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Arsenic-Bearing Carbonate Waters: Geochemical and Thermodynamic Analysis of Their Genesis, Transformation of Arsenic Migration Species, and Models for the Genesis of Hydrogenic As Sulfide Mineralization

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Abstract—Analysis of hydrogeochemical materials on As distribution in CO_2-bearing (carbonate) waters in various regions and the thermodynamic simulation of geochemical processes in rock–CO_2-bearing water systems made it possible to constrain the optimal conditions for As transfer from rocks into carbonate waters and the accumulation of this element in the waters. The problem was solved with regard for the various rates of As transitions from rocks to water: (a) high rates of As transitions from rocks in compliance with the ion exchange mechanism and (b) low rates of As transitions from rocks in compliance with the mechanism involving the decomposition of As-bearing minerals. Various mechanisms of As extraction from rocks result in the compositional diversity of the aqueous phase and various As migration species in CO_2-bearing waters, which, in turn, control the equilibrium concentration levels of this element. The principally important boundary conditions of As enrichment in CO_2-bearing waters are high P_{CO_2} and R/W ratios in the geochemical systems, a preliminary increase in the Cl concentration in the CO_2-bearing waters, and the origin of these waters at high-density heat fluxes. As migration species were simulated for the model solutions and real carbonate waters of various geochemical types, and it is demonstrated that the predominant As species are oxygen-bearing $HAsO_2^0$, and AsO_2^- at a subordinate role of the sulfide $HAs_2S_4^{2-}$, and $As_2S_4^{2-}$ – species even at high $\sum S^{2-}$ in the system. Two models of the genesis of solid As sulfides in CO_2-bearing waters are analyzed: (1) with oxygen-bearing species ($HAsO_2^0$, and AsO_2^-), which occur most widely, and (2) with sulfide species ($As_2S_4^{2-}$, $HAs_2S_4^-$, and $As_4S_7^{2-}$), which occur not as widely.

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INTRODUCTION

Alpine geological structures show close spatial and genetic relations between their low-temperature As ore mineralization and carbonate waters with high As concentrations [1–8]. In essence, these relations indicate that most low-temperature As sulfide deposits include discharge sites of carbonate waters with high As concentrations. There are extensive geochemical data [1–5] indicating that As-bearing ore mineralization could not serve as a source of As for these CO_2-bearing waters but, conversely, the carbonate waters containing As themselves provided the basis for the development of both ancient and modern As ore mineralization. There are a number of Alpine regions in which As- and CO_2-bearing waters are widespread and in which these waters are most closely genetically interrelated with As ore mineralization. Examples of these regions are provided by the Greater Caucasus (Fig. 1), some of the youngest structures in the Carpathians (Fig. 2), western states of the United States, Japan, Kamchatka, the Kurile Islands, and New Zealand. Table 1 summarizes typical chemical analyses of such waters.

In these regions, the participation of As-bearing carbonate waters in the formation of low-temperature ore mineralization follows from the coincidence of the discharge site of carbonate waters with zones of As sulfide mineralization, the restriction of all of them to the same tectonic and hydrogeological structures, and from the genetic trends of the geochemical processes in these structures (precipitation but not dissolution of sulfides [1]).

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† Deceased May 10, 2007

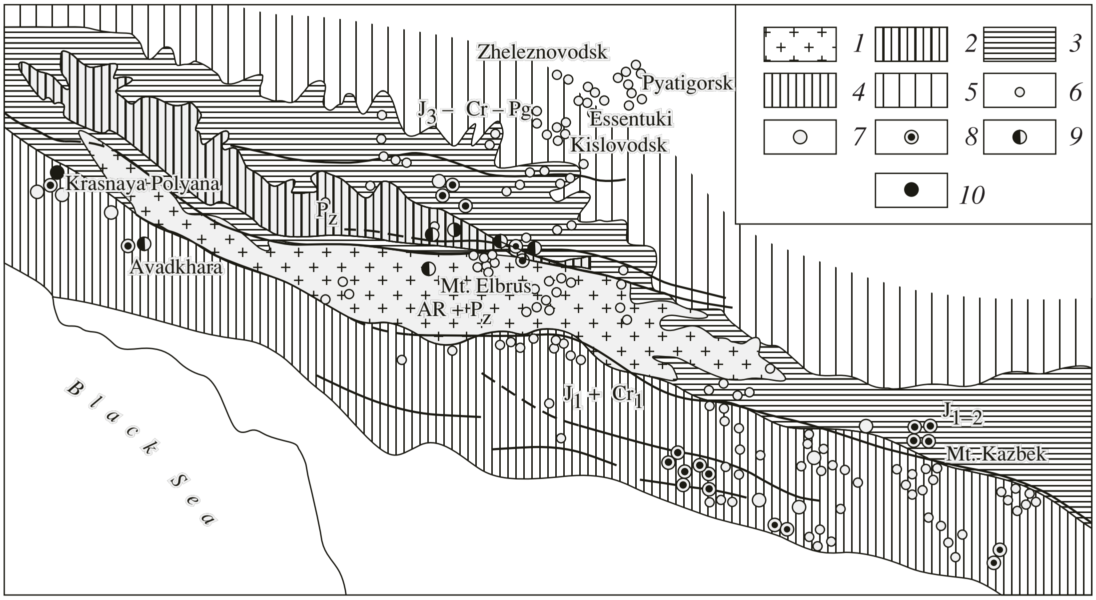

Fig. 1. Distribution of As-bearing carbonate waters in the Greater Caucasus [5].

Aquifer complexes: (*1*) Archean–Paleozoic crystalline rocks; (*2*) volcanic, sedimentary, and metamorphic Paleozoic rocks; (*3*) sandy shale Early–Middle Jurassic rocks (northern slope); (*4*) sandy shale, volcanic, and carbonate Early Jurassic–Early Cretaceous rocks (southern slope); (*5*) carbonate Late Jurassic–Paleogene rocks (northern slope). As concentrations in carbonate waters (mg/l): (*6*) <0.5; (*7*) 0.5–1.0; (*8*) 1–10; (*9*) 10–15; (*10*) >15.

Paragenetic relations between low-temperature As deposits and As-bearing carbonate waters are controlled by common conditions under which the hydrothermal solutions responsible for the development of the ore mineralization are formed and modern As- and CO_2-bearing waters are generated. It is self-evident that the coincidence of these conditions can most probably occur in the youngest structures. In light of the aforesaid, As-bearing carbonate waters are now regarded as the successors of hydrothermal ore-forming solutions [1, 3, 5]. Hence, modern As-bearing carbonate waters are produced during the final evolutionary stage of hydrothermal systems and inherit their "inheritors" to which ore-forming solutions give way in hydrogeological structures and which are spatially combined with As mineralization. The analysis of relations between As ore mineralization and As-bearing carbonate waters demonstrates that the younger the mineralization, the stronger its relations with modern hydrogeological systems with carbonate waters. The evolutionary history of the hydrothermal solutions that produced the low-temperature mineralization was proved to be closely related to the hydrogeological evolution of these structures and to all of their hydrodynamic, geothermal, and hydrogeochemical features that control the directions, velocities, and movement times of the solutions and the time during which the chemical composition of the ore-forming solutions is formed [1–7].

Hence, the problems to be solved for understanding the principles of genetic links between As-bearing CO_2 waters and As sulfide mineralization are as follows: (i) what are the genetic reasons for the development of As-bearing CO_2 waters and what are the genetic prerequisites for the ability of As species to form sulfide deposits, and (ii) what is the geochemical mechanism forming As sulfide ore mineralization from these species. In preparing this manuscript, we used our results obtained during the study of more than 1000 occurrences of CO_2 waters in various regions of the former Soviet Union, mostly in the Greater Caucasus, Carpathians, and Pamirs, as well as in the Czech Massif, Polish Sudetes, and California. Some of these results were published in our earlier papers [5, 10], and here we will widely use these materials, which are appended in this publication with the thermodynamic analysis of the processes that we examined earlier but could not comprehensively explain.

GEOCHEMICAL PHENOMENOLOGY OF AS-BEARING CARBONATE WATERS

Naturally occurring hydrogeological environments are known to contain two geochemical types of As-bearing carbonate waters, whose relations to low-temperature sulfide As ore mineralization are different.

First, these are thermal As-bearing sulfide waters that currently form sulfide As mineralization (As_2S_3 and AsS). These thermal waters occur in hydrogeological structures of modern Quaternary and Late Quaternary magmatism (Steamboat Springs 60–175°C, Norris 100–200°C, and Sulfur Bank 80–130°C in the western United States; Osoreyama 100°C and Tamagawa 98°C

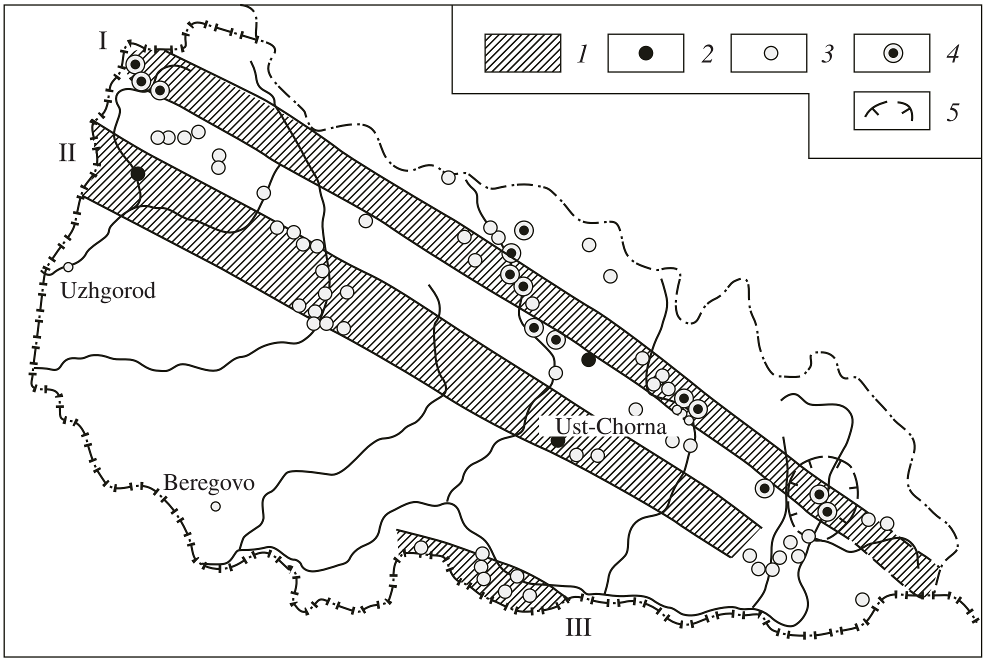

Fig. 2. Distribution of carbonate waters with high Sb and As concentrations in tectonic and metallogenic zones of the Carpathians. (*1*) Tectonic and metallogenic zones: (*I*) Petros; (*II*) Perechin–Rahov; (*III*) Pripanovskaya. Chemical composition of carbonate waters: (*2*) HCO_3–Cl–Na, Ch–HCO_3–Na; (*3*) HCO_3–Na, HCO_3–Ca; (*4*) carbonate waters with Sb concentrations of ~1–10 mg/l; (*5*) area with carbonate waters containing up to 50 mg/l As.

in Japan; Wairakei 130–260°C and Broadlands 100–260°C in New Zealand; and the Uzon caldera 60–102°C in Kamchatka. The geochemistry of these waters is as follows: Cl–Na, Cl–HCO_3–Na composition at a few mg/l of CO_2 and in the pervasive presence of sulfide sulfur species (H_2S and HS^-) in concentrations from a few to a few tens mg/l and low (no higher than –300 mV) redox potential [2, 3, 6–9, our data].

We have demonstrated [10] that a temperature increase to higher than 80–100°C activates abiogenic sulfate reduction $SO_4^{2-} + 10H^+ + 8e = H_2S + 4H_2O$ ($SO_4^{2-} + 9H^+ + 8e = HS^- + 4H_2O$), and thus, an increase in the temperature at which As-bearing waters are formed is inevitably associated with an increase in the sulfide S concentration in these waters. The total H_2S + HS^- concentration in thermal As-bearing waters can reach tens to hundreds of mg/l, with P_{H_2S} increasing thereby to 0.1 atm and more [7].

The speciation of sulfide S (H_2S and HS^-) is the principal geochemical factor controlling the origin of thermal carbonate waters, with these species predetermining the geochemical characteristics of the waters and their complexation and mineral-forming potential. Empirical materials and results of thermodynamic simulations point to very strong links between the concentration of sulfide S species and the Eh–pH characteristics of the aqueous solutions. These links become even stronger with increasing temperature of the carbonate waters: the higher the temperature, the more significant the shift of the data points toward higher H_2S and HS^- concentrations (Fig. 3) and, correspondingly, lower Eh.[1] This is associated with a decrease in the standard Eh^0 value for the sulfate–sulfide sulfur redox pair. Thermal sulfide waters of this type contain much lower As concentrations than those in cold sulfide-free carbonate waters. Indeed, these waters most commonly contain a few mg/l of As (Table 1).

The second type comprises cold and weakly thermal As-bearing waters, which are most widely spread in hydrogeological structures of Tertiary and Late Quaternary tectonic–magmatic activity (Fig. 1). These are Azatavan 42°C and Dzhulfa 40°C in the Lesser Caucasus; Khudes 8°C, Chuchkur 8°C, and Avadkhara, Chvizhipse 15°C in the Greater Caucasus; Rahov 10°C in the Carpathians; Kudowa 15°C in the Sudetes; and Sinegorsk 9°C in Sakhalin Island. The geochemistry of these waters is characterized by high CO_2 concentra-

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[1] This diagram and analogous diagrams below were constructed in the following manner. They are based on variations in the Eh–pH characteristics of the aqueous phase depending on P_{CO_2} and the R/W (rock/water) ratio in the geochemical system. Each line in the diagram corresponds to a certain P_{CO_2}. Points on the lines correspond to specified R/W ratios, which were varied here from 0.01 to 1000, with their increase indicated by a large arrow. Small arrows point to the concentrations of components obtained in our simulations at the highest R/W ratios.)

Table 1. Chemical composition (mg/l, ppm) of As-bearing carbonate waters [5–7, 9, and our data]

Parameter	Lesser Caucasus			Greater Caucasus				
	Azatavan	Dzhulfa	Upper Isti-Su	Chuchkur	Uchkulan	Khudes	Upper Karmadon	Vazhas-Tskharo
t°C	42	40	64–70	7.5	12	7–8	50	10
pH	6.7	6.8	7.1	6.6	6.4	6.7	6.6	6.9
Eh	+100	+150	+50	+150	+170	+90	+50	+150
Na + K	11645	7044	1902	1990	1310	2316	2368	4690
Ca	710	276	28	433	129	321	380	206
Mg	90	138	44	191	120	290	68	196
Cl	17700	7150	1095	1780	945	1354	3936	3260
SO_4	750	939	580	192	169	216	65	n.a.
HCO_3	2105	5890	2735	4245	2635	6386	921	7452
As	40–120	20	4.8	37.5	11	15	7.0	6.8
As/Sb	>400	>200	50	~100	~110	>150	3140	>130
B	400–600	150	20	50	50	70	60	150
Na/K	5.9	33.5	50	70	65	56	2.9	51
Gas composition	CO_2, CH_4, H_2	CO_2, CH_4	CO_2, H_2S	CO_2	CO_2, CH_4	CO_2	CO_2, H_2S	CO_2, CH_4
CO_2	1400	1150	600	1200	1500	1700	700	1500
$H_2S + HS^-$	n.a.	n.a.	7.0	n.a.	n.a.	n.a.	n.a.	n.a.
Chemical composition formula	$M_{36.1}\frac{\mathrm{Cl91HCO_36}}{\mathrm{(Na+K)92}}$	$M_{21.2}\frac{\mathrm{Cl84HCO_330}}{\mathrm{(Na+K)92}}$	$M_{6.5}\frac{\mathrm{HCO_351Cl35}}{\mathrm{(Na+K)94}}$	$M_{8.8}\frac{\mathrm{HCO_356Cl43}}{\mathrm{(Na+K)90}}$	$M_{5.3}\frac{\mathrm{HCO_349Cl36}}{\mathrm{(Na+K)78}}$	$M_{10.9}\frac{\mathrm{HCO_370Cl26}}{\mathrm{(Na+K)73}}$	$M_{7.8}\frac{\mathrm{Cl87HCO_312}}{\mathrm{(Na+K)82}}$	$M_{15.4}\frac{\mathrm{HCO_351Cl43}}{\mathrm{(Na+K)88}}$

Carpathians	Sakhalin	Kamchatka		Japan	New Zealand			United States
Kvasy, Rahov	Sinegorsk [1]	Uzon [6]	Nalychevo [9]	Osoreyama, ppm [7]	Boadlands, ppm [2, 7]	Waitapu, ppm [2, 7]	Wairakei, ppm [2, 7]	Steamboat Springs, ppm [2, 7]
10	7	94	75	100	260	275	244	90
6.1	6.1	7.6	6.4	7.3	6.2	9.8	8.6	7.9
+100	+105	–65	–	–	–	–	–	–
11669	6688	1085	5240	4220	1180`	1015	1545	751
310	260	77.4	285.6	553	2.4	10	17	16
210	208	5.7	30.1	8.3	0.03	0.06	0.1	1
15410	6195	1740	1673	7025	1668	1450	2260	900
n.a.	36	86.0	466.5	63	6.5	52	36	130
6427	8944	24.4	621	–	–	–	35	305
28–50	60	7.0	7.7	39.5	3.2	3.1	4.8	3
5–28	–	–	–	–	–	7.75	12	6
352	470	~100	70	343	48	–	29	48
40	52	11.8	4.8	7.9	4.9	5.54	5.86	8.75
CO_2, CH_4	CO_2, CH_4, H_2	CO_2, H_2S	CO_2	CO_2, H_2S	CO_2, H_2S	CO_2	CO_2,CH_4, N_2, H_2S	CO_2
2400	3000	–	457	–	117	90	92	91
n.a.	n.a.	11.3	n.a.	11	103	n.a.	1.8	n.a.
$M_{34.1}\frac{\mathrm{Cl80HCO_320}}{\mathrm{(Na+K)91}}$	$M_{25}\frac{\mathrm{Cl54HCO_345}}{\mathrm{(Na+K)90}}$	$M_{3.0}\frac{\mathrm{Cl95}}{\mathrm{(Na+K)90}}$	$M_{4.7}\frac{\mathrm{Cl70HCO_315}}{\mathrm{(Na+K)74Ca21}}$	Cl-Na	Cl-Na	Cl-Na	Cl-Na	Cl-Na

tions (Tables 1, 2), the complete absence of sulfide S, and low positive values of the redox potential. These oxygen- and sulfide-free waters now cannot produce As sulfide mineralization but contain very high (the highest for carbonate waters) As concentrations, commonly as high as tens of mg/l at a maximum of 100–120 mg/l (at Azatavan). The discharge sites of these waters (Dzhulfa and Sinegorsk) commonly bear ancient As sulfide mineralization (orpiment and realgar) and are thus regarded by most researchers as relics of the hydrothermal solutions that produced this sulfide mineralization. Now these carbonate waters do not form any sulfide As mineralization and, judging from the absence of sulfide S compounds from them, cannot form this mineralization any more. However, the frequent presence of As sulfide mineralization (orpiment and realgar) in their near-surface discharge zones testifies that the hydrogeological evolution of these carbonate waters included a highly thermal stage that was characterized by the presence of sulfide S and the precipitation of As sulfide mineralization.

GEOCHEMISTRY AND GENESIS OF As-BEARING CARBONATE WATERS

Below we will consider the genetic features of As-bearing carbonate waters that were utilized as the basis for our physicochemical simulations of the geochemical processes that formed these waters:

(1) As-bearing carbonate waters are generated at the significant addition of CO_2 (together with $H_2S + HS^-$ at higher temperatures) to them. According to the change in the CO_2 solubility in water depending on temperature, its dissolved concentrations are at a maximum ($n \times 100$ to $n \times 1000$ mg/l) in cold As-bearing carbonate waters and at a minimum ($n \times 100$ mg/l) in thermal waters, although the spontaneous CO_2 concentrations in these waters can be much higher. Aver'ev [1] has demonstrated that As concentrating is correlated with an increase in CO_2 concentrations in the As-bearing waters. Because hydrogeochemical systems are open with respect to CO_2, As-bearing waters are sodic (see [10] for explanations of the reasons), have HCO_3–Cl–Na, Cl–HCO_3–Na, or, more rarely, HCO_3–Na and Cl–Na (the most thermal) composition at usually high HCO_3^- concentrations (which decrease with increasing temperature), and the minimum Ca concentrations. Because of this, carbonate waters with the highest As concentrations are characterized by very high $mHCO_3^-/mCa^{2+}$ ratios and, correspondingly, plot in the extreme "carbonate" position in the Hardy–Engster diagram, occurring, in fact, at the "carbonate pole" of the origin of groundwaters (Fig. 4). This means that CO_2 inflowing into the geochemical systems from outside is the leading component predetermining the geochemistry and genesis of these waters. This was previously demonstrated by studying the isotopic composition of the carbonate system of CO_2-bearing waters in the Carpathians: an increase in the CO_2 concentration in the groundwaters ensures their high HCO_3^- concentrations [11]. Because of this, As-bearing carbonate waters usually display paragenetic As–HCO_3^- links (Fig. 5). In addition to the illustration of these links in the As–HCO_3^- system, the figure also displays the fact that, depending on the conditions under which the carbonate waters are formed, these links can be modified. For example, hydrogeological structures in the Lesser Caucasus, whose carbonate waters are affected by an anomalously high heat flux, have higher As concentrations in waters with lower HCO_3^- concentrations than those in the Greater Caucasus.

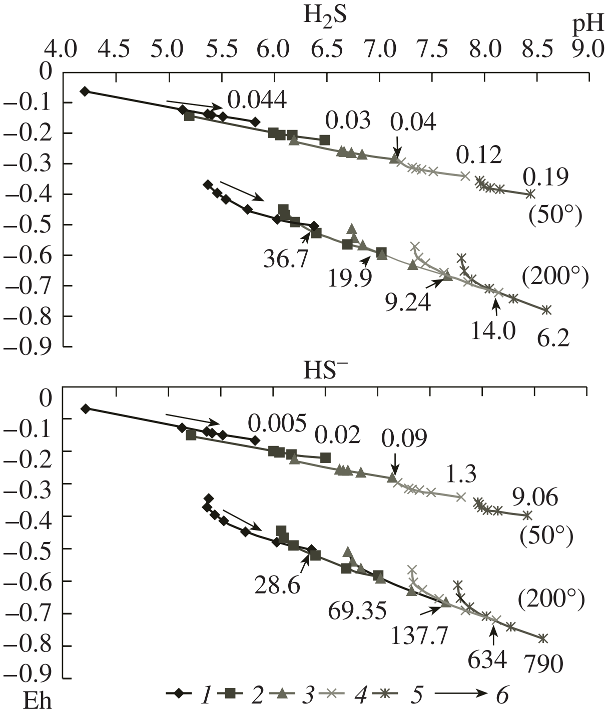

Fig. 3. Variations in equilibrium H_2S and HS^- concentrations (mg/kg) in the aqueous phase of the system carbonate rock–water in an Eh–pH diagram depending on P_{CO_2} and the R/W ratio (from –2 to 3), which are specified in the system by the GIBBS computer program; (log)P_{CO_2}: (*1*) 1; (*2*) 0; (*3*) –1; (*4*) –2; (5) –3.4; (*6*) increase in the R/W ratio in the modeled hydrogeochemical systems.

(2) Carbonate As-bearing waters are formed in hydrogeological structures made up of sandy–shale and volcanic–sedimentary rocks in hydrogeochemical systems open with respect to CO_2. It was statistically proved that the highest As concentrations are more often contained in Cl-rich carbonate waters produced in shaly (sand–clay) rocks, most commonly of Tertiary age. These are, for example, carbonate waters at Azatavan in the Lesser Caucasus, Sinegorsk in Sakhalin,

Table 2. Composition of gases in some As-bearing carbonate waters [9 and our data]

Locality	Temperature, °C	Composition of spontaneous gases, vol %							
		CO_2	CH_4	H_2	O_2	AsH_3	N_2 + rare gases	Ar + K +Xe	He + Ne
G. and L. Caucasus									
Zhulfa									
Well 5	25	99.1	0.145	–	–	–	0.755	0.0072	0.0016
Well 14		98.8	0.187	–	–	0.001	1.013	0.005	0.0016
Well 7/64	39–40	99.5	–	–	0.1	–	0.4	–	–
Well 8/64	42	98.1	–	–	0.3	–	1.6	–	–
Nagadzhir, Well 3	20	100	–	–	–	–	–	–	–
Chvizhipse, Well 4	15.5	95.0	–	0.8	0.2	–	4.0	–	–
Avadkhara	10	98.8	0.34	–	–	–	0.86	–	–
U. Karmadon									
Well 10	52	98.0	–	0.9	–	–	1.10	–	–
Azatavan	42	89	10	1.0	–	–	–	–	–
Carpathians									
Rahov									
Well 2-R	8–10	97.85	0.19	–	0.06	–	1.90	–	–
Well P-K	6–10	94.835	0.135	0.0107	0.02	–	4.956	0.039	0.00097
Sakhalin									
Sinegorsk									
Well 9	7	98.69	1.31	–	–	0.0001	0.01	–	–
Well 8	7	94.45	5.40	–	–	–	0.15	–	–
Well 14	8.3	98.8	–	–	–	–	1.2	–	–
Well 18	10	98.6	–	–	–	–	1.3	–	–
Kamchatka									
Nalychevskie	74.3	93.43	0.74	–	–	–	5.8	–	–

and Rahov in the Carpathians. Structures composed of these rocks are artesian basins or fracture–vein systems characterized by clearly pronounced complete (i.e., reaching the chloride stage) horizontal and vertical hydrogeochemical zoning. A classic example is the Orduban artesian basin in eastern Nakhichevan at the Lesser Caucasus, in which the transit of carbonate waters through Upper Cretaceous carbonate rocks from the alimentation area to discharge zones is associated with a systematic change in the chemical composition of the waters from HCO_3–Na (Sirab) to Cl–HCO_3–Na (Dzhulfa–Darry-Dag) and ends with the formation of the Cl-richest (up to 7–10 mg/l Cl) carbonate waters with high (20–40 mg/l) As concentrations in the deepest part of the structure. Still higher Cl concentrations were detected in As-bearing carbonate waters in the Chatminskii Miocene halogen-bearing basin in the Armenian folded zone (Azatavan, 100–120 mg/l As, 10–15 g/l Cl^-) and carbonate waters in the Rahov field in the Petros zone in the Carpathians (up to 50 mg/l As, ~15 g/l Cl^-). The evolution of carbonate waters with the maximum As concentrations through a stage of chloride waters is an inevitable condition, which is associated with and genetically predetermines the accumulation of the maximum As concentrations. If carbonate waters did not reach the chloride stage in their hydrogeological evolution but stopped at the hydrocarbonate stage, the As concentrations in these waters are much lower. A classic example of these waters is the carbonate HCO_3-Na waters in shale and carbonate rocks in the southwestern Lesser Caucasus (Avadkhara, Chvizhipse, Atsetuka, Grushevaya Polyana, and others) and carbonate waters at Kudowa in the Sudetes, which contain a few mg/l of As. This is, however, merely an obvious aspect of the problem, namely acknowledging the fact that high As concentrations are spatially restricted to the chloride zones of hydrogeological structures. At the same time, the genetic relations in the As–Cl^- system itself are much more complicated and not fully understood as of yet. The point is that As-bearing

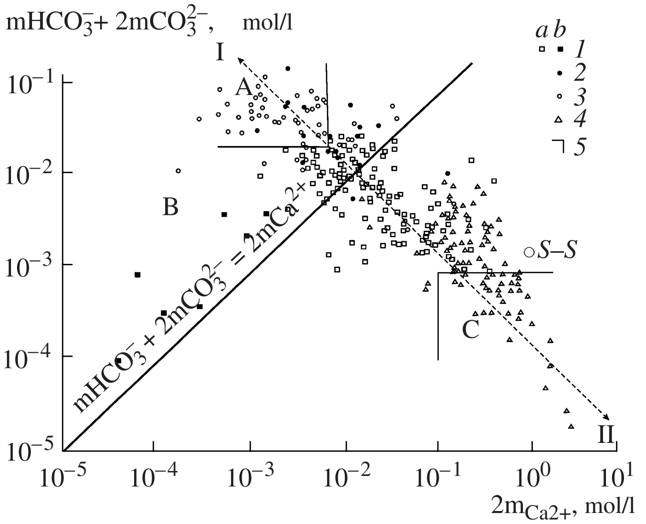

Fig. 4. Data points of carbonate waters in Alpine structures and brines in artesian basins in a $m\mathrm{HCO}_3^- + 2m\mathrm{CO}_3^{2-}$ vs. $2m\mathrm{Ca}^{2+}$ diagram (constructed with the use of data on the chemical composition of carbonate and highly thermal waters in the Greater and Lesser Caucasus, Carpathians, Czech Massif, Kamchatka, Sakhalin, California, New Zealand, and brines in the western Turkmen, northern Crimea, northern Caucasian, Kura, northern Sakhalin, and Kambeiskii basins). Geochemical types of brines, carbonate and thermal waters: (*1*) Cl–Na($\mathrm{HCO}_3^- + \mathrm{CO}_3^{2-}$ < 5% mg-equiv.); (a) cold and weakly thermal brines; (b) highly thermal carbonate As-bearing waters; (*2*) Cl–Na($\mathrm{HCO}_3^- + \mathrm{CO}_3^{2-}$ > 5% mg-equiv.); (*3*) Cl–HCO_3–Na, HCO_3–Cl–Na; (*4*) Cl–Ca–Na; (*5*) waters: (*A*) carbonate cold and weakly thermal waters with the maximum As concentrations, (*B*) highly thermal carbonate waters containing *n* mg/l As; (*C*) brines with the highest Zn, Pb, Fe, and Mn concentrations; S–S is the position of As-bearing high temperature brines at Salton Sea, California. Compositional trends of the geochemical metamorphism of brines in rocks: (*I*) sodic (carbonate), (*II*) calcic.

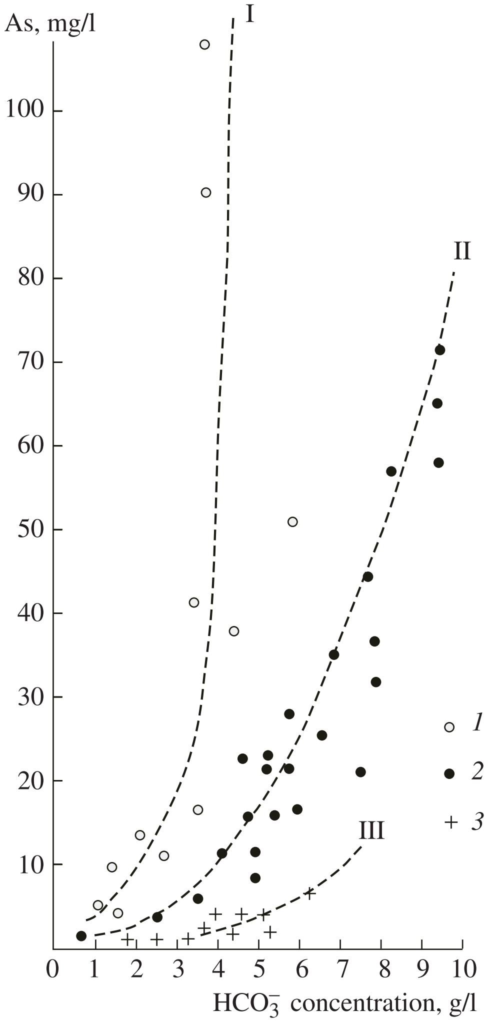

Fig. 5. Dependence between As and HCO_3^- concentrations in cold As-bearing waters in structures in the Greater and Lesser Caucasus, Carpathians, Sudetes, and Sakhalin.

Data points of As-bearing carbonate waters: (*1*) in structures of the Lesser Caucasus (Armenian folded area); (*2*) structures in the Greater Caucasus, Petros zone in the Carpathians, and Sakhalin; (*3*) southwestern structures in the Greater Caucasus (Abkhasian tectonic zone and Krasnaya Polyana structures) and Sudetes.

Dependences for: (*I*) Armenian folded area; (*II*) central structures in the Greater Caucasus, Petros zone in the Carpathians, and Sakhalin; (*III*) southwestern structures in the Greater Caucasus and Sudetes.

waters in the overwhelming majority of Alpine hydrogeological structures are indeed very rich in Cl, but not all carbonate chloride waters contain high As concentrations. For example, chloride carbonate waters widespread in the Carpathians often contain no As at all, or its concentrations are at a minimum (from *n* to *n* × 10 μg/l). In the Greater Caucasus, elevated As concentrations in carbonate waters are restricted to the central parts of the structures, which are characterized by a high (>3 μcal/cm^2 s) density of the heat flux, and high-Cl carbonate waters in the marginal parts of the carbonate water province of the Greater Caucasus contain practically no As (shale structures in the Mara and Khumara areas in the west and in Dagestan and Khevsuretia in the east). The situation in the Lesser Caucasus is analogous: high As concentrations are contained only in chloride carbonate waters in the Armenian folded zone [5]. Paragenetic As–Cl links manifest themselves only (a) in certain hydrogeological structures with the youngest As sulfide ore mineralization and/or (b) in structures with anomalous geothermal regimes. As an example, Fig. 6 demonstrates that the As–Cl paragenetic relations are discernible in New Zealand only in the Rotunda structure, whereas these relations in all other structures are weak and poorly pronounced [12]. In the Petros zone, the youngest tectonic structure in the Carpathians, most of its chloride carbonate waters are rich in Sb, and elevated As concentrations in the car-

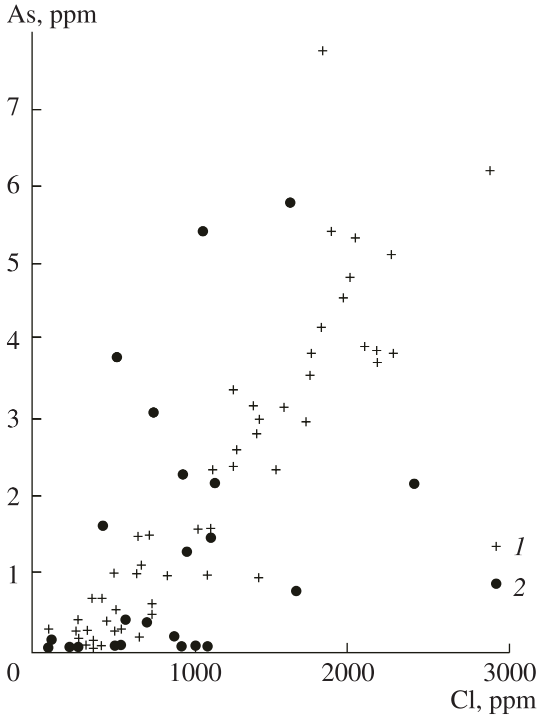

Fig. 6. Dependences between As and Cl$^-$ concentrations in thermal waters in New Zealand: (*1*) Rotorua area; (*2*) other areas [12].

bonate waters occur only in the Rahov group of CO$_2$ waters, which are formed in the youngest part of this zone (Fig. 2).

As and Cl are geochemically different elements, and thus, in discussing their association, it is reasonable to analyze only their interaction effects. The detailed analysis of paragenetic links between As and Cl indicates that chloride carbonate waters become As-bearing when formed in cold Alpine structures in geothermally tense structures due to their proximity to magmatic chambers or because of high heat fluxes. As a result, we arrived at the conclusion [5] that As-bearing carbonate waters are generated by geochemical processes in a thermohydrogeological zone activated by the preliminarily formed elevated Cl concentrations in the carbonate waters. The nature of these geochemical processes with the participation of the Cl$^-$ ion is not fully understood, but its most realistic explanation seems to be that As becomes volatile and is expelled from rocks when the Cl concentrations of the solutions and their temperature increase. The arguments for this concept are as follows. It has been established by the experiments of Krasintseva [13, 14] that B, As, and CH$_4$ are expelled from sedimentary rocks at 200°C under the effect of water vapor. The transfer of these components into the aqueous phase is activated in Cl–Na solutions [14, 15]. Analogous conclusions concerning As follow from the data in [16], in which it is demonstrated how efficient As thermometamorphic removal from sedimentary (particularly shale) rocks can be. Because of this, higher grade metamorphic rocks (shales and others) bear lower As concentrations, which further decrease toward final metamorphic stages [16]. The effect of As^{3+}–Cl$^-$ complexation cannot appreciably activate As extraction from rocks because (i) as will be demonstrated below, the concentrations of $\mathrm{AsCl}_4^- \; {}^-$ and AsCl_5^{2-} complexes in the modeled aqueous phase and naturally occurring chloride carbonate solutions are negligibly low, and (ii) our computer simulations of the effect of increasing NaCl concentration (from 1 to 100 g/l) in the aqueous phase on its As leaching from various rocks have proved the absence of this effect.

(3) The chemical composition of modern As-bearing carbonate waters shows features indicating the "memory" of the temperatures of these waters during their high-temperature ore-forming evolution. Since these waters are relics of ore-forming hydrothermal solutions, it is reasonable to believe that the temperatures were of the order of a few dozen to a few hundred degrees Celsius. The problem can be solved based on the geochemical features of modern As-bearing waters and the geochemical "memory" recorded in their geochemistry. One of the manifestations of this memory is the Na/K ratio of the waters. Normally when carbonate waters are formed, an increase in their Cl concentration is associated with an increase in their Na concentration, and hence, an increase in the mineralization of these waters (and, correspondingly, in their Cl concentration) means an increase in their Na/K ratio. Because of this, the Na/K ratio of carbonate waters is usually higher than 100. When As-bearing carbonate waters are formed, the situation is opposite: an increase in the As concentrations of carbonate waters takes place at increasing K concentrations and, correspondingly, decreasing Na/K ratios. The K concentration in the As-richest waters, for example, in the Greater and Lesser Caucasus (Azavatan, Upper Kardamon, Isti-Su, and others) reaches $n \times 100$ to 1000 mg/l and even more, and the Na/K ratio of these waters correspondingly decreases to 3–50 (Table 1).

It is known from the geochemistry of thermal waters that the main reason for a decrease in the Na/K ratio during the interaction of carbonate waters with rocks is an increase in the temperatures at which these interactions take place. The experiments conducted by Ellis and Mahon [17] and our experiments on the development of the chemical composition of thermal waters carried out in 1973–1978 have demonstrated that the Na/K ratios known to occur in the As-richest carbonate waters are reached at temperatures of 150–250°C. This allowed us to propose that high-As waters should be formed under thermobaric conditions anomalous for these structures. Indeed, their hydrogeology and geothermal characteristics confirm this conclusion: structures with regionally elevated As concentrations in their carbonate waters (for example, in the northern and southern slopes of the Greater Caucasus) contain these waters in zones with the densest heat fluxes and the highest geothermal gradients, i.e., in zones with the maximum level of the high temperature surfaces. This is expressed as the restriction of the As-richest carbonate waters to deep fault zones and areas of Late Quaternary magmatism (Fig. 1). More detailed temperature determinations with the use of equations proposed in [18, 19] for relations between the Na/K ratios of thermal waters and their formation temperatures demonstrates that the As richest waters were indeed produced at temperatures of 180–200°C. The evaluation of the temperatures by the diagram of Ellis and Mahon [17], which illustrates relations between the atomic Na/K ratio of thermal waters and their temperatures in various regions worldwide indicates that the Na/K ratios found in As-rich waters in, for example, the Caucasus were formed within practically the same temperature range of 150–250°C. Hence, various approaches to the evaluation of the temperatures at which As-richest carbonate waters were formed from the Na/K ratios of these waters indicate that these waters were most probably formed at a temperature of approximately 200°C.

(4) The Eh–pH states of As-bearing carbonate waters are controlled by various systems. As is an element of variable valence (5 and 3) in various hydrogeochemical systems. All processes of As geochemical transformations in carbonate waters occur under the effect of certain systems controlling the Eh–pH states. These systems are different in cold (weakly thermal) sulfide-free and thermal sulfide waters. The original pH-controlling system in the first type of these waters is the carbonate system, which is formed by inflowing deep endogenic and thermally metamorphosed CO_2 ($CO_2 + OH^-_{rock} = HCO_3^-$) and maintains pH within 4.5–8.5 (and, correspondingly, specifying the usually positive Eh values). The other Eh- and pH-controlling system of these waters is the system of Fe^{2+}, which maintains low positive or, more rarely, negative Eh values in the systems of carbonate waters [$Fe^{2+} + 3H_2O = Fe(OH)_3 + 3H^+ + e$].

In the context of this research, much more important Eh- and pH-controlling systems are those of thermal sulfide carbonate waters. When these waters are formed in deeper sitting hydrogeological structures, the carbonate and Fe^{2+} systems gradually give way to the S^{2-}/S^o, CO_2/CH_4, and H^+/H_2° systems. Among them, the $S^{2-} = S^o + 2e$ or $H_2S = S^o + 2H^+ + 2e$ is kinetically more active, more often dominates in controlling geochemical processes in thermal sulfide waters, and maintains As in its As^{3+} state. The H_2S concentration of As-bearing carbonate waters reaches 100–300 mg/l and increases with decreasing pH and increasing P_{CO_2}. The concentration of the other sulfide component HS^- increases to a few hundred mg/l with increasing alkalinity of the solutions and, particularly, with increasing temperature (Fig. 3).

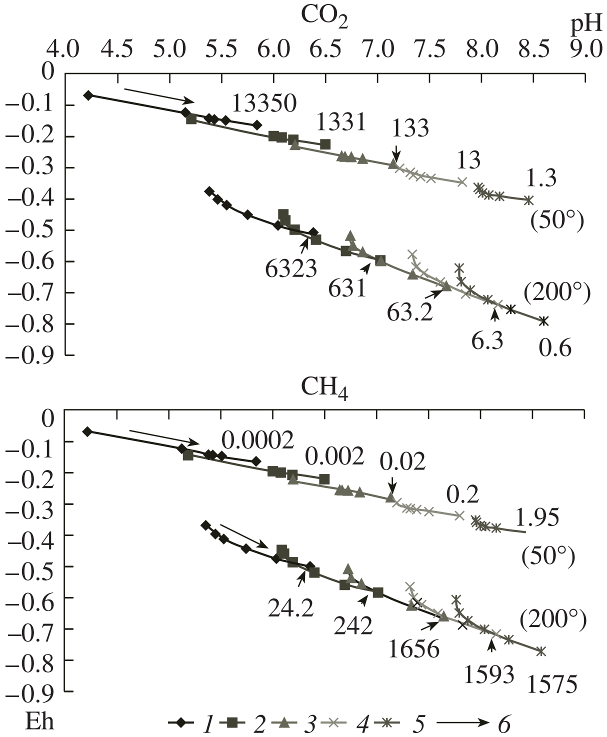

Fig. 7. Variations in equilibrium CO_2 and CH_4 concentrations (mg/kg) in the aqueous phase in an Eh–pH diagram depending on the temperature and R/W ratio (from –2 to 3), which is specified in the modeled hydrogeochemical systems by the GIBBS computer program; log P_{CO_2}: (*1*) 1; (*2*) 0; (*3*) –1; (*4*) –2; (5) –3.4; (*6*) systematic increase in the R/W ratio in the systems.

In deeper Alpine structures, the Eh–pH systems of carbonate waters are affected by hydrogen, and the CO_2/CH_4 system ($CO_2 + 4H_2 = CH_4 + 2H_2O$ or $CO_2 + 8H^+ + 8e = CH_4 + 2H_2O$) is formed, which is very important in the context of this study. We modeled the process forming high CH_4 concentrations in the aqueous phase and the CH_4 to CO_2 proportions at various boundary conditions. The results are presented in Figs. 7 and 8. CO_2 and CH_4 are geochemical antagonists: these are alternative components in the gas composition of groundwaters at deep levels. In deep hydrogeological structures, at a temperature increase and a decrease in the CO_2 partial pressure at increasing H_2 concentrations, the role of CO_2 is played by CH_4 (Fig. 8), which becomes the principal indicator of a decrease in the Eh of groundwaters to low negative values. However, the transition to this system does not completely terminate aqueous As migration, and its concentrations in these systems are maintained at a few mg/l. This is another (still poorly understood) aspect of aqueous As migration, which is characterized by other relations with chemical components and is prone to be related to another calcic trend in the geochemical evolution of chloride brines (Fig. 4). An example of this evolution of

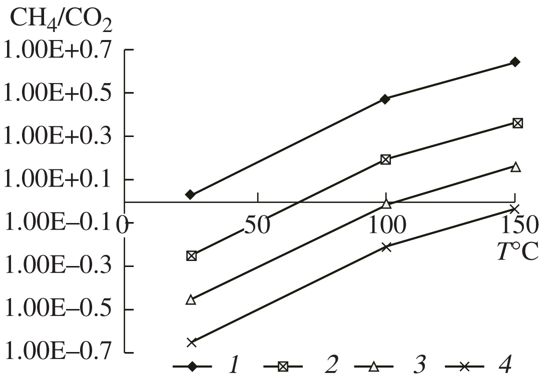

Fig. 8. Calculated changes in the CO_2/CH_4 ratios in natural groundwaters of $Cl–HCO_3–Na$ composition (mineralization 14 g/l) in the Akhtyrskaya structure (Azov–Kuban basin, depth 2700 m, Paleogene) at increasing temperature and decreasing P_{CO_2} (R/W = 10, GIBBS computer program); $\log P_{CO_2}$: (*1*) –3.4; (*2*) –2; (*3*) –1; (*4*) 0.

brines is provided by As-bearing (with 12 mg/l As) highly thermal (340°C) Cl–Na–Ca (40000 mg of Ca) brines (mineralization 300 g/l) at Salton Sea, California. The gas components are dominated (80–90%) by CO_2 (1500 mg/kg) and contain 10–20% $\sum CH_4 + H_2S + H_2$. An even more typical example is the As-bearing (a few mg/l As) brines in the Terek–Caspian basin (Jurassic, Cretaceous, and Paleogene units). These are highly thermal waters that are formed at a depth of up to 4000 m and have a temperature of 75–130°C. The gas component of these waters contains 80–90% CH_4 and no more than a few percent CO_2. The As geochemistry in the Ca-rich waters of these structures is yet to be studied in detail.

Finally, in deep Alpine structures releasing H_2, a significant role is played by the H^+/H_2° system, which decreases Eh to low negative values and diminishes the As valence. The Greater Caucasus is known to host $Cl–HCO_3–Na$ waters whose gas composition contains several percent H_2. These waters precipitated AsS. H_2 is a component of thermal waters in zones of Alpine tectonism, and P_{H_2} in systems of thermal carbonate waters reaches 0.1 bar and more.

GEOCHEMICAL PROCESSES TAKING PLACE AT THE DISCHARGE OF As-BEARING CARBONATE WATERS AT THE SURFACE AND PRECIPITATES FROM THESE WATERS

In systems of As-bearing carbonate waters, orpiment As_2S_3 and realgar AsS are formed when these waters approach the surface or discharge at it. Below we will consider the geochemical phenomena favorable for this near-surface precipitation of sulfides and the processes associated with it. These processes are different for various types of As-bearing carbonate waters (cold sulfide-free and thermal sulfide-bearing, with their different Eh- and pH-controlling systems).

In sulfide-free carbonate cold and weakly thermal waters, the main pH-controlling system is the carbonate system, and the main process affecting the chemical composition of these waters at the surface is their degassing (spontaneous escape of a nonequilibrium CO_2 amount at the surface), which leads to an increase in the pH of these waters near the surface. The study of the near-surface evolution of these carbonate waters demonstrates that the reasons of this phenomenon can be briefly summarized as follows [10].

At $P_{CO_2} = 10^{-3.4}$ near the surface, the CO_2 concentration in carbonate waters becomes lower than the equilibrium concentrations needed to maintain high HCO_3^- concentrations in the waters. Consequently, the homogeneous system of carbonate waters undergoes disproportionation $2HCO_3^- = H_2CO_3 + CO_3^{2-}$ with the subsequent hydrolysis reaction $CO_3^{2-} + H_2O = HCO_3^- + OH^-$, which is more significant as a pH-controlling reaction than the reaction of HCO_3^- hydrolysis. As a result, the pH of the system acquires high values (up to 8.5 and more). The evolution of these sulfide-free carbonate waters near the surface ends with the formation of carbonate ($CO_3^{2-} + Ca^{2+} = CaCO_3$) travertines, with which elements migrating in the waters precipitate. This process acts as an efficient precipitator of As. According to the Paneth–Fayans rule [10], these travertines precipitate together with much As and Sb contained in the carbonate waters. Simultaneously the oxidation reaction $Fe^{2+}_{(aq)} \longrightarrow Fe^{3+}_{(aq)} \longrightarrow Fe(OH)_{3\,(sol)})$ proceeds with the precipitation of Fe hydroxides at the discharge sites of the carbonate waters and with the coprecipitation of As and Sb. When studying the composition of travertine in the Lesser Caucasus, we have found out that the As concentration in the total mass of carbonate–ferrous travertine ranges from 0.001 to *n*%. For cold and weakly thermal sulfide-free carbonate waters of this evolutionary stage away from a source of sulfide sulfur, this is the only mode in which As-bearing solid phases can be formed.

A principally different trend of near-surface geochemical processes is typical of thermal carbonate waters containing sulfide sulfur. Our conclusions are based on materials obtained by studying thermal carbonate waters in the Greater and Lesser Caucasus., Czech Massif, Kamchatka, and California. The geochemistry of these thermal waters approaching the surface is determined by the evolution of the Eh- and pH-controlling systems that were acquired by the thermal waters at deep levels of the hydrogeological structures. These are the carbonate, S^{2-}/S^0, CO_2/CH_4, and H^+/H_2 systems. We have established previously [20] that, if more than one potential-controlling system can act in groundwaters, the potential is most probably controlled by a system with the highest reaction rate. Because of this, the fastest and most kinetically effective system in situations considered here is S^{2-}/S^0. Its evolution includes two stages: during the first of them, the concentrations of reduced species $\sum S\ (H_2S + HS^-)$ increase. However amazing, this phenomenon can be explained by an increase in the R/W ratio in the system during the boiling of the solutions and the resultant removal of H_2O, as was considered in detail in [21]. Consequently, the Eh of the carbonate–sulfide waters continues to decrease in the system to negative values. However, during the second stage, the system rapidly reaches a metastable state in the newly established acidic medium, and this triggers a series of oxidation processes $2H_2S + O_2 = 2S^\circ + 2H_2O$ and $S^\circ + 4H_2O = SO_4^{2-} + 8H^+ + 6\,e$ (or, in the resultant form, $4S + 4H_2O = 3H_2S + H_2SO_4$). Because of this, the discharge zones of thermal As-bearing waters are marked by the development of acidic solutions, with pH decreasing to 3–4 and Eh increasing to +200 and more.

In the course of the redox transformations of thermal carbonate sulfide waters, the migration modes of As can vary depending on the Eh–pH conditions. For example, As sulfide species occurring in sulfide waters are transformed into its oxygen species in the newly formed oxygen-bearing solutions: $As_2S_4^{2-} + 2O_2 \longrightarrow 2AsO_2^- + 4\ S$. These transformations of As migration species facilitate its retaining in near-surface aqueous solutions at newly established Eh–pH parameters, because of which the As concentrations increase (to a few mg/l) even in the most acidic Na–Ca waters [6, 22]. However, other Eh–pH systems also act in these discharge zones of carbonate–sulfide waters. The most important of these Eh- and pH-controlling systems are CO_2/CH_4 and H^+/H_2°. These systems are less reactive, and may maintain high concentrations of their reduced components (CH_4 and H_2) in the discharge zones (As-bearing waters in foredeeps and foreland basins). The Eh decrease in these situations is more radical. Waters with high CH_4 and, particularly, H_2 concentrations in their gas composition are characterized by negative Eh values and the reduction of all elements of variable valence: As, Sb, Se, Cu, etc. During the discharge of sulfide carbonate waters, As can be either retained in the aqueous phase or from orpiment As_2S_3 and realgar AsS in association with antimonite Sb_2S_3 depending on the newly established temperatures and Eh–pH parameters. It was demonstrated in [8] that sulfide-forming processes of this type occur at temperatures of 75–100°C, within a broad range of negative (up to –100 mV) and positive (up to +150 mV) Eh values. The possible driving forces of these mineral-forming processes were explained within the framework of the following three hypothetical models: boiling, mixing at cooling, and oxidation [8].

METHODOLOGY AND TECHNIQUES OF OUR THERMODYNAMIC SIMULATIONS OF THE ORIGIN OF As-BEARING CARBONATE WATERS AND THE BOUNDARY CONDITIONS

Our methodological principles applied in this research were as follows. The genesis of the major genetic types of mineralized waters in the Earth's crust, their geochemical states, and concentrations of chemical elements in them are controlled by boundary conditions: R/W ratio (the rock/water mass ratio), P_{CO_2} in the hydrogeochemical systems, and interaction temperatures, which are determined and formalized by real naturally occurring geological, hydrogeological, and geothermal situations and eventually predetermined the resultant effect of the geochemical processes in natural hydrogeochemical systems.

The above definition may be explained as follows. Universal geochemical processes deterministically act in naturally occurring systems and control the chemical composition of groundwaters (dissolution, crystallization, oxidation–reduction, dissociation, complexation, and ion exchange), but the efficiency of these processes and their results are determined by probabilistically established boundary conditions, which are specified by natural geological, hydrogeological, and geothermal situations. It is principally important that various boundary conditions may lead to different geochemical effects of the same geochemical processes. The ranges of these geochemical effects turned out to be extremely wide, so that it is possible to reproduce all known geochemical types of mineralized waters, with extremely broadly varying concentrations of chemical elements in them, by merely varying the boundary conditions of geochemical processes in the rock–water systems. It is also important to stress that variations in the boundary conditions may result in principally new geochemical features of groundwaters and in the occurrence of new geochemical processes. These methodological principles were utilized as the basis for our computerized thermodynamic analysis of geochemical processes playing the leading role in the formation of carbonate waters with high As concentrations in various lithological rock types [carbonate and sandy-clay (shale)]. In simulating water–rock interactions, we used the average composition of these rocks according to Vinogradov (1962), and their mineralogical composition was assumed according to Rozen et al. (2000).

Our thermodynamic simulations were centered on the resolution of the following two principal problems:

(1) How various boundary conditions (P_{CO_2}, R/W ratios, temperature, and an increase in the Cl concentration in the groundwaters) may affect As transfer from the rocks to water.

(2) How these boundary conditions may affect the migration species of As in carbonate waters; what kind of an evolution of the boundary conditions results in soluble migration species of As; and which evolution of

these conditions facilitates the decomposition of these species and the precipitation of solid sulfides.

Thermodynamic simulations of this type can be carried out based on the known boundary conditions (P_{CO_2}, temperature, and R/W ratios) under which the waters are formed. The data reported above allow us to formulate these boundary conditions.

Carbon dioxide partial pressures in hydrogeochemical systems producing As-bearing waters. Typical carbonate waters have P_{CO_2} of the order of 1 bar (and higher), which decrease to $10^{-3.4}$ bar at the discharge sites of these waters due to degassing. Depending on the temperature, these partial pressures correspond to different CO_2 concentrations in carbonate waters. The variations in the concentrations of dissolved CO_2 in the aqueous phase depending on P_{CO_2} in the hydrogeochemical system and the specified R/W ratios and temperatures are shown in Fig. 7.

Temperature. The results of geochemical thermometry with the use of the Na/K ratio definitely indicate that the maximum temperatures at which As-bearing carbonate waters are formed are within the range of 150–200°C.

Mass ratios of interacting rocks and groundwaters R/W. Hydrogeological analysis demonstrates that As-bearing carbonate waters are generated at relatively sluggish water exchange in hydrogeological structures, which ensures long-lasting interactions between the carbonate waters and rocks and results in the origin of waters with high Cl concentrations. The rocks composing these hydrogeological structures are fine-grained and are characterized by low permeability (10^{-4} to 10^{-5} mD), low porosity (5–10%), and correspondingly, low velocities of carbonate waters in them. Water exchange in these structures takes hundreds and, perhaps, even thousands of years and is favorable for rock–water interactions in compliance with not only external diffusion but also with internal diffusion kinetics. This allows the profound recycling of the As-bearing rocks and explains the fact that brief experiments modeling rock–water interactions at high temperatures and pressures fail to reproduce the high As concentrations occurring in natural carbonate waters. The intensity of As transfer from rocks into groundwaters increases with increasing temperature [10], which partly explains the restriction of carbonate waters with elevated As concentrations to zones of maximum geothermal tension. The low porosity of the water-hosting rocks maintains high ratios between the interacting rock and groundwater masses R/W. Our earlier specialized studies indicate that the geochemical composition (Cl–HCO_3–Na and HCO_3–Cl–Na) typical of carbonate waters with the maximum As concentrations can be obtained by simulating rock–water interactions in hydrogeochemical systems with R/W = 50. Considered together with the general geochemical situation of these waters, this led us to assume the maximum R/W ratios of 50–100 in our simulations.

We conducted our simulations using the GIBBS (HCh) computer program, which was designed by Yu.V. Shvarov and makes use of the minimization of the free energy of the hydrogeochemical systems [23]. This program allows the researcher to vary the boundary conditions (R/W ratio and temperature) and rock compositions with which the aqueous phase interacts. This, in turn, enabled us to conduct simulations for elucidating the roles of various boundary conditions in forming the compositions of the aqueous and solid phases and for identifying the optimal conditions under which various geochemical processes can occur. Varying the boundary conditions, we managed to imitate the precipitation of sulfide minerals and to constrain the boundary conditions favorable for this process. In describing the equilibrium state of the hydrogeochemical system, we utilized 70 simple and complex species that can occur in the aqueous phase. The Gibbs free energy of several compounds were published in [10]. The thermodynamic parameters of certain As compounds and reactions in the system As(III)–S(II)–O–H were compiled from [24]. In our research we used simpler descriptions of As(III) species considered in this paper ($HAsO_2^\circ$ and AsO_2^- instead of $H_3AsO_3^\circ$ and $H_2AsO_3^-$).

We used various modifications for the thermodynamic simulations of rock–water interactions. The GIBBS program permitted us to conduct these simulations with regard for transition mechanisms of elements from rocks to water with various rates: (a) slow processes of the destruction (transformation) of mineral crystalline structures and (b) faster ion-exchange processes. The As concentration in rocks was specified as that of As_2O_3 according to A.P. Vinogradov. When As was assumed to be incorporated into the crystalline structures of minerals, the extraction rate of this element corresponded to the dissolution rates of these minerals. If As presumably occurred in an ion-exchange setting, its extraction rate corresponded to the dissolution rate of the chloride minerals. The method applied for the solution of this analogous problem is described in detail in [10] with reference to equilibrium kinetic models.

THERMODYNAMIC ANALYSIS OF THE ORIGIN AND TRANSFORMATIONS OF As MIGRATION SPECIES IN CARBONATE WATERS AT VARIOUS MECHANISMS OF As TRANSFER INTO THE AQUEOUS PHASE

Various mechanisms responsible for the extraction of elements from rocks into the aqueous phase predetermine the various chemical composition of this aqueous phase and, correspondingly, various concentrations of chemical elements that can be contained and interact in this aqueous phase. The total mineralization of the resultant solutions produced by various mechanisms extracting As from rocks was proved to be similar, but the proportions of components in this mineralization varied. For example, the ion exchange mechanism yielded higher Na concentrations and, correspondingly, higher Na/Ca ratios. Depending on the contamination proportions in components in the aqueous phase, various mechanisms generated different migration species of elements.

AQUEOUS PHASE COMPOSITION AND As MIGRATION SPECIES FORMING AT LOW EXTRACTION RATES OF ELEMENTS FROM ROCKS ACCORDING TO THE MECHANISM WITH THE DESTRUCTION OF CRYSTALLINE STRUCTURES IN OPEN SYSTEMS AT VARIOUS P_{CO_2}, R/W RATIOS, AND TEMPERATURES

Upon reaching equilibrium in these systems, we obtained an aqueous phase of Cl–HCO_3–Na composition, which is metamorphosed into a Cl–Na composition at high (200–300°C) temperatures. In the context of this research, the most important feature of this aqueous phase is its low (even at high R/W ratios) As concentrations, which only slightly increase at high (200°C) temperatures (Table 3). At this mechanism and this composition of the aqueous phase, the effect of the solute components on the degree of As complexation is at a minimum, and As-bearing species are dominated (98–99%) by oxygen-bearing compounds ($HAsO_2^0$, and AsO_2^-).[2] The reasons for this are different: low sulfur concentrations for sulfur-bearing compounds ($As_2S_4^{2-}$ and $HAsS_4^-$) and very low stability of Cl-bearing complexes ($AsCl_n^{3-n}$), because of which even high Cl^- concentrations produced in the aqueous phase fail to produce any significant concentrations of As chloride complexes. The slowness of the transfer of elements from various rocks somewhat equalizes their geochemical differences and, hence, also the differences between the As concentrations and its migration species forming in the aqueous phase of carbonate and sand–clay rocks. These are oxygen As compounds whose concentrations depend only on the pH of the solution, P_{CO_2}, and temperature (Table 3). Oxygen-bearing As compounds in carbonate waters are characterized by broad Eh–pH ranges of their stability. Variations in the acid–basic characteristics of the solutions result in transformations of these species $HAsO_2^0 = H^+ + AsO_2^-$ and in the retainment of As in the aqueous phase. Because of this, $HAsO_2^0$ is a typomorphic As species in acidic and near-neutral carbonate waters with elevated Eh (Fig. 9), and AsO_2^- is characteristic of $P_{CO_2} = 10^{-3.4}$ alkaline waters with low Eh. The $HAsO_2^0 \longrightarrow AsO_2^-$ transformation decreases the As concentration in the solution (because of its lower leaching capability) but does not prevent its further migrations and expands the pH range of this migration. Hence, relatively high As concentrations (2–8 ng/l) in natural solutions are also typical of weakly alkaline (pH 8.6) CO_2-poor thermal (Broadlands and others) waters and even so-called inversion Cl–HCO_3–Na CH_4–CO_2 thermal waters at deep levels of the Eastern Fore-Caucasian (Terek–Caspian) artesian basin. However, the typomorphic predominant, and most significant species of the carbonate waters is nevertheless $HAsO_2^0$, and thus, As concentrations in carbonate waters increase most actively in acidic carbonate solutions, which are characterized by the highest P_{CO_2} values (Fig. 10). The temperature plays a thereby incomparably less significant role than that of increasing P_{CO_2}.

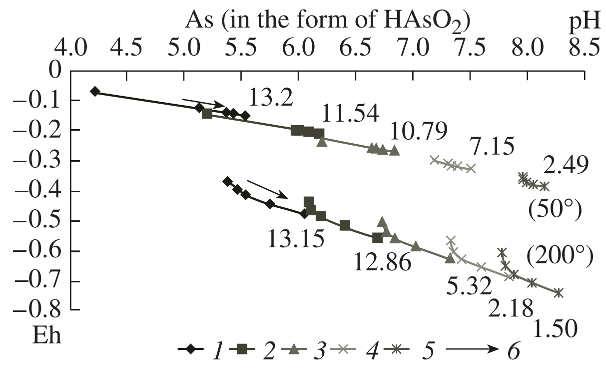

Fig. 9. Variations in the calculated As concentrations (in the form of $HAsO_2^0$, mg/kg) in the aqueous phase of the system carbonate rock–water in an Eh–pH diagram depending on P_{CO_2}, temperature, and R/W ratio (from –2 to 2) specified in the system (low extraction rates according to the mechanism of crystalline lattice destruction, GIBBS computer program); $\log P_{CO_2}$: (*1*) 1; (*2*) 0; (*3*) –1; (*4*) –2; (*5*) –3.4; (6) systematic increase in the R/W ratio in the modeled hydrogeochemical systems.

AQUEOUS PHASE COMPOSITION AND As MIGRATION SPECIES FORMING AT HIGH EXTRACTION RATES OF ELEMENTS FROM ROCKS ACCORDING TO THE MECHANISM OF ION EXCHANGE IN OPEN SYSTEMS AT VARIOUS P_{CO_2}, R/W RATIOS, AND TEMPERATURES

The mechanism of ion exchange was proved to be much more efficient for the transfer of elements from rocks into aqueous phases (Table 4). Upon reaching equilibrium, these systems form an aqueous phase of

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[2] For the sake of convenience, oxygen- and sulfur-bearing As migration species will be referred to below as complex compounds, although they are not exactly such from the standpoint of physical chemistry.

Table 3. Variations in the concentrations of As and its migration species formed during interaction between H_2O and carbonate rocks at low extraction rates of elements from the rocks according to the mechanism of the destruction of crystalline structures (GIBBS computer program, temperatures 25–200°C, P_{CO_2} from $10^{-3.4}$ to 10 bar)

$\log P_{CO_2}$	As concentration, mg/kg					Concentrations $\sum S$, mg/kg at R/W = 100	As migration 'species, % at R/W = 100*	
	$\log R/W$							
	–2	–1	0	1	2		$HAsO_2^0$	AsO_2^-
	25°C							
–3.4	0.0013	0.013	0.13	1.32	1.79	1.21	80.34	18.63
–2	0.0013	0.013	0.13	1.32	9.99	0.06	97.34	2.63
–1	0.0013	0.013	0.13	1.32	10.05	0.09	99.27	0.58
0	0.0013	0.013	0.13	1.32	13.10	0.25	99.65	0.13
1	0.0013	0.013	0.13	1.32	13.20	0.30	99.97	0.03
	50°C							
–3.4	0.0013	0.013	0.13	1.32	3.44	6.13	76.15	18.87
–2	0.0013	0.013	0.13	1.32	7.64	1.28	94.55	5.03
–1	0.0013	0.013	0.13	1.32	10.99	0.52	98.63	1.16
0	0.0013	0.013	0.13	1.32	11.68	0.38	99.35	0.25
1	0.0013	0.013	0.13	1.32	13.24	0.73	100.0	0.06
	100°C							
–3.4	0.0013	0.013	0.13	1.16	2.05	10.76	63.87	35.73
–2	0.0013	0.013	0.13	1.32	8.05	6.07	87.41	12.13
–1	0.0013	0.013	0.13	1.32	13.20	6.02	96.59	3.0
0	0.0013	0.013	0.13	1.32	13.20	3.38	99.43	0.66
1	0.0013	0.013	0.13	1.32	13.20	1.39	100.0	0
	200°C							
–3.4	0.0013	0.013	0.13	1.32	2.54	141.46	59.22	40.32
–2	0.0013	0.013	0.13	1.32	2.73	105.97	79.87	20.05
–1	0.0013	0.013	0.13	1.32	5.73	40.98	92.77	7.22
0	0.0013	0.013	0.13	1.32	13.20	15.54	98.19	1.81
1	0.0013	0.013	0.13	1.32	13.20	11.59	99.6	0.40

Note: Concentrations of sulfide and chloride complex compounds in this system are at a minimum: no significant $As_2S_4^{2-}$ and $HAs_2S_4^-$ concentrations can be formed because of the low $\sum S$ concentrations, and the formation of $AsCl_n^{3-n}$ (in a concentration of >0.001%) requires high Cl^- concentrations, which are higher than even those high Cl^- concentrations ($n \times 10$ g/kg) produced in the systems at high R/W ratios.

$Cl–\sum S–HCO_3–Na$ composition, which is transformed into a $Cl–\sum S–Na$ composition with increasing temperature. At this composition, we obtained high (much higher than those known in natural waters) As concentrations, which form all possible solute compositions (oxygen, sulfide, and even chloride) in the aqueous phase. The variations in their concentrations at various $\sum S$ and $Cl^–$ concentrations and P_{CO_2} values are reported in Table 4. The faster transfer of As from rocks into the aqueous phase gives rise to a difference between its concentrations in the aqueous phases of various rocks (in this case, carbonate and sand–shale, silt, etc.): at R/W = 10–100, sand–shale and silt rocks yield somewhat higher As concentrations.

A distinctive feature of the chemical composition of the aqueous phase produced at high extraction rates of elements from rocks during ion exchange is a much higher mineralization of these solutions and higher concentrations and significance of As compounds with $Cl^–$ and $S^{2–}$. Nevertheless, the proportions of various types of As species are still contrastingly different: oxygen >> sulfide >> chloride. As before, the aqueous phase is dominated by $HAsO_2^0$, and AsO_2^- is prone to occur in alkaline solutions with low P_{CO_2}, with this tendency strengthening with increasing temperature. Hence, the maximum AsO_2^- concentrations (up to 39%) are reached at a temperature of 200°C, whereas the P_{CO_2} decreases. The reason for the low significance of the sulfide species is the relatively low $\sum S$, which are transformed into sulfide sulfur compounds (Table 4). Their significant concentrations are formed at temperatures of 150–200°C (the increase is particularly significant for $HS^–$ at decreasing P_{CO_2}), and correspondingly, sulfide As compounds are dominated by $As_2S_4^{2-}$, whose concentration increases with the beginning of P_{CO_2} decrease. [3] An increase in the concentrations of sulfide species ($As_2S_4^{2-}$ and $HAs_2S_4^{2-}$) with increasing sulfide S concentration occurs owing to the transformation of oxygen species ($2AsO_2^- + 4H_2S = As_2S_4^{2-} + 4H_2O$ or $2AsO_2^- + 4HS^- = As_2S_4^{2-} + 4OH^-$). Finally, high $Cl^–$ concentrations (>70 g/kg) produced in the aqueous phase at R/W ratios increasing to 100 overcome the low stability of chloride As complexes and form the $AsCl_4^-$ and $AsCl_5^{2-}$ chloride complexes. However, their concentrations in the system are relatively low even at high $Cl^–$ concentrations: these complexes can occur in significant concentrations only at high P_{CO_2}, high R/W ratios, and relatively low temperatures (50–100°C). This means that chloride As complexes cannot occur in significant concentrations in natural carbonate waters in naturally occurring environments without high $Cl^–$ concentrations in the aqueous phase, which is commonly formed at lower R/W ratios.

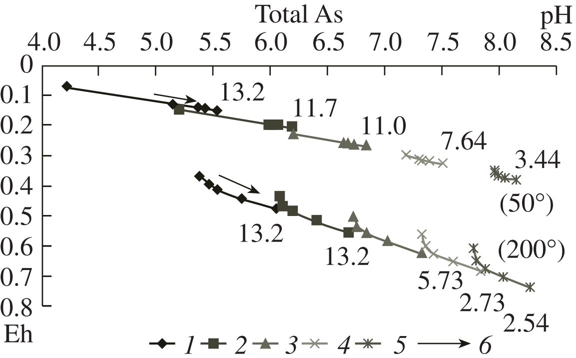

Fig. 10. Variations in the calculated total As concentrations (mg/kg) in the aqueous phase of the system carbonate rock–water in an Eh–pH diagram depending on P_{CO_2}, temperature, and R/W ratio (from –2 to 2) specified in the system (low extraction rates, GIBBS computer program); $\log P_{CO_2}$: (*1*) 1; (*2*) 0; (*3*) –1; (*4*) –2; (*5*) –3.4; (*6*) systematic increase in the R/W ratio in the modeled hydrogeochemical systems.

It is now possible to compare the results of our simulations of the interaction of a carbonate aqueous phase with various rock types at various kinds of rock–water interactions. It was established that the relatively fast ion-exchange interaction of carbonate waters with fine-grained rocks leads to much more significant As extraction from the rocks. As follows from Table 3, fast ion-exchange interactions yield one order of magnitude higher As concentrations (up to 1000 mg/l) in the aqueous phase.

This, however, provokes the question as to why the maximum As concentrations in naturally forming carbonate waters are usually no higher than a few dozen mg/l and reach no higher than 100 mg/l under the most favorable conditions (Table 1).

This is partly explained by As coprecipitation during the deposition of travertine at the discharge sites of carbonate waters of HCO_3–Cl–Na and Cl–HCO_3–Na composition. We mentioned above that As concentrations in the carbonate–ferrous travertine masses range from 0.01 to *n*%. However, the material balance of As in individual travertine massifs does not correspond to

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[3] This conclusion is in conflict with statements in [24], in which it was convincingly proved that the opposite process of the replacement of sulfide compounds by oxygen ones is more probable at high temperatures. However, in the situation with our high-temperature simulations, the concentrations of sulfide S compounds are relatively high, and, according to the mass action law, they are able to transform oxygen compounds into sulfides. As will be demonstrated later, high temperatures of natural carbonate waters with lower concentrations of sulfide S can transform sulfide As species into oxygen species of this element.

Table 4. Concentrations of various S, Cl, and As species in carbonate waters at various temperatures in carbonate rocks depending on P_{CO_2} at R/W = 100 (high rates of As extraction from rocks in compliance with the ion exchange mechanism, GIBBS computer program)

Parameter		50°C					100°C				
		$\log P_{CO_2}$					$\log P_{CO_2}$				
		1	0	–1	–2	–3.4	1	0	–1	–2	–3.4
pH		5.292	5.801	6.306	6.808	7.508	5.358	5.867	6.372	6.874	7.573
Eh (V)		–0.095	–0.134	–0.175	–0.215	–0.271	–0.181	–0.228	–0.274	–0.321	–0.385
$\sum Cl$	mg/kg	74593	74577	74570	74570	74572	74582	74572	74572	74578	74575
$\sum S$	mg/kg	3199	3340	3404	3437	3444	2197	2294	2339	2361	2360
$\sum SO_4^{2-}$	%	99.99	100.00	100.00	100.00	99.99	99.98	99.98	99.96	99.92	99.68
HS^-		2.70E-05	5.94E-05	1.84E-04	5.81E-04	3.08E-03	0.002	0.01	0.02	0.07	0.31
H_2S		4.59E-04	3.12E-04	3.03E-04	3.01E-04	3.18E-04	0.02	0.02	0.02	0.02	0.01
$\sum As$	mg/kg	735	735	734	735	537	735	735	730	727	667
$HAsO_2^0$	%	58.32	97.72	99.60	98.97	95.09	82.74	98.99	98.79	96.11	81.02
AsO_2^-		0.02	0.10	0.32	1.01	4.89	0.09	0.34	1.09	3.38	14.26
$As_2S_3^0$		0.01	0.01	0.01	0.01	0.01	0.036	0.036	0.036	0.036	0.018
$HAs_2S_4^-$		1.98E-05	4.54E-05	1.43E-04	4.57E-04	1.94E-03	0.002	0.005	0.016	0.054	0.125
$As_2S_4^{2-}$		4.60E-07	3.40E-06	3.43E-05	3.48E-04	7.40E-03	0.00036	0.00336	0.035	0.360	4.180
$As_4S_7^{2-}$		1.34E-08	9.92E-08	1.00E-06	1.01E-05	1.26E-04	0.00005	0.00044	0.005	0.047	0.255
$AsCl_4^-$		24.39	1.26	0.04	1.22E-03	9.32E-06	12.01	0.43	0.01	4.05E-04	2.73E-06
$AsCl_5^{2-}$		16.26	0.86	0.03	8.41E-04	6.40E-06	4.76	0.17	0.01	1.63E-04	1.10E-06

Parameter		150°C					200°C				
		$\log P_{CO_2}$					$\log P_{CO_2}$				
		1	0	–1	–2	–3.4	1	0	–1	–2	–3.4
pH		5.485	5.997	6.502	6.999	7.693	5.746	6.254	6.755	7.252	7.935
Eh (V)		–0.273	–0.326	–0.379	–0.431	–0.5	–0.378	–0.437	–0.493	–0.548	–0.624
$\sum Cl$	mg/kg	46555	46552	46556	46557	46557	74583	74581	74586	74586	74586
$\sum S$	mg/kg	1043	1104	1136	1136	1145	1286	1336	1358	1378	1390
$\sum SO_4^{2-}$	%	99.36	99.19	98.59	97.29	94.19	94.86	94.38	93.50	90.87	83.68
HS^-		0.10	0.29	0.92	2.31	5.61	0.99	2.43	4.60	8.07	15.88
H_2S		0.55	0.51	0.50	0.40	0.20	4.16	3.19	1.90	1.06	0.43
$\sum As$	mg/kg	827	831	893	1086	1086	914	1092	1085	1083	1082
$HAsO_2^0$	%	97.67	98.30	91.48	76.41	60.83	90.14	79.80	78.52	71.74	39.74
AsO_2^-		0.26	0.86	2.56	6.71	26.42	0.58	1.64	5.12	14.69	39.26
$As_2S_3^0$		0.06	0.06	0.06	0.03	0.002	0.10	0.05	0.01	1.58E-03	3.37E-05
$HAs_2S_4^-$		0.05	0.15	0.44	0.49	0.09	0.79	0.95	0.39	0.11	4.49E-03
$As_2S_4^{2-}$		0.04	0.40	3.82	13.31	12.36	2.74	10.65	13.90	11.77	2.42
$As_4S_7^{2-}$		0.02	0.17	1.64	3.05	0.22	3.11	6.82	1.89	0.24	0.00
$AsCl_4^-$		1.72	0.05	1.45E-03	3.91E-05	2.56E-07	2.29	0.06	1.89E-03	5.58E-05	2.71E-07
$AsCl_5^{2-}$		0.12	3.58E-03	1.03E-04	2.76E-06	1.81E-08	0.21	0.01	1.78E-04	5.25E-06	2.56E-08

the As mass that should have been leached according to the ion exchange mechanism over the whole lifetime of the hydrogeological system of waters forming these massifs. Hydrogeological materials testify that the lifetime of these systems of carbonate waters varies from 10^5 to 10^6 years. Thus we believe that active As transfer from rocks to the aqueous phase, which was recognized when the ion exchange was simulated, is hardly plausible compared to less active As transfer during the decomposition of the crystalline structures of minerals. This led us to the conclusion that As is transferred from rocks to the aqueous phase of carbonate waters mostly via the mechanism of the destruction of primary As-bearing minerals under the effect of CO_2 and their replacement by newly formed As-free supergene minerals. Our simulations demonstrate that the complex of these supergene minerals is fairly diverse (kaolinite, siderite, quartz, and others). The most important boundary conditions ensuring As transfer from rocks via this mechanism are P_{CO_2} and the R/W ratio in the hydrogeochemical systems. We obtained As concentrations approaching those in naturally occurring carbonate waters at P_{CO_2} of about 1–10 bar and R/W = 50–100 (Table 3). In hydrogeological terms, this means that the carbonate waters are produced in relatively weakly permeable rocks, at a sluggish water exchange, and at correspondingly long times of carbonate water formation in the hydrogeological structures. Our simulation results indicate that hydrogeological systems with these R/W ratios and P_{CO_2} can generate a chemical composition of carbonate waters typical of As-bearing waters (Cl–HCO_3–Na composition at Cl concentrations of *n* to $n \times 10$ g/l and HCO_3^- concentrations of *n* g/l).

AS MIGRATION SPECIES IN CARBONATE WATERS

As follows from the results of our thermodynamic simulations, well soluble As migration species can be formed in carbonate waters within broad Eh–pH ranges. At variations in the Eh–pH parameters, earlier migration As species "adjust" to newly formed situations and, changing their composition, remain retained in the aqueous phase. This adjustment may proceed in two manners: (1) mutual concurrent transformations of oxygen and sulfide species at changes in the concentrations of sulfide sulfur and temperatures and (2) replacement of protonated ($HAsO_2^0$ and $HAs_2S_4^-$) species by nonprotonated ones (AsO_2^-, $As_2S_4^{2-}$, $As_4S_7^{2-}$, and others) at variations in the pH of the solutions. Below we will consider the transformations of oxygen and sulfide As species within the Eh–pH range of naturally occurring carbonate waters. The benchmark data for this analysis are presented in Table 5.

The $HAsO_2^0$ and AsO_2^- oxygen species are predominant in both sulfide-free and sulfide-bearing carbonate waters. They account for almost 100% of all As species in sulfide-free waters, and their concentrations in sulfide waters are also high. The original As species for these compounds is AsO_2^-, which is transformed into $HAsO_2^0$ ($AsO_2^- + H^+ = HAsO_2^0$) with the transition to acidic carbonate aqueous solution. Correspondingly, the abundances and variations in the concentrations of these species in carbonate waters are of an opposite direction and depend mostly on P_{CO_2} in the hydrogeochemical system. At deep levels of hydrogeological structures, at high P_{CO_2}, in sulfide-free solutions with pH < 7, the carbonate waters are strongly dominated (>95%) by $HAsO_2^0$. As the carbonate waters approach the surface and progressively degas, their pH increases (to >7), and the AsO_2^-- concentration in them increases.

Another important factor affecting the $HAsO_2^0$ and AsO_2^- distributions and their relations with other As species is temperature. It was established (Table 5) that a temperature increase in a system of oxygen and sulfide As species induces an increase in the concentrations of $HAsO_2^0 + AsO_2^-$, which progressively replace sulfide complex compounds. For example, in highly thermal Broadland waters (260°C), the overall $HAsO_2^0$ + AsO_2^- concentrations approach 100% even at very high concentrations of H_2S > 100 mg/l, and much As of the sum of these compounds is contained in the form of AsO_2^- (32%).

Cold and weakly thermal sulfide-free carbonate waters containing $HAsO_2^0$ have the highest As concentrations among all types of As-bearing natural waters (Table 1). Even in near-surface environments, these waters contain the highest (approaching 100 mg/l and even more) As concentrations. There are two major types of boundary conditions that control $HAsO_2^0$ concentrations in natural carbonate waters. One of them is the R/W ratio in the hydrogeochemical systems. Table 3 and Fig. 9 demonstrate how the As concentrations (in the form of $HAsO_2^0$) increase in carbonate waters with increasing R/W ratio. Hydrogeologically, this means that the As concentrations in the form of $HAsO_2^0$ increase with decreasing intensity of water exchange in the hydrogeological structures and at increasing interaction surface between these waters and rocks. The other boundary condition is a high P_{CO_2} in the hydrogeochemical systems, which have in these situations a major CO_2 source. Situations of this kind are typical of hydrogeological structures in areas of Alpine tectonism and magmatism. A decrease in the P_{CO_2} occurring at the discharge site of carbonate waters results in an

Table 5. Calculated As migration species in carbonate cold sulfide-free and thermal sulfide-bearing waters

Parameter		Sulfide-free waters						Thermal sulfide-bearing waters			
		Azavatan	Dzhulfa	Chuchkur	Uchkulan	Khudes	Kvasy Rahovsky	Isti-Su	Uzon	Oso-reyama	Broadlands
t (°C)		42	40	7.5	12	7.5	10	67	94	100	260 $\longrightarrow$ 100
pH_{meas}		6.7	6.8	6.6	6.4	6.7	6.1	7.1	7.6	7.3	6.2 $\longrightarrow$ 8.6**
Eh, mV_{calc}		–0.148	–0.155	–0.084	–0.129	–0.136	–0.027	–0.248	–0.283	–0.384	–
SO^{2-}_{4meas}	mg/kg	750	939	192	169	216	n.a.	580	86.0	63.0	6.5
$\sum S\ (H_2S + HS^-)$	mg/kg	9.85E-10*	6.02E-13*	1.09E-15*	4.33E-13*	6.30E-10*	–	7.0	11.3	11	103
$\sum As$	mg/kg	120	20	37.5	11	15	50	4.8	7.0	39.5	3.2
$HAsO_2^0$	%	99.27	98.52	99.49	98.76	99.39	99.79	35.73	83.49	90.17	67.4
AsO_2^-	%	0.28	0.78	0.22	0.50	0.34	0.11	0.26	0.50	6.84	32.54
$As_2S_3^0$	%	6.03E-11	9.10E-22	2.78E-25	5.56E-19	1.34E-08	–	6.99	1.50	0.01	<0.01
$HAs_2S_4^-$	%	1.31E-15	2.22E-29	1.17E-35	1.40E-26	4.42E-13	–	39.89	9.16	0.13	<0.01
$As_2S_4^{2-}$	%	1.39E-16	5.32E-30	2.08E-37	6.28E-28	1.25E-14	–	15.21	5.08	1.39	<0.01
$As_4S_7^{2-}$	%	2.37E-27	2.60E-52	3.66E-63	6.95E-48	4.29E-24	–	1.92	0.27	0.01	<0.01

Notes: * Calculated $\Sigma(H_2S + HS^-)$.

** Speciation for Broadlands was calculated at 260 and 100°C; the data of the table correspond to 260°C).

increase in their alkalinity and leads, correspondingly, to the $HAsO_2 \longrightarrow AsO_2^-$ transformations, which always means a decrease in the As concentration in naturally occurring waters. This is caused by the geochemical processes occurring when carbonate waters approach the surface and outpour at it. Previously we considered the geochemical processes occurring thereby. Because of them originally acidic (pH 6.2) thermal waters at Broadlands, New Zealand, are transformed into alkaline waters (pH 8.6) as the temperature decreases from 260 to 100°C, and these waters precipitate an amorphous precipitate with elevated As concentrations but not sulfide minerals [7]. As is shown in Table 5, oxygen As species ($HAsO_2^0 + AsO_0^-$) are predominant even in the most thermal waters (>200°C), and they can form the highest As concentrations in the carbonate waters. We believe that (a) these high concentrations may be typical of carbonate waters at deep, highly thermal levels of Alpine hydrogeological structures, and (b) they provide the basis for hydrothermal solutions that can (and do) form sulfide As mineralization.

The sulfide As species ($As_2S_4^{2-}$, $HAs_2S_4^-$, and $As_4S_7^{2-}$) are produced only in thermal carbonate waters with sulfide S compounds. The quantitative analysis of the possible distribution of sulfide As species in carbonate waters (Table 5) indicates that the concentrations of these species in the thermal sulfide carbonate waters are not as high as was thought previously [6]. The major two factors that facilitate the formation of sulfide As species and constrain their abundances in thermal waters are (1) the initial $SO_4^{2-} + H_2S + HS^-$ concentrations and (2) the temperature. The reasons for this are as follows. First of all, the analysis of the distributions of sulfide As species in certain naturally occurring carbonate waters indicates that these distributions depend on the initial SO_4^{2-} concentrations and the intensity of its biogenic and abiogenic transformations into various sulfide sulfur species: the higher the initial SO_4^{2-} concentrations, the greater the number of the derived sulfide sulfur species, the wider the pH range (at equal other parameters) of the As sulfide complexes, and the greater the shift of this range toward alkaline conditions. For example, in the course of our thermodynamic simulations of interactions between carbonate waters and sandy clay rocks and the numerical experiment with carbonate waters from a diversity of their occurrences, we determined that significant $As_2S_4^{2-}$ concentrations occurred at temperatures of 50–100°C and high sulfide sulfur concentrations (approaching 1 g/l) within a pH range of up to 9 and Eh of –400 mV. Another principally important factor controlling the formation and distributions of sulfide As species is the temperature of the carbonate waters. As is displayed in Fig. 5, natural carbonate waters contain significant As concentrations only at temperatures of no higher than 100°C. A further temperature increase leads a decrease in their concentrations because of their substitution for the $HAsO_2^0$

and AsO_2^- oxygen species. For example, the thermal carbonate waters at Broadlands, New Zealand (260°C), contain all of their As in the form of oxygen species ($HAsO_2^0$ + AsO_2^-), and their percentage among all As compounds approaches 100% (Table 5). We regard this fact as an argument in support of the conclusions [24] in which the substitution of sulfide complexes for oxygen ones was theoretically predicted for a situation with a significant temperature increase. At the same time, it should be emphasized that these figures are not absolute. The phenomenon considered here depends not only on the temperature but also on the initial concentrations of sulfide and sulfate sulfur. This is quite obvious: according to the mass action law, the higher the sulfate and sulfide sulfur concentrations in a given carbonate water, the higher its resistance to temperature-dependent replacement of its sulfide As species by oxygen ones. We have demonstrated this phenomenon in the course of the thermodynamic simulations of ion-exchange interactions of carbonate waters with sand–clay rocks, when these waters formed very high (>1 g/l) sulfur concentrations (Table 4). In these situations, we obtained As sulfide species stable to temperatures of 200°C. These situations are, however, little probable in natural carbonate waters: real hydrogeological situations with much lower concentrations of sulfate and sulfide sulfur in the waters contain no As sulfide complexes able to remain stable to such high temperatures. The following conclusions can be drawn as summarizing this section:

(1) Naturally occurring carbonate waters are characterized by high concentrations of oxygen As species and much less significant concentrations of its sulfide species.

(2) Under natural conditions forming carbonate waters, two group of processes can take place that decrease the concentrations of sulfide As species: (a) a temperature increase with depth at which carbonate waters are formed, particularly in zones of modern and Alpine tectonism and magmatism, which result in the transformations of sulfide As species into oxygen species and a decrease in their concentration to minimum values; and (b) the escape of H_2S from the carbonate waters (degassing) during their discharge and the aeration and oxidation of these and other sulfide sulfur species (HS^- and others) contained in the carbonate waters depress the stability of sulfide As species and transform them into oxygen species according to the schemes $As_2S_4^{2-} + 2O_2 \longrightarrow 2AsO_2^- + 4S$. This constrains a fairly narrow hydrogeochemical zone in which As sulfide species are stable. This zone corresponds to the deep levels of hydrogeological structures with the following characteristics: temperatures of 50–100°C, high $H_2S + HS^-$ concentrations, and negative Eh values (at a broad pH range).

(3) An increase in the $\sum S(II)$ concentrations increases the amount of As in the form of soluble sulfide complexes, decreases the As concentrations able to form its solid sulfides, and correspondingly, increases the As concentrations retained in the aqueous phase.

All of this means that solid As_2S_3 and AsS phases from dissolved sulfide species can be formed only within narrow ranges of Eh–pH and the concentrations of $H_2S + HS^-$ and As.

DISCUSSION OF THE RESULTS FROM THE STANDPOINT OF THE HYDROGENIC GENESIS OF LOW-TEMPERATURE As SULFIDE MINERALS

First, the following two remarks should be made:

(1) The position of sulfide As minerals is shown in the Eh–pH diagrams published in [25, 26]. However, our task was more complicated, because we had to constrain the position of solute sulfide and oxygen species in the Eh–pH field of solid sulfides. As was demonstrated earlier these dissolved compounds have Eh–pH characteristics plotting them deep in the solid sulfide field.

(2) Experience in studying hydrogeological structures whose geochemical evolution ends with hydrogenic ore-forming processes [27, 28] suggests that there is no need to invoke the inflow of sulfide waters into these structures from outside to establish geochemical barriers: these sulfide waters are formed in situ in the hydrogeological structures themselves, and the geochemical barriers are formed when certain boundary conditions are imposed onto these waters. It was established that hydrogenic mineralization most commonly results from the systematic hydrogeochemical evolution of the hydrogeological structures under certain boundary conditions (R/W ratio, P_{CO_2}, and temperature) under which the groundwaters are formed. In its optimal expression, this systematic hydrogeochemical evolution of the structure should inevitably produce successive cycles of its metallogenic evolution, which starts with the concentration of ore elements in the groundwaters and ends with the precipitation of these elements in the zones of geochemical barriers. In systems with As-bearing carbonate waters, these phenomena are clearly pronounced, and the produced concentrations of dissolved As compounds are sufficient for the deposition of solid sulfides.

In the previous sections of this publication, we discussed the causes of As enrichment in carbonate waters and the migration species of this element in the waters, and now we can consider the probable processes and boundary conditions of As deposition from these waters in the form of a solid sulfide phase.

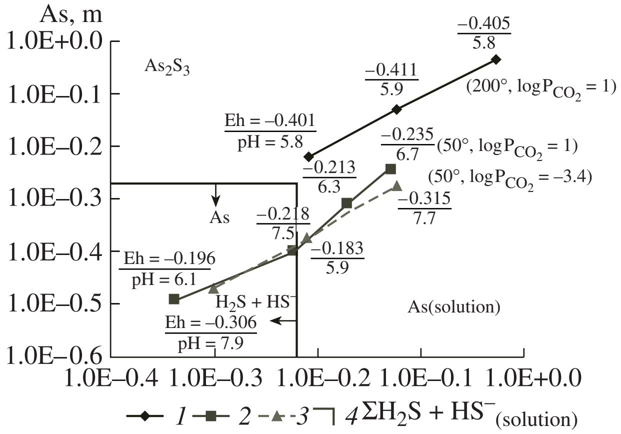

Fig. 11. Calculated $As_2S_{3solid}/As_{solution}$ boundaries in the model $HAsO_2^0(AsO_2^-)_{solution}–\sum H_2S + HS^-_{solution}$ depending on temperature, P_{CO_2}, pH, and Eh. The diagram also shows the boundaries of the actual As – $\sum H_2S + HS^-$ concentrations in naturally occurring carbonate waters (GIBBS computer program): (*1*) 200°C at $P_{CO_2} = 1$ bar; (*2*) 50°C at $P_{CO_2} = 1$ bar; (*3*) 50°C at P_{CO_2} $10^{-3.4}$ bar; (*4*) boundaries of the actual $\sum As$ and $\sum H_2S + HS^-$ concentrations in carbonate waters.

MODELS FOR THE HYDROGENIC ORIGIN OF As SULFIDES

Carbonate waters may contain two types of original solute As species that can lead to the formation of As sulfide minerals: (a) oxygen compounds $HAsO_2^0$ and AsO_2^- and (b) sulfide complexes $As_2S_4^{2-}$, $HAs_2S_4^-$, and $As_4S_7^{2-}$. Obviously, these diverse As migration species in carbonate waters and their various geochemical behavior under boundary conditions forming these waters may be considered within the framework of various models for mineral-forming processes producing As sulfides.

Model for the genesis of As sulfides in the system $HAsO_2^0(AsO_2^-) - \sum S^{2-}$. Figure 2 presents the calculated conditions under which minerals are formed in this system and shows the boundaries between $As_2S_{3solid}–As_{solution}$ in this system at various Eh–pH parameters and $H_2S + HS^-$ at various temperatures. We also consider it necessary to show the position of the real As and $\sum S^{2-}$ concentrations in carbonate waters in order to reveal relations between these conditions of mineral-forming processes and the actual parameters of natural carbonate waters. The following conclusions can be drawn from these materials:

(1) The calculated As and $\sum S^{2-}$ concentrations needed for the deposition of sulfides at 200°C lie outside the actual ranges of their concentrations in carbonate waters, and thus, sulfide formation in the system is optimal at 50°C (which agrees with the conclusions in [8]).

(2) Inasmuch as As species in carbonate waters at 50°C are strongly dominated by oxygen compounds, it is reasonable to assume that the basis of the mineral-forming processes at $P_{CO_2} = 1$ bar and pH < 7 is provided by reactions like $2HAsO_2^0 + 3H_2S = As_2S_{3sol} + 4H_2O$. At the same time, it is quite evident that, at a decrease in P_{CO_2} to $10^{-3.4}$ at the same temperatures and an increase in pH to 7.9, the significant reactions are $2AsO_2^- + 3HS^- + 5H^+ = As_2S_{3solid} + 4H_2O$. The problem of an H_2S and HS^- source is thereby readily soluble, because these sulfur compounds become typomorphic of carbonate waters starting at 50°C. The problem here is not so much the source of $\sum S^{2-}$, as its concentration at which As sulfide form becomes probable in natural carbonate waters. Figure 11 also illustrates that As sulfides can be most plausibly and efficiently formed in the system if $\sum S$ (H_2S + HS^-) decreases. This is explained by the fact that a decrease in their concentrations leads to a shift from As and $H_2S + HS^-$ concentrations improbable for carbonate waters to values quite probable for these waters (the boundary between $As_2S_{3solid}/As_{solution}$ and $As_{solution}$ shifts at 50°C to the region of such realistic concentrations).

Another important observation is as follows: a decrease in P_{CO_2} from 1 to $10^{-3.4}$ bar (as is typical of near-surface environments where carbonate waters discharge) shifts the region where sulfides are formed toward higher pH (and lower Eh), which may mean an increase in the probability of AsS formation by the reaction $AsO_2^- + HS^- + 3H^+ + e = AsS + 2H_2O$. This is more consistent with the position of the sulfide in the Eh–pH diagram according to [26].

As can be seen, the optimal formation of As sulfides in the model takes place at decreasing temperatures in the carbonate waters and the degassing of CO_2 and H_2S from them. In natural environments this corresponds to an increase in the probability of the precipitation of these minerals in the discharge zones of carbonate waters, when their temperature decreases and they lose much of their CO_2 and H_2S.

Model $As_2S_4^{2-}$ ($HAs_2S_4^-$ and $As_4S_7^{2-}$)–H^+. The action of this model is based on the binding of S^{2-} from the aforementioned solute sulfide complexes with the H^+ cation with the formation of H_2S and solid As_2S_3 and AsS precipitates in acidic solutions. The action of the model can be represented as follows:

$$As_2S^{2-}_{4solution} + 2H^+ = As_2S_{3solid} + H_2S$$

$$As_2S^{2-}_{4solution} + 2H^+ + H_{2gas} = 2AsS_{solid} + 2H_2S$$

$$HAs_2S_4^- + H^+ = As_2S_{3solid} + H_2S$$

$$HAs_2S_4^- + H^+ + H_{2gas} = 2AsS_{solid} + 2H_2S$$

$$As_4S_7^{2-} + 2H^+ = 2As_2S_{3solid} + H_2S$$

$$As_4S_7^{2-} + 2H^+ + 2H_{2gas} = 4AsS_{solid} + 3H_2S.$$

Obviously, the higher the H^+ concentration in the system, the more efficient its mineral-forming action. The model pertains to acidic solutions. Data obtained on redox processes in systems with carbonate waters led us to suggest that these transformations can occur during the formation of H_2 via underwater Fe(II) oxidation by the reaction $Fe^{2+} + H_2O \longrightarrow Fe^{3+} + 1/2\ H_2$. Gaseous H_2 is fairly often produced in carbonate waters, particularly at high Fe^{2+} concentrations and low redox potential values [29]. This hypothesis of orpiment and realgar formation in carbonate waters as a result of transformations of their dissolved As sulfide compounds in acid solutions is chemically plausible. However, if the geochemistry of natural carbonate waters is considered, the question arises as to what As and $\sum S^{2-}$ concentrations are needed for the aforementioned processes and reactions to form orpiment and realgar and whether these concentrations in natural carbonate waters are high enough. In order to evaluate these mineral-forming concentrations and conditions under which they can be transformed into As_2S_3 and AsS, we conducted quantitative thermodynamic simulations of the processes described by the reactions presented above and constrained the boundaries of As_2S_{3solid} and $AsS_{solid}/As_{solution}$ in the As–H_2S system at various Eh–pH parameters and various temperatures at which the carbonate waters are formed (Fig. 12). As the previous figure, this one shows the position of the As and $\sum S^{2-}$ concentrations in natural carbonate waters in order to display how these calculated concentrations needed for the precipitation of the minerals are related to the actual concentrations in natural carbonate waters. As a result, we determined that, first, sulfides can be formed according to the "sulfide" model within a broad temperature range (25–200°C), the optimum temperatures are close to 100°C, and, second, these minerals can be precipitated only at low pH of the solutions (<5). Obviously, As sulfide minerals cannot be formed from near-neutral and, particularly, alkaline solutions anywhere within the temperature range typical of carbonate waters: the precipitation of these minerals requires high As concentrations (from *n* to *n* × 10 g/kg), which are unrealistic for carbonate and any naturally occurring waters. It is also important to stress that the higher the temperatures of the system are, the lower Eh values of the solution are needed for mineral precipitation.

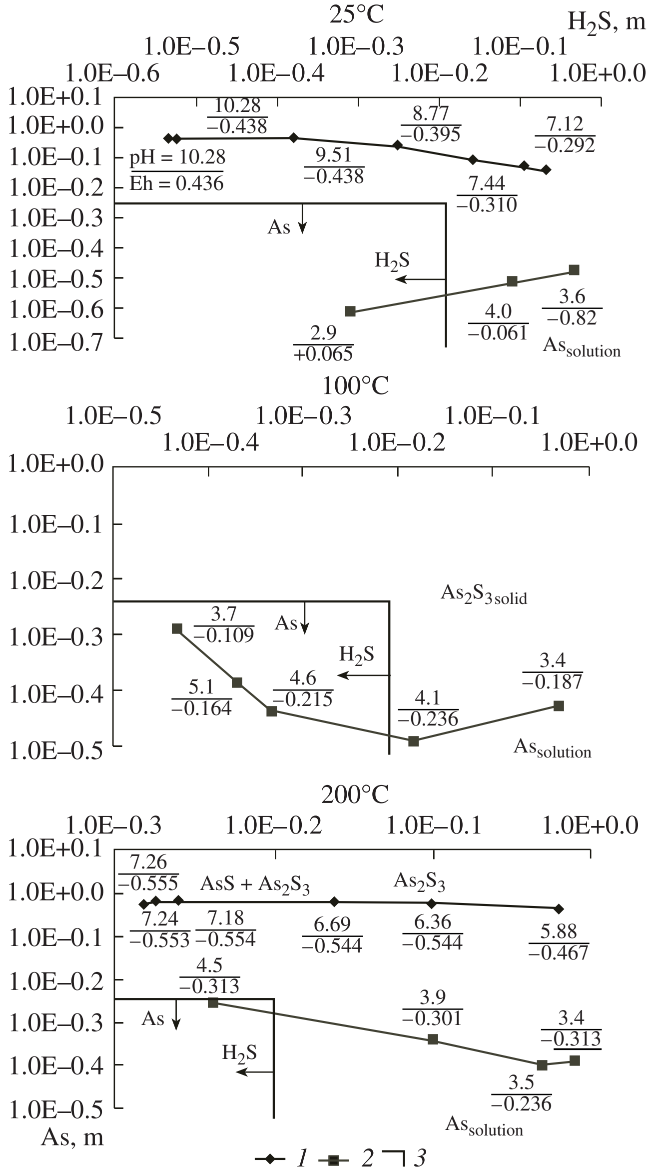

Fig. 12. Calculated $As_2S_{3solid}/As_{solution}$ boundaries in the model $As_2S_4^{2-}$, $HAs_2S_4^{2-}$ – H^+ for sulfide As species depending on temperature, pH, and Eh. The diagram also shows the boundaries of the actual As and H_2S concentrations in natural carbonate waters (GIBBS computer program): (*1*) calculation series at elevated pH; (*2*) calculation series at decreased pH; (*3*) boundaries between the actual As and H_2S concentrations in natural carbonate waters.

It follows from the materials and considerations presented above that the conditions of efficient action of the "sulfide" model in hydrogeological structures requires the following geochemical conditions. Obviously, the minerals should be formed in zones of the near-surface discharge of carbonate–sulfide waters, which form sulfide solutions with low pH at discharge. As was demonstrated in the previous section of this paper, these solutions are formed in the near-surface zones of hydrogeological structures in areas of active volcanism, and exactly those system are often thought to form As ore mineralization [6, 21].

COMPARISON OF THE EFFICIENCY AND SIGNIFICANCE OF THE "OXYGEN" AND "SULFIDE" MODEL FOR THE GENESIS OF As SULFIDES

It follows from the materials presented in this paper that the "oxygen" model should be regarded as more widely applicable to and more significant for the genesis of As sulfide minerals. Arguments in support of this statement are as follows:

(1) The amount of As oxygen compounds in the aqueous phases of the modeled and naturally occurring systems is normally much higher than the concentrations of As sulfide compounds. The maximum percentage of $\sum HAs_2S_4^- + As_2S_4^{2-}$ among other migration species of As in natural carbonate waters can occasionally reach ~55% (Table 5) but is normally much lower.

(2) Under the boundary conditions of the origin of natural carbonate waters, As sulfide species are systematically replaced by oxygen species of this element. This tendency is particularly clearly pronounced (a) in near-surface discharge sites of carbonate waters, when sulfide sulfur compounds become metastable and are transformed [$H_2S \longrightarrow S^0$, $S^0 \longrightarrow SO_4^{2-}$ (H_2SO_4), and $As_2S_4^{2-} \longrightarrow AsO_2^-$] and (b) when the temperature of the aqueous phase increases to 100–150°C and all As sulfide species are completely transformed into its oxygen species (Table 5) (because a temperature increase is associated with a more rapid increase in the stability of oxygen but not sulfide complex compounds). This means that the stability regions of sulfide As species are very narrow and correspond to the deep levels of hydrogeological structures with temperatures below 100°C.

(3) The "oxygen" model is characterized by a very broad Eh–pH range of its efficient action (Fig. 11). This model is more applicable to real geochemical and temperature processes typical of the hydrogeological zones of carbonate water action, particularly in near-surface zones, with the replacement of sulfide by oxygen As species. The efficient action of the "sulfide" model is restricted to low pH of the solutions at low (!) Eh values: a very unusual situation, because natural hydrogeological environments are characterized by other relations between their Eh and pH.

Hence, following Zotov et al. [21], we conclude that natural mineral-forming waters should be dominated by hydroxide complexes ($H_3AsO_3^0$ in [21]), with these compounds playing the decisive role in the formation of As solid sulfides. Nevertheless, As sulfide complexes can still be formed in thermal carbonate waters, so that the "sulfide" model can be applicable to certain hydrogeological and geochemical situations, when the pH values of the solutions drastically decrease. In the previous section of this paper, we have briefly outlined these situations: these are the discharge zones of sulfide-rich thermal waters that can resist the replacement of sulfide As species by its oxygen compounds.

Our materials also led us to conclude that they are best compatible with the model of cooling and oxidation, among the hypothetical genetic models proposed for the genesis of orpiment and realgar in [8].

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