores r > 100–200 nm; mesopores - 1.5-2.0 < r < 100-200 nm, micropores – r < 1.5-1.6. The latter are divided into ultramicropores r < 0.6-0.7 nm and supermicropores 0.6-0.7 < r < 1.5-1.6. Limestones are mainly represented by mesopores. Theoretically, in a layer consisting of one-dimensional spherical particles, the average pore size will be equal to the size of the empty space formed with a single-layer staggered arrangement of three spheres. In this case, the pore radius is $r = 0{,}154 \cdot d(I)$ = 30.6 nm, which corresponds to mesopores. Non-metamorphosed limestones have the highest specific surface area, and limestones with a medium degree of metamorphism have the smallest specific surface area. For the ideal case, spherical particles of the same diameter $d(I)$, specific surface area S_{sp}, are given by the expression:

$$S_{sp} = 6/\rho \cdot d(I) \qquad (1)$$

where ρ is the limestone density.

The concentrating of ore elements and $\delta^{34}S_{sulfide}$ in limestones is caused by the leading role of the hydrogenic mechanism. Regardless of the source of $\delta^{34}S_{sulfide}$ entering the basin, under conditions of the high specific surface area of limestones, ore elements, mainly lead and $\delta^{34}S_{sulfide}$, pass into the mobile form in the groundmass and eventually accumulate in the organic matter.

To assess the surface layer of limestones effect on the formation of mineralization, let us consider the mesostructures of this layer.

Mesoscopic physics or mesoscopics (MS) studies the physical properties of small size particles, the systems with sizes larger than atomic ones whose characteristics depend on the particle size, i.e. it is an intermediate layer between micro- and macrophysics. Characteristic of MS is the size and the number of particles in the sample. Mesoscopic bodies are those whose properties are determined by the behavior of one microscopic particle.

Let us consider the substance, including limestones, in the composition of the surface layer $d(I)$ and the $d(II)$ layer. To calculate the thickness of the surface layer $d(I)$ in work [15], for framework hydrocarbons, the relation is given:

$$d(\mathrm{I}) = 0{,}17 \times 10^{-9} \nu(\mathrm{m}) \qquad (2)$$

It follows from equation (2) that the thickness of the surface layer $d(I)$ is determined by the molar (atomic) volume of the element ($\nu = M/\rho$, where M is the molar mass g/mol), ρ is density (g/cm^3)).

To determine the surface energy (σ) there is used the empirical dependence [13]:

$$\sigma = 0{,}7 \cdot 10^{-3} \cdot T_m, \tag{3}$$

where T_m is the temperature of the massive sample melting without considering the surface and transition layers [16].

The surface layer *d(I)* is a nanostructure (Table 2), where the first kind size effects are observed, determined by the entire group of atoms in the system, which are inherent only to nanoparticles and nanostructures [17]. In this *d(I)* layer, there occurs reconstruction and relaxation with atoms associated with rearrangement of the surface layer [[18], [19]].

In the *d(I)* layer, all physical parameters are subject to size effects, including the surface energy. A.I. Russanov, 1967, p. 190, shows that equation (VIII.55) is valid in the case of small radii of curvature, when *r* ≈ *d(I)*)), and that its value depends linearly on the *h* size:

$$\sigma = K \cdot d(I), \tag{4}$$

where K is the coefficient of proportionality that depends on the temperature and the phase composition.

The $d(II)$ layer extends approximately to the size of $d(II) \approx 9d = d_\infty$ [[15], [16]]. From this size, dimensional properties begin that are called the second kind size effects. This size for nanostructures is associated with a certain critical parameter: the mean free path of carriers in transition phenomena, the dimensions of domain walls, the diameter of the Frank-Read loop for dislocation glide, and so on [19]. Some of the effects, such as the surface energy, are constant.

According to formulas (1) and (3), there is determined the thickness and the surface energy of a number of sulfides and oxides (Table 2).

Calcium oxide which is a part of limestone ($CaCO_3$), has the surface layer thickness $d(I)$ = 16.64 nm. The surface layer of limestones, in terms of particle size and distance between them, is included in the mesoscopic system of bodies (MS) and can be considered as a subsystem of a large closed system. These particles are characterized by the manifestation of quantum properties determined by the phase coherence length (h_φ) that can vary over a wide range. In MS always $h_\varphi \le 10^{-6}$ м = 1 micron.

Table 2 – The surface energy and the thickness of the Ba, Pb, Zn sulfides and Ca, Ba oxides surface

Compound	σ, J/m^2 (T-300K)	μ, (g/mol)	ρ, (g/cm^3)	ν, cm^3/mol	The surface layer thickness, nm
sulfides					
BaS	0.385	169.40	4.25	39.86	39.86
PbS	0.195	239.96	7.60	31.49	31.48
ZnS	0.240	97.44	4.09	23.83	23.82
oxides					
CaO	0.436	56.08	3.37	16.64	16.64
BaO	0.389	153.34	5.72	26.81	28.81

It is known that the physical quantities characterizing the subsystem fluctuate, exchanging energy and particles with the environment [20].

In work [21], a model was proposed according to which the nano- and mesophases existing in the surface layers of crystals regulate the relationship between the crystal and the medium, selectively interacting with the substance-carrying complexes and reducing the probability of their "wrong" unloading. Continuously moving into the bulk of the crystal, by means of a solid-phase transformation, nano- and mesophases drop these elements into defective areas of mating with the matrix, where they form their own phases of micron or meso sizes. This fact is the reason for changing $\delta^{34}S_{sulfide}$ from the textural features of ores, the basis of which is their formation in limestone nanostructures, cracks, and pores.

It was shown in works [[15], [19]] that for nano- and mesostructures the size effects take the form:

$$\begin{aligned} A(r) &= A_0\left(1 - d(I)/r\right),\ r >> d(I), \\ A(r) &= A_0\left(1 - d(I)/d(I) + r\right),\ 0 < r < d(I). \end{aligned} \tag{5}$$

Here $A(r)$ is a variable physical property depending on the particle size *(r)* of the surface nanolayer with the thickness of $d(I)$, A_0 is the physical property of the massive sample.

In the layer $d(I)$, all elements are nanoluminophores [16], which can be considered as sensitive molecular probes for studying the structure, including limestones. Small changes in the local structure in the layer $d(I)$ lead to significant changing the characteristics of the layer, which follows from formula (5); for this, instead of $A(r)$, it is necessary to use the amount of ore elements, including the sulfur isotope [[22], [23]].

The following models are used to describe the mesostructure of porous bodies: a lattice; a percolation; a capillary; fractal ones. Let us consider the relationship between fractality and the thickness of the surface layer of limestones.

It is known [24] that the sizes of geomaterials and elements blocks of the earth's crust are not arbitrary but make a certain discrete series in which the ratio of the block sizes of the n-th order to the size of neighboring blocks of the order (n+1) and (n–1) satisfies some fundamental ratio: the universal principle of material divisibility during destruction:

$$L_{(n-1)}/L_n = A = 2{,}618 \approx 3, \qquad (6)$$

where A is an ideal size ratio.

To determine the sides of the corresponding block sizes L_n in the hierarchy of scales, there is used the relationship [25]:

$$L_n = \begin{cases} (2-6)\cdot 10^{\left(\frac{n-11}{2}\right)} \text{ for } n = 2k\text{-}1, \\ (1\text{-}2)\cdot 10^{\left(\frac{n-10}{2}\right)} \text{ for } n = 2k. \end{cases} \qquad (7)$$

Here k is an integer that changes from 1 to 9; L_n is a characteristic siz of the block of the n order.

The limestone surface layer thickness that mainly consists of CaO (Table 2), is 16.64 nm, which relates this layer to a nanostructure [24].

The established regularities that connect the difference in the concentration of $\delta^{34}S_{sulfide}$ with textural factors indicate that one of the influencing factors of the heavy sulfur isotope mineralization and concentration is the effect of nanostructures and of pores and cracks that arise during the division of geomaterials. These factors explain the formation of stratiform deposits of lead-and-zinc mineralization with carbonate orogenic structures.

It should be noted that the impurities adsorption (including $\delta^{34}S_{sulfide}$) is developed in the mesoporous structure of limestone due to the formation of adsorption layers on the surface of these mesopores, which lead to the volumetric filling of these pores by the mechanism of capillary condensation that is described by the Kelvin equation [[25], [26]].

Let's consider the model of the hydro-therm movement in a fractured medium, in this case limestone, which is an aqueous solution with ore-forming elements, sulfur isotopes, and other components thereof.

To solve the problem, there is used the level of movement of an aqueous solution with the density *ʃ(r,z,t),* which moves according to the *β(t)* dependence in a crack of radius *r*, length *L*, in the direction *z*, with the use of the diffusion equation:

$$\frac{\partial f(r,z,t)}{\partial t} = a^2\left[\frac{\partial^2 f(r,z,t)}{\partial z^2} + \frac{1}{r}\cdot\frac{\partial}{\partial r}\left(r\frac{\partial f(r,z,t)}{\partial r}\right)\right], \qquad (8)$$

where $a^2 = D$ is the coefficient of the solution diffusion.

The solution of equation (8) is given in work [14]. Denoting the flow density *ʃ(r,z,t)* by *ρ (r, z, t),* at $z = \upsilon t$, where υ is the speed of the flow at the point *z* at the instant of time *t* and assuming the movement of the phase separation as automodel *β(t) = β0t*, there is used the asymptotic representation of Bessel functions and obtained:

$$\rho(r,z,t) = \frac{D^{3/2}}{\pi^{5/2}}\sqrt{\frac{L}{r}}\cdot\frac{1}{\upsilon\cdot\beta_0\cdot t}. \qquad (9)$$

Assuming that the speed of solution movement *(z,t)* depends only on the hydrothermal solution ρ density, and if the crack is not filled with solution (ρ = 0), then the solution moves in it with the maximum speed $\upsilon = \upsilon_{max}$, and when the crack is filled, the speed of solution movement in the crack falls to a complete stop ($\upsilon = 0$), when $\rho = \rho_{max}$.

$$\rho = \rho_{max}\left(1 - \frac{\upsilon}{\upsilon_{max}}\right), \quad 0 \le \upsilon \le \upsilon_{max}. \qquad (10)$$

If to assume in equation (10) that under the density of the liquid flow there is taken the degree of deposition of metals from the solution, the isotope of sulfur and other elements, and under the speed of the flow is taken as the speed of their deposition (that is proportional to the diffusion coefficient D), there are obtained the experimental regularities presented in work [27] that reflect equations (9, 10) obtained in this work. Thus, formula (9) shows a significant dependence of the solution flow density on the diffusion coefficient, i.e. its rheology. According to the Newton's classical theory, it is equal to $D = \nu$, where ν is the kinematic coefficient of viscosity [19]. Let's consider the solution viscosity from the position of the thermodynamic approach, determine the kinematic viscosity ν using the response function [15], then the kinematic viscosity ν is determined as follows:

$$\nu = \frac{kT}{c}\cdot\frac{W}{G^0_{см}}\cdot\overline{N}, \tag{11}$$

where $\overline{N}kT = pV = (V=1) = p$ is pressure in the solution flow; W is kinetic energy of the solution particles (molecules) ($W=m\upsilon^2/2$), $G^0_{см}$ is Gibbs energy of the solution; m is the particle mass, υ is their speed, c = const. Taking into account that $G^0_{см}$ = σS, where S is the unit area of the nanolayer surface, there is obtained the equation of the relationship between the solution viscosity and the surface tension σ of the nanoparticles of the surface layer of the crack in limestone:

$$\nu = \frac{1}{c}\cdot\frac{p}{2\sigma S}\cdot m\upsilon^2. \tag{12}$$

It follows from equation (12) that the hydrothermal flow in limestone cracks is proportional to its surface energy σ. The validity of the relation D = ν ~ 1/σ is obvious.

Let's consider a model of the crock formation in limestone. It should be noted that hydrothermal solutions that move along the existing cracks (open porosity of the layer, stress cracks, crack formation in a nanolayer of limestone, etc.) form new cracks under the action of pressure, temperature, capillary forces, dissolution of calcite, and at low values of the movement speed, the hydrothermal branching of small cracks, along the characteristic length of the cracks is maximal. With increasing pressure, one crack is practically formed with small branching of small feathering cracks having the critical radius r_k [21] that can be determined by the expression:

$$r_k = \frac{2\sigma V}{RT} = \frac{4\sigma\cdot V}{m\upsilon^2}, \tag{13}$$

where σ is the surface energy of the capillary material, in this case limestone, V is the molar volume, R is the universal gas constant, T is temperature.

Equation (13) makes it possible to estimate the critical hydrothermal flow velocity υ using the fracture and fluid characteristics. Using (13), a formula was obtained for calculating the number of cracks N per unit area of limestone:

$$N = \frac{1}{k_B \ln 2}\sqrt{\ln\left(1-\frac{2\sigma}{\upsilon}\right)}, \tag{14}$$

where k_B is the Boltzmann constant. The product $k_B ln_2$ is the energy equivalent of one unit of information.

The number of cracks per unit area of a limestone layer cannot be arbitrarily large and it is proportional to its porosity that is in turn determined by the principles of the closest packing of limestone particles.

Discussion of the results

The established pattern of changes in the heavy isotope of sulfur $\delta^{34}S_{sulfide}$ from the texture of barite-galena ores in limestones indicates a possible reason for the formation of mineralization in porous limestones due to the effect of their surface nanolayer. With the leading role of the heterogeneous mechanism of ore formation and heavy sulfur isotope formation in ores and their replenishment in the organic matter, an important role is played by a high specific surface of the nanolayer of ore-bearing limestones. It is shown that the thickness $d(I)$ of the surface layer is determined by one fundamental parameter: the molar (atomic) volume, and the surface energy of the limestone nanolayer is determined by the Tolman temperature. It determines the continuous transition into the bulk of the substance of the elements formed on the surface layer in its defective areas, forming the actual ore phases and the heavy isotope of sulfide sulfur associated with them, which is determined by equation (5).

The effect of pressure and temperature of hydrothermal ore-forming solutions in the mesostructures of porous limestones leads to the formation of crack development that obeys the principle of material divisibility and forms additional conditions for mineralization in these formed layer cracks.

The model of hydrothermal solution movement in a crack coincides quite well with the well-known model presented in the work by V.S. Golubev (reports of the Academy of Sciences of the USSR, 1978, Vol. 238, No. 6. P. 1318-1320), taking into account the fact that in this case the velocity of the solution is associated with the density of the solution, and in the mentioned work, the liquid density is associated with the liquid filtration through a porous medium. The established relationship between the fluid flow density and the diffusion coefficient made it possible to establish the relationship between the kinematic viscosity of the hydro-therm and the surface tension of the crack surface layer along which the fluid moves. It is the higher, the lower the kinematic viscosity, all the other things being equal. The critical velocity of the hydro-therm movement through the crack is determined. Using this regularity, the regularity of the number of cracks per unit area of limestone is obtained. It is determined by the surface energy and kinematic viscosity of the solution. From this it follows that the number of cracks is related to the porosity of limestone through the surface energy of these pores.

Conclusions

There was established the dependence of the flux density of the hydrothermal solution on its diffusion; the relationship between kinematic viscosity and pressure in the solution flow, the velocity, the mass of particles, and the Gibbs energy of the mixture were obtained; the relationship between the viscosity of the solution and the surface tension of the limestone particles nanolayer was obtained; the critical radius of crack formation was determined. The resulting constraint equations are applicable for the numerical analysis in order to assess the effect of ore-bearing hydrotherms on ore deposition processes and to evaluate the efficiency of crack formation and their role in ore deposition, taking into account kinematic viscosity under thermodynamic conditions of the ore-bearing limestone horizon occurrence.

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Үшқатын III (Орталық Қазақстан) кен орнының барит-қорғасынды кенденуінің қалыптасуының математикалық моделі

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ТҮЙІНДЕМЕ
Шөгінді жыныстардағы қорғасын, барит стратиформды кен орындарының генезисі полиметалл кендерінің қорын толықтыру тұрғысынан үлкен қызығушылық тудырады. Жұмыстың мақсаты-кеуектердегі кен ерітінділерінің қозғалысының математикалық моделі мен сипаттамаларына негізделген кеуектер мен жарықтардың нано бетінің әсерін ескере отырып, әктастарда кендердің гидрогендік түзілу заңдылығын анықтау. Кеннің қалыңдығы мен сульфидті минералдардың құрамына кіретін әктастар мен минералдардың беткі қабатының қалыңдығы есептелген. Нәтижелер олардың заттың қалған бөлігінен ерекше, физикалық қасиеттері бар наноқұрылымдар екенін көрсетеді, бұл әртүрлі текстуралық

типтегі кендерде ауыр күкірт изотопының түзілу заңдылығымен расталады. Әр түрлі тығыздығы, кинематикалық тұтқырлығы, жылдамдығы бар гидротермалардың әктастардың жарықтары мен тесіктерінде кенденудің пайда болу қарқындылығына, сондай-ақ бөлшектеу жарықтары айналасында жаңа жарықтардың пайда болуына әсері бағаланды. Гидротермалар ағынының тығыздығының сұйықтықтың диффузиясына тәуелділігі анықталды. Кинематикалық тұтқырлық теңдеуі ерітінді ағынындағы қысымнан, оның қозғалу жылдамдығынан, кенді құрайтын элементтер бөлшектерінің массасынан және Гиббс энергиясының термодинамикалық жағдайында күкірт изотоптарынан алынады. Ерітіндінің тұтқырлығының жарықтар мен кеуектердегі әктас бөлшектерінің наноқабатының беттік керілуімен байланысы көрсетілген, бұл энергия неғұрлым көп болса, кенді құрайтын ерітінділердің қозғалыс жылдамдығы соғұрлым көп болады, бөлшектенетін жарықшағының айналасында жаңадан пайда болған жарықтардың тармақтары азаяды. Математикалық модель кен қабатының термодинамикалық жағдайында әктастардың жарықтары мен кеуектерінің наноқұрылымдық қабатының әсерін ескере отырып, жарықтардың кендену заңдылығын сандық талдау үшін қолданылады.

Түйін сөздер: Үшқатын III, стратиформды кен орындары, Атасу кен ауданы, изотоптық құрамы, математикалық моделі.

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Математическая модель формирования барит-свинцового оруденения месторождения Ушкатын III (Центральный Казахстан)

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АННОТАЦИЯ

Генезис стратиформных месторождений свинца, барита в осадочных породах представляет огромный интерес с точки зрения восполнения запасов полиметаллических руд. Целью работы является установление закономерности гидрогенного формирования руд в известняках с учётом влияния наноповерхности пор и трещин на основе математической модели движения и характеристик рудоносных растворов в порах. Рассчитаны толщины поверхностного слоя известняков и минералов входящих в состав рудовмещающей толщи и сульфидных минералов. Результаты свидетельствуют о том, что они являются наноструктурами обладающими особыми отличными от остальной части вещества, физическими свойствами, что подтверждается закономерностью формирования тяжелого изотопа серы в рудах различных текстурных типов. Оценено влияние гидротерм обладающих различными плотности, кинематической вязкости, скорости на интенсивность формирования оруденения в трещинах и порах известняков, а также возникновении новых оперяющих трещин вокруг трещин расчленения. Установлена зависимость плотности потока гидротерм от диффузии жидкости. Получено уравнение кинематической вязкости от давления в потоке раствора, скорости его движения, массы частиц рудообразующих элементов и изотопов серы в термодинамических условиях определяемых энергий Гиббса. Показано связь вязкости раствора поверхностным натяжением нанослоя частиц известняка в трещинах и порах, свидетельствующая о том, что чем больше эта энергия, тем больше скорость движения рудообразующих растворов, тем меньше ветвлений вновь образованных трещин вокруг трещины расчленения. Математическая модель применима для численного анализа закономерности оруденения в трещинах с учетом влияния наноструктурного слоя трещин и пор известняков в термодинамических условиях залегания рудоносного пласта.

	Keywords: Ушкатын III, стратиформные месторождения, Атасуйский рудный район, изотопный состав, математическая модель

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