Hydrodynamic and Geochemical Conditions of the Formation of Stratiform Zn–Pb Ore Mineralization by Chloride Solutions

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Abstract—Ore mineralization is formed by postsedimentary (concentrated by evaporation to stage SW2) chloride brines metamorphosed in hydrogeochemical systems that are closed with respect to CO_2, evolve according to "calcic" trend, and have high $2mCa^{2+} > mHCO_3^- + 2mCO_3^{2-}$ ratios. In these situations at high R/W ratios (10–100) and temperatures (100–200°C), these brines concentrate ore elements (Zn, Pb, Fe, and Mn) that are geochemical analogues of Ca. The sulfide precipitation of these elements occurs under the effect of carbonate rocks at the abiogenic sulfate reduction of S(VI) of the original brines at low Eh values, which are created in carbonate rocks at higher (>100°C) temperatures. This origin of sulfide mineralization is intensified at decreasing R/W ratios during the dilution of the original brines by elision waters and an increase in the temperature. The hydrodynamics of these ore-forming brines is controlled by the elision hydrogeological regime, which is defined in hydrogeological structures by the geostatic pressure. The brines migrate into the zones of geochemical barriers during the relaxation of hydrogeological structures toward their equilibrium hydrostatic state. Hydrogeological structures, optimal for the precipitation of ore mineralization, are hydrodynamically active and able to maintain a steady (during 10^5–10^6 years) inflow of ore-forming brines into the zones of geochemical barriers and the maximum number of water-exchange cycles at these barriers. Modern analogues of these structures are miogeosyncline foredeeps with Cl–Na–Ca chloride brines with high concentrations of ore elements and overall flow rates ranging from 0.n to n m^3/year. Stagnate hydrogeological platform structures in hydrostatic equilibrium cannot ensure water exchange needed for ore formation, and, hence, the brines of these structures are not able to deposit the ore elements contained in them, in spite of the high concentrations of these elements.

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INTRODUCTION

Now it is virtually unanimously acknowledged [1–10] that chloride brines of salt-forming basins provide the genetic basis for the origin of stratiform base-metal ore formations. These formations are more and more often classed with so-called hydrogenic ore formations [6–9]. However competent these concepts of the "hydrogenic genesis" of stratiform ore formations are, their scientific meaning is quite distant from the actual hydrogeology and hydrodynamic situation at evolving hydrogeological structures. A typical example is the paper [10], which provides a sound geological basis but obvious shortcomings of this type. The authors consider hypothetical "fracture–exfiltration" and "ground–exfiltration" systems in which ore mineralization is produced by fictitious variations in the Eh–pH parameters during mixing with arbitrarily assumed types of groundwaters (which are not justified either hydrogeologically or hydrogeochemically): alkaline, sulfate, bicarbonate, etc. These waters reportedly produce some "alkaline–hydrogen sulfide" barriers,

whose genesis and functioning mechanisms remain obscure.

These papers leave uncertain the following issues:

—how brines with high concentrations of ore elements and able to generate ore mineralization are formed;

—what is the source of ore elements for these ore-forming brines;

—what are the driving forces of the migrations of these brines toward zones of ore deposition;

—what are the geochemical barriers during ore-forming processes and what is the genesis of these barriers. It remains unclear as to whether the inflow of sulfide waters into the zones of geochemical barriers is always required, whether or these barriers can be formed immediately within the zone of ore deposition.

A notable breakthrough among these publications was made in publications by L.G. Bogashova (1991 and others), which provided insight into the nature of geochemical processes responsible for the origin of chloride solutions with high concentrations of ore ele-

ments and proposed a brine–gravitational model for the genesis of stratiform ore formations.

This model was underlain by the following issues:

—genetic links between the evolution of salt-forming basins and the development of stratiform mineral deposits;

—the concept of the decisive role of clarke concentrations of ore elements in rocks in the origin of chloride solutions with high concentrations of ore elements in these rocks;

—the actual volumes of the brines produced during the evolution of salt-forming basins.

The model is based on the long-lasting gravitational filtration of brines through sedimentary rocks and the associated process of equally long-lasting evolution of the salt-forming basins.

Although well justified geochemically, this model also suffers from abstracting from the actual regional hydrogeology of artesian basins and is at variance with the concepts of the reasons, driving forces, and directions of groundwater migrations in naturally occurring and evolving hydrogeological structures.

These uncertainties and misinterpretations led us to publish a series of papers that expounded the hydrogeochemical and hydrogeodynamic fundamentals of the problem of the genesis of stratiform Zn–Pb ore mineralization and the principles of the pertinent geochemical processes. This paper is the second in this series. Our previous publication [11] revealed the geochemical conditions and reasons for the concentration of ore elements (Zn, Pb, Fe, and Mn) in the chloride brines of structures containing halide formations. This paper is devoted to the hydrodynamic and geochemical processes that facilitate the transportation of ore-forming brines to the zones of geochemical barriers and the geochemical nature of the genesis of these barriers.

This paper is based on the hypothesis, which was formulated in our previous publications, that the source of ore elements for chloride brines are terrigenous (clayey) rocks in salt-forming basins, and the deposition of sulfides from these solutions occurs, under appropriate $P–T$ boundary conditions, in situ, under the effect of genetically related carbonate rocks. The following problems will be discussed in this paper:

* how brines that became enriched in ore elements when filtering through clayey (terrigenous) rocks migrate to the zones of geochemical barriers in carbonate rocks;

* how the Eh–pH conditions are created in the carbonate rocks that result in the precipitation of ore elements in the form of solid phases and in the origin of base-metal ore mineralization;

* which compounds are the sources of sulfide ions for the ore-forming brines and which processes form them.

Prior to discussing the scientific meaning of this publication, it is pertinent to stress the following issue

that predetermines it. Zn–Pb and Cu stratiform deposits are commonly considered in modern metallogenic publications to be genetically similar hydrogenic deposits, related to the action of geochemically similar chloride brines. However, our experience convinces us that these deposits are, in fact, not as close as they are commonly thought to be. This can be clarified as follows.

Genetic relations between Zn–Pb and Cu stratiform deposits to chloride brines are far from unambiguous. It is well known that Zn–Pb deposits are spatially restricted to carbonate formations, whereas Cu deposits are related to variegated terrigenous formations [7, 10], and these types of mineral deposits notably differ in the character of their genetic links with certain types of chloride brines. The relations between Zn–Pb deposits and chloride brines is fairly simple: structures with stratiform Zn–Pb ore mineralization practically always contain brines with high concentrations of these elements, but the occurrence of these brines does not necessarily imply that they form stratiform ore mineralization. The genetic links between the brines and stratiform Cu mineralization is much more complicated. This mineralization is known to be spread much more widely (a very important comment was made in [10]: globally speaking, areas with Zn–Pb mineralization seem to "overbuild" extensive belts with Cu mineralization). This implies that Cu mineral deposits were produced by a more diverse and extensive complex of favorable geological, hydrogeological, and geochemical conditions. This can be interpreted as implying that the relations between hydrogenic Cu deposits and ore-forming brines should be more common, clear, and simple. This is, however, not the case, and there are significant hydrogeochemical inconsistencies with this concept, which indicate that the problem is more complicated.

(1) High Cu concentrations, commensurable with those of Zn and Pb, of chloride brines in the deep structures of artesian basins (even the highest temperature ones) are very rare. These high Cu concentrations in the brines are formed in other lithological formations (red beds with high Fe^{3+} contents, which were produced in arid oxygen-rich environments) and hydrothermal situations (chloride brines with oxidized states with respect to Cu) [7]. These are different–open, infiltration but not closed, elision hydrodynamic systems. In these closed elision systems, high Cu concentrations in brines are formed very rarely and only in certain hydrogeological structures (for example, in the brines of Zechstein, which are genetically related to the Mansfeld type of Cu deposits). However, the Cu concentration in brines in most hydrogeological structures, even those in areas with stratiform Cu deposits, are no higher than n mg/l [11]. These natural materials are consistent with the results of our thermodynamic simulations of the interaction of brines at various evaporation concentration stages with terrigenous rocks. The Cu concentrations in the resulting brines are always three to four orders

Table 1. Hydrogeological zoning of artesian systems in the Earth's crust (modified after [14])

Hydro-geological zone	Stage of lithogenesis	Genesis of ground-waters	Nature of formation pressures	Relations to the surface, migration directions of groundwater	Genesis of groundwater resources
Infiltration		Infiltration and sedimentogenic	Hydrostatic pressure controlled by an externally determined head	Cyclic water exchange with the surface	Infiltration
Elision	Early and middle catagenesis	Sedimentogenic (talassogenic). Relics of seawaters at various stages of their evaporation concentrations. Ancient infiltration waters	Geostatic compaction of hydraulically permeable rocks. Increase in the formation pressures controlled by the elision of water from the compacted subsiding clayey rocks. Development of suprahydrostatic pressures in the zones of the most significant subsidence and compaction of the rocks	No links with the surface. Lateral – vertical water migration	No external feeding areas. Water supply via the compaction of clays and the separation of pore and loosely bound waters
Thermohydrodynamic	Late catagenesis and metagenesis	Sedimentogenic, revived, ancient infiltration waters in supra- and subcritical states	Suprahydrostatic pressures determined by the geothermal field	No links with the surface. Predominantly vertical water migration	No external feeding areas. Water supply via the dehydration of rocks, separation of strongly bound, crystallization, and chemically bound waters, dehydration and decarbonatization

of magnitude lower than the Zn and Pb concentrations [11].

(2) In contrast to stratiform Zn and Pb deposits, whose relations with chloride Zn- and Pb-bearing brines result from a rather short sequence of favorable conditions, the origin of stratiform deposits of Cu, an element of variable valence, is, according to our hydrogeochemical data, a complicated phenomenon. The origin of these deposits requires a more complicated succession of geochemical transformations of the solutions. These transformations should involve (a) a systematic transition from oxygen- and copper-bearing brines to oxygen-free waters with low positive Eh values that are able to transform Cu^{2+} to Cu^+ and produce minerals like cuprite (Cu_2O); (b) the evolution of these oxygen- and sulfide-free waters at geochemical barriers into sulfide waters with low negative Eh, from which copper sulfides can precipitate. These processes are complicated by fairly intricate Cu migration modes in brines, including not only chloride but also hydroxide species. Because of this, the data and considerations presented below for the geochemistry and geochemical links of chloride solutions with stratiform deposits of Zn and Pb do not pertain to analogous deposits of Cu.

This paper is underlain by a synthesis of empirical generalization of naturally occurring hydrogeochemical phenomena in ore-generating systems and their quantitative analysis based on the method of the thermodynamic simulation of geochemical processes analogous to those in natural hydrogeological and hydrogeochemical systems.

STARTING POINTS

These points can be briefly summarized as follows [5, 8, 11–13]:

(1) Ore-forming chloride brines are produced in geological structures that passed through the stage of halogenesis and preserved relics of brines that were formed during certain evaporation concentration stages (usually no higher than SW2) and were metamorphosed during their geochemical evolution in terrigenous rocks. These brines are produced and geochemically evolve mostly in the elision hydrodynamic zone. Its position in the generalized hydrodynamic and hydrogeochemical zoning of the Earth's crust and its hydrogeological characteristics are presented in Table 1.

(2) It was demonstrated previously [8, 11–13][1] that ore elements (Zn, Pb, Fe, and Mn) contained in the chloride brines of artesian basins in halide formations show similarities with Ca. Because of this, the highest concentrations of these elements are restricted to brines

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[1] It should be mentioned that Bogashova (1981, 1983) used the example of pore solutions expelled from rocks at the Stebnokovskoe deposit to demonstrate that ore elements (Zn, Pb, and Cu) can enrich chloride brines during their metamorphism simultaneously with the increase in the Ca concentration.
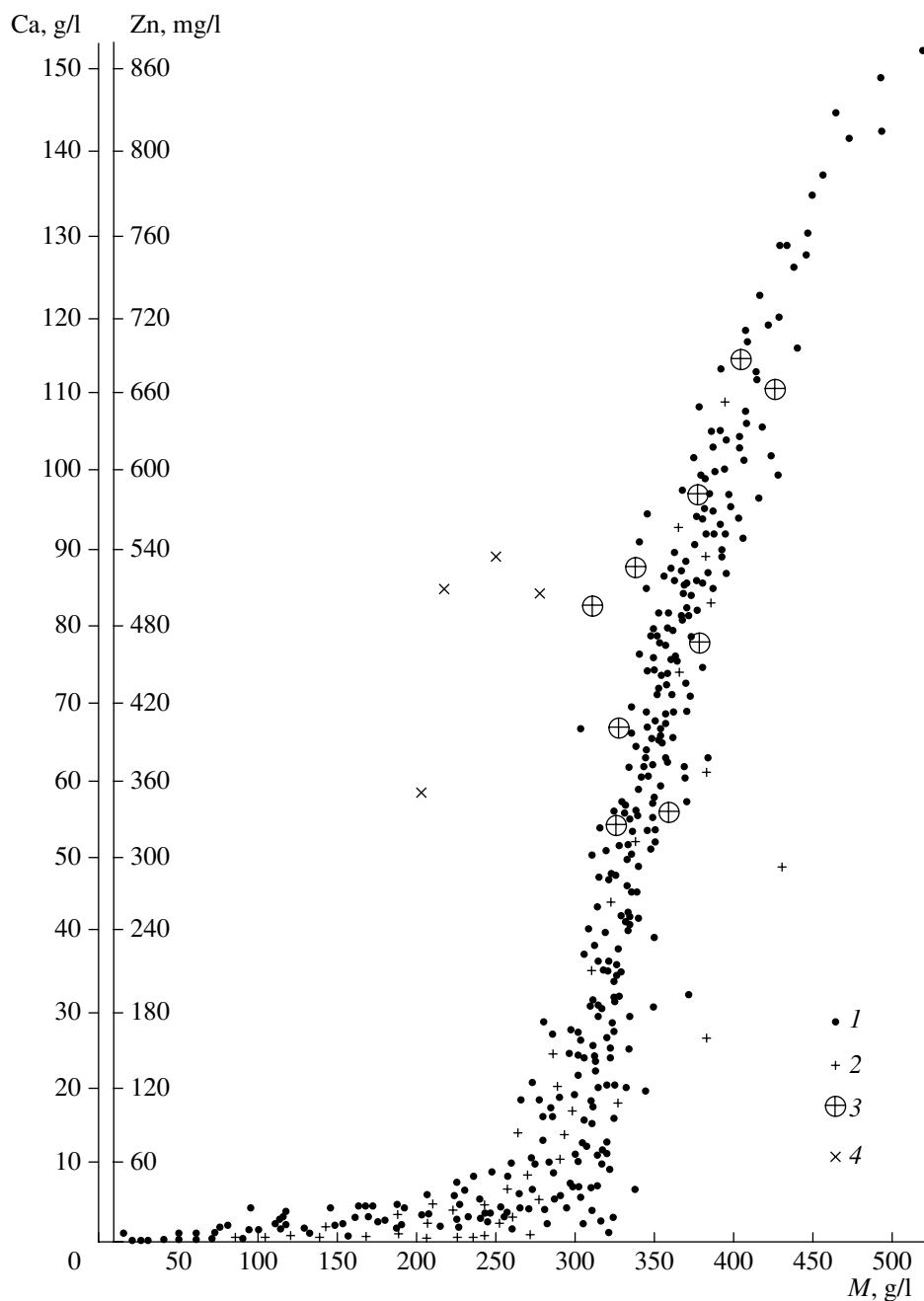
Fig. 1. Correlation between the Z and Ca concentrations in chloride brines from basins with halide formations (Michigan, Pripyat', Angara–Lena, Silesian, Central Polish, Harz, and Californian). Constructed with the use of materials of L.S. Balashov, E.V. Pinneker, A.V. Kudel'skii, A. Hermann, S. Frape, Mckibben, L. Hardies, and our data. (*1*) Concentrations of Ca; concentrations of Zn: (*2*) in brines generated in carbonate formations, (*3*) in brines generated in terrigenous formations, (*4*) in high-temperature chloride brines in halide-bearing Alpine structures.

evolving according to the calcic metamorphic trend [11]. An increase in Ca concentration in these chloride brines is always associated with an increase in the concentration of bivalent ore elements (Zn, Pb, Fe, and Mn) (Fig. 1). We quantified the depth of this calcic metamorphism of chloride brines that is required for an increase in their concentration of ore elements. Our diagram, which is based on the principles in [15], demon-

strates the position of brines with the highest concentrations of ore elements in the system $2m\text{Ca}^{2+} - m\text{HCO}_3^- + 2m\text{CO}_3^{2-}$ (Fig. 2). As follows from this plot, chloride brines with the highest concentrations of ore elements are the most metamorphosed calcic brines, which plot in the extremely calcic region of this diagram. The processing of extensive empirical data on the distribution
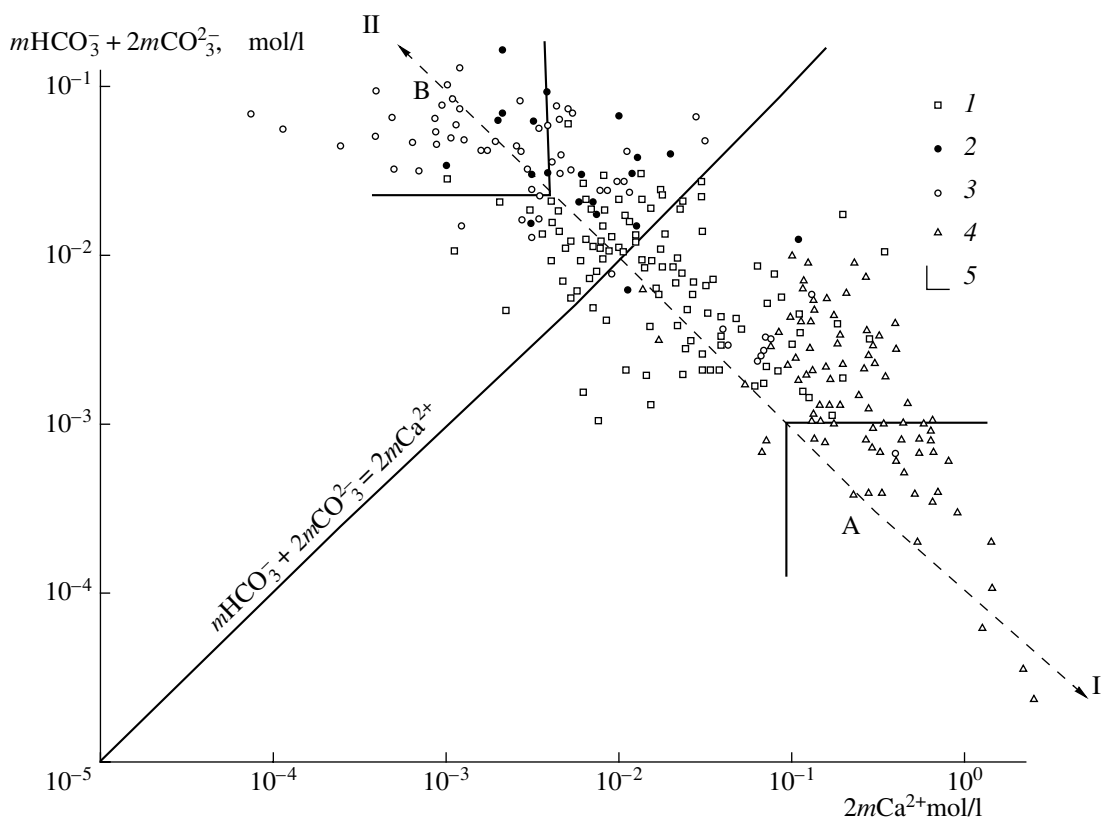
Fig. 2. $(m\mathrm{HCO_3^-} + 2m\mathrm{CO_3^{2-}}) - 2m\mathrm{Ca^{2+}}$ diagram for the composition of chloride brines from artesian basins with halide formations (based on data on the chemistry of brines from the Western Turkmenia, Northern Crimean, Fore-Caucasian, Kura, Nortehrn Sakhalin, and Kambeiskii basins) and CO_2-bearing waters in Alpine structures. Geochemical types of brines and CO_2-bearing waters: (*1*) Cl–Na($\mathrm{HCO_3^-} + \mathrm{CO_3^{2-}} < 5\%$ mg-eq); (*2*) Cl–Na($\mathrm{HCO_3^-} + \mathrm{CO_3^{2-}} > 5\%$ mg-eq); (*3*) Cl–$\mathrm{HCO_3}$–Na, $\mathrm{HCO_3}$–Cl–Na; (*4*) Cl–Na–Ca, Cl–Ca–Na; (*5*) compositional fields of (A) brines with the highest concentrations of Zn, Pb, Fe, and Mn, (B) CO_2-bearing waters with the highest concentrations of As and Sb. Geochemical metamorphic evolution of brines in rocks: (I) calcic, (II) sodic (carbonate).
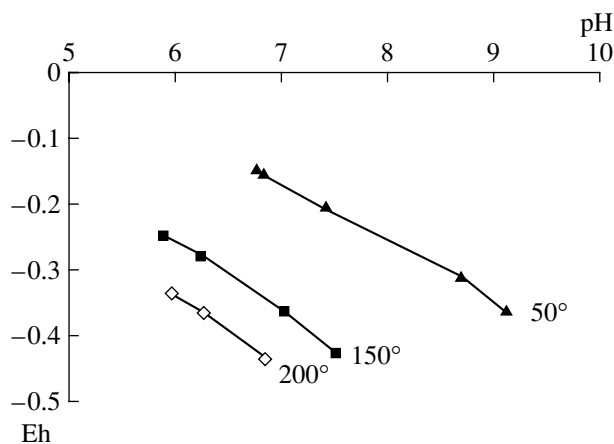
Fig. 3. Changes in the Eh–pH states of brines (SW2) metamorphosed in terrigenous rocks during migration into carbonate formations as functions of temperature and the R/W ratio (GIBBS computer program). Data points in the lines denote various R/W ratios of the interactions, and numerals correspond to the temperatures of these interactions specified in the simulations.

of ore elements in chloride brines demonstrates that the maximum increase in the concentrations of ore elements in chloride brines requires the maximum excess of $2m\mathrm{Ca^{2+}}$ over $m\mathrm{HCO_3^-} + 2m\mathrm{CO_3^{2-}}$, and an increase in the concentration of $\mathrm{HCO_3^-}$, i.e., a shift in the geochemical evolution of the brines toward carbonates always negatively affects the concentrations of ore elements in the brines. In these situations, their concentrations always decrease.

(3) The geochemical sense of the processes of the accumulation of ore elements analogues of Ca in chloride brines during their metamorphism in rocks is the exchange reaction $\mathrm{Mg^{2+}_{brine}} - \mathrm{Ca^{2+}}(\mathrm{Zn^{2+}},\ \mathrm{Pb^{2+}},\ \mathrm{Fe^{2+}},\ \mathrm{Mn^{2+}})_{\mathrm{rock}}$. Because of this, the maximum concentrations of ore elements occur in metamorphosed solutions at the latest stages of their evaporation concentration with the highest Mg concentrations [8, 11].

(4) The concentrations of ore elements increase most actively during the metamorphism of the brines in

Table 2. Changes in the composition of SW2 brines interacting with terrigenous (clayey) rocks at increasing R/W ratio and temperatures (GIBBS computer program)

SW2 + clays	100°C			150°C			200°C		
R/W	1	10	100	1	10	100	1	10	100
pH	6.941	6.388	6.407	6.763	6.184	6.221	6.739	6.258	6.141
Eh, ,	−0.263	−0.213	−0.213	−0.338	−0.280	−0.283	−0.424	−0.37	−0.359
Solution composition, mg/kg									
H_2O	1.00E+06	1.00E+06	1.03E+06	1.00E+06	1.00E+06	1.03E+06	1.00E+06	1.00E+06	1.03E+06
H	7.55E–01	1.98E+00	2.66E+00	7.00E–01	2.83E+00	3.43E+00	6.95E–01	1.84E+00	3.97E+00
O	1.19E+04	1.16E+04	5.45E+03	1.18E+04	9.91E+03	3.67E+03	1.13E+04	8.42E+03	2.73E+03
K	2.78E+03	3.25E+03	8.00E+03	2.78E+03	3.25E+03	8.00E+03	2.78E+03	3.25E+03	8.00E+03
Na	8.47E+04	8.83E+04	1.24E+05	8.47E+04	8.83E+04	1.24E+05	8.47E+04	8.83E+04	1.24E+05
Ca	6.68E+02	1.45E+03	5.40E+03	8.33E+02	1.10E+03	5.96E+03	5.23E+02	8.00E+02	5.73E+03
Mg	1.26E+04	1.19E+04	5.51E+03	1.25E+04	1.14E+04	4.49E+03	1.25E+04	1.10E+04	4.17E+03
Fe	2.30E+01	7.96E–01	1.10E+00	5.66E–01	1.89E+00	2.78E+00	1.31E+00	3.54E+00	7.60E+00
Mn	6.32E+05	6.32E–04	6.32E–03	6.32E–05	6.32E–04	6.32E–03	6.32E–05	6.32E–04	6.32E–03
Al	7.87E+07	4.69E–07	2.68E–06	9.03E–06	5.05E–06	1.14E–05	6.32E–05	3.90E–05	5.07E–05
Si	1.12E–01	6.09E+00	1.61E+01	4.52E–02	3.14E+00	1.56E+01	1.79E–02	6.81E–01	1.53E+01
Ti	5.15E–04	5.15E–03	5.15E–02	5.15E–04	5.15E–03	5.15E–02	5.15E–04	5.15E–03	5.15E–02
P	5.37E–07	4.23E–07	1.08E–07	9.53E–07	2.21E–06	2.90E–07	3.39E–06	5.11E–06	6.66E–07
S	5.92E+03	5.75E+03	2.65E+03	5.90E+03	4.86E+03	1.71E+03	5.65E+03	4.12E+03	1.13E+03
F	7.30E–01	5.94E+00	3.75E+00	7.30E–01	7.30E+00	7.42E+00	7.30E–01	7.30E+00	1.31E+01
Cl	1.58E+05	1.64E+05	2.23E+05	1.58E+05	1.64E+05	2.23E+05	1.58E+05	1.64E+05	2.23E+05
Br	4.58E+02	4.58E+02	4.58E+02	4.58E+02	4.58E+02	4.58E+02	4.58E+02	4.58E+02	4.58E+02
C	9.56E+00	3.09E+01	3.97E+01	9.01E+00	6.41E+01	7.11E+01	8.47E+00	5.88E+01	1.50E+02
Ba	2.04E–01	2.18E–01	5.80E–01	3.41E–01	4.23E–01	1.54E+00	4.21E–01	5.92E–01	3.02E+00
Sr	4.48E+00	4.48E+01	4.48E+02	4.48E+00	4.48E+01	4.48E+02	4.48E+00	4.48E+01	4.48E+02
Pb	9.51E+00	9.24E+01	8.07E+02	1.07E+01	1.02E+02	8.33E+02	7.77E+00	7.34E+01	6.06E+02
Zn	4.15E+01	4.15E+02	4.19E+03	4.11E+01	4.12E+02	4.12E+03	4.21E+01	4.21E+02	4.25E+03
Cu	4.20E–03	1.33E–02	4.25E–02	2.42E–02	7.67E–02	2.38E–01	8.00E–02	2.52E–01	7.77E–01
N	6.00E–02	6.00E–01	6.00E+00	6.00E–02	6.00E–01	6.00E+00	6.00E–02	6.00E–01	6.00E+00

terrigenous rocks [8, 11]. The concentrations of ore elements in chloride brines increase during this metamorphism with increasing R/W ratio and interaction temperature (Table 2). The increase in the concentrations of these elements in the brines of terrigenous rocks is higher by four to five orders of magnitude than the corresponding increase in these concentrations in brines interacting with carbonate rocks at the same boundary conditions (Table 3).

(5) We believe that these differences are related to the different redox conditions in the brines of terrigenous and carbonate rocks (Table 3). The Eh–pH conditions in brines in terrigenous rocks are more favorable for the leaching of the elements from the rocks and their enrichment and retainment in the aqueous phase. The Eh–pH situation in brines contained in carbonate rocks is less favorable for the retainment of elements in the aqueous phase. Table 3 summarizes the results of our simulations of the geochemical interactions of brines with clay and carbonate rocks. It can be seen that the brines of carbonate rocks are characterized by much higher gradients of the Eh decrease with decreasing R/W ratios and increasing interaction temperatures in the rock–water systems.[2] It should be mentioned that the study of temperature variations in the Eh–pH characteristics of brines in carbonate rocks led us to two conclusions that are crucial for the solution of the problem formulated above: (i) a drastic decrease in the Eh of brines occurs with an increase in the interaction temperatures of brines with rocks (Fig. 3), and (ii) a signif-

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[2] It was demonstrated statistically in [11] that natural brines generated in carbonate rocks have much lower Eh values than those in the brines and mineralized waters of terrigenous rocks. Because of this, hydrogeological structures in carbonate rocks are the most favorable for the development of natural sulfide waters.

Table 3. Changes in the Eh-pH characteristics of the SW2 aqueous phase and its concentrations of elements (mg/kg) in clays and carbonate rocks as functions of temperature and the R/W ratio (GIBBS computer program)

Element	Carbonates, R/W = 10				Clays, R/W = 10		
	Temperature, °C						
	100	150	200	250	100	150	200
Fh	−0.294	−0.361	−0.436	−0.555	−0.213	−0.280	−0.370
pH	6.32	6.09	6.01	6.62	6.39	6.18	6.26
Zn	4.6E–03	9.1E–03	1.6E–02	7.1E–02	4.2E+02	4.1E+02	4.2E+02
Pb	2.9E–04	2.9E–03	1.1E–02	9.0E–03	9.2E+01	1.0E+02	7.3E+01
Cu	4.7E–03	2.8E–02	7.1E–02	1.3E–02	1.3E–02	7.7E–02	2.5E–01
Fe	2.9E–06	1.8E–04	1.4E–02	4.0E+00	8.0E–01	1.9E+00	3.5E+00
Mn	4.2E–04	4.2E–04	4.2E–04	3.8E–04	6.3E–04	6.3E–04	6.3E–04
F	4.1E+00	4.3E+00	4.3E+00	3.9E+00	5.9E+00	7.3E+00	7.3E+00
Ca	7.5E+03	7.6E+03	8.6E+03	3.8E+03	1.4E+03	1.1E+03	8.0E+02
Sr	2.8E+01	2.8E+01	2.8E+01	2.8E+01	4.5E+01	4.5E+01	4.5E+01

Element	Carbonates, R/W = 100				Clays, R/W = 100		
	Temperature, °C						
	100	150	200	250	100	150	200
Fh	−0.262	−0.332	−0.407	−0.515	−0.213	−0.283	−0.359
pH	5.85	5.72	5.65	6.20	6.41	6.22	6.14
Zn	7.9E–02	1.3E–01	1.7E–01	2.8E–01	4.2E+03	4.1E+03	4.1E+03
Pb	4.8E–03	3.2E–02	1.3E–01	4.3E–02	8.1E+02	8.3E+02	6.1E+02
Cu	5.4E–03	7.1E–02	3.5E–01	1.4E–01	4.2E–02	2.4E–01	7.8E–01
Fe	7.5E–07	1.7E–05	4.5E–04	1.2E–01	1.1E+00	2.8E+00	7.6E+00
Mn	4.2E–03	4.2E–03	3.8E–03	3.8E–03	6.3E–03	6.3E–03	6.3E–03
F	4.6E+00	1.1E+01	2.2E+01	1.6E+01	3.8E+00	7.4E+00	1.3E+01
Ca	8.6E+03	1.0E+04	1.1E+04	7.8E+03	5.4E+03	5.8E+03	5.7E+03
Sr	2.8E+02	2.8E+02	2.5E+02	2.5E+02	4.5E+02	4.5E+02	4.5E+02

icant increase in the temperatures (>150°C) results in very unusual relations between Eh and pH in the brines. These unusual relations manifest themselves in a negative correlation between the temperature of the solutions and the range of their pH variations (Fig. 3). Consequently, our high-temperature solutions with low Eh have pH of about 6.2–6.7, which leads to very unusual geochemical situations when an Eh decrease in high-temperature solutions results not in an increase in their pH but in its decrease, and, as a consequence, the brines with low values of their redox potential are acidic. Of course, the question that should be answered here is which potential-determining systems control this decrease in the Eh of brines in carbonate rocks. We are prone to believe that this phenomenon is related to the temperature transformation of organic compounds that are contained in the carbonate rocks and pass into the brines. Our simulations demonstrate that a temperature

increase results in the transformation of much of the organic matter and also, perhaps, the carbonate components of the rocks into CH_4 and other hydrocarbons, which are ignored in the simulations. The concentrations of CH_4 (together with H_2) in brines at temperatures of more than 150°C increase to $n \times 10^0$ mol/kg, which is much higher (by a few orders of magnitude) than the concentrations of CO_2, HCO_3^-, and CO_3^{2-}, i.e., equilibrium in the potential system CO_2/CH_4 is strongly shifted toward CH_4. There is likely the redox reaction $CO_2 + + 4H_2 = CH_4 + 2H_2O$, and it results in a drastic decrease in Eh.

This decrease in the Eh of brines in carbonate rocks is coupled with a significant decrease in the concentrations of all ore elements in these solutions. It is worth mentioning that the most significant decrease in the concentrations in the brines of carbonate rocks are typ-

ical of Zn, Pb, and Fe, i.e., elements that are typomorphic of classic stratiform base-metal formations of the Mississippian type. Hence, the Eh states developing in the high-temperature hydrogeochemical systems of carbonate rocks make it impossible for the ore elements to occur in the aqueous phase and facilitate their precipitation in the form of solid sulfide phases.

These materials gave rise to the idea of the barrier geochemical role of carbonate rocks. The idea was expressed in the form of the following hypothesis [11]: the source of ore elements for chloride ore-forming brines is the terrigenous (clayey) rocks of salt-forming basins, and the elements are precipitated in situ in the form of sulfides at appropriate thermodynamic conditions under the effect of carbonate rocks.

HYDRODYNAMIC REASONS FOR THE MIGRATION OF ELISION ORE-FORMING BRINES INTO RESERVOIRS IN CARBONATE ROCKS AND THE TIME NEEDED FOR THESE MIGRATIONS

Here we are supposed to explain the mechanisms of the elision[3] migrations of brines from deep levels of hydrogeological structures, to determine the driving forces of this process, and to elucidate the geochemical evolution of these brines. This is needed not only to clarify the general metallogenic aspect of the problem but is also necessary for determining the methods and succession of operations of the thermodynamic simulations. As follows from materials in the reviews [6, 10], stratiform ore mineralization is produced by the lateral–vertical migrations of ore-forming brines from terrigenous into carbonate rocks. In essence, this is a hydrogeological process that can be understood only on the basis of hydrogeological concepts (particularly those developed in oil geology) concerning the nature and mechanisms of elision processes [16–23].

Causes of the migrations of ore-forming brines. It should be preliminarily emphasized that the key geological structural element in the development of stratiform ore mineralization is a peripheral zone of a platform bounded by a miogeosyncline foredeep and the systems of these deep miogeosyncline foredeeps themselves [6, 7, 10]. For example, the Midcontinent system of the United States, which hosts one of the largest stratiform base-metal deposits, comprises the whole southeastern part of the North American Platform and the neighboring miogeosyncline zone of the fore-Appalachians. The origin of these ore formations is genetically related to the evolution of a Permian salt-forming basin. The major ore-forming hydrogeological structure of this system is the fore-Appalachian deep, which was characterized by active subsidence in the Permian and provided ore-forming solutions for the ore-generating systems of the Midcontinent [6, 10]. All of these

structures and their analogues elsewhere that host stratiform ore formations are genetically related to salt-forming basins [8, 10], all of them passed through an evolutionary stage of deep sedimentation subsidence, and their geologic histories include stages of elision evolution. The elision evolution of hydrogeological structures is not only controlled by the regional hydrogeological conditions (as is the case with the infiltration zone) but also affects these conditions via generating water flows of variable intensity and direction (preferably from the centers of the structures toward their peripheries) and with various geochemical characteristics. There are certain prerequisites for the development of such flows of brines.

(1) First of all, geostatic stress arising during the subsidence of clay formations results in their contraction and compaction, a process coupled with a systematic decrease in the porosity of the rocks. The dynamics of the changes in the porosity of the terrigenous rocks during their subsidence and compaction in sedimentogenic basins was examined most thoroughly by oil hydrogeologists [16, 17, 19–21]. According to these materials, the porosity of the rocks varies from 90% during early sedimentation stages to 20% during intermediate stages (at depths of 1.5–2.0 km) and 1–2% during the final stages (at depths of up to 5 km). This means that the R/W ratios of the hydrogeochemical systems developing during these stages systematically increase to 10 and further to 50–100, and this predetermines the intensification of the geochemical interaction of the brines and rocks. In compliance with the long-term possibilities of the exchange reactions Mg $\longrightarrow$ Ca (Zn, Pb, Fe, Mn), this results in the active enrichment of ore elements in the brines. Their concentrations can thereby approach the concentration of Ca, and Zn concentration can even exceed it [11].

Another important consequence of the subsidence of hydrogeological structures and the increase in their geothermal tension is the development of suprahydrostatic formation pressures in the artesian systems. Pressures in elision zones can exceed their hydrostatic pressures by factors of 2.0–2.5 [14]. The two major reasons for these suprahydrostatic pressures are as follows. Their main cause is the compaction of clayey sediments during the subsidence of the structures. Because of this, the formation pressure in the compacted sediment is higher than the hydrostatic pressure and becomes to exceed the piezometric levels in adjacent rockreservoirs (both sub- and superjacent). As a result, the formation pressures of the brines (their piezometric levels) in elision artesian systems approach the gradient of the geostatic (lithostatic) pressure as the subsidence depth of the sediments, their density, and degree of compaction increase (Fig. 4).

(3) Finally, subsided elision structures are characterized by tension and brine temperatures in the artesian systems much higher than 100°C (the maximum known temperatures [9] of thermal water seeps in geosyncline

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[3] Elision stems from the Latin word *elidere* "to strike out."
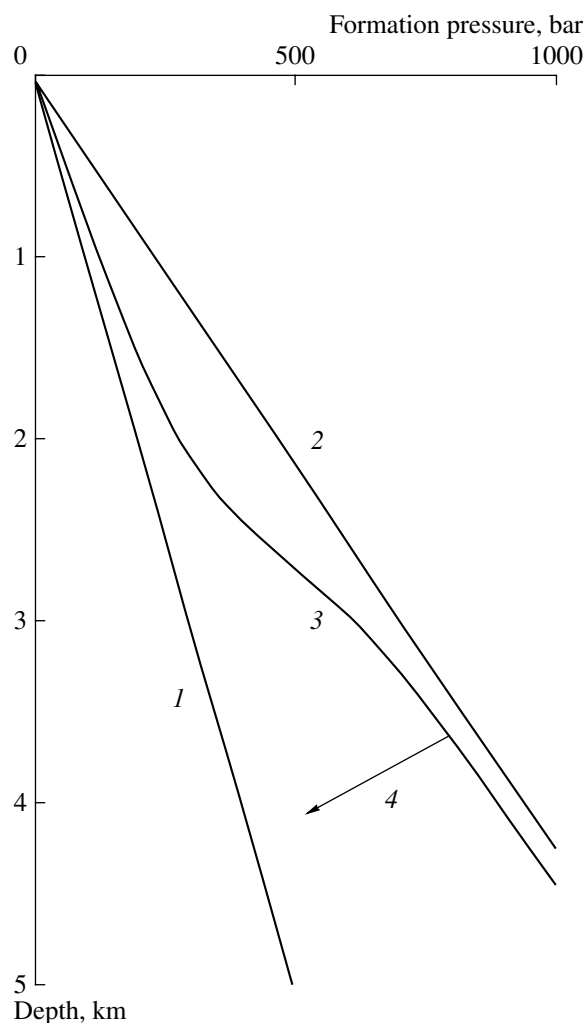
Fig. 4. Typical variations in the formation pressure with the depth at which groundwaters are generated in elision hydrogeological structures. Formation pressures: (*1*) hydrostatic equilibrated; (*2*) geostatic (limiting); (*3*) actual formation pressures in elision hydrogeological structures; (*4*) relaxation of formation pressure during the hydrodynamic evolution of the structures with time.

ancient infiltration solutions and mineralized waters with high concentrations of ore elements into adjacent reservoirs.

Beginning with the publications [16–18], this problem has been actively explored, and now a quite comprehensive understanding has been achieved for the dynamics of the segregation of elision waters and the factors controlling this process [14, 19–23]. It is known that the evolution of terrigenous rocks from silt to shale is associated with the loss of 90% of their water, and the mass of this water is fairly significant. For example, according to [5], the compaction of 1 m³ of an average clay to shale can produce 3.5×10^3 l of water. The subsidence of a sediment to a depth of 3000 m can result in a release of up to 75% of its water. Even more significant values were quoted in [14] (for the western Turkmenia basin) and in [19]. The elision separation of water is characterized by the systematic changes in the types of the released waters. Free and pore waters are expelled at depths of up to 3000–3500 m (temperatures of 100°C), bound waters are released beginning with depths of 3500 m (temperature of more than 150°C), and dehydration waters from clay and other hydrous minerals are separated at depths of up to 10 km.

This separation of brines from sedimentary rocks during their compaction is coupled with a geochemical evolution of the solutions, which ends during the final stages with the generation of less mineralized solutions. Their mineralization usually decreases to 20–10 g/l, but it is known that even less mineralized waters can occur at significant depths of >3000 m. For example, the Triassic rocks in Mangyshlak contain chloride waters with mineralization of only 0.8 g/l at a depth of 3500 m. Geochemically, this final stage of the separation of the least mineralized waters from rocks is accompanied by the release of organic hydrocarbons from them [19]. It is important that the final stage is characterized by a change in the geochemical evolution of the brines from a calcic to sodic (carbonate) trend [24]. This phenomenon corresponds to the changes in the chemistry of fluid inclusions during the final (calcic) stages of the ore-forming stratiform process [25].

Finally, it is pertinent to mention another issue that is important for the theory of ore formation and concerns an increase in the permeability of clayey rocks to the filtration of chloride mineralized waters as compared to fresh water. The maximum increase in the permeability of these rocks occurs within the mineralization range of 5–20 g/l [26]. Moreover, the permeability of clays further increases under the effect of an anomalous geothermal field. Starting at 50–60°C, the permeability of clays to mineralized waters increases, and hence, the region of elevated temperatures in the sedimentary cover corresponds to the enhancement of hydrodynamic activity [26]. Hence, it is reasonable to expect that deep levels are characterized by an increase in the vertical component of the migrations of groundwaters and a change in the ratio of the lateral and verti-

structures are as high as 330–340°C). The increase in geothermal tension in these structures also causes, along with the activation of the ion-exchange transition of ore elements from the rock into the brine (a process that leads to a significant increase in the Zn/Ca ratio [11]), very significant catagenetic transformations of the rocks, and above all, their further dehydration with the removal of strongly bound and crystallized water. The transition of the aqueous phase of the rocks from the bound to free state is associated with a 30–40% increase in its volume [14], and this further enhances the suprahydrostatic formation pressure in the hydrogeological structures and their susceptibility to lateral–vertical migrations into adjacent reservoirs. The integral result of these processes in the elision zone is the migration of the produced postsedimentation and

cal components of their migration with an increase in the latter. In this context, the recognition of thermohydrodynamic zones in deep-seated hydrogeological structures [14] seems to be much more important for the theory of ore formation than it is thought now.

Quantitative analysis of the timing and dynamics of the elision migrations of ore-forming brines from terrigenous formations to adjacent reservoirs. It was mentioned above that the compaction of sedimentary rocks, and increase in the geostatic pressure, and an increase in the geothermal tension in the deepest zones are associated with the development of very high formation pressures, whose gradients approach those of geostatic pressures (Fig. 4). The ensuing disequilibrated hydrodynamic states (systems) with very high geostatic pressures relax toward equilibrated hydrostatic states via the expelling of excess waters into adjacent reservoirs. An important issue is the direction of these migrations. In the hypothesis of the gravitational filtration of sediments [8], they moved to lower levels under the effect of gravity. However, this hypothesis ignores flows that occur in aquifers and the piezometric levels controlling them. For example, in the salt-forming basing of the Caucasian foredeep, the gravitational migration of brines into the complex beneath the salt-bearing formation is hampered by the elision flow from the underlying terrigenous formations [27], and the resulting migration of the groundwaters is determined by the relations between the piezometric levels of these counteracting flows. One of the key points of hydrogeology postulates that the migration of groundwaters in any system of aquifers in an artesian basin is determined by the relations between the piezometric levels in the aquifer complexes. The migration of the elision water proceeds from the zones of piezometric maxima to those of piezometric minima [28]. Brines usually migrate from sedimentogenic elision systems away from the subsidence center with the maximum geostatic pressure in lateral and, particularly, vertical directions. Aquicludes, particularly those at a significant geothermal tension, cannot preclude this process [26]. These key points are in principal agreement with the results of hydrodynamic simulations conducted to understand the genesis of stratiform ore mineralization [29].

Below these phenomena will be analyzed on a quantitative basis. The relations between the geostatic and hydrostatic processes in artesian systems were explored fairly thoroughly in regional hydrogeology, and the time needed for the relaxation of unequilibrated artesian systems to hydrostatic ones was also evaluated. Figure 5 demonstrates the relations between the geostatic and hydrostatic formation pressures in natural hydrogeological structures of various ages. It was established that younger structures have artesian systems more distant from their relaxation level. This puts forth the question as to what time is needed for the relaxation of an artesian system to its hydromechanically equilibrated hydrostatic pressure. To answer this question we present Table 4, which quotes the times needed for the relaxation of formation pressure and the passage of artesian systems to equilibrium hydrostatic states depending on the sizes of the geological structures, the lithological types of their rocks, and their piezoconductivity. It is demonstrated that the time needed for the relaxation, i.e., the expelling of free and pore waters from the reservoir of the elision systems during lithological transformations of the rocks in large regional hydrogeological structures (stratiform ore formations are hosted by exactly these structures) is of the order of a few million years. This means that Paleozoic structures containing chloride solutions with high concentrations of ore elements should inevitably pass through an evolutionary stage of hydrodynamic elision relaxation, and their brines should migrate from terrigenous (clayey) lithological complexes to adjacent (carbonate) reservoirs.

Finally, the question should be answered as to why some of these brines are still retained in Paleozoic hydrogeological structures. To solve this problem, it is expedient to examine hydrogeological materials on the filtration velocities of brines in Paleozoic structures [31–33]. Judging from these materials, the deep levels of Paleozoic structures, which are, in fact, dehydrated elision thermohydrodynamic systems [32], are characterized by migration rates of the brines of the order of $n \times 10^{-3}$ to $n \times 10^{-4}$ m/year. This means that no hydraulic elision of brines from these deep-seated structures can take place. The time needed for filtration water exchange in these structures is no less than 50–100 m.y. and more. In their hydrodynamic meaning, these structures that underwent elision relaxation but partly retain the relict brines are quasistagnant (equilibrium) systems that cannot release their brines to other hydrodynamic systems. The brines of these structures are syngenetic with respect to the host rocks and retain the age of their origin of the order of a few million years.

A noteworthy fact is that the filtration velocities of the brines are comparable with the velocities of tectonic motions in the Earth's crust and the rates of variations in the relations between discrete parts of hydrogeological structures: all of them are of the order of $0.0n$ to $0.000n$ m/year [14]. This means that the migrations of brines in ancient Paleozoic structures are controlled by extremely slow tectonic motions in various parts of the Earth's crust. Only these processes can disturb the hydromechanical equilibria in these hydrogeological structures. These processes can disturb the hydrogeochemical conditions in both these structures themselves and the adjacent structures that contain carbonate reservoirs.

METHODS OF THERMODYNAMIC SIMULATIONS OF THE GENESIS OF ZN AND PB SULFIDES IN CARBONATE ROCKS: BOUNDARY CONDITIONS

The essence of our methodological principles is as follows [11].
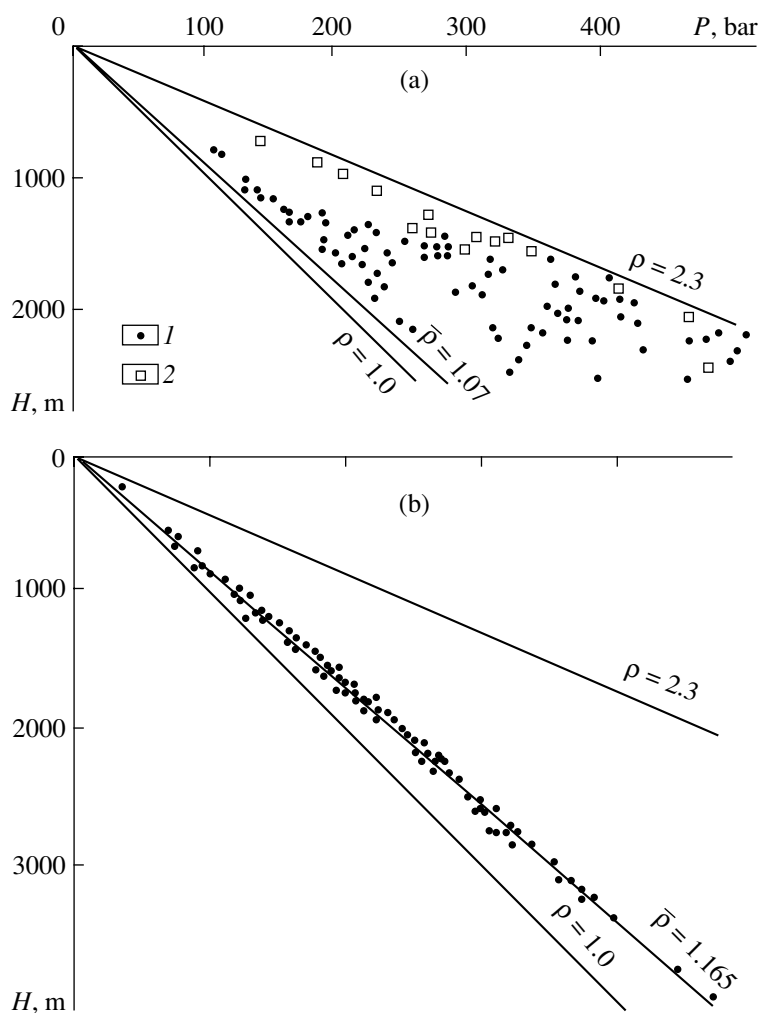
Fig. 5. Distribution of formation water pressures in sedimentation basins as functions of the depth and density (ρ) of brines (modified after [30]). (a) Unrelaxed in closed systems: (*1*) Gulf of Mexico basin; (*2*) Iranian basin (for example, in an unequilibrated hydrodynamic system). (b) Relaxed to the hydromechanically equilibrated distribution of the formation pressures of water with an average density ρ = 1.165 (for example, in a relaxed equilibrated hydrodynamic system, as in the Volga–Urals territory).

The genesis of the major types of mineralized waters and brines, their geochemical states, and their concentrations of chemical elements are controlled by a complex of boundary conditions (R/W ratios in the geochemical systems, P_{CO_2}, and the interaction temperatures), which are defined by natural geological, hydrogeological, and geothermal situations and eventually predetermine the results of geochemical processes in natural hydrogeochemical systems.

Some points here should be clarified. Naturally occurring systems are deterministically affected by universal geochemical processes (dissolution, crystallization, redox processes, dissociation, complexation, and ion exchange), which define the chemistry of groundwaters and whose efficiency and results are determined by the probabilistically occurring boundary conditions and geothermal situations. It is principally important that different boundary conditions lead to different geochemical consequences of the same geochemical processes. The ranges of these geochemical consequences turn out to be extremely wide, so that practically any geochemical types of mineralized waters and brines with broadly varying concentrations of chemical elements can be obtained by varying the boundary conditions of geochemical processes in rock–water systems. It is important to stress that a change in the boundary conditions results in absolutely new geochemical characteristics of the groundwaters and triggers principally new geochemical processes in them. We utilized these principles as the basis for our thermodynamic analysis of geochemical processes generated by the migration of brines with high concentrations of ore elements from terrigenous (clayey) rocks to carbonate lithological complexes.

Boundary conditions specified for the simulations. The systems discussed in this publication are thermodynamically closed with respect to CO_2 [11], and, thus,

the R/W ratio and the temperatures of water–rock interactions are of crucial importance. Inasmuch as these systems occur outside the infiltration zone and are elision relict systems, their R/W ratios should be determined based on the changes in the porosity of the rocks during lithological processes. The original (during sedimentation processes) porosity of clayey (terrigenous) rocks is of the order of tens of percent and decreases to 10–1% when the rocks are compacted. This means that the final R/W ratios of the clay–water system reached in elision processes should tend towards 100. Carbonate rocks have much better characteristics as reservoirs than those of terrigenous rocks: their porosity approaches 10% and is only occasionally lower. Because of this, the R/W ratio of carbonate systems receiving brines from clayey rocks decreases to approximately 10. The boundary conditions in terms of temperature are determined based on the analysis of relations between the temperatures in deep hydrogeological structures and data on the temperatures of ore-forming fluids. The latter data were obtained by studying fluid inclusions in ore minerals from stratiform deposits. Their relations are as follows. Judging from [5, 9, 25], the temperatures of fluid inclusions in ore minerals from stratiform deposits of the Mississippian type range from 50 to 200°C. These temperature correspond to the values known to occur in artesian structures. For example, the usual temperatures of mineralized waters and brines in miogeosyncline artesian basins at depths of 2000–3000 m are 100–130°C, occasionally rising to 275–330°C [9]. Because of this, the optimum temperatures for the simulations were assumed equal to 100–250°C.

We simulated geochemical processes generated by the flows of brines from clayey (terrigenous) formations into carbonate lithological complexes. For the complex of brines generated via evaporation concentration and metamorphosed in clayey rocks, we had to select a concentration stage whose geochemical characteristics most closely approached those of ore-forming solutions. This was done using materials on the composition of fluid inclusions in ore minerals from stratiform deposits [25]. For example, fluid inclusions in sphalerite containing 83–124.6 g/kg Cl⁻ correspond to metamorphosed brines of stages SW1 (72–130 g/kg) and SW2 (160 g/kg). Because of this, the initial composition of the brines introduced into the ore-forming process was assumed to be equal to those of brines SW2, metamorphosed into the "calcic" geochemical type, and enriched in ore elements as a result of interaction with clays. The compositions of these solutions are presented in Table 2, and the conditions under which they are generated were discussed in detail in our earlier paper [11]. This brine was brought into carbonate rocks at various interaction temperatures (50–200°C) and R/W ratios typical of carbonate rocks (100 ⟶ 10). Inasmuch as we consider elision hydrogeological systems, the ore-generating brines were successively diluted by natural low-mineralization waters and pure

Table 4. Characteristics times of formation pressure relaxation [30]

Water-bearing rocks	Values, orders of magnitude		
	formation-pressure conductivity factor, $cm^2 \ s^{-1}$	characteristic sizes of the artesian systems, m	characteristic relaxation times, years
Sandstones and limestones	10^4–10^5	10^3	10^{-2}–10^{-3}
		10^5	10^2–10^1
		10^6	10^4–10^3
Sands and gravels	10^3	10^3	10^{-1}
		10^5	10^3
		10^6	10^5
Siltstones	10^2	10^2	10^{-2}
		10^3	10^0
		10^5	10^4
Clayey rocks	10^0	10^2	10^0
		10^3	10^2
		10^5	10^6

Note: In addition to the parameters listed in the table, the relaxation time of formation pressures depend on the hydraulic permeability of the rocks, temperature, concentrations of components in the groundwaters, and other characteristics and boundary conditions of the hydrogeological structures. Note that the relaxation times of the chemical compositions of brines and their temperatures can differ from the hydrodynamic relaxation times [30].

water in the course of simulations. Simultaneously we modeled interactions with the same rocks without dilution by less mineralized waters and evaluated the correspondence of these opposite situations to, and their effect on, the intensity of the formation of ore-element sulfides in the solid phase.

Methods used in the thermodynamic simulations. Proceeding from naturally occurring hydrogeological situations of the migration of groundwaters and their successive interactions with the host carbonate rocks, the methods selected as optimal in application to our problems were those able to account for those successive geochemical interactions in dynamic hydro-geochemical systems. Because of this, our simulations were conducted by the method of flow-through stepwise reactors in its single-wave and multiwave modifications. In the method of stepwise flow-through reactors, the hydrogeochemical system is subdivided into a series of discrete subsystems of reactors. The original solution started to interact with the rock in the first reactor, after which the resultant solution flowed into the second reactor and started to interact there with the fresh rock of this reactor, and so on. In the course of this process, the solution changed its composition when passing through a series of reactors and also changed the composition of the rock via producing newly-

formed minerals. We simulated two variants of the situations:

* geochemical processes of interactions between brines and carbonate rocks took place in each cell, and the mineralization of the solutions systematically decreased. This decrease in the mineralization of the solutions was achieved via dilution in the proportions of 1 : 1, 1 : 2, etc., and also as $i = 1+$ kg of H_2O;

* solution in each cell was not diluted but acquired mineralization formed via interaction with the rocks.

We also used the method of a multiwave stepwise reactor. This method differs from the previous one in that it deals with the geochemical interactions of not a single solution portion but a series of waves of brine that successively inflow into the hydrogeochemical system of the reactors. In this method, the term *wave* is used as a synonym of a solution portion and is denoted *w*. The overall number of the waves used in the multiwave reactor method reached 100. As in the previous method of single-wave reactor, the movements of the waves were coupled with (i) the successive dilution of the solutions and (ii) the retainment of their original mineralization with the systematic accumulation of certain compounds in the resulting solutions as a consequence of interaction with rocks.

In the course of simulations, we calculated the compositions of the aqueous and solid phases and assayed the balance of elements between their masses passing into the solid phase and those remaining in the aqueous phase. The simulations were carried out by the GIBBS(HCh) computer program, which was developed by Yu.V. Shvarov and is underlain by the minimization of the free energy of the hydrogeochemical system. This program enables the researcher to widely vary the boundary conditions (R/W ratios and temperatures) and the compositions of rocks interacting with the brines. This, in turn, makes it possible to conduct numerical simulation experiments to elucidate the role of various boundary conditions in the generation of the compositions of the aqueous and solid phases and to determine the optimum conditions of various geochemical processes. By varying the boundary conditions, we imitated the formation of the sulfide mineral phase and determined the boundary conditions favorable for its origin. In describing the equilibrium state of the hydrogeochemical system, we assumed 70 simple and complex species that can probably be formed in the aqueous phase and occur as components of the solid phases. Their Gibbs free energies were quoted in many of our earlier publications [34].

With regard for situations created in nature by the elision process, we took into consideration the increase in the concentrations of organic matter (in the form of C_{org}) in the solutions interacting with rocks. The material into which brines with high concentrations of ore elements were introduced was assumed to be carbonate rocks with the average concentrations of chemical elements cited for them in reference books and specialized publications [35, 36].

GENESIS OF SULFIDE MINERALIZATION IN CARBONATE ROCKS: THERMODYNAMIC SIMULATION OF THE PROCESSES GENERATED BY FLOWS OF BRINES FROM TERRIGENOUS TO CARBONATE ROCKS

It was established previously [11] that, according to their effect on the distribution of ore elements in chloride brines, lithological formations in which brines are metamorphosed can be subdivided into two marginal types: (a) terrigenous, which are the sources of ore elements for the brines and maintain the accumulation of these elements in the brines, and (b) carbonate, whose geochemical role involves the precipitation of these ore elements as a solid phase in the form of sulfides. We assumed that the process of sulfide transformations of sulfur and the precipitation of ore elements in the form of sulfides occurs in situ as a consequence of sulfate reduction, $S(VI) \longrightarrow S(II)$, in the original solutions inflowing into the carbonate rocks. These processes can be activated at low Eh, which are generated by carbonate rocks (Table 3, Fig. 3). In naturally occurring hydrogeological situations, this process results in widespread sulfide (with hydrogen sulfide) waters in carbonate lithological formations [11].

This paper presents the results of our quantitative analysis of the validity of this hypothesis and the thermodynamic simulations conducted to solve the following two problems:
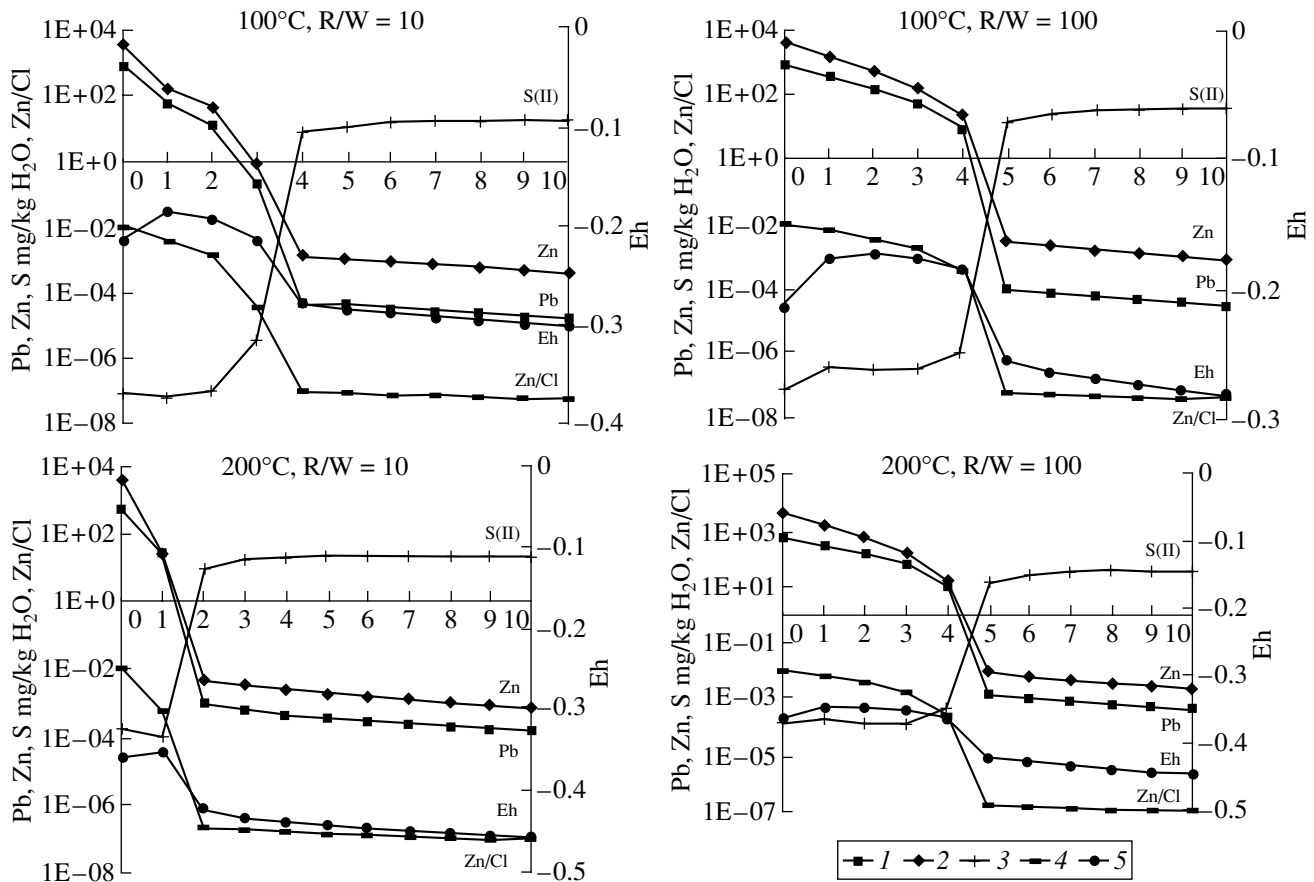
(1) we calculated the concentrations of sulfur that can be generated in carbonate rocks under various boundary conditions during the flows of brines from terrigenous rocks;

(2) we constrained the boundary conditions optimal for the precipitatiion of Zn and Pb sulfides from the brines in carbonate rocks.

The solution of these problems yielded the following results.

Quantitative Thermodynamic Analysis of the Origin of Sulfide Sulfur in Brines Flowing into Carbonate Rocks

First of all, it should be mentioned that our hypothesis that sulfide sulfur is generated by carbonate rocks was proved valid. The migration of chloride solutions into carbonate rocks is coupled with an increase in concentrations of sulfide sulfur in them to $n \times 10^2$–$n \times 10^3$ mg/kg. As will be demonstrated below, these concentrations are sufficient for the precipitation of Zn and Pb sulfides. The dynamics of the increase in the concentration of sulfide sulfur in brines at various R/W ratios during their interactions with carbonate rocks, temperatures, and degree of dilution of the original brines is shown in Fig. 6. It can be seen that the dynamics of the variations in the sulfide sulfur concentrations in the resultant solutions is quite uniform at any boundary conditions specified for the simulations. The overall principal situation with this dynamics is quite
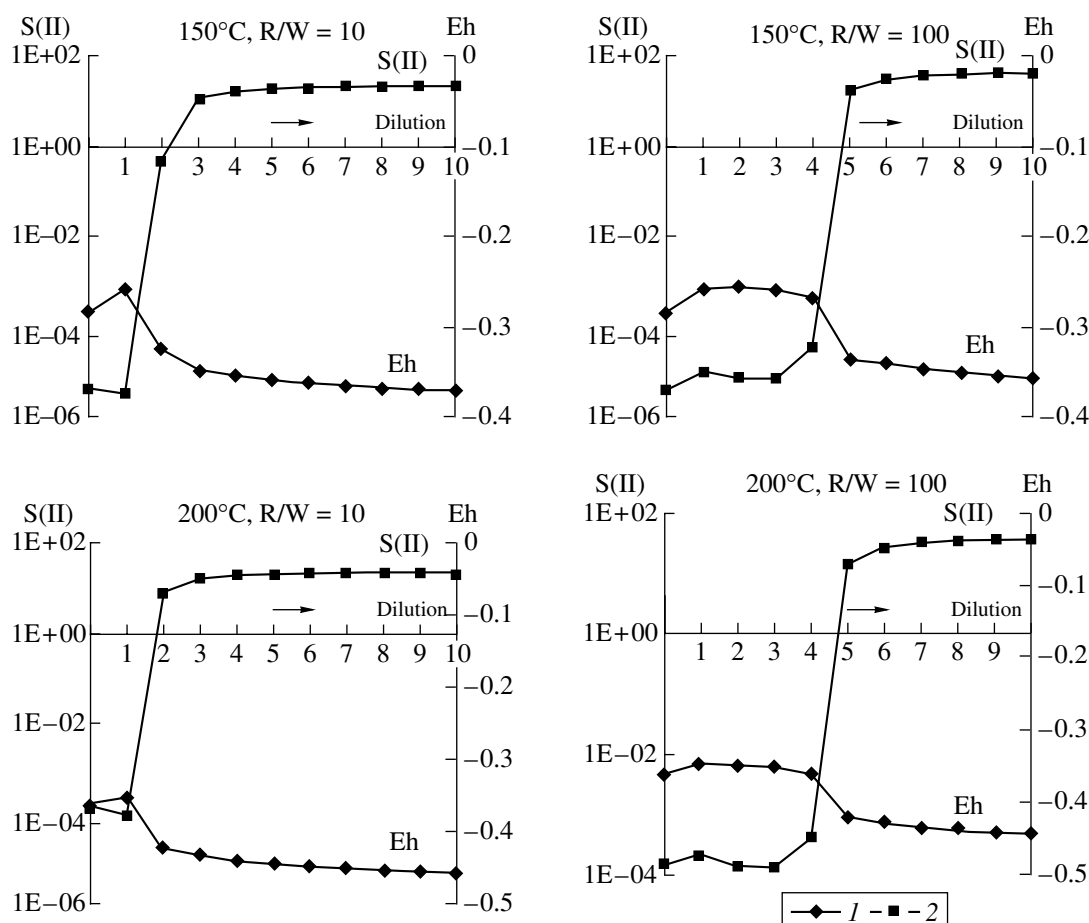
Fig. 6. Dynamics of variations in the concentrations of sulfide sulfur S(II), Pb, and Zn, the Zn/Cl ratio, and the Eh of brines during their migration from terrigenous to carbonate rocks at temperature of 100 and 200°C, various R/W ratios, and degrees of dilution (1–10). (1) Pb; (2) Zn; (3) S(II); (4) Zn/Cl; (5) Eh.

uniform. The introduction of the original brines into carbonate rocks is associated with the quick transformation S(VI) $\longrightarrow$ S(II) and a rapid increase in the $HS^- + H_2S/SO_4^{2-}$ ratios, which is, in turn, controlled by the temperature at which the brines interact with carbonate rocks: the higher this temperature, the higher this ratio (Fig. 7). The kinetics of the S(VI) $\longrightarrow$ S(II) transformations is controlled by the R/W ratio in the forming hydrogeochemical systems, the degree of dilution of the brines by elision waters, and the temperature. The final result of these transformations is uniform regardless of the boundary conditions: the interactions between the brines (solutions) and carbonate rocks during the final stages of the process occur at quite uniform concentrations of sulfur [$n \times 10^2$ to $n \times 10^3$ mg/kg for S(II)] in the resultant solutions. We believe that this uniformity is an indication of the fact that the system receives relatively little varying (in both amount and mass) concentrations of S(VI). The S(VI) $\longrightarrow$ S(II) transformation under these conditions is a stationary process, which is maintained by a constant gradient in S(VI) during the inflow of brines into carbonate rocks. This is a geochemical reactor that maintains constant

final ratios of the inflowing brines with S(VI) and newly produced S(II). The operation of this reactor is based on the fact that the original brines contain a cer-
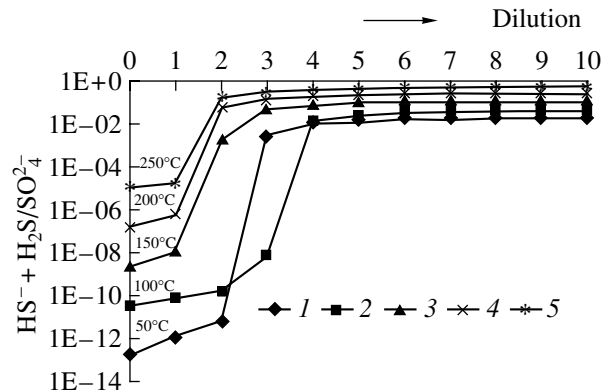
Fig. 7. Dynamics of variations in the $HS^- + H_2S/SO_4^{2-}$ ratios in brines interacting with carbonate rocks at R/W = 10 depending on the temperature and dilution of the original brines (GIBBS computer program). Interaction temperatures (°C): (1) 50, (2) 100, (3) 150, (4) 200, (5) 250.
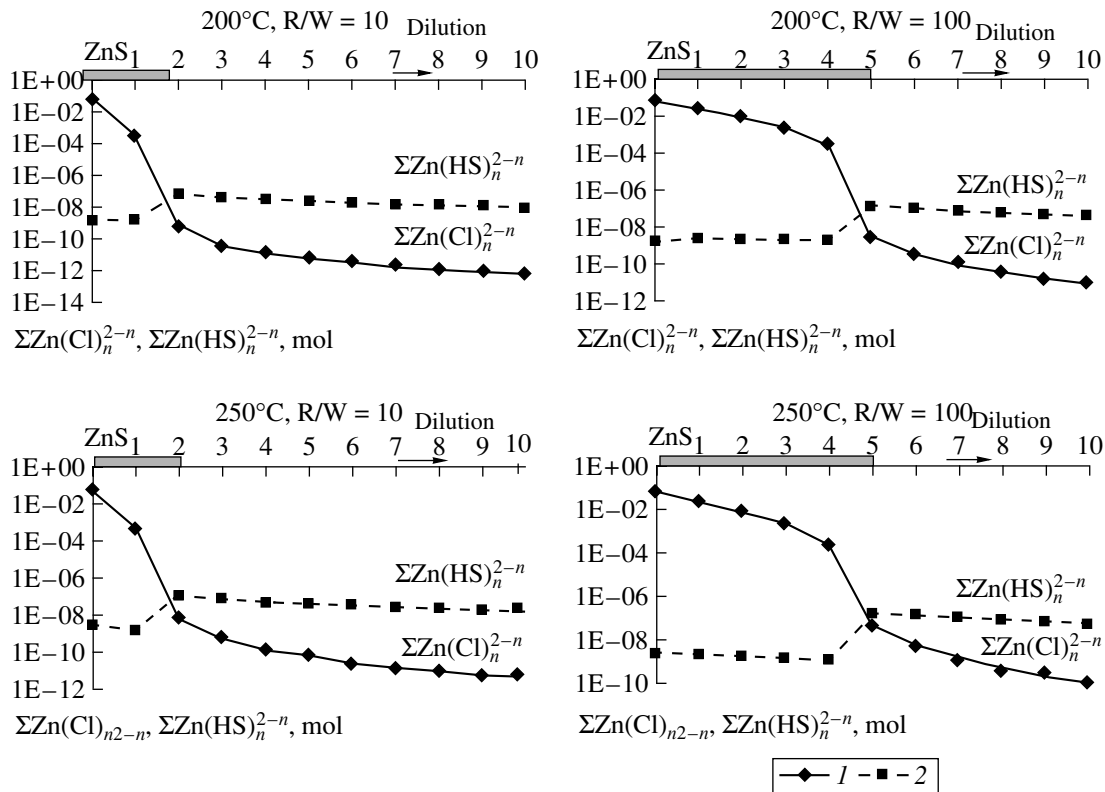
Fig. 8. Dynamics of variations in the concentrations of sulfide sulfur S(II) and Eh in brines during their interaction with carbonate rocks at temperatures of 150 and 200°C depending on the R/W ratio and the dilution of the original brines (GIBBS computer program). (*1*) S(II); (*2*) Eh.

tain mass of S(VI) that should be transformed into S(II) at low Eh generated in the carbonate rocks, particularly at high temperatures (100–250°C) (Fig. 8). This figure demonstrates that the relations between the Eh of the brines and their concentrations of sulfide sulfur are the opposite. These high temperatures and low Eh ensure the abiogenic sulfate reduction $SO_4^{2-} + 10H^+ + 8e \longrightarrow H_2S + 4H_2O$, $SO_4^{2-} + 9H^+ + 8\,e = HS^- + 4H_2O$, which always acts when brines migrate through carbonate rocks. This abiogenic sulfate reduction is activated with increasing interaction temperature of the brines and carbonate rocks, which is generally consistent with the main conclusions in [37]. It is important to emphasize that the differences in the generation of sulfide sulfur in our systems manifest themselves not in the final concentrations (it was demonstrated that these concentrations are quite uniform) but in the kinetics of the increase in these concentrations depending on temperature and the R/W ratio of the interaction of the brines and carbonate rocks. The unusual feature of this process is the fact that the maximum gradient in the S(II) concentrations is reached in the resultant solutions at

the minimum R/W ratios, i.e., at the lowest ratios of the interacting masses of the rocks and brine. At these low R/W ratios (10 and lower), the gradient of the increase in the concentrations of S(II) (i.e., the tempo of the increase in these concentrations) is at a maximum, and the maximum S(II) concentrations approach the initial stages of brine dilution (stages 1 and 2), whereas the analogous concentrations at R/W = 100 are reached only during stages 4–5.

*Boundary Conditions and Factors Favorable
for the Precipitation
of Zn and Pb Sulfides from Chloride Brines
in Carbonate Rocks*

This precipitation, which was indicated in the simulations by a decrease in the concentrations of Zn and Pb in the resultant brines (Fig. 6) and by the formation of sphalerite and galena in the solid phase of the system, takes place in the zone of the highest gradients of the increasing concentration of S(II) and the maximum S(II)/S(VI) ratios. The maximum amounts of sulfide minerals in the newly formed solid phase during this

Fig. 9. Variations in the proportions of the concentrations of chloride and hydrosulfide complexes in brines due to the S(VI) $\longrightarrow$ S(II) transformations when the brines filter through carbonate rocks. (*1*) Total for chloride complexes; (*2*) total for hydrosulfide complexes. Shaded bars correspond to the ranges where ZnS precipitates.

metamorphic stage of the brines at the most favorable precipitation conditions (which will be considered below) were as high as 36–40% for sphalerite and 10% for galena. Geochemically, the transformations of sulfur during the early stages of the inflow of brines into carbonate rocks are a typical zone of a contrasting geochemical barrier. Figure 6 summarizes all geochemical characteristics produced during this process. It can be seen that the decrease in Zn and Pb concentrations is the most rapid during this stage of the drastic increase in the concentration of S(II) in the resultant brines, and this metamorphic stage of brines is characterized by the formation of Zn and Pb sulfides. This is, however, only the explicit aspect of the genesis of sulfide sulfur and its effect on the origin of sulfide minerals. The implicit aspects of the process, caused by the transformations of the chemical composition of the brine in carbonate rocks, are as follows.

(1) First of all, these transformations are accompanied not only by a decrease in Zn and Pb concentrations but also by a drastic decrease in Zn/Cl and Pb/Cl ratios in the resultant solutions (Fig. 6). This provides evidence that the decrease in Zn and Pb concentrations in the resultant brines is caused not only by the dilution of the brines by elision waters but also by the decrease in their absolute masses as a consequence of geochemical

processes that lead to the precipitation of sulfide minerals.

(2) An increase in the concentrations of sulfide sulfur in the resultant solutions is ensued by transformations of Zn and Pb chloride complexes (which are strongly predominant in the original brines) into hydrosulfide complexes and by the precipitation of Zn and Pb sulfide minerals according to the scheme

$$ZnCl_n^{2-n} \longrightarrow Zn(HS)_n^{2-n} \longrightarrow ZnS.$$
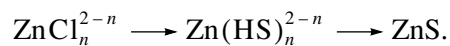
The stability of the Pb and Zn hydrosulfide complexes during all complexation stages at high temperatures is a few orders of magnitude higher than the stability of chloride complexes of these metals (under the same conditions). Because of this, the appearance of sulfide sulfur in the brines during their inflow into carbonate rocks results in an excess of the concentrations of hydrosulfide complexes over the concentrations of chloride compositions (Fig. 9), which provides the basis for the further transformations of hydrosulfide complexes into solid sulfides. The dynamics in the compositional evolution of the brines during their inflow into carbonate rocks and the changes in Zn and Pb concentrations in these brines are shown in Figs. 5–7.

Table 5. Changes in the concentrations of components with the inflow of brines from terrigenous rocks into carbonate formations (R/W = 100 ⟶ R/W = 10, 150°C, dilution i = 1 + kg H$_2$O for stages 1–10)

Component	0	1	2	3	4	5	6	7	8	9	10
mg/kg H$_2$O											
Na	123698	13826	8239	6188	5095	4403	3917	3552	3265	3031	2836
K	7998	1075	714	576	499	448	411	382	358	337	320
Ca	5961	960	617	480	406	359	327	303	285	270	258
Mg	4486	420	211	140	107	86.85	74.01	64.97	58.25	53.04	48.88
Sr	448	63.50	43.28	34.45	31.04	28.07	25.86	24.12	22.69	21.47	20.41
Cu	0.238	0.021	0.00093	0.00060	0.00044	0.00034	0.00027	0.00022	0.00019	0.00016	0.0014
Pb	832	51	0.00021	0.00014	0.00010	0.00008	0.00006	0.00005	0.00004	0.00004	0.00003
Zn	4117	49	0.00037	0.00024	0.00017	0.00013	0.00011	0.000088	0.000075	0.000064	0.000056
Cl	222643	24464	14458	10779	8827	7595	6732	6087	5582	5172	4830
S	1708	319	248	234	225	218	213	208	203	199	196
Zn/Cl	1.85E–02	1.09E–03	1.38E–08	1.20E–08	1.06E–08	9.51E–09	8.61E–09	7.87E–09	7.24E–09	6.71E–09	6.25E–09
pH	6.221	5.948	6.065	6.153	6.215	6.263	6.293	6.318	6.339	6.357	6.374
Eh (V)	–0.283	–0.258	–0.324	–0.347	–0.355	–0.36	–0.363	–0.366	–0.368	–0.369	–0.371
I	2.972	0.565	0.362	0.281	0.236	0.207	0.186	0.171	0.158	0.148	0.139
Mineralization	372000	41200	24500	18400	15200	13100	11700	10600	9770	9080	8510

Precipitation of ZnS and PbS

Zone of gradient S(VI) ⟶ S(II) reduction and precipitation of ZnS and PbS

Zone of constant residual concentrations of S(II), Zn, Pb; neither ZnS nor PbS are precipitated

Table 6. Changes in the concentrations of components with the inflow of brines from terrigenous rocks into carbonate formations (R/W = 100 ⟶ R/W = 10, 100°C, dilution $i = 1 + $ kg H_2O for stages 1–10)

Component	0	1	2	3	4	5	6	7	8	9	10
mg/kg H_2O											
Na	123698	74033	44339	29554	21486	16609	13413	11185	9558	8324	7359
K	7997	5740	3826	2742	2099	1687	1404	1199	1045	925	830
Ca	5399	3397	2308	1757	1438	1222	1071	962	880	816	764
Mg	5057	2934	1565	944	634	457	350	281	234	201	176
Sr	438	340	233	169	131	106	88.6	76.0	66.4	58.9	53.0
Cu	0.0420	0.021	0.010	0.006	0.002	0.002	0.00110	0.00084	0.00066	0.00053	0.00043
Pb	806	357	157	58.53	8.86	0.000113	0.000083	0.000063	0.000049	0.000040	0.000033
Zn	4187	1538	529	169	24.37	0.0031	0.0023	0.0017	0.0014	0.0011	0.0009
Cl	222643	130702	77549	51381	37204	28647	23054	19170	16341	14202	12534
S	2648	1970	1440	1150	973	878	816	766	724	688	658
Zn/Cl	1.88E–02	6.38E–03	3.70E–03	1.78E–03	3.55E–04	5.89E–08	5.33E–08	4.87E–08	4.48E–08	4.15E–08	3.87E–08
pH	6.407	5.889	5.88	5.903	5.94	6.003	6.067	6.122	6.17	6.212	6.249
Eh (V)	–0.213	–0.175	–0.173	–0.176	–0.184	–0.255	–0.264	–0.269	–0.274	–0.278	–0.281
I	3.478	2.475	1.682	1.217	0.935	0.752	0.626	0.535	0.467	0.414	0.372
Mineralization	373000	221010	131944	87924	63998	49605	40195	33640	28849	25214	22374

Precipitation of ZnS and PbS

Zone of S(VI) ⟶ S(II) reduction and precipitation of ZnS and PbS

Zone of constant residual concentrations of S(II), Zn, Pb; neither ZnS nor PbS are precipitated

Table 7. Zn and Pb concentrations (mg/kg) during the inflow of the original brines into carbonate rocks at R/W equal to 10 and 100 and the successive dilution of the original brines ($I = 1 + $ kg of H_2O)

T, °C	R/W = 10 Dilution stages										
	0	1	2	3	4	5	6	7	8	9	10
100 Pb	7.9E+02	6.1E+01	1.3E+01	2.1E–01	5.3E–05	4.1E–05	3.3E–05	2.7E–05	2.3E–05	2.0E–05	1.7E–05
Δ		7.3E+02	7.7E+02	7.9E+02	7.9E+02	7.9E+02	7.9E+02	7.9E+02	7.9E+02	7.9E+02	7.9E+02
Zn	4.1E+03	1.7E+02	4.5E+01	7.8E–01	1.4E–03	1.1E–03	8.9E–04	7.3E–04	6.2E–04	5.3E–04	4.6E–04
Δ		3.9E+03	4.0E+03	4.1E+03	4.1E+03	4.1E+03	4.1E+03	4.1E+03	4.1E+03	4.1E+03	4.1E+03
150 Pb	8.1E+02	5.1E+01	2.1E–04	1.4E–04	9.8E–05	7.6E–05	6.1E–05	5.0E–05	4.2E–05	3.6E–05	3.2E–05
Δ		7.6E+02	8.1E+02	8.1E+02	8.1E+02	8.1E+02	8.1E+02	8.1E+02	8.1E+02	8.1E+02	8.1E+02
Zn	4.0E+03	4.9E+01	3.7E–04	2.4E–04	1.7E–04	1.3E–04	1.1E–04	8.8E–05	7.5E–05	6.4E–05	5.6E–05
Δ		4.0E+03	4.0E+03	4.0E+03	4.0E+03	4.0E+03	4.0E+03	4.0E+03	4.0E+03	4.0E+03	4.0E+03
200 Pb	5.9E+02	2.6E+01	9.3E–04	6.0E–04	4.4E–04	3.4E–04	2.7E–04	2.2E–04	1.9E–04	1.6E–04	1.4E–04
Δ		5.7E+02	5.9E+02	5.9E+02	5.9E+02	5.9E+02	5.9E+02	5.9E+02	5.9E+02	5.9E+02	5.9E+02
Zn	4.2E+03	2.5E+01	4.9E–03	3.2E–03	2.3E–03	1.8E–03	1.4E–03	1.2E–03	9.9E–04	8.5E–04	7.4E–04
Δ		4.1E+03	4.2E+03	4.2E+03	4.2E+03	4.2E+03	4.2E+03	4.2E+03	4.2E+03	4.2E+03	4.2E+03
250 Pb	3.4E+02	1.4E+01	2.5E–03	1.6E–03	1.2E–03	9.0E–04	7.3E–04	6.0E–04	5.1E–04	4.3E–04	3.8E–04
Δ		3.2E+02	3.4E+02	3.4E+02	3.4E+02	3.4E+02	3.4E+02	3.4E+02	3.4E+02	3.4E+02	3.4E+02
Zn	4.2E+03	2.8E+01	7.6E–03	4.9E–03	3.6E–03	2.7E–03	2.2E–03	1.8E–03	1.5E–03	1.3E–03	1.1E–03
Δ		4.2E+03	4.2E+03	4.2E+03	4.2E+03	4.2E+03	4.2E+03	4.2E+03	4.2E+03	4.2E+03	4.2E+03

T, °C	R/W = 100 Dilution stages										
	0	1	2	3	4	5	6	7	8	9	10
100 Pb	7.9E+02	3.6E+02	1.6E+02	5.9E+01	8.9E+00	1.1E–04	8.3E–05	6.3E–05	4.9E–05	4.0E–05	3.3E–05
Δ		4.3E+02	6.3E+02	7.3E+02	7.8E+02	7.9E+02	7.9E+02	7.9E+02	7.9E+02	7.9E+02	7.9E+02
Zn	4.1E+03	1.5E+03	5.3E+02	1.7E+02	2.4E+01	3.1E–03	2.3E–03	1.7E–03	1.4E–03	1.1E–03	8.9E–04
Δ		2.6E+03	3.6E+03	3.9E+03	4.1E+03	4.1E+03	4.1E+03	4.1E+03	4.1E+03	4.1E+03	4.1E+03
150 Pb	8.1E+02	3.9E+02	1.9E+02	8.2E+01	8.7E+00	5.9E–04	4.3E–04	3.3E–04	2.6E–04	2.1E–04	1.7E–04
Δ		4.2E+02	6.2E+02	7.3E+02	8.0E+02	8.1E+02	8.1E+02	8.1E+02	8.1E+02	8.1E+02	8.1E+02
Zn	4.0E+03	2.5E+03	4.9E+02	1.4E+02	1.2E+01	7.2E–03	5.3E–03	4.0E–03	3.1E–03	2.5E–03	2.1E–03
Δ		2.5E+03	3.5E+03	3.9E+03	4.0E+03	4.0E+03	4.0E+03	4.0E+03	4.0E+03	4.0E+03	4.0E+03
200 Pb	5.9E+02	2.8E+02	1.4E+02	6.6E+01	1.0E+01	1.5E–03	1.1E–03	8.5E–04	6.7E–04	5.4E–04	4.4E–04
Δ		3.1E+02	4.5E+02	5.3E+02	5.8E+02	5.9E+02	5.9E+02	5.9E+02	5.9E+02	5.9E+02	5.9E+02
Zn	4.2E+03	1.6E+03	5.2E+02	1.6E+02	1.7E+01	8.9E–03	6.5E–03	4.9E–03	3.9E–03	3.1E–03	2.6E–03
Δ		2.6E+03	3.6E+03	4.0E+03	4.1E+03	4.2E+03	4.2E+03	4.2E+03	4.2E+03	4.2E+03	4.2E+03
250 Pb	3.4E+02	1.6E+02	7.5E+01	3.3E+01	5.2E+00	4.2E–03	3.0E–03	2.3E–03	1.8E–03	1.5E–03	1.2E–03
Δ		1.8E+02	2.6E+02	3.1E+02	3.3E+02	3.4E+02	3.4E+02	3.4E+02	3.4E+02	3.4E+02	3.4E+02
Zn	4.2E+03	1.6E+03	5.5E+02	1.7E+02	1.8E+01	1.4E–02	1.1E–02	8.0E–03	6.3E–03	5.1E–03	4.2E–03
Δ		2.6E+03	3.7E+03	4.1E+03	4.2E+03	4.2E+03	4.2E+03	4.2E+03	4.2E+03	4.2E+03	4.2E+03

Note: The solid line shows the boundary of the complete precipitation of Zn and Pb from the original brines listed in column 1; Δ are the amounts of Zn and Pb precipitating from the original solutions.

Effect of the dilution of the original brines by weakly mineralized elision waters or "pure" waters. Geochemically, the most significant precipitation of sulfide minerals occurs simultaneously with the dilution of the original brines by elision waters or "pure" water. The precipitation of sulfide minerals from undiluted brines is delayed until much later stages of the process, and this precipitation itself is much less contrasting and intense (in terms of mass). The reason for this is the further increase in the mineralization of the undiluted brines when they migrate through carbonate rocks [38] and an increase in the complexation of ore elements in these brines (in the form of both chloride and hydrosulfide species). Correspondingly, the possibility of the extraction of ore elements from them for the precipitation of solid sulfides at the same concentrations of S(II) decreases. The effect of the dilution of ore-forming brines on the precipitation of sulfide minerals has been discussed for a long time [5, 39–41]. H. Barnes [41] was among the first to demonstrate in 1965 that dilution by water results in the precipitation of sphalerite from Zn sulfide complexes. It is pertinent to add that it was proved in our earlier publication [42] that the action of the sulfide barrier is the most efficient at low concentrations of sulfide sulfur (0.n to n mg/l), whereas its high concentrations diminish the geochemical activity of this barrier and lead to the passage of Zn and Pb into soluble hydrosulfide complexes. It was demonstrated that an increase in $\Sigma S(II)$, due to an increase in the concentrations of hydrosulfide complexes like $Me(HS)_n^{2-n}$, expands the range of thermodynamically permissible Pb and Zn concentrations in sulfide waters and, correspondingly, leads to the dissolution of earlier solid sulfides.

Based on the simulations, we examined the effect of the transformation of hydrosulfide complexation on the formation of MeS during the dilution of the original brines. The essence of this phenomenon is the transformations of complex compounds according to the scheme $Me(Cl)_n^{2-n} \longrightarrow Me(HS)_n^{2-n} \longrightarrow MeS$. As the brines come into carbonate rocks, already the initial increase in the S(II) concentrations is associated with (i) the decomposition of $Me(Cl)_n^{2-n}$ complexes in the brines with the crystallization of sphalerite and galena, which are formed during the very early interaction stages (it was demonstrated earlier [42] that chloride complexation of Zn and Pb in brines cannot, in fact, hamper the precipitation of MeS from them, because $pK_{Zn(Cl)_n^{2-n}}$ at 150°C is only 2–3 at SP_{ZnS} of the order of $n \times 10^{-25}$); and (ii) the remaining ore elements form hydrosulfide complexes (Fig. 9), so that their predominant migration modes are $Me(HS)_3^- – Me(HS)_2^0$, and $Me(HS)^+$. The further dilution of the brines results in shifts in equilibria in the system $Me(HS)_3^- \longrightarrow Me(HS)_2^0 \longrightarrow$

$Me(HS)^+$. [4] The last and the simplest hydrosulfide compound $Me(HS)^+$ is the least stable: 150°C $pK_{Me(HS)^+}$ at 150°C is ~7, and, thus, its formation cannot preclude the further origin of brines with MeS. Consequently, the precipitation of solid sulfides during the dilution of the brines is further intensified, as also follows from the results of our simulations: the percentages of sphalerite and galena in the solid phase increase. The most probable scheme of their formation is $Me(HS)^+ \longrightarrow MeS + H^+ (Me(HS)_2^0 \longrightarrow MeS + H_2S)$.

Tables 5–6 illustrate how quickly our diluted system gets rid of Zn, Pb, and S via the precipitation of solid ZnS and PbS. It can be seen that the precipitation of ore elements in the form of their sulfides from diluted brines is practically complete.

The opposite situation occurs in undiluted brines during an increase in their mineralization and concentrations of S(II). The equilibrium in the system of hydrosulfide complexes is shifted toward more coordination-saturated complexes of high general stability. Moreover, a significant increase in the concentration of S(II) and the origin of highly stable coordination-saturated hydrosulfide complexes is associated not only with the retainment of Zn and Pb in the sulfide waters but also with the dissolution of earlier solid sulfides [41]. As a result, the undiluted brines can retain high concentrations of Zn (and Pb) up to much later reactors, and the precipitation of Zn(Pb) is far from complete even in the last reactors. This is in good agreement with the distribution of chalcophile elements in natural sulfide brines. We examined sulfide brines from the Fore-Uralian, Fore-Carpathian, and Fergana basins, which contain significant concentrations of S(II) (from n to $n \times 100$ mg/l). Their maximum Zn concentrations approached 1 mg/l, and those of Pb were close to 0.2 mg/l. This phenomenon is universal and is typical of all sulfide waters, in which the precipitation of Pb and Zn sulfides is never complete.

This led us to the conclusion that the complete precipitation of Zn and Pb from sulfide solutions can occur only upon their dilution, with Zn and Pb sulfide precipitation the more complete, the more diluted the solutions (because this precipitation of the minerals is not hampered by the accompanying processes of complexation). During this dilution of the original brines, the persistence of the barrier properties of ore-forming systems is controlled by the boundary conditions that can preclude or facilitate the precipitation of sulfides at barriers. Our systems have two such conditions: the R/W ratio and temperature.

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[4] This decrease in the concentrations of sulfide sulfur due to the dilution of the original brines is clearly illustrated in Tables 5, 6, which list analyses (in mg/kg) of resultant solutions. This decrease is not as apparent in generalizing Figs. 6–8 whose logarithmic scale somewhat beclouds the differences in the concentrations.

Effect of the R/W ratios. It is known that the lower R/W ratio in carbonate rocks causes a more rapid increase in the concentrations of sulfide sulfur, a more rapid decrease in the Eh of the solutions, and the more active precipitation of Zn and Pb sulfides (Figs. 6–9, Tables 5–7). Indeed, at R/W ratios equal to 10, the maximum S(II) concentrations are reached at any temperatures already at one- to threefold dilutions. An increase in the R/W ratios to 100 shifts the zone of the maximum increase in S(II) to five- sixfold dilutions, and, correspondingly, the amounts of the precipitating Zn and Pb sulfides diminish throughout the whole zone. Thus, the lower the R/W ratios of the systems (i.e., the lower the mineralization of the solutions), the farther the shift of the systems to the early stages of sulfide complexation [Me(HS)+]. Accordingly, the conditions become more favorable for the precipitation of sulfides in the solid phase. As a consequence, less mineralized brines occur at lower R/W ratios, and elements are contained in these brines in the form of species more favorable for the precipitation of sulfides (because of the simpler and less stable initial sulfide complexes).

Effect of a temperature increase on the transformation of sulfur systems and the origin of sulfide minerals. This temperature increase leads to two important consequences. First, a temperature increase intensifies the yield of S(II) compounds in the process of abiogenic sulfate reduction ($SO_4^{2-} + 10H^+ = H_2S + 4H_2O$; $SO_4^{2-} + 9H^+ = HS^- + 4H_2O$) and intensifies the formation of S(II) during the dissociation of $HS^- \longrightarrow H^+ + S^{2-}$ and $H_2S \longrightarrow HS^- + H^+$.

It is demonstrated in [37] that a temperature increase to 150–300°C shifts the $SO_4^{2-} \longleftrightarrow (H_2S + HS^-)$ redox equilibrium toward reduced S species, and the equilibrium redox potential of the system in near-neutral solutions decreases to –400 and –500 mV. It is also important that a temperature increase is associated with an increase in the degree of dissociation of $HS^- \longrightarrow H^+ + S^{2-}$ and $H_2S \longrightarrow HS^- + H^+$. Judging from the materials presented in [43], the pK of HS^- dissociation decreases from 12 to 6 as the temperature increases from 50 to 250°C. Consequently, much S^{2-} is released to participate in the precipitation of sulfide minerals. Analogously, an increase in the temperatures specified in the simulations shifts the maximum in the S(VI) $\longrightarrow$ S(II) reduction toward the early reactors of our system (Fig. 7), and the gradient of these transformations increases. Because of this, the maxima in the S(II) concentrations systematically shift to earlier dilution stages (reactors), and, correspondingly, the precipitation of ZnS and PbS becomes more rapid and massive in the temperature succession of 100 < 150 < 200 < 250°C.

Another consequence of a temperature increase is the intensification of the decomposition of hydrosulfide complex compounds in response to the decrease in the pH of the resultant solutions with increasing tempera-

ture. It was mentioned above that an increase in the solution temperatures to 200–250°C leads not only to a decrease in the redox potential but also to a decrease in the pH (Fig. 3). As a result, a decrease in pH brings about the decomposition of Zn and Pb hydrosulfide complexes with the formation of $MeS(Me(HS)_2^0) + H^+ \longrightarrow MeS + H_2S$.

Sulfide Precipitation in Systems with Single- and Multiwave Stepwise Reactors

(1) In the system of a single-wave flow-through reactor, Zn and Pb sulfides are formed not everywhere in the system but only within its narrow initial zone in which the S(II) concentration drastically increases and which, in fact, possesses the barrier characteristics of the system. The precipitation of the whole mass of ore elements contained in the original solutions is spatially restricted only to this narrow local gradient barrier zone of the system, in which the S(II) concentration increases, along with the S(II)/S(VI) ratio. No solid sulfides can be formed outside this zone, although the S(II) concentrations there are relatively high. In our system, this is caused by the absolute depletion of the mass of ore elements, i.e., their reserves can be precipitated. It follows from Tables 5 and 6 that all this mass is already precipitated, and it is obvious that the continuation of sulfide precipitation requires a new portion of brines with analogous concentrations of ore elements. Only in this situation can be expected the lateral shift of the ore-forming zone along the stratum of carbonate rocks with organic matter (i.e., having a high ore-generating potential) according to the filtration of brines that are able to precipitate ore minerals. The results of the simulation of the genesis of stratiform mineral deposits in [29] demonstrate that exactly these hydrodynamic situations are needed to produce such deposits.

We expected to simulate the lateral "roll" displacement of the ore-generating zone by using the method of the multiwave stepwise reactor and increasing the number of brine waves passing through the system. However, the results obtained at the same boundary conditions point only to an increase in the masses of sphalerite and galena (up to 36–40% of the solid phase for sphalerite) in the same narrow local zone of our geochemical barrier (Fig. 10). This phenomenon is of dualistic nature. On the one hand, the multiwave character of the reactor results in a significant increase in the mass of the sulfide ore material in the geochemical barrier zone. On the other hand, the multiwave character of the model does not lead to the farther shift of the ore-forming zone along the bed. There can be only one explanation of this phenomenon: the "productivity" and "capacity" of the geochemical barrier at the specified boundary conditions are so large that it does not pass any farther newly coming masses of ore elements but instead precipitates them and increases the mass of

solid sulfides. Evidently, the farther advance of the ore-forming zone along the bed, together with the filtration of the brines, is possible only after the depletion of the whole capacity of the geochemical barrier. This obviously implies that the lateral displacement of the ore-forming zone in the hydrogeological structure requires multiple water exchange with the long-lasting inflow of ore-forming brines.

DISCUSSION OF THE RESULTS FROM THE STANDPOINT OF THE OPTIMUM HYDRODYNAMIC AND GEOCHEMICAL CONDITIONS OF THE EVOLUTION OF NATURAL HYDROGEOLOGICAL STRUCTURES FOR THE DEVELOPMENT OF STRATIFORM Zn AND Pb ORE MINERALIZATION

In the course of our research, which was partly described in our earlier paper [11], we determined that hydrogenic stratiform Zn–Pb deposits are produced by the systematic hydrogeochemical and geochemical evolution of hydrogeological structures. During their evolution, these structures acquire the abilities (i) to concentrate significant masses of ore elements in chloride brines and (ii) to precipitate these masses in the form of sulfide minerals. This historical–geological evolution of the hydrogeological structures must involve a systematic succession of inevitable phenomena (prerequisites), which are summarized into a vector of the ore-forming potential of chloride brines and lead to the precipitation of Zn–Pb ore mineralization at geochemical barriers.

Prerequisites favorable for the development of high concentrations of ore elements in chloride brines and for the precipitation of sulfide minerals. These prerequisites involve:

(1) The metamorphism of connate relict brines (SW2 and higher) in a hydrogeochemical system thermodynamically closed with respect to CO_2, a condition required for the evolution of chloride brines according to the "calcic" trend at constant relations $2mCa^{2+} > mHCO_3^- + 2mCO_3^{2-}$;

(2) The occurrence of high R/W ratios in the system, which activate the release of ore elements–geochemical analogues of Ca (Zn, Pb, Fe, and Mn) into the aqueous phase;

(3) High temperatures (150–250°C) at which the brines interact with terrigenous rocks, which occur due to either (i) the deep subsidence of the hydrogeological structures (at normal geothermal gradients) or (ii) a high heat flux in these structures, which activate the $Mg \longrightarrow Ca$ (Zn, Pb, Fe, Mn) exchange reactions;

(4) An elision hydrodynamic regime in the hydrogeological structures with predominantly terrigenous rocks, whose aquifer systems are under suprahydrostatic pressures of geostatic genesis and ensure the
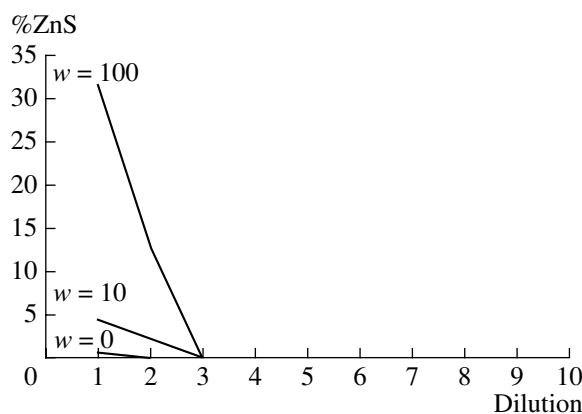

Fig. 10. Amount of precipitated sphalerite in a geochemical barrier zone as a function of the number of waves (*w*) (GIBBS computer program, 150°C).

migration of their various relict waters (of free pore, bound dehydration, and other types) into adjacent carbonate rocks;

(5) The development of a high potential for the abiogenic sulfate reduction $S(VI) \longrightarrow S(II)$ in the migrating brines at decreasing Eh in the carbonate rocks; the development of a sulfide geochemical barrier in these rocks, whose growth gradient is maintained by the dilution of the original brines, a temperature increase, and a decrease in the R/W ratios in the newly-formed hydrogeochemical systems.

However, even the origin of this succession of favorable prerequisites still does not guarantee the development of ore mineralization. It is now clear enough that deep-seated hydrogeological structures with halide formations often contain chloride brines with high concentrations of ore elements [11] but are not accompanied by stratiform ore mineralization. Structures with accompanying Zn–Pb ore deposits always have chloride brines with high concentrations of these ore elements, but far from all structures with these brines have ore mineralization. Brines with high Zn and Pb concentrations are spread much more widely than the corresponding ore mineralization itself. For example, the deep levels of the Angara–Lena, Tungusska, and Pripyat platform artesian basins are vast reservoirs of chloride brines with high concentrations of ore elements, but neither these structures themselves nor their surrounding rocks bear economic Zn–Pb mineralization. In structures in the Uralian foredeep, chloride brines contain much lower concentrations of ore elements, but these structures bear much more significant Zn–Pb mineralization. At the same time, the basins of Zechstein in Western Europe and, particularly, Midcontinent in the United States host both chloride brines and large Zn–Pb deposits. It is quite obvious that (i) the occurrence of chloride brines in hydrogeological structures is only a necessary but not sufficient condition of the origin of Zn–Pb mineral

Changes in the Zn concentration, mg/kg of H_2O
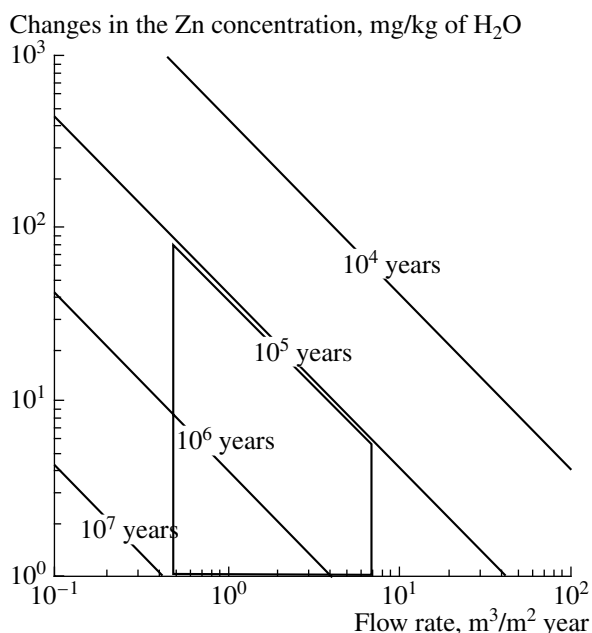
Fig. 11. Model for the relations between the flow rates of brines, their Zn concentrations, and the time needed to form a stratiform ore deposit like Pine Point [29].

deposits, and (ii) there should be more general universal hydrogeological phenomena that control the origin of stratiform mineralization and enable the implementation and geochemical efficiency of the aforementioned prerequisite.

Characteristics of the hydrogeological evolution of geological structures optimal for the origin of stratiform Zn–Pb mineralization. Our hydrogeological analysis of the genesis of stratiform mineral deposits indicates that the key point of this problem is not so much the origin of the brines themselves as certain characteristics of the hydrogeological evolution of the geological structures that produce these brines and facilitate their migration into the zones of geochemical barriers and the precipitation of ore mineralization.

Now we can determine which geological structures are optimal for the development of stratiform Zn–Pb mineralization and which of their hydrodynamic characteristics make the ore-forming process in them efficient. Currently available materials enable us to answer these questions: on the one hand, there are the results of the serious mathematical and hydrodynamic modeling of the genesis of stratiform ore mineralization (the time needed for its origin, the concentrational parameters of the chloride brines, and the volumes and flow rates of these brines [29]). On the other hand, extensive materials are now available on the regional hydrodynamic evolution of hydrogeological structures that contain chloride brines [8, 16, 19–23, 31–33]. The synthesis of these data provides insight into the ore-forming roles of various hydrogeological structures and makes it possi-

ble to identify their features favorable for ore-forming process.

Figure 11 presents the results of the mass-transfer simulations of the time needed for brines to form a stratiform Zn–Pb deposit like Pine Point depending on the Zn concentrations in the brines and the flow rates of the brines through the structure (preparatorily, we conducted a paleohydrogeological reconstruction of the ore-forming structure and assayed its hydrodynamics using the finite-difference method). It can be seen that the usual time needed to form a mineral deposit is 10^5–10^6 years and decreases with increasing Zn concentrations in the ore-forming brines and, particularly, with increasing flow rates of these brines. Assuming the usual Zn concentrations in the brines (from 10 to 100 mg/kg) and the amounts of elision solutions close to those produced by terrigenous rocks in nature (a few cubic meters) and normalizing them to one year [14], we evaluated the time commonly needed to produce a large mineral deposit, such as Pine Point, at 10^6 years. It is important to emphasize that a decrease in the amount of the solutions coming into the ore-forming system (<1 m^3/year) increases the time needed to form the deposit to 10^7 years. This leads us to the obvious conclusion that the time of the development of stratiform deposits is a function of the hydrodynamic characteristics of the structure: the development of the deposit requires that the flow rates of brines through the ore-forming structure were no less than a few cubic meters per year, and the origin of ore deposits becomes less realistic if these flow rates are lower. This, in turn, leads to the conclusions that ore-forming structures should be hydrodynamically active hydrogeological systems.

Let us now return to the first section of this paper, particularly, to Table 4, which characterizes the relaxation time of the structure to a hydrodynamically equilibrated state in elision artesian systems. It can be easily seen that this relaxation time (of the order of 10^5–10^6 years) roughly corresponds to the characteristic time of the ore-forming process in Fig. 11. Hence, the time needed to form a typical stratiform mineral deposit corresponds to the time of one cycle of elision relaxation during the hydrodynamic evolution of the hydrogeological structure from an unequilibrated geostatic to an equilibrated hydrostatic state.

This leads us to the following three important conclusions:

(1) The ore-forming process, which is based on the migration of solutions into the zones of geochemical barriers, is the result of the implementation of the relaxation potential of the hydrogeological structure, which occurs from an unequilibrated geostatically tensed state to an equilibrated hydrostatic state. The driving force and mechanism of this shift is the relaxation potential.

(2) The time needed to produce stratiform ore mineralization in a hydrogeological structure should be constrained by the time during which the structure preserves this potential.

(3) The transition of the structure from unequilibrated geostatic to equilibrated hydrostatic states means the termination of the process of effective ore formation. In terms of hydrogeology, the development of a stagnant regime in the structure implies that it loses its ore-forming potential.

These conclusions make understandable the characteristics of hydrogeological structures necessary for these structures to be able to generate stratiform Zn–Pb ore mineralization. First of all, the structures should be hydrodynamically active (water-exchanging) but not stagnant. This conclusion follows from the results of our simulations, which demonstrate that efficient ore formation requires a constant inflow of ore-forming brines into the zones of geochemical barriers and the continuous replacement of these brines by newly arriving brine portions in the ore-forming reactor. It was demonstrated that the mass of sulfide minerals precipitating in the zones of geochemical barriers increases proportionally to the number of solution waves inflowing into the ore-forming reactor. Hence, the maximum ore-forming potential should be typical of structures not only having high concentrations of ore elements in their brines but also able to maintain the maximum number of water-exchange cycles during the hydrogeological ore-forming evolution.

Based on the materials presented previously, we can provisionally list the hydrodynamic parameters of these optimal hydrogeological structures able to form ore mineralization: their overall rate flows of chloride brines with high concentrations of ore elements should be of the order of $0.n$–n m^3/year, the velocities of the brines in these structures should be of the order of $0.n$–n m/year, and the time of the ore-forming activity of the hydrogeological structures should be of the order of $0.n$–n years.

Modern analogues of these hydrogeological structures are artesian basins, such as the Western Turkmenia basin and the Eastern Caucasian Foredeep, which are situated in Alpine miogeosyncline zones bounded by platform structures. For example, the Western Turkmenia basin is characterized by a modern flow rate of 3×10^{-3} km^3/year [14] and "yields" Cl–Ca–Na brines with high concentrations of Pb, Zn, Fe, and Cd for a long time [44].

A much lower ore-forming potential is typical of deep-seated platform structures with stagnant hydrodynamic regimes, such as the deep levels of the Pripyat', Angara–Lena, and other basins that are hydrostatically equilibrated and have only residual fragments of quasielision regimes [32]. Such stagnant structures have lost their ability to move the brines and, correspondingly, are not able to implement their ore-forming potential. The velocities of brines in these structures are

of the order of $0.n$ to n cm/year, and their water exchange (if any) lasts, for example, for 50–60 m.y., as in the Angara–Lena basin [31]. These values are much greater than the time needed to produce such a significant deposit as Pine Point. This means that such water exchange and dynamics of the brines cannot create the ore-forming tension required for the origin of a significant mass of sulfide minerals. In this water-exchange situation, only the very first waves of the ore-forming solutions can enter the zone of the sulfide geochemical reactor, and the multiple replenishment of the solution waves and the corresponding concentrating of newly formed ore minerals will not take place.

Hence, these situations are characterized by the alternative: either (i) the deposit should be formed over a time period of several dozen million years (which is hardly probable), or (ii) the action only of the first waves of the ore-forming brine can produce lean mineralization ($0.n$ to n% of the overall mass of newly formed minerals). The latter scenario seems to be more realistic and consistent with naturally occurring situations. Thus, such stagnant hydrogeological structures with high concentrations of ore elements cannot maintain active ore formations and cannot be optimal for this process.

In conclusion, we would like to mention the inconsistency between naturally occurring situations and the results of our thermodynamic simulations of the origin of stratiform Zn–Pb ore mineralization. In our simulations, the dilution of the original brines brought about ore-forming solutions whose mineralization was much lower than that known to occur in fluid inclusions in ore minerals. We believe that this inconsistency provides evidence that the mineralization of solutions that can form ore mineralization can be lower than that found in the inclusions (particularly considering the fact that the inclusions occur at extremely high R/W ratios). Obviously, the pivoting point of the ore-forming process is not the mineralization of the solutions but the relations and interactions in the Me^{2+}–$Cl^- \longrightarrow HS^-$ system, which are controlled by the Eh–pH boundary conditions. Correspondingly, the lower the mineralization of the ore-formed solutions becomes, the weaker complexation is in them, and the more favorable these solutions are for sulfide precipitation.

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