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Geochemistry of Soda Waters of the Chulym–Yenisei Artesian Basin (West Siberia)

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Abstract—Results of studies of soda waters of the Chulym–Yenisei artesian basin are presented. It is shown that these waters are ubiquitous within Cretaceous or Jurassic sediments at depths of ~100–300 m to 1.5–2.3 km. According to the formation conditions, mineralization, and pH, they are divided into three groups: Type I waters spread to a depth of 600 m and have pH = 7.4–8.4 and TDS ≤ 0.5 g/L, type II waters occur at depths of 0.6–2.3 km and are characterized by pH = 8.0–8.9 and TDS = 0.7–4.1 g/L, and type III waters ("Omega") form a local segment among type II waters and have a unique composition: high alkalinity (pH = 9.0–10.3) and low mineralization (TDS = 0.2–0.6 g/L). We focus special attention on type III waters and present results of studies of their microcomponent, gas, and isotope compositions. The cause of their low salinity and high pH is explained for the first time. Taking into account the isotope data (δD, $\delta^{18}O$, and $\delta^{13}C$), we have established the infiltration origin of soda waters of the three types and the biogenic source of their carbon dioxide. Calculations of equilibria in the water–host-mineral system have shown that all soda waters are in disequilibrium with many primary aluminosilicate minerals but are in equilibrium with a wide range of carbonates and clays. In passing from type I to type III waters, the number of minerals in equilibrium with water continuously increases (albite, microcline, muscovite, and biotite). Taking into account the data obtained, we present schemes of formation of different types of soda waters in the studied basin at different stages of the evolution of the water–rock–gas–organic-matter system and estimate the time of each stage.

Keywords: soda waters, conditions of water spread, chemical and isotope compositions, water–rock system, formation mechanisms, equilibrium, Chulym–Yenisei basin

INTRODUCTION

Special attention has recently been focused on soda waters, which result from the interaction of water with aluminosilicate minerals. This problem is of great scientific interest. Soda waters are an object of contradictions in modern hydrogeochemistry (Shvartsev, 2004). The mechanism of soda water formation was long ascribed to cation exchange processes. It was first proposed by soil scientists to explain the formation of soda in steppe solonetz and solonchak (K.K. Gedroits, W.P. Kelley, I.N. Antipov-Karataev, V.A. Kovda, K.Ya. Kozhevnikov, etc.). Later, this idea was supported by some hydrogeologists (V.A. Sulin, A.N. Buneev, G.N. Kamenskii, E.V. Pinneker, J.I. Drever, etc.). Today it is actively developed by Popov and Abrakhmanov (2013) and other researchers (Blake, 1989; Kimura, 1992; Matthess et al., 1992; Appelo and Postma, 1994; Gavrishin, 2005; Shvartsev and Wang, 2006).

The cation exchange hypothesis cannot account for many details of the formation of soda waters and thus receives criticism and stimulates the search for new approaches to the solution of the soda waters problem. One of them is the long-known geological hypothesis implying the formation of soda during weathering of massive crystalline and sedimentary rocks (F.F. Clark, M.I. Kuchin, I.P. Gerasimov, E.N. Ivanova, Yu.R. Nikol'skaya, E.V. Posokhov, K.F. Filatov, etc.), but it cannot explain the selective concentration of Na in the solution, although all cations, including Na, K, Ca, and Mg, pass into water during weathering of aluminosilicates. Researchers are trying to solve the problem in two ways: (1) Elucidation of the relationship of soda waters with the type of weathered rocks. Posokhov (1969) is the most dogmatic in this regard: He believes that a favorable environment for the formation of soda waters is created only in massifs of alkali granites rich in Na-feldspars and in sandstones, sands, and conglomerates, which are the product of destruction of igneous rocks of corresponding mineral composition. (2) Elucidation of the relationship of soda formation with a certain climate, which supposedly controls the temperature differentiation of salts and changes the element mobility, the sorption capacity of weathering products, the intensity of biological cycles of elements, etc. Summarizing the data on sodic soils in the south of West Siberia, Bazilevich (1965) concludes that the separation of Na bicarbonates

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from Ca and Mg salts in solutions, necessary for soda accumulation, proceeds through sorption, because Ca and Mg have a higher absorption energy than Na. Both approaches are highly vulnerable and are not confirmed by particular data (Shvartsev et al., 2007). Therefore, the search for a solution to the problem of soda formation continues (Kazantsev, 1998; May, 1998; Jankowski and McLean, 2001; Shvartsev et al., 2007; Krainov et al., 2012; Christian et al., 2016). Of great interest is the concept of the calcium and soda trends of groundwater evolution developed by Krainov et al. (2012). Unfortunately, the authors of this concept have not considered the mechanism of the formation of shallow-depth soda waters.

In our opinion, the problem of soda waters is simply solved in terms of the general theory of water–rock interaction, which is now actively developed by scientists all over the world. This theory is based on results of laboratory experiments on the dissolution of minerals in different geochemical media and at different temperatures and on results of physicochemical modeling of various hydrogeochemical processes and calculation of equilibria in the water–rock system. But what is the most important is that it is based on numerous results of geological and hydrogeological observations in hypergenesis zone, sedimentary basins, hydrothermal systems, at the bottom of seas and oceans, etc. (Pinneker et al., 1983; Shvartsev et al., 2007; Shvartsev, 2008).

In the framework of this theory, soda formation is considered to be a certain stage of water–rock interaction, which begins when the groundwater is saturated with calcite. This saturation usually takes place at water TDS (total dissolved solids) of >0.6 g/L and pH > 7.4. When these values are reached, a geochemical barrier arises for Ca and Mg in the solution, because calcite and montmorillonite begin to form. These minerals bind Ca and Mg, hampering their concentration in the aqueous solution, and thus ensure a relative increase in Na concentration in the solution under disequilibrium–equilibrium conditions of the water–rock system.

Having analyzed the huge factual material on soda waters in many world regions, we concluded (Shvartsev et al., 2007) that soda formation is a natural stage of the evolution of the water–aluminosilicate system, which begins when the water–calcite equilibrium is established. This stage always takes place if water does not leave rock before the soda formation stage is reached. The less water exchange, the more likely the beginning of soda formation.

It might seem that the problem of the mechanisms of soda water formation is solved. But we discovered unusual deep-seated (0.6–1.3 km) soda waters in the Chulym–Yenisei artesian basin, which are highly alkaline (pH = 9.5–10.3) but lowly mineralized (TDS = 0.2–0.4 g/L) (Lepokurova, 2012; Shvartsev and Lepokurova, 2014). Therefore, the main goal of this research was to establish the mechanisms of formation of low-mineralization soda waters on the background of their other types. Under soda waters we imply groundwaters with predominant hydrocarbonate + carbonate anions and Na cations and with pH > 7.0.

THE CHULYM–YENISEI ARTESIAN BASIN

The Chulym–Yenisei artesian basin is located in the southeast of the West Siberian artesian area (Kiryukhin and Tolstikhin, 1987) (Fig. 1). Its territory lies within the zone of

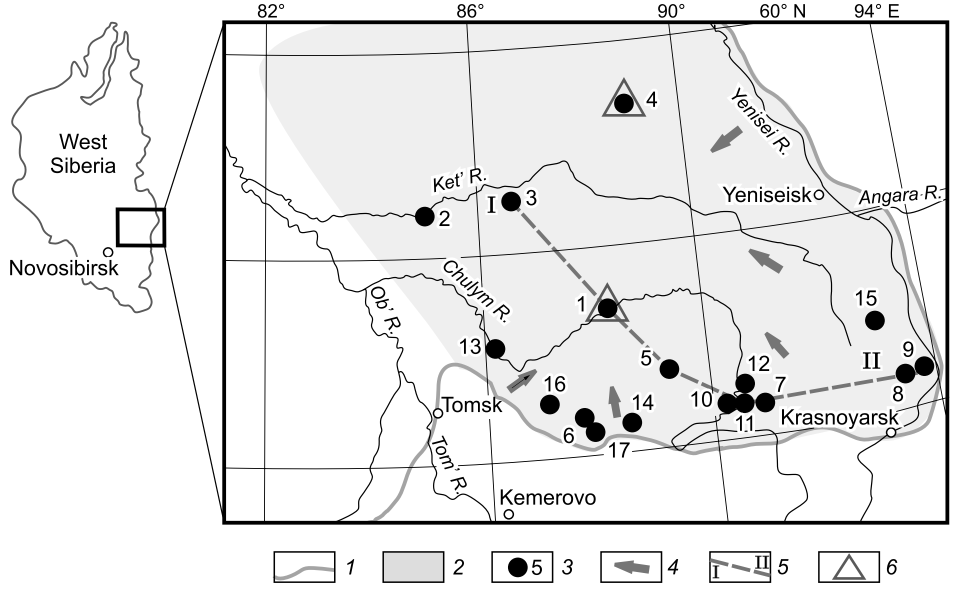

Fig. 1. Map of the location of wells. *1*, border of the West Siberian artesian basin of the first rank (Kiryukhin and Tolstikhin, 1987); *2*, area of the Chulym–Yenisei artesian basin of the second rank; *3*, wells and their numbers (1, Chulymskaya, 2, Beloyarskaya-1 (Tomsk Region), 3, Maksimkin Yar, 4, Kasskaya, 5, Belogorskaya, 6, Mariinskaya, 7, Achinskaya, 8, Sukhobuzinskaya-1, 9, Sukhobuzinskaya-2, 10, Beloyarskaya-2 (Kemerovo Region), 11, Inginskaya, 12, Sekretarskaya, 13, Asinovskaya, 14, well in the Stupitsyno Village, 15, well in the Dubrovino Village, 16, well in the Malaya Peschanka Village, 17, well in the Raevka Village); *4*, direction of groundwater flow; *5*, line of hydrogeochemical section; *6*, wells that discharged highly alkaline waters (pH > 9).

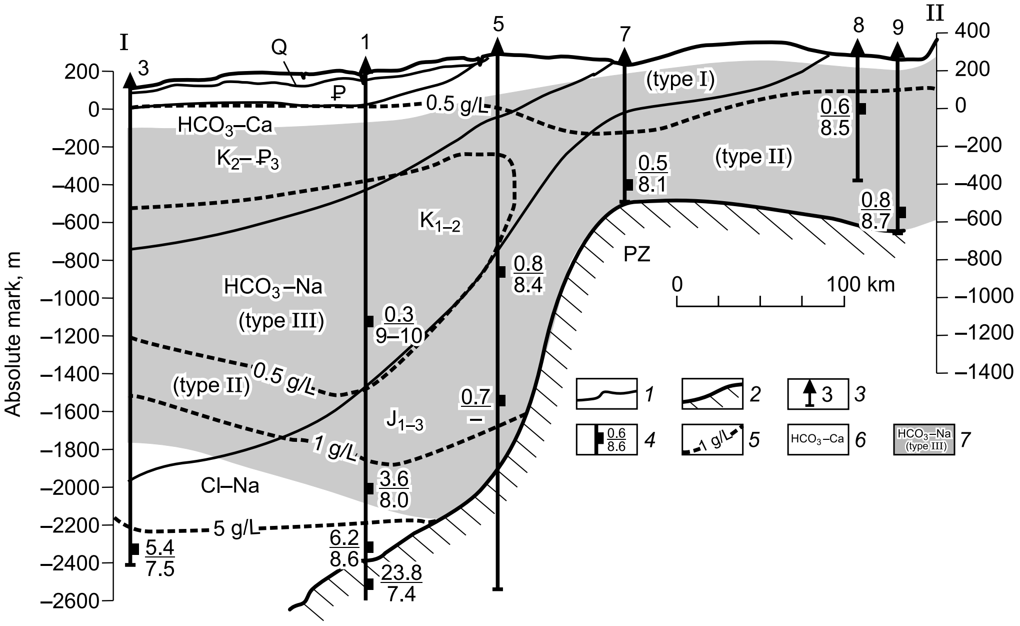

Fig. 2. Schematic hydrogeochemical section. *1*, geologic boundaries; *2*, upper boundary of the basement; *3*, well and its number; *4*, sampling interval: above the line—TDS, g/L, below the line—pH; *5*, isomineral contours; *6*, chemical composition of waters; 7, soda waters area (parenthesized Roman numerals mark the type of soda waters).

the poorly studied Tegul'det mesotrough of the Outer belt (Kontorovich, 2002) of the East Siberian Plate (southeastern margin), at its junction with the Altai–Sayan folded area. The basin section is formed by a folded basement composed of pre-Jurassic rocks and by gently pitching Mesozoic and Cenozoic platform deposits resting on it. The shallowest depth of the basement (0.6 km) is observed in the zone of transition to the Altai–Sayan folded area (Fig. 2). Toward the northwest, the surface of the basement submerges and reaches a maximum depth of 3 km in the area of the Kasskaya BH-4. The resulted depression is filled with thick continental Cretaceous and Jurassic sand–clay deposits, which outcrop in the southeast.

The basin has the following specifics: (1) the absence of salt-bearing and carbonate rocks (except for up to 2 m thick intercalates of authigenic limestone), (2) domination of sandy rocks over argillaceous ones in the upper part of the section, to a depth of 1500–1600 m, and (3) nearly the complete absence of a regional Cretaceous–Paleogene argillaceous confining bed typical of the entire West Siberian artesian basin. The latter two factors favor the percolation of fresh infiltration waters to a depth of 0.7–1.8 km (Sidorenko, 1970; Zaitsev, 1972; Pinneker, 1991).

The Cretaceous aquiferous sediments (Neocomian and Albian–Aptian strata, Simonovka and Sym Formations) are formed by quartz and quartz–feldspathic sandstones with clay and pebble interbeds. The specific well discharge is 0.1–2.0 L/s. The Jurassic rocks are fine-grained sandstones, siltstones, mudstones, and clays with a large amount of plant material, with pyrite, siderite, and calcite inclusions, and, in the south, with beds of brown coal (Achinsk Coal Basin). The specific well discharge is 0.1–0.5 L/s. Soda waters in the Chulym–Yenisei artesian basin are widespread. From depths of 100–300 m to 1.5–2.3 km, they are ubiquitous independently of the type of host rocks (Fig. 2). They are probably most abundant in the southeast of the basin, where a freshwater catchment area is located. Toward the center of the West Siberian artesian basin, the lower boundary of the soda water zone rises to an absolute level of 0.7–0.8 km (Sidorenko, 1970; Zaitsev, 1972; Uchiteleva, 1974). Below the soda water zone, there are HCO_3–Cl–Na waters, then, Cl–HCO_3–Na waters, and, finally, Cl–Na waters, whose TDS rapidly increases with depth and reaches 24 g/L in the central part of the basin. The waters stay highly sodic at TDS ≥ 3–5 g/L.

THE CHEMICAL COMPOSITION OF SODA WATERS

Soda waters spread in the basin are diverse in chemical composition (Table 1). Their TDS varies from 0.2 to 4.1 g/L (Fig. 3), and pH, from 7.4 to 10.3. This diversity gives grounds to divide the waters into three types (Table 1).

Soda waters of type I are localized in the upper part of the Cretaceous and Jurassic rock section stripped in the south of the Chulym–Yenisei basin, at depths of down to 600 m (Fig. 3). These are low-mineralization waters with TDS = 0.2–0.5 g/L and pH = 7.4–8.4. No correlation between pH and TDS is observed (Fig. 4). In the upper hydrodynamic (active water exchange) zone such waters occur sporadically at the sites with low water exchange, which ensures their saturation with calcite and, hence, their sodic composition in the plain relief environment.

Soda waters of type II occur at greater depths, 0.6–2.3 km, in Cretaceous and Jurassic deposits. They have higher mineralization (TDS = 0.7–4.1 g/L) and pH = 8.0–8.9 (Figs. 3 and 4). An increase in salinity of these waters is usually accompanied by an increase in pH, which follows the general regularity specific to other regions (Pinneker et al., 1983; Shvartsev et al., 2007). The salinity of water and the content of soda components in it increase with depth and with the time of the disequilibrium water–rock interaction (Shvartsev, 1991).

Soda waters of type III have a unique composition: high alkalinity (pH = 9.0–10.3) but low mineralization (0.2–0.6 g/L). No correlation between pH and TDS is observed (Fig. 4). Such waters were found at great depths in two wells in the central and northern parts of the basin: Chulymskaya well (at depths of 1266–1277 m) and Kasskaya well (in the depth intervals 640–710, 815–835, 870–910, and 1030–1040 m). In both wells, the waters are confined to Cretaceous continental sandy deposits (Table 1). Note that the deposits of the Ilek Formation (Borodkin and Kurchikov, 2010) hosting highly alkaline low-mineralization waters are formed by sands, sandstones, and siltstones. The sands and sandstones are mostly quartz–feldspathic. They contain up to 50% quartz and up to 40% acid and basic plagioclases and K–feldspars. The sandstones contain up to 2% iron oxides, up to 2.8% siderite, and 4–29% carbonates. The predominant accessory minerals are epidote group minerals (up to 70% of the heavy fraction), green hornblende (up to 45%), and ilmenite + magnetite (up to 25%). The clays are hydromicas, montmorillonite, and chlorite (up to 2%) (Poyarkova, 1961; Rychkova, 2006; Devyatov et al., 2010).

Hence, soda waters of type III are intermediate between soda waters of types I and II and occur mostly in the continental deposits of the Ilek Formation. Sampling of deeper horizons in the Kasskaya well showed the presence of soda waters in the deposits of the Itat Formation (J_2) at depths of 1169–1665 m, but these waters have a much lower pH (8.8) and a higher TDS (1.1 g/L), which permits them to be considered waters of type II (Table 1). Therefore, we associate such soda waters with Cretaceous deposits only (Fig. 2).

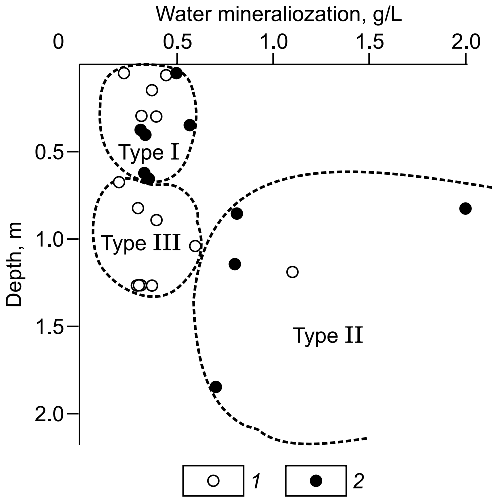

Fig. 3. Variation in TDS of soda waters with depth. *1*, Cretaceous deposits; *2*, Jurassic deposits.

Highly alkaline waters of type III are pressure waters flowing out in the Chulymskaya well, which permits their therapeutic application under the name Omega. Therefore, their chemical, gas, and isotope compositions have been studied in detail for more than 15 years. As seen from Table 2, these waters have a rather stable composition throughout the observation period: They are steadily of low mineralization but highly alkaline, contain HCO_3-Na (soda), have low concentrations of SO_4, Cl, Ca, Mg, K, Fe, B, and DOC ions but high concentrations of SiO_2 (16–31 mg/L), and keep a temperature of 19 to 21 °C at their mouth. Minor compositional variations within a year are due to the influence of the upper-horizon waters, which partly mix with alkaline waters when rising to the surface. The highest pH values (10.3 and 10.1) were established in February and April, respectively, i.e., in winter, when there is the minimum probability of mixing of deep water with groundwater. Therefore we believe that reservoir waters always have pH > 10, TDS < 0.3 g/L, SiO_2 > 30 mg/L, and DOC < 2.0 mg/L. Above- and below-localized waters are characterized by lower pH (7.8–8.6) but higher TDS values (Table 1). In the area of the Chulymskaya well, the groundwater at a depth of 50 m is fresh (0.6 g/L), of HCO_3–Ca composition. The salinity of the below-localized waters gradually increases to 3.6 g/L at the expense of soda and chloride components. With depth, their TDS increases to 4–24 g/L, and the waters are of Cl–Na composition (Table 1).

We also studied the microcomponent composition of the Chulym–Yenisei basin waters in three year periods (Table 3). In general, the waters are poor in almost all microcomponents, i.e., the latter are poorly concentrated in alka-

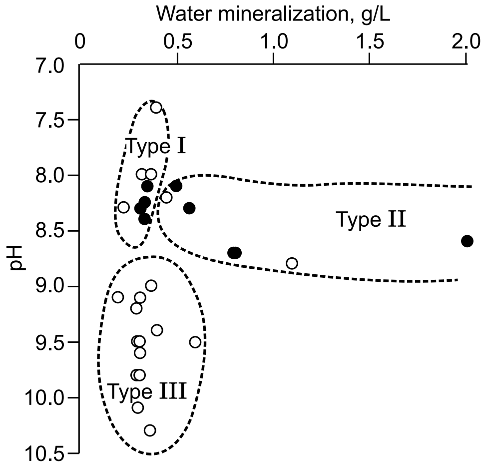

Fig. 4. TDS vs. pH of soda waters. Designations follow Fig. 3.

Table 1. Typical samples of soda waters from the Chulym–Yenisei basin

Well	Depth, m	Age of rocks	Type of waters	pH	Σ	HCO_3^-	CO_3^{2-}	SO_4^{2-}	Cl^-	Ca^{2+}	Mg^{2+}	Na^+
					g/L	mg/L						
1	50	Ꝑ	–	7.3	0.6	421	0.5	4.2	1	98	18.3	11
	1266–1271	$K_{1–2}$	III	9.6	0.3	162	36.2	9.6	1	1	0.1	94
	2172–2181	$J_{1–3}$	II	8.5	3.6	2165	6.5	3.5	398	15	3.7	1052
	2287–2292	$J_{1–3}$	II	8.0	4.1	1659	2.5	33.0	1086	17	7.5	1312
	2647–2652	PZ	–	7.8	24	1372	0.1	1148	12316	158	34	8810
2	1997–2005	$K_{1–2}$	–	8.6	1.8	172	13.2	5.8	902	9	0.7	650
3	2404–2476	$J_{1–3}$	–	7.5	5.4	98	0.7	4.7	3179	288	5.4	1764
4	640–710	$K_{1–2}$	III	9.1	0.2	104	18.4	0.1	8	7	6.0	35
	815–835	$K_{1–2}$	III	9.2	0.3	214	18.2	0.5	32	6	4.0	100
	870–910	$K_{1–2}$	III	9.4	0.4	250	23.6	2.0	28	6	5.0	115
	1030–1040	$K_{1–2}$	III	9.5	0.6	323	37.5	3.0	38	6	4.0	164
	1175–1200	$J_{1–3}$	II	8.8	1.1	598	78.3	6.0	78	11	5.0	341
5	1139–1146	$J_{1–3}$	II	8.7	0.8	540	16.7	32.0	23	39	1.0	190
6	816–829	$J_{1–3}$	II	8.6	2.0	1300	17.0	5.0	97	10	5.0	540
7	500–800	$J_{1–3}$	I	8.1	0.5	260	8.6	5.0	3	4	0.5	100
8	200–500	$J_{1–3}$	I	8.3	0.6	400	4.0	2.0	0.3	1	0.5	143
9	800–900	$J_{1–3}$	II	8.7	0.8	570	15.2	2.0	20	24	6.0	175
10	398	$J_{1–3}$	I	8.4	0.3	230	4.4	4.0	6	5	0.5	83
11	382	$J_{1–3}$	I	8.3	0.3	220	7.2	10.0	2	10	0.1	80
12	632	$J_{1–3}$	I	8.2	0.3	250	1.6	0.1	0.5	6	0.1	85
13	300	$K_{1–2}$	I	7.4	0.4	294	0.4	4.8	3	50	17.1	22
14	150–160	$K_{1–2}$	I	8.0	0.4	270	3.8	7.0	3	35	12.0	45
15	3–101	$J_{1–3}$	I	8.1	0.5	350	15.0	0.1	1	35	12.0	78
16	50–54	$K_{1–2}$	I	8.3	0.2	150	1.6	10.0	1	14	12.0	41
17	63–66	$K_{1–2}$	I	8.2	0.4	250	2.2	45.0	16	66	6.6	61

Note. Σ, TDS of waters; dash, non-soda waters, data are given for comparison. The well numbers follow Fig. 1.

Table 2. Chemical composition of highly alkaline waters in the Chulymskaya well at depths of 1266–1277 m, mg/L

Sampling date	pH	Σ	HCO_3^-	CO_3^{2-}	SO_4^{2-}	Cl^-	Ca^{2+}	Mg^{2+}	Na^+	SiO_2
26.12.1994	9.5	311	162	28	1.5	7.1	2.0	<0.1	85	26.6
28.04.1995	9.5	302	161	28	4.4	7.1	2.0	<0.1	87	26.4
29.09.1995	9.6	320	150	33	20.4	7.1	2.0	<0.1	94	20.6
21.11.1995	9.8	313	130	46	14.8	10.6	3.0	<0.1	95	26.4
24.02.2000	10.3	268	73	82	2.0	4.9	4.0	2.0	89	30.1
28.06.2000	9.8	304	141	50	2.5	4.2	2.0	1.0	92	–
23.08.2000	9.5	315	169	30	8.8	4.2	2.0	2.0	88	–
07.10.2000	9.0	369	209	12	13.2	17.7	5.0	0.2	99	26.2
28.09.2006	9.6	311	162	36	9.6	1.5	0.4	0.1	94	16.1
11.08.2010	9.3	316	178	19	8.3	1.8	1.2	0.5	85	22.1
06.04.2011	10.1	296	102	65	7.7	1.7	0.7	0.1	94	31.0
12.07.2013	9.1	318	180	30	11.4	1.8	3.0	0.1	91	23.8
05.07.2014	9.5	320	170	36	8.0	1.8	2.2	0.1	88	23.8

Note. Σ, TDS of waters; dash, no data.

Table 3. Microcomponent composition of Omega alkaline waters, μg/L

Component	Concentration			Average in hypergenesis zone (Shvartsev, 2008)	Component	Concentration			Average in hypergenesis zone (Shvartsev, 2008)
	February 2010	August 2010	July 2013			February 2010	August 2010	July 2013	
pH	9.9	9.3	9.1	13.0	Rb	0.14	0.24	0.27	1.86
Li	–	3.1	2.0	0.19	Sr	–	33.0	24.7	183
Be	0.05	–	–	77.9	Y	0.006	0.007	–	–
B	3.4	12.3	8.2		Zr	0.019	0.022	0.04	1.2
F	180	–	–	480	Nb	0.002	B.d.l.	–	0.45
Al	20	31.2	25.8	226	Mo	0.43	0.71	0.55	1.75
P	–	45.9	48.6	58	Ag	0.01	–	B.d.l.	0.26
Sc	3.70	2.44	–	0.07	Sn	0.003	0.09	0.08	0.39
Ti	0.64	1.3	B.d.l.	17.4	Sb	0.02	0.04	0.03	0.68
V	–	0.01	0.02	1.34	Te	0.006	–	–	–
Cr	–	0.64	0.51	3.03	J	22.0	–	–	8.0
Mn	–	1.9	0.6	54.5	Cs	0.01	0.01	0.04	0.26
Fe	–	10.7	11.9	481	Ba	0.9	2.5	2.7	18.3
Co	0.003	B.d.l.	B.d.l.	0.39	W	–	0.11	0.13	–
Ni	0.13	0.08	B.d.l.	3.58	Pb	0.39	0.08	0.59	2.97
Cu	1.59	0.23	0.61	5.58	Cd*	1.1	3.6	5.3	240
Zn	14.1	36.7	5.98	41.4	Bi*	–	0.39	0.38	–
Ga	0.31	0.60	0.45	0.37	La*	5.0	0.8	5.1	670
Ge	1.1	2.3	–	–	Ce*	8.1	9.8	16.1	–
As	0.9	2.7	3.0	1.5	Sm*	1.6	1.7	6.0	–
Se	0.13	–	B.d.l.	0.72	Th*	–	B.d.l.	0.4	240
Br	66.0	–	–	85.2	U*	–	3.1	3.1	1310.0

Note. Dash, not determined, B.d.l., below detection limit.
*Measured in ng/L.

line waters, especially Mn, Co, Ni, Zr, Nb, Cd, Sn, La, Th, U, and V, whose concentrations are hundreds of times lower than those in the hypergenesis zone waters. Only the concentrations of Sc, I, Ga, and As are higher than the average ones in the waters of the upper hydrodynamic zone, i.e., these elements are more actively concentrated in alkaline waters.

Nitrogen (76–77%) prevails among the gases of the studied waters, next is oxygen (18–19%), and sometimes methane is also present in a small amount (<0.5%). Hydrogen sulfide was noted in the waters till 1994 but was not detected later. The presence of oxygen also indicates an inflow of gases of atmospheric genesis specific to groundwater and aeration zones, which again indicates a partial mixing of deep waters with groundwater. The nitrogen composition of the gas of deep waters and their low mineralization show their similarity to the nitrogen-containing hydrotherms in Transbaikalia (Plyusnin et al., 2013; Shvartsev et al., 2015).

THE ISOTOPE COMPOSITION OF WATER AND WATER-DISSOLVED CARBON

To establish the genesis of both fresh highly alkaline and other regional soda waters, we studied the isotope composition of water and water-dissolved carbon, using five samples of HCO_3–Na waters: one sample of type I water, one sample of type III water, and three samples of type II water. For comparison, we present data on the above-localized HCO_3–

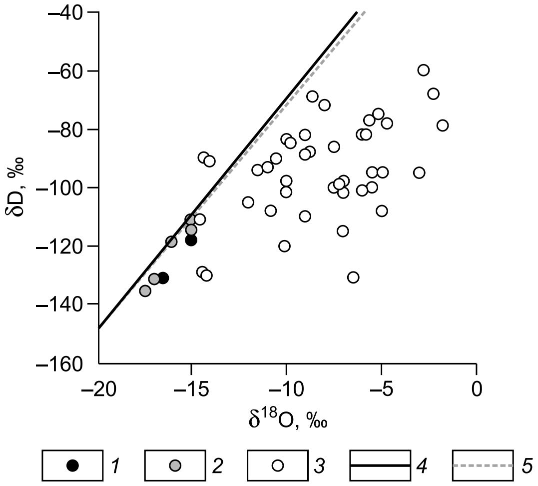

Fig. 5. Distribution of hydrogen and oxygen isotopes in the regional groundwater. *1*, HCO_3–Ca freshwater; *2*, HCO_3–Na water; *3*, saline Cl–Na water; *4*, Craig line $\delta D = 8\delta^{18}O + 10‰$ (Craig, 1961); *5*, local meteoric-water line $\delta D = 7.8\delta^{18}O + 6‰$ (Polyakov et al., 2008).

Table 4. H, O, and C isotope compositions of soda waters and other regional groundwaters

Object		Number of analyses	Depth, m	$\delta^{13}C$	δD	$\delta^{18}O$
				‰		
HCO_3–Na waters in Cretaceous and Jurassic deposits	Well 1	1	1266–1271	–30.3	–130.8	–16.8
	Well 2	1	500	–18.7	–118.7	–16.0
		1	740	–19.8	–115.3	–14.9
		1	2000	–21.3	–111.4	–15.0
	Well 13	1	300	–26.2	–135.7	–17.4
Fresh HCO_3–Ca waters in Paleogene deposits		3–6	≤200	–18.0 to –25.7 –20.2	–131.1 to –118.0 –124.7	–16.4 to –14.9 –15.7
Saline Cl–Na waters in Jurassic and pre-Jurassic deposits (Golyshev and Ivanov, 1983)		47	≥2500	–1.7 to –23.1 –9.3	–61 to –132.0 –95.0	–1.6 to –15.5 –7.9

Note. Above the line—range of isotope values; below the line—average value.

Ca and below-localized Cl–Na waters (Table 4). The small number of soda water samples does not permit considering each type separately. The estimated δD and $\delta^{18}O$ values of soda waters of the three types, like those of fresh waters of the active water exchange zone, indicate their infiltration nature, because their figurative points are arranged close to the local isotope line of meteoric waters (Polyakov et al., 2008) that differs insignificantly from the global line of meteoric waters (Craig, 1961) (Fig. 5). Only the points of deeper-seated Cl–Na waters lie far from the meteoric-water line, which is due to traces of sedimentation water (Golyshev and Ivanov, 1983).

Carbon of dissolved HCO_3^- of the soda waters has a light isotope composition, $\delta^{13}C(HCO_3^-)$ = –18.7 to –30.3‰, because CO_2 resulted from the oxidation of dispersed organic material in the rocks. Thus, no influence of depth factors is observed.

EQUILIBRIUM BETWEEN GROUNDWATER AND MINERALS OF THE HOST ROCKS

To clarify the mechanisms of formation of soda waters of different types, we calculated the indices of their saturation with major minerals of the host rocks, based on the available data on their chemical composition and using the HydroGeo software (Bukaty, 2002). The results of calculation are presented in graphical form (Figs. 6 and 7).

The obtained data show that the soda waters of all three types are in equilibrium with widespread carbonates (calcite, dolomite, siderite, rodochrosite, and, partly, magnesite), montmorillonites, illite, and even albite (only waters of types II and III). The type III waters are the most oversaturated; they are characterized by low mineralization but high alkalinity. These waters are also partly saturated with microcline, muscovite, and biotite. Hence, the latter minerals do not dissolve but form under these conditions. Independently of the water mineralization and alkalinity, they are all in disequilibrium with many primary aluminosilicates of the terrigenous part of water-bearing rocks: basic plagioclases, olivine, pyroxenes, hornblende, epidote, etc. The equilibrium fields of these minerals lie beyond the presented plots. It is remarkable that even at low salinity, the soda waters reach an equilibrium even with albite (except for type I waters) and microcline (only type III waters). The reason is the high alkalinity of waters, especially those of type III.

Thus, the water–rock system is equilibrium–disequilibrium: The soda waters of different types are in equilibrium with certain minerals but are in disequilibrium with others, i.e., the earlier established regularity is preserved (Shvartsev et al., 2007). For example, type I waters are in equilibrium only with montmorillonites, partly with illite and calcite, and seldom (one of three points) with dolomite, magnesite, and siderite. Type II waters are in equilibrium with montmorillonites, illites, and calcite; most of them, with dolomite, magnesite, and siderite; and some waters are in equilibrium even with albite and, less often, microcline, muscovite, and Mg-chlorite. In contrast to waters of types I and II, all waters of type III are in equilibrium with calcite, siderite, and albite; most of them, with dolomite, microcline, muscovite, biotite, and Mg-chlorite; and many waters are in equilibrium with magnesite (Figs. 6 and 7). The number of minerals in equilibrium with water increases continuously from type I to type III soda waters. All these regularities are important for understanding the mechanisms of formation of soda waters of different compositions, which we consider below.

FORMATION OF THE CHEMICAL COMPOSITION OF SODA WATERS

Soda waters of type I are groundwaters occurring at shallow depths and interacting with the host loose rocks for a short time. Since these waters are in disequilibrium with most of minerals of the host rocks, they dissolve these minerals to form mainly montmorillonites and illite. That is,

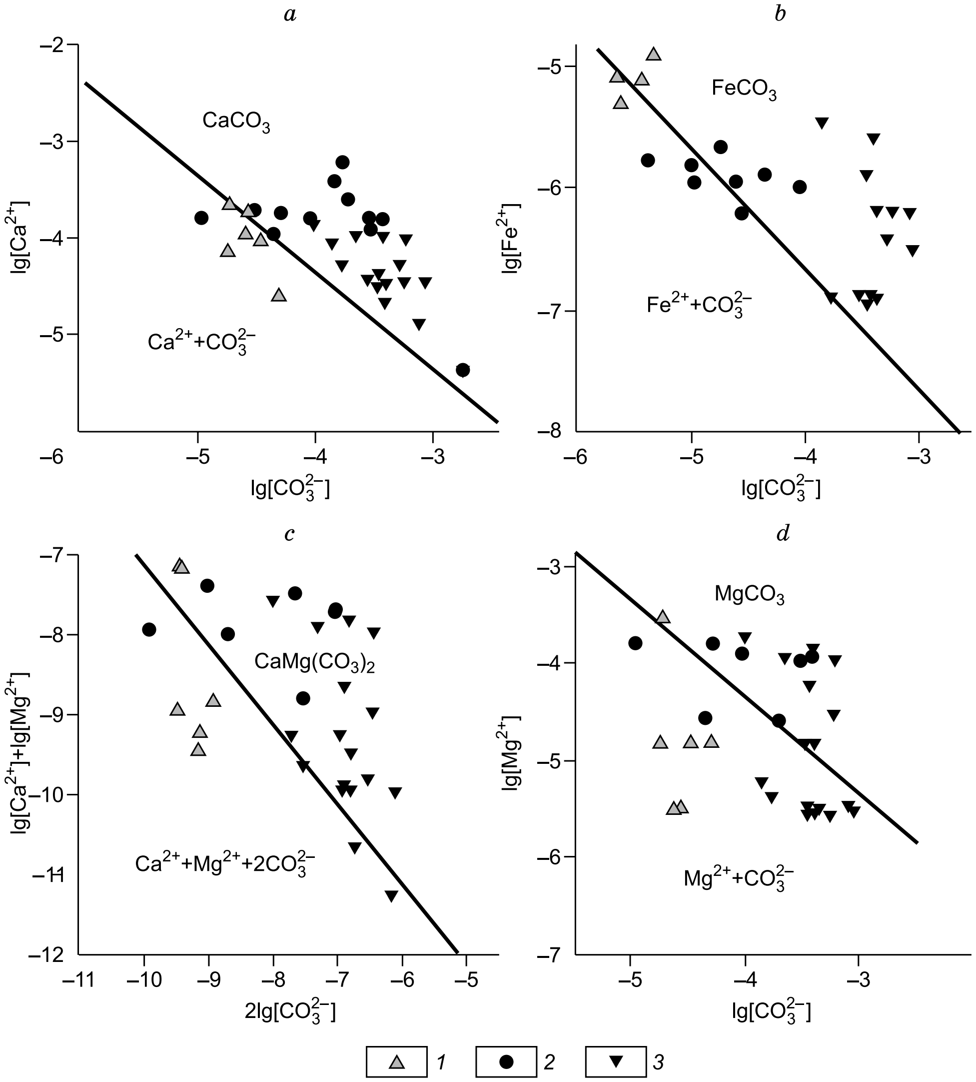

Fig. 6. Equilibrium between soda waters and calcite (*a*), siderite (*b*), dolomite (*c*), and magnesite (*d*) at 25 °C. Soda waters of: *1*, type I; *2*, type II; *3*, type III.

chemical weathering takes place, which is accompanied by the transfer of all chemical elements into solution and their partial deposition in the form of the above minerals. The geochemical barriers formed for some chemical elements, namely, K, Mg, Ca, Si, and Al, remove them from the solution. Since the secondary mineral formation under these conditions is insignificant, most of the above elements are concentrated in the solution, thus increasing its mineralization.

In places where water exchange is especially slow, there is an equilibrium between water and calcite because of the low permeability of deposits. Thus, an additional barrier for Ca appears, the portion of this element bound by secondary minerals increases, and the portion of Ca concentrated in the solution decreases. This phenomenon is local; therefore, soda waters are also of local occurrence and usually appear in rocks with high contents of Na.

Soda waters of type II are localized at great depths. These are groundwaters or artesian waters. They interact with the host rocks for a longer time and therefore are in equilibrium with illite, montmorillonite, calcite, and, locally, some other minerals. The geochemical barrier for Ca is ubiquitous, and the element loses its capability for concentration in solution. At the same time, other elements that also have regional geochemical barriers can continue to be partly concentrated in solution. This depends on the type of forming secondary mineral. The fact is that clay minerals, such as kaolinite, montmorillonite, illite, etc., bind the elements passing from dissolving minerals into solution not completely but partly. This is the case of Si, Mg, Na, Fe, etc. We discussed this issue in detail earlier (Shvartsev et al., 2007; Shvartsev, 2013).

At the early stages, groundwater dissolves aluminosilicates by the reaction

$$2.33NaAlSi_3O_8 + 1.16CaAl_2Si_2O_8 + 8H_2O + 4CO_2 = Na_{0.33}Al_{2.33}Si_{3.67}O_{10}(OH)_2 + Ca_{0.33}Al_{2.33}Si_{3.67}O_{10}(OH)_2 + Ca^{2+} + 2Na^+ + 4HCO_3^- + 2H_4SiO_4\,, \qquad (1)$$

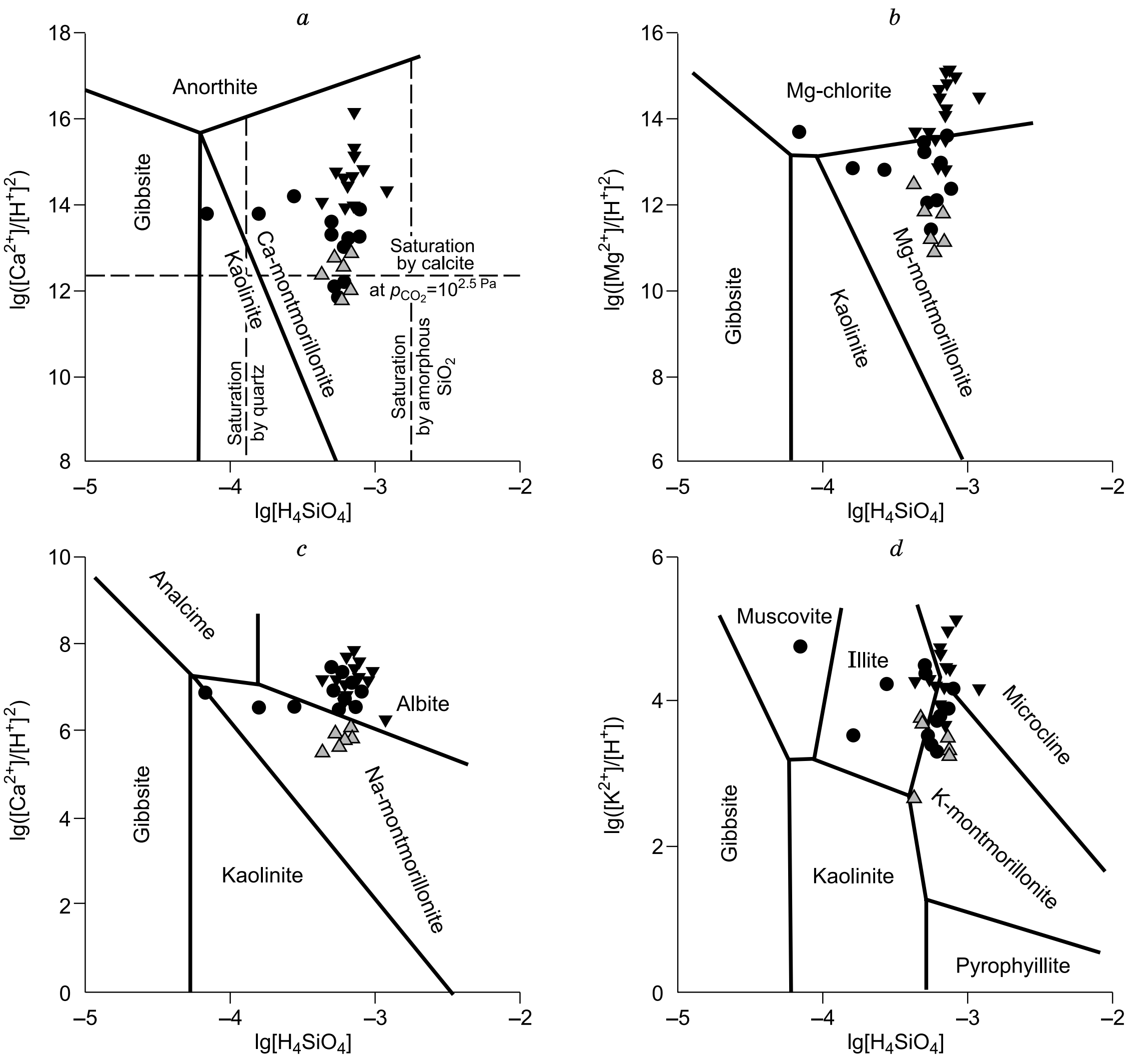

Fig. 7. Equilibrium diagrams for Ca- (*a*), Mg- (*b*), Na- (*c*), and K-containing (*d*) aluminosilicate minerals at 25 °C, with the composition of soda groundwater. Designations follow Fig. 6.

i.e., the cationic composition of water is completely determined by the initial composition of dissolving aluminosilicates.

After the establishment of an equilibrium between water and carbonates, the situation changes, and the above reaction looks as follows:

$$2.33NaAlSi_3O_8 + 1.16CaAl_2Si_2O_8 + 7H_2O + 3CO_2 = Na_{0.33}Al_{2.33}Si_{3.67}O_{10}(OH)_2 + Ca_{0.33}Al_{2.33}Si_{3.67}O_{10}(OH)_2 + CaCO_3 + 2Na^+ + 2HCO_3^- + 2H_4SiO_4. \quad (2)$$

The appearance of a geochemical barrier for Ca favors concentration of Na in the solution, which has no geochemical barriers at this stage of the water–rock system evolution. As a result, secondary carbonates form, and the Ca concentration in water does not increase.

Soda waters of type III form a local segment among waters of type II (Fig. 2). As mentioned above, they occur in quartz–feldspathic sands, sandstones, and conglomerates of Lower Cretaceous deposits (Ilek Formation). This fact is of crucial importance. Sandstones strongly dominate over clays and mudstones in the considered geologic section, which ensures a more prolonged interaction of water with the host rocks and, correspondingly, transition to the next stage of evolution of the water–endogenous aluminosilicates system. At this stage, there are a ubiquitous equilibrium between groundwater and albite and a local equilibrium between groundwater and microcline, chlorite, and many other minerals, e.g., chalcedony, which is in equilibrium with the waters under study (Fig. 8).

The transition of groundwater to their equilibrium with albite and other sodium and potassium aluminosilicates is favored not only by an increase in Na and K concentrations in the solution but also by an increase in pH values. Why does this transition take place?

Hydrolysis of aluminosilicates yields alkalies (Shvartsev et al., 2007; Shvartsev, 2008; Krainov, 2012), which are partly neutralized by acids (mineral or organic). Neutralization of alkalinity by carbonic acid by the reaction

$$OH^- + CO_2 = HCO_3^- \qquad (3)$$

is the most common in nature, as confirmed by analyses for HCO_3^-.

If there are no acids in the system, as in the waters under study, its pH will grow in proportion to the degree of aluminosilicate dissolution. As a result, an equilibrium between water and minerals, especially carbonate and aluminosilicate ones, is established more rapidly (Shvartsev et al., 2015). After the establishment of an equilibrium, these minerals no longer dissolve and begin to form. As a result, the number of dissolving minerals in the system decreases, whereas the number of forming minerals increases. At the certain stage of the system evolution, such an equilibrium is established between water and most minerals of the host rocks. Of course, there is no complete equilibrium in the system, because an equilibrium between water and many Ca-, Mg-, and Fe-aluminosilicates of deep genesis (anorthite, fayalite, forsterite, diopside, sphene, etc.) is impossible.

Although dissolution of minerals in water never stops, the evolution of the water–aluminosilicates system reaches a moment when most of the elements passing into the solution are bound by newly formed minerals: Ca-calcite, montmorillonite, zeolites and other aluminosilicates, Mg-glaucophane, talc, chlorite, zeolites, Na-albite, zeolites, K-illite, muscovite, microcline, biotite, phlogopite, Fe-siderite, Fe-aluminosilicate, etc. Thus, not only chemical but also dynamic equilibria are established in the system; they ensure the equality of the elements entering and leaving the solution. An increase in water mineralization also stops, and the waters remain lowly mineralized but highly alkaline.

Such is the case with soda waters of type III, which is confirmed not only by their low salinity and high alkalinity but also by the presence of a large number of secondary minerals in the section. For example, calcite is spread not unevenly but everywhere and amounts to 4–30%; hydromica and montmorillonite amount to ≤10–15%; siderite, ≤3%; chlorites, ≤2%, etc. (Poyarkova, 1961; Devyatov et al., 2010; Vakulenko et al., 2010).

Hence, throughout the geologic time after the formation of sedimentary rocks in the study area, the terrigenous part of clastic rocks dissolved, and a large number of secondary minerals formed, which took a significant portion of elements from the solution. It is important that each stage of the water–rock interaction yields a definite set of secondary minerals whose composition changes with time. This determines the formation of different types of water in the geologic section (in our case, different types of soda waters).

To sum it up, note that the water–endogenous aluminosilicates (even transformed to sedimentary varieties) system is of crucial importance, because it governs the composition of forming types of groundwater, which determines the course of evolution in inanimate nature (Shvartsev, 2010, 2013, 2015). Even the stage of evolution of soda waters overwhelms by a diversity of their types (Posokhov, 1969; Shvartsev et al., 2007). This diversity is still greater with regard to the systems including CO_2 (Shvartsev, 2008; Kopylova et al., 2011; Krainov et al., 2012; Plyusnin et al., 2013; Shvartsev et al., 2017). Each type of soda waters formed at the certain microstage of evolution of the water–rock–gas(O_2, CO_2, CH_4, N_2)–organic-matter system. Highly alkaline ultrafresh soda waters are a unique equilibrium–disequilibrium system evolving under conditions when most of chemical elements borrowed from the host rocks are bound by formed secondary minerals. As a result, a dynamic equilibrium is established between the number of elements entering the solution and the number of elements leaving it, which ensures a stable composition of water and does not lead to an increase in its salinity, although its interaction with the rocks continues. Such cases are rare in sedimentary basins. The Chulym–Yenisei basin is unique in this respect.

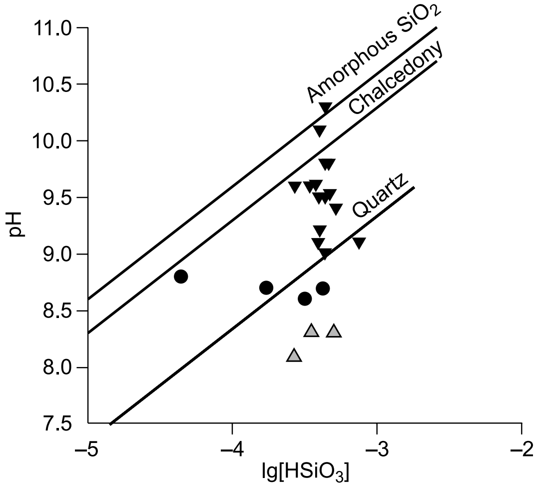

Fig. 8. Equilibrium between the regional soda waters and Si-minerals. Designations follow Fig. 6.

CONCLUSIONS

In the Chulym–Yenisei basin, soda waters are spread in the host rocks of different types at depths of ~100–300 m to 1.5–2.3 km, i.e., in Cretaceous and Jurassic deposits. They are characterized by TDS = 0.2–4.1 g/L and pH = 7.4–10.3. Based on this diversity, we divided the studied soda waters into three types. Type I waters occur in the upper part of the section, to a depth of 600 m, and have pH = 7.4–8.4 and TDS ≤ 0.5 g/L. Type 2 waters occur much deeper (0.6–2.3 km) and show higher TDS (0.7–4.1 g/L) and pH values = 8.0–8.9. An increase in their salinity is usually accompanied by an increase in their pH. Type III waters have a unique composition: Being highly alkaline (pH = 9.0–10.3), they are of low mineralization (0.2–0.6 g/L). They form a local segment among type II waters and differ strongly from the above- and below-localized waters in lower mineralization and higher pH. The chemical, microcomponent, and gas compositions of type III waters (“Omega”) have been studied in more detail. The isotope compositions of water and water-dissolved carbon (δD, δ^{18}O, and δ^{13}C) indicate the infiltration origin of soda waters of the three types.

Calculations of equilibria in the water–host-mineral system have shown that all soda waters are in disequilibrium with many primary aluminosilicate minerals of the terrigenous part of the host rocks (basic plagioclases, olivine, pyroxenes, hornblende, epidote, etc.) but are in equilibrium with widespread carbonates (calcite, dolomite, siderite, rodochrosite, and, partly, magnesite), montmorillonites, illite, chlorite, and even albite (only waters of types II and III) and, partly, with microcline, muscovite, and biotite (only waters of type III). In passing from type I to type III waters, the number of minerals in equilibrium with water continuously increases. Thus, the freshest type III waters form the largest amount of secondary minerals, which is due to their high alkalinity.

Taking into account the geologic conditions and the results of calculation of equilibria in the water–rock system, we present schemes of formation of different types of soda waters in the studied basin. Each type of soda waters is the result of a certain stage of evolution of the water–rock–gas–organic-matter system. The latest stage corresponds to the formation of type III waters under domination of sandstones over clay and mudstones and in the absence of organic and mineral acids from the geologic section. This stage is characterized by the establishment of both chemical and dynamic equilibria, when most of the chemical elements passing into the aqueous solution form secondary mineral products and are not concentrated in the solution. The solution keeps a stable salinity but continues to interact with the host rock and thus becomes more alkaline.

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