

Geochemistry of Sodic Waters in the Datong Intermountain Basin, Shanxi Province, Northwestern China

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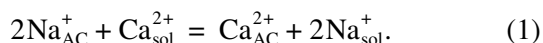
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Abstract—The paper presents a critical analysis of current concepts of the origin of sodic waters. The example of the Datong Basin with widespread sodic waters is employed to demonstrate that these waters typically have salinities of 0.6–4.5 g/l at pH of 7.8–8.8. It was determined that sodic waters are in equilibrium with calcite and clay minerals (montmorillonite and kaolinite) and, sometimes, also with analcime but are never in equilibrium with anorthite, albite, forsterite, microcline, and muscovite; i.e., the water–rock system is in equilibrium–unequilibrium state. The degree of evaporation concentration of salts is in places as high as a few tens. The complex analyses of conditions under which sodic waters are formed indicates that these waters are produced during a certain weathering stage of aluminosilicates, after the groundwaters have reached equilibrium with calcite. The time when this equilibrium can be reached is controlled by the intensity of the water exchange.

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INTRODUCTION

Sodic waters are widespread in the Earth's crust, and their genesis is extensively discussed in the literature [1–16]. This problem still raises vivid debates, and the following two major alternative hypotheses were put forth to solve it. According to the geological hypothesis, sodium bicarbonate is produced by the weathering of massive crystalline and sedimentary rocks (F.F. Clarke, M.I. Kuchin, I.P. Gerasimov, E.N. Ivanova, Yu.R. Nikol'skaya, E.V. Posokhov, K.F. Filatov, and others). The proponents of the other, ion exchange, hypothesis believe that sodium bicarbonate is formed when Na absorbed in colloid complexes [AC] is forced out of them by Ca dissolved in the water (K.K. Gedroits' reaction):



This hypothesis is popular, first of all, among soil scientists (K.K. Gedroits, W.P. Kelly, I.N. Antipov-Karataev, V.A. Kovda, K.Ya. Kozhevnikov, and others) and some hydrogeologists (V.A. Sulin, A.N. Buneev, G.N. Kamenskii, E.V. Pinneker, V.G. Popov, S.R. Krainov, J.J. Driver, and others). Some researchers tried to somehow combine the ideas of both hypotheses (N.I. Bazilevich, N.M. Strakhov, I.P. Gerasimov, and others).

The unsolved problem concerning the conditions under which sodic waters can be formed hampers the further evolution of hydrogeochemistry, because this problem is pivotal for understanding not only the inter-

action mechanisms of waters and rocks but also the conditions under which other geochemical types of waters can be produced [14–16]. Obviously, the solution for this problem calls for further research. In this context, northwestern China attracts keen interest because of sodic waters widespread in its basins. An illustrative example of the latter is the Datong Basin, which was examined by Chinese researchers together with the authors of this publication. The basin is dominated by terrigenous and magmatic rocks and contains widespread loess deposits, which are famous in northern China. The long-lasting evolution of this area in continental environments makes this basin suitable for studying the geochemical processes producing sodic waters.

GEOCHEMISTRY OF GROUNDWATERS IN THE DATONG BASIN

The Datong Basin in Shanxi Province, 600 km west of Beijing (Fig. 1), is an intermountain depression bordered by mountain chains composed of Archean gneisses, granites, and basalts, Cambrian and Ordovician limestones, and Carboniferous, Permian, and sometimes Jurassic shales and sandstones. The depression itself is filled with Neogene–Quaternary sandy–clayey terrigenous deposits, whose thickness locally reaches 1000 m but mostly does not exceed a few hundred meters. We examined the uppermost of the aquifers hosted in the Cenozoic deposits [17, 18].

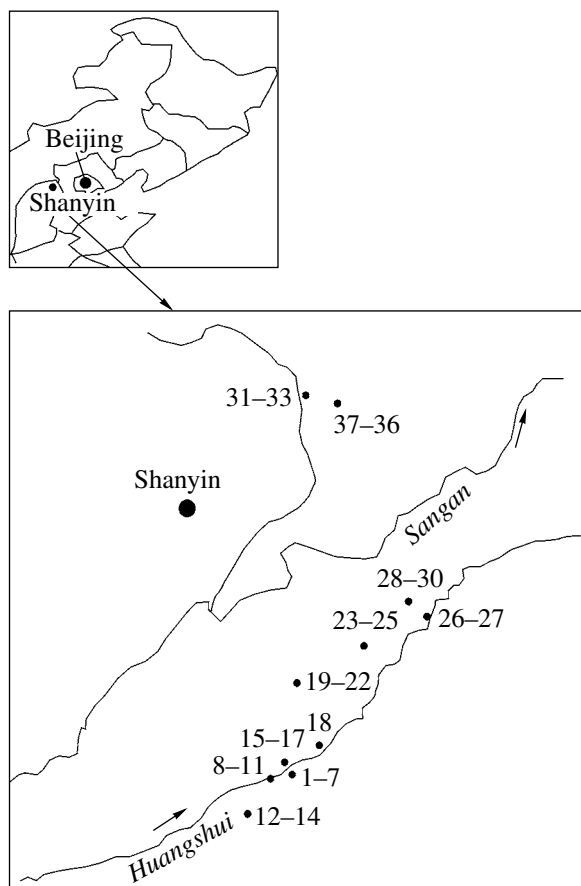


Fig. 1. Schematic map of the water sampling sites in wells within the Datong Basin.

Water occurs in this aquifer at depths of 5–60 m from the surface. The waters are often artesian, with the piezometric level usually situated at depths of 2–10 m or, occasionally, even above the Earth's surface.

These characteristics make this aquifer convenient as a local source of drinking water, although the quality of the waters themselves sometimes does not meet the standards (see below). The alimentation areas of the groundwaters are restricted predominantly to the surrounding mountain edifices.

All of our water samples were taken from wells that were equipped with shallow-depth pumps and drilled in populated areas as local water sources. In one village, water was sampled in a number of wells; the map in Fig. 1 cannot show all of them because of scale. Due to these reasons, the same points at the map can be labeled with different sample numbers because, in fact, these numbers can pertain to different closely spaced sampling sites. All of our 36 water samples were taken in December of 1999, when the water temperature varied between 8.5 and 12.5°C.

The landscape topography of our study area corresponds to a typical steppe, whose climate is continental, with cold winters and hot summers and with precipita-

tion ranging from 250 to 400 mm/year and evaporation from 900 to 1000 mm/year. Because of this, the area is extensively affected by continental salinization.

The chemical composition of the Datong groundwater is illustrated by the data in Table 1. As can be seen from these data, the waters have a variable composition and salinity, with the overall mineralization ranging from 0.4 to 4.5 g/l, pH from 7.8 to 8.8, and with the overwhelming predominance of sodic waters. Considering only chemical components whose concentrations are higher than 50 mg-equiv. %, all of the waters belong to the $\text{HCO}_3\text{-Na}$ type, i.e., are sodic (Fig. 2). With regard for the elements with concentrations of >25 mg-equiv. %, the waters can be subdivided into six types, again with the strong predominance (77.8%) of $\text{HCO}_3\text{-Na}$ and $\text{HCO}_3\text{-Na-Mg}$ types, i.e., sodic waters (Table 2).

The first two types of hydrocarbonate Na–Ca and Na–Mg waters with mineralization of up to 0.92 g/l and pH 7.8–8.4 are leaching waters, whose genesis is controlled by the degree of their interaction with the host aluminosilicates. At the same time, it should be stressed that even these freshwaters (except for only those from two sites) are saturated with respect to calcite (Fig. 3), a feature that makes impossible their enrichment in Ca and transforms them into Na and Mg types. The reasons for this will be discussed in more detail below.

The third, $\text{HCO}_3\text{-Cl-Na-Mg}$ type of waters is characterized by a higher salinity, from 0.6 to 1.9 g/l, and elevated concentrations of the chlorine ion (18.5–262 mg/l) and, sometimes, the sulfate ion (185 mg/l in sample 25). All of the aforementioned characteristics testify to the initial stages of continental salinization in these groundwaters.

The fourth type comprises the most alkaline (pH 8.0–8.8) $\text{HCO}_3\text{-Na}$ waters with an overall mineralization of up to 0.8–3.0 g/l, i.e., typical sodic waters. Analogous sodic waters compose the fifth and sixth types, but these are complicated by the processes of continental salinization, which resulted in elevated concentrations of the sulfate and chlorine ions and values of the Cl/SO_4 ratio as high as 0.4–2.9, which is typical of waters related to continental salinization.

It follows that the Datong Basin ubiquitously (with the exception of only four sampling sites) contains sodic waters, whose salinity varies from 0.6 to 4.5 g/l and whose pH is from 7.8 to 8.8. These waters comprise five varieties corresponding to various degrees of continental salinization and, perhaps, the effect of oxidizing sulfide minerals. In order to get a better insight into the conditions producing each of the water types, below we consider their equilibrium with rocks.

EQUILIBRIUM BETWEEN GROUNDWATERS AND THE MAJOR MINERALS OF ROCKS

First of all, let us consider the interaction of waters with calcite, which is widespread among both the primary and the secondary minerals. As was mentioned

Table 1. Chemical composition of groundwaters in the Datong Basin

No.	T, °C	pH	Ca	Mg	Na	K	Cl	HCO ₃	CO ₃	SO ₄	F	M*	Br	NO ₃	PO ₄
			mg/l												
1	9.3	7.93	13.9	27.1	119	6.23	20.9	464	0.9	1.6	0.62	654	0.114	3.82	1.64
2	9.3	7.81	29.4	93.7	858	24.3	518	1201	1.5	552	1.12	3279	0.281	2.34	0.95
3	8.5	7.95	32.3	35.0	107	16.4	63.1	467	1.0	4.7	0.74	727	0.161	6.03	0.06
4	10	8.13	16.5	33.0	89.6	7.95	15.9	434	1.4	2.0	0.39	601	0.009	2.94	0.67
5	8.1	7.98	23.9	32.9	77.6	7.91	41.3	358	0.6	21.1	0.38	564	0.091	39.3	0.42
6	9.3	8.1	12.0	27.8	161	6.45	58.6	473	1.4	28.6	0.63	769	0.143	1.38	0.39
7	9.6	8.12	11.9	29.4	122	6.78	42.1	414	1.3	23	0.41	651	0.094	6.41	0.46
8	9.4	7.81	27.1	26.8	116	6.20	30.8	477	0.7	0.8	1.21	687	0.101	1.16	0.28
9	9.7	8.29	22.3	31.4	106	7.55	43.4	439	2.0	0.3	0.89	653	0.09	1.32	0.41
10	9.5	8.11	20.1	34.8	107	7.97	72.8	405	1.3	0.3	0.57	650	0.029	7.39	0.8
11	10	8.31	18.4	19.0	69.9	4.65	16.7	313	1.5	0.2	0.34	444	0.053	3.53	0.21
12	9.6	7.93	35.2	9.37	51.5	2.71	3.2	287	0.6	1.0	0.43	391	0.044	2.32	0.16
13	10	8.16	20.9	17.4	66.6	4.28	10.5	314	1.1	0.5	0.11	435	0.051	0.14	7.36
14	9.2	7.90	19.4	22.5	69.0	4.98	10.3	344	0.6	0.6	0.23	472	0.048	4.16	0.57
15	9.5	8.52	14.5	64.2	675	15.7	357	1392	10.8	122	0.96	2652	0.736	11.3	2.27
16	8.6	8.08	18.1	24.7	109	5.96	18.5	444	1.2	0.5	0.2	622	0.083	25.1	0.71
17	9.9	8.55	11.0	42.7	422	10.2	123	1085	9.0	54.2	0.78	1758	0.288	10.4	1.55
18	12.5	8.05	15.1	21.4	76.9	4.90	39.4	263	0.7	26.3	0.26	448	0.063	7.31	0.21
19	9.1	8.84	9.02	34.1	223	8.01	89.0	622	11.5	3.8	0.72	1001	0.193	6.42	1.39
20	9.1	8.33	23.4	36.5	202	9.66	42.7	725	3.6	0.1	0.54	1044	0.095	5.39	1.29
21	9.7	8.40	12.1	29	222	6.94	42.7	687	4.0	10.6	0.54	1015	0.093	1.44	1.39
22	9.5	8.44	16.4	34.6	213	8.18	37.3	727	4.7	0.9	0.56	1043	0.093	0.38	1.34
23	9.2	7.95	17.8	41.0	179	9.75	79.0	553	1.1	43.8	1.81	926	0.125	1.49	1.73
24	9.5	8.37	16.1	30.7	107	7.10	20.2	458	2.5	0.6	0.62	643	0.086	7.39	0.24
25	9.8	7.96	32.8	90.1	387	22.9	262	926	2.0	185	1.57	1909	0.587	1.88	3.62
26	10	8.22	10.1	22.3	181	5.27	50.6	526	2.1	6.8	1.95	806	0.043	0.66	2.55
27	10	8.15	17.0	31	196	7.43	81.6	541	1.8	39.6	1.71	917	0.105	0.68	1.52
28	10	8.29	11.6	25	105	5.94	40.0	366	1.7	0.2	0.48	562	0.043	5.91	0.14
29	9.2	7.83	58.3	141	1090	41.5	803	1605	2.1	668	3.47	4412	0.836	3.96	10.2
30	9.5	8.37	14.1	25.7	107	5.87	17.2	430	2.3	0.5	0.49	603	0.096	2.13	0.32
31	7.9	7.87	30.9	62.6	400	18.2	128	857	1.6	321	4.21	1824	0.329	61.6	4.33
32	7.8	8.02	45.0	51.2	596	50.6	277	1208	4.0	292	4.06	2528	0.408	55.6	3.41
33	9.4	8.83	112.0	49.9	634	15.3	305	1360	14.6	331	0.52	2822	0.491	25.6	4.16
34	9.2	8.43	9.28	20.3	590	4.91	106	1073	6.7	318	9.65	2138	0.079	39.1	2.17
35	9.4	8.35	17.9	104	687	26.4	348	1268	9.7	446	2.32	2909	0.436	18.9	1.73
36	10.0	8.02	19.0	49.0	813	11.6	330	1347	4.7	442	6.99	3023	1.238	20.3	1.91

Table 1. (Contd.)

No.	T, °C	pH	Sr	Si	Zn	Pb	Cd	Mn	Fe	Al	Cu	Li	As ³⁺	As ⁵⁺	As _{tot}
			mg/l			µg/l									
1	9.3	7.93	0.29	6.12	3.6	102	0.08	78.1	14.6	10	1.2	1.5	223	138	361
2	9.3	7.81	0.69	5.72	8.3	1.74	0.11	127	27.4	18	1.4	7.8	220	147	367
3	8.5	7.95	0.57	6.83	4.9	1.15	0.15	185	84	9	3	8.6	50	45	95
4	10	8.13	0.53	5.76	6.3	0.84	0.18	73.2	83.6	49	2.6	3.7	250	154	404
5	8.1	7.98	0.46	7.2	20.1	1.62	0.16	175	18.2	594	16	2.9	290	63	353
6	9.3	8.1	0.32	6.83	11.3	1.05	0.08	125	293	156	5.3	3.5	692	155	847
7	9.6	8.12	0.31	6.54	26	1.14	0.15	93.3	441	146	4.7	2.6	542	132	674
8	9.4	7.81	0.49	6.46	4.6	0.84	0.11	101	16.2	13	2.3	2.8	4.7	2.9	7.6
9	9.7	8.29	0.44	4.92	14	0.1	0.07	160	28.3	30	2.6	2.5	591	376	967
10	9.5	8.11	0.52	5.83	6.5	0.64	0.12	88.6	25.2	37	1.7	1.6	281	226	507
11	10	8.31	0.43	7.55	7.6	1.02	0.1	58.4	138	38	2.4	4.7	84	67	151
12	9.6	7.93	0.34	6.97	3.3	0.81	0.02	114	16.3	17	1.8	1.9	2.4	8.6	11
13	10	8.16	0.42	6.59	6.2	0.62	0.09	80.5	12	25	1.6	3.6	176	132	308
14	9.2	7.90	0.28	5.43	10.3	0.59	0.07	88.1	34.6	34	1.3	2.7	1060	872	1932
15	9.5	8.52	0.54	4.26	7.9	1.94	0.21	25.6	381	48	3.4	8.3	22	22	44
16	8.6	8.08	0.49	7.06	12.3	0.82	0.15	40.3	178	42	2.1	5.7	109	82	191
17	9.9	8.55	0.39	4.37	6.1	1.28	0.07	10.1	128	57	1.3	6.0	6.3	0.1	6.4
18	12.5	8.05	0.47	6.37	5.6	1.35	0.12	34	137	52	1.8	3.9	78	68	146
19	9.1	8.84	0.47	5.01	8.0	0.46	0.09	18.6	132	5.1	1.0	4.6	108	71	179
20	9.1	8.33	0.5	4.89	4.9	0.94	0.07	110	124	47	2.1	4.3	108	82	190
21	9.7	8.40	0.37	5.09	6.1	0.87	0.05	41.5	179	52	2.6	5.7	69	56	125
22	9.5	8.44	0.46	5.48	8.2	1.28	0.06	74.3	416	212	2.7	3.6	99	71	170
23	9.2	7.95	0.47	6.69	0.3	0.76	0.4	91.1	61.3	6	2.1	1.9	99	68	167
24	9.5	8.37	0.46	6.23	4.3	1.41	0.21	30.3	128	53	2.9	3.8	136	142	278
25	9.8	7.96	0.82	5.49	6.9	2.37	0.12	370	350	70	3.4	6.7	460	351	811
26	10	8.22	0.31	5.18	3.5	0.52	0.09	83.3	191	2.0	3.5	4.9	367	193	560
27	10	8.15	0.41	5.25	6.6	0.63	0.11	90.4	114	59	2.4	5.8	267	191	458
28	10	8.29	0.41	5.66	7.7	0.7	0.02	13.6	45.3	30	1.9	2.7	144	103	247
29	9.2	7.83	1.48	4.85	21	0.34	0.12	169	65.2	54	4.2	50	11	13.4	24.4
30	9.5	8.37	0.45	5.64	3.8	0.82	0.05	33.7	38.0	30	2.5	3.9	157	128	285
31	7.9	7.87	1.28	5.26	15.6	12.8	0.03	4.03	12.6	1.0	1.6	61	1.4	1.2	2.6
32	7.8	8.02	1.45	7.2	18.9	2.05	0.06	7.19	109	83	6.3	103	6.8	6.4	13.2
33	9.4	8.83	3.02	12.7	29.1	3.07	0.14	34.3	263	77	4.7	27.0	19.0	1.0	20.0
34	9.2	8.43	0.29	4.1	13.6	1.02	0.02	3.06	80.6	71	1.8	16	3.6	9.4	13
35	9.4	8.35	1.46	5.51	19.3	1.62	0.11	90.5	63.2	51	1.7	56	1.4	7.2	8.6
36	10.0	8.02	1.47	4.90	17.4	1.50	0.13	74.6	813	75	3.3	37	0.8	8.3	9.1

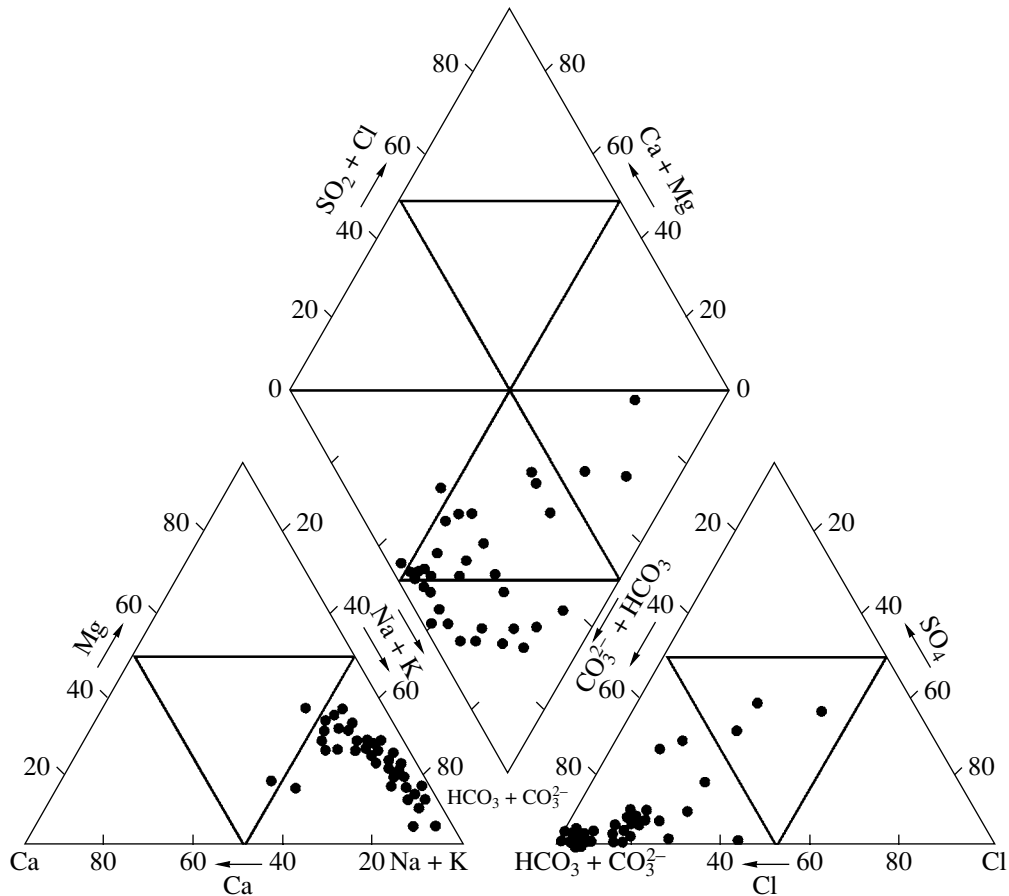


Fig. 2. A.M. Piper's diagram with data on the Datong basin.

above, practically all of the water types (except those from two sampling sites 12 and 18) are in equilibrium with calcite (Fig. 3), a fact demonstrating that Ca cannot be concentrated in these waters unless the character of the geochemical environment is modified.

At the same time, most points in the diagram for the equilibrium of groundwaters with calcic aluminosilicates (Fig. 4) plot within the stability field of kaolinite, and only some points lie within the field of montmorillonite, with which groundwaters are in equilibrium.

The waters equilibrated with Ca-montmorillonite simultaneously contain the highest concentrations of Ca and Si and are characterized by high pH, regardless of the salinity of these waters (samples 5, 11, 16, 29, 32, and 33). The other points plot within the field of equilibrium with kaolinite due to the simple reason that they have low concentrations of Ca and have insufficiently high pH. It is also important to mention that the waters are, in principle, not in equilibrium with endogenic Ca

Table 2. Chemical types of groundwaters, mg/l

No.	Chemical type	Number of analyses	pH		Overall mineralization		Samples
			range	average	range	average	
1	HCO ₃ -Na-Ca	1	—	7.93	—	390	12
2	HCO ₃ -Na-Mg	15	7.8–8.4	8.10	436–926	605	1, 3–5, 7–9, 11, 13, 14, 18, 23, 24, 28, 30
3	HCO ₃ -Cl-Na-Mg	3	7.9–8.1	8.05	622–1909	1060	10, 16, 25
4	HCO ₃ -Na	13	8.0–8.8	8.36	770–3577	1751	6, 17, 19–22, 26, 27, 32–36
5	HCO ₃ -SO ₄ -Na	1	—	7.87	—	1822	31
6	HCO ₃ -Cl-Na	3	7.8–8.5	8.06	2652–4409	3473	2, 15, 29

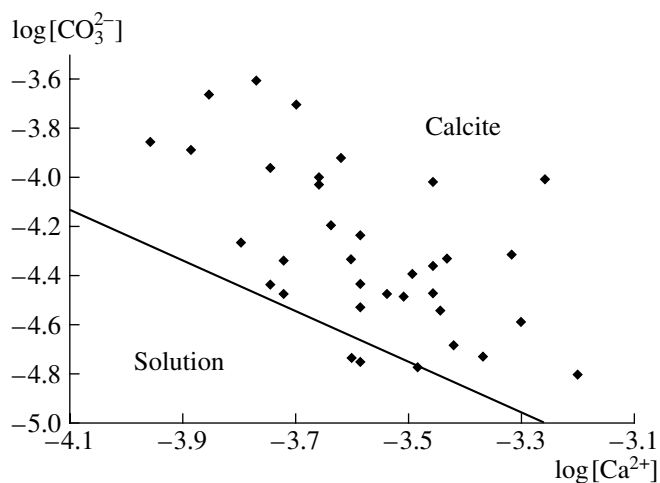


Fig. 3. Equilibrium of groundwaters with calcite in the Datong basin.

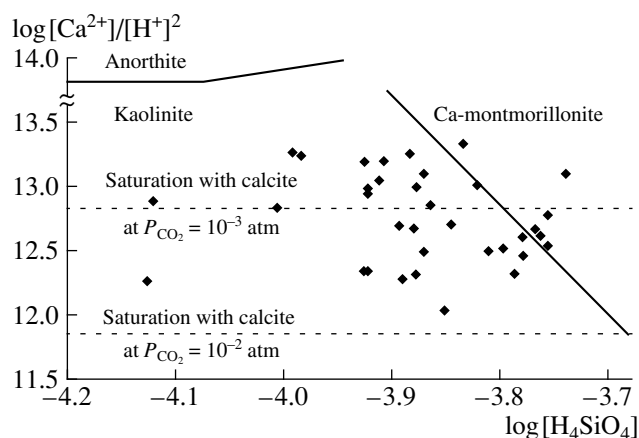


Fig. 4. System $\text{HCl-H}_2\text{O-Al}_2\text{O}_3\text{-CO}_2\text{-CaO-SiO}_2$ at 25°C with data on the composition of groundwaters in the Datong basin.

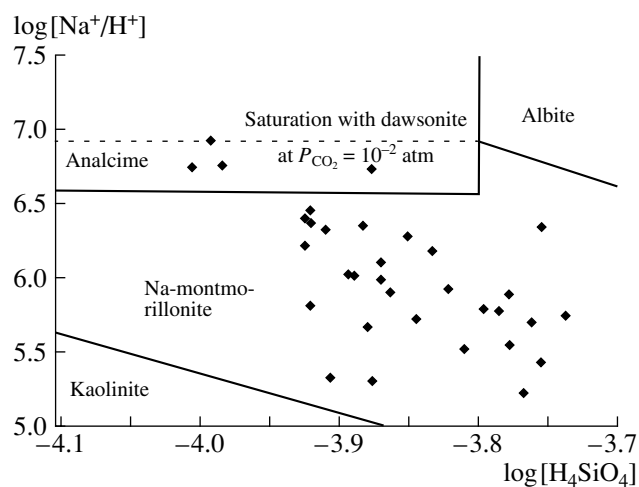


Fig. 5. System $\text{HCl-H}_2\text{O-Al}_2\text{O}_3\text{-CO}_2\text{-Na}_2\text{O-SiO}_2$ at 25°C with data on the composition of groundwaters in the Datong Basin.

minerals, for example, with anorthite, whose equilibrium field is located much higher.

In the diagram showing equilibria between groundwaters and sodic aluminosilicates (Fig. 5), most of the points lie within the stability field of Na-montmorillonite but not kaolinite. The only exceptions are six points, two of which (6 and 13) fall into the stability field of kaolinite and four (15, 17, 34, and 35) lie in the field of analcime. None of the samples showed equilibria with albite. Hence, if equilibria of water with kaolinite and Na-montmorillonite are compared, preference should be given to the latter mineral.

The situation with equilibria of water with magnesian aluminosilicates is different (Fig. 6), because many of these points, similarly to the points corresponding to equilibria with calcic aluminosilicates, fall within the kaolinite stability field, less points fall into the Mg-montmorillonite field, and only one (point 33) lies in the stability field of Mg-chlorite. It is important to emphasize that all of the waters are far from equilibria with primary magnesian aluminosilicates, for example, forsterite and anorthite. In Fig. 6, the field of forsterite lies outside it, at $\log[\text{Mg}^{2+}]/[\text{H}^+]^2 = 16.26$.

Finally, in the diagram showing equilibria with potassic aluminosilicates (Fig. 7), all of the points lie within the illite stability field. At the same time, all of these waters are not equilibrated only with muscovite, whose field is displayed in this figure, but also with potassic feldspar, whose field is beyond the boundaries of this figure.

Hence, all of the primary aluminosilicates (anorthite, albite, forsterite, muscovite, potassic feldspar, and others) are not in equilibrium with groundwaters and can dissolve under these conditions and produce secondary minerals (kaolinite, montmorillonite, illite, calcite, and others). Thereby, much of the chemical elements that passed into solution due to the incongruent dissolution of the primary minerals are incorporated into the secondary products, whereas other (mobile) elements are concentrated in the solution.

GENESIS OF THE CHEMICAL COMPOSITION OF GROUNDWATERS

According to the conditions under which the waters of the basin were formed, these waters can be classified into two types: (i) leaching waters and (ii) waters of continental salinization.

As was mentioned above, the waters of the first type comprise fresh waters whose overall mineralization is <1.0 g/l and pH ranges from 7.8 to 8.4 (Table 2). These waters are formed by the congruent and incongruent dissolution of minerals of the water-hosting rocks, and the cation composition of the waters (except their Fe and Al concentrations) is close to the composition of the dissolved minerals. Some complications are related only to the behavior of Ca, whose concentration in the waters can increase only until equilibrium with calcite

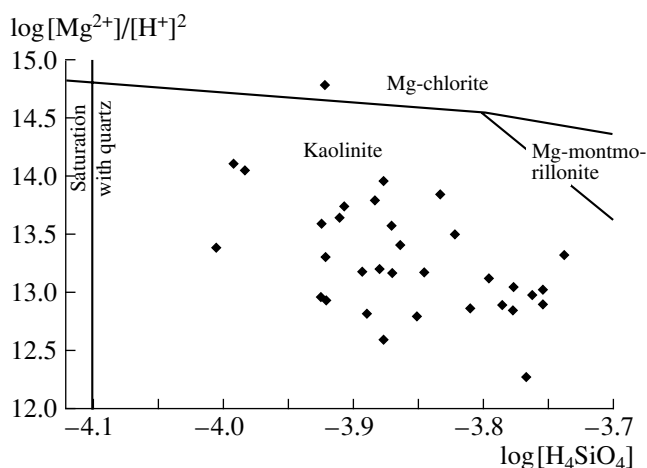


Fig. 6. System $\text{HCl-H}_2\text{O-Al}_2\text{O}_3\text{-CO}_2\text{-MgO-SiO}_2$ at 25°C with data on the composition of groundwaters in the Datong Basin.

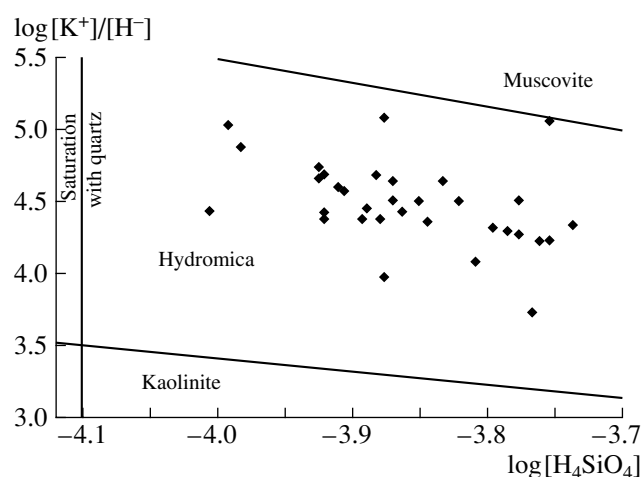


Fig. 7. System $\text{HCl-H}_2\text{O-Al}_2\text{O}_3\text{-CO}_2\text{-K}_2\text{O-SiO}_2$ at 25°C with data on the composition of groundwaters in the Datong Basin.

is established. At an overall mineralization of <0.5 g/l, equilibrium with calcite is commonly not reached and the Ca concentrations in the waters are controlled by the compositions of the dissolved rocks. At an overall mineralization of >0.5 g/l and $\text{pH} > 7.5$, this equilibrium is achieved and calcite does not dissolve but crystallizes. Because of this, the Ca concentrations in these waters do not increase with increasing salinity and do not exceed 112 mg/l (Fig. 8).

Mg behaves similarly to Ca and its barrier is Mg-montmorillonite (Fig. 6). Equilibrium with this mineral is reached at a salinity higher than that required for equilibrium with calcite. Because of this, the Mg concentrations in the waters are higher but still never exceed 140 mg/l.

The situation with Na is different. Although this element participates in the formation of Na-montmorillonite, its amount in this mineral is insignificant, and, hence, the concentrations of this element increase more rapidly with increasing overall mineralization (Fig. 8).

If the groundwaters of points 4, 10–13, and 30 are assumed as typical leaching waters, their average overall mineralization is 491 mg/l, pH is 8.1, and the concentration of Cl^- is 12.3, that of SO_4^{2-} is 1.2, and that of HCO_3^- equals 343 mg/l (Table 3); i.e., these are typical

leaching waters, which are widespread throughout the world [13].

Waters related to continental salinization are characterized by higher pH and salinity, elevated concentrations of sulfate and chlorine ions, and Cl/SO_4 ratios of >1 . These waters are exemplified by the waters of points 2, 15, 17, 25, 29, and others (Table 1), whose mineralization varies from 1.7 to 4.4 g/l and pH is 7.8–8.6, and which have concentrations of Cl from 120 to 800 mg/l and SO_4 from 0.93 to 668 mg/l. The average concentrations of chemical elements in these waters are presented in Table 3.

If average data on typical waters of continental salinization are compared with analogous data on leaching waters, it can be seen that the degree of evaporative concentration of the former corresponds for overall mineralization from 3.1 to 7.3 (at an average of 5.7) for concentrations of Cl^- from 5.5 to 46 (at an average of 12.3), for SO_4^{2-} from 20 to 334 (at an average of 263), and for Na from 4.2 to 10.2 mg/l (at an average of 9.1) (Table 3). Hence, the increase in the concentrations of elements during evaporative concentration is uneven: the most significant increase is typical of SO_4^{2-} , Cl^- , and Na^+ and the minimum increase is characteristic of Ca^{2+} .

Table 3. Comparative analysis of the compositions (mg/l) of typical waters related to continental salinization and leaching

Water type	Overall mineralization	pH	Cl^-	SO_4^{2-}	HCO_3^-	F^-	Ca^{2+}	Mg^{2+}	Na^+
1. Leaching (average of 6 samples)	491	8.12	12.3	2.7	343	0.93	20.8	21.2	75.6
2. Continental salinization (average of 5 samples)	2804	8.13	412	316	1241	1.58	29.2	86.3	686
Average ratios of waters of type 2 to those of type 1	5.71	1.0	33.5	117	3.61	6.86	1.40	4.07	9.07

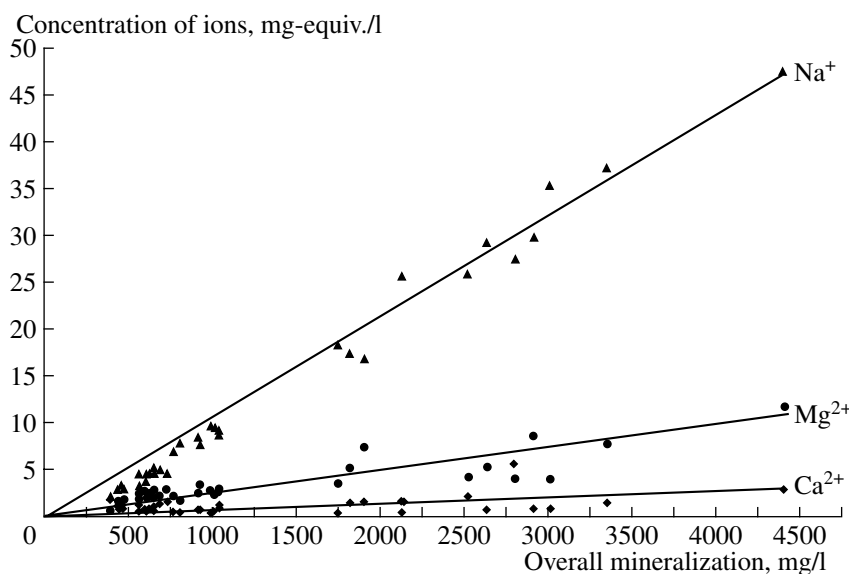


Fig. 8. Dependence of the cation composition of waters on their overall mineralization.

The reasons for this situation were revealed previously: Ca^{2+} is incorporated into calcite crystallizing from the solution, and Mg^{2+} and Na^{+} are accommodated in montmorillonite (although their concentrations in this mineral are different). It thus remains to explain the reasons for the unequal concentration of Cl^{-} and SO_4^{2-} in the waters in question (Fig. 9). In this context, it is pertinent to emphasize that groundwaters of continental salinization are at some sites enriched in the sulfate ion more strongly than in the chlorine ion, with this difference greater in salinization than in leaching waters (the former ion is concentrated almost one order of magnitude more significantly than the latter one). These facts definitely testify that the waters of these sites had an additional source of SO_4^{2-} . Hence, the degree of continental concentration should be assayed using Cl^{-} but not SO_4^{2-} , because the former ion has no sources other than atmospheric precipitation.

Table 4 briefly characterizes the samples of groundwaters with the highest concentrations of the sulfate ion. These data indicate that the overall mineralization of these waters ranges from 1.8 to 4.4 g/l, and their pH is from 7.8 to 8.8. These waters simultaneously contain elevated concentrations of SO_4^{2-} and Cl^{-} , a fact definitely pointing to the process of continental salinization. The degree of evaporative concentration of salts in these waters ranges from 10 to 65, averaging at 28.6.

The overwhelming majority of samples show equal degrees of the concentrating of the sulfate and chlorine ions, as follows from the Cl/SO_4 ratios. The only exceptions are sample 29, for which SO_4^{2-} losses can be suggested, and samples 31 and 34, which obviously had

additional sources of this ion. These could be either sulfide minerals, which are contained in the sedimentary rocks of the basement, or anthropogenic sources of sulfur.

Assuming that all chlorine resulted from evaporative concentration, we arrived at the conclusion that 88% of the sulfate ion also resulted from the evaporation process, with only 12% of the sulfates having another source, most probably, sulfides because traces of anthropogenic sources should have been inevitably discernible elsewhere.

The principal components of groundwaters are, as was mentioned above, HCO_3^{-} and Na^{+} , which dominate (in equivalent terms) over other anions and cations (Figs. 8, 9). Below, we consider their sources in more detail.

GENESIS OF SODIC WATERS

As was demonstrated above, in spite of their high degree of evaporative concentration, all of the waters are not in equilibrium with the primary endogenic minerals and can dissolve them. Aluminosilicates dissolve mostly in compliance with the hydrolysis mechanism. The minerals dissolve incongruently, but, as was demonstrated by Alekseev [19], these dissolution reactions proceed through the passage of all elements of the crystalline structures into solution and the simultaneous precipitation of secondary minerals. Of course, the latter include phases equilibrated with the solution [13, 20].

This fact is very important because it highlights the mechanism responsible for the selective concentration of chemical elements in the aqueous solution: *compounds in equilibrium with a solution form secondary*

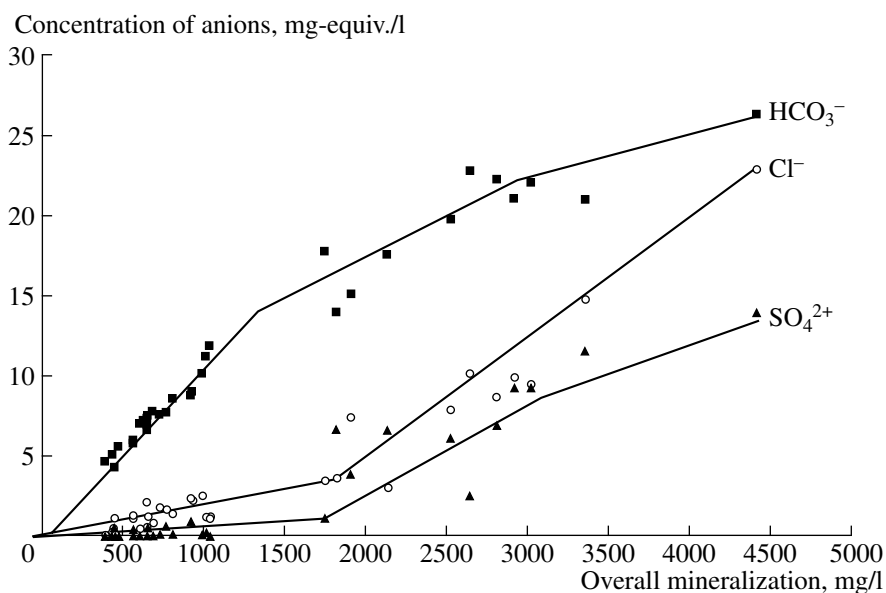


Fig. 9. Dependence of the concentrations of major anions in waters on their overall mineralization.

phases, and elements that are not involved in the precipitation process become enriched in this solution. The solution as a whole is, thereby, not equilibrated with the dissolving minerals. This state of the water–rock system is quite common, and some minerals always dissolve while others precipitate from naturally occurring solutions. This conclusion was confirmed by one of the authors based on very extensive factual data on various water types and geochemical environments and was referred to as the equilibrium–unequilibrium state [9, 13, 20–24], which is intrinsically controversial and determines the progressive evolution of interactions in water–rock systems. It is important that various stages of these interactions are characterized by the pre-

cipitation of different secondary minerals. In our situation, both clay minerals (kaolinite, montmorillonite, illite, and others) and calcite are formed, a fact important for understanding the processes that form sodic waters.

The interaction of water with aluminosilicates proceeds according to the hydrolysis mechanism, and this reaction can be written in the most general form as [25]

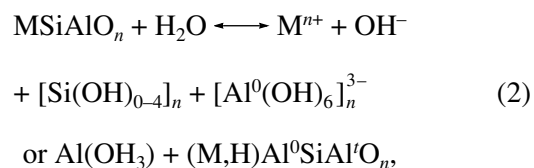
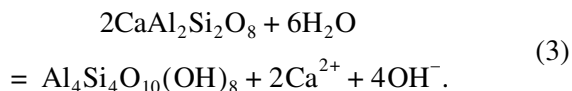


Table 4. Composition (mg/l) of waters anomalous in terms of SO_4^{2-} concentrations and their degree of salt concentration by continental evaporation

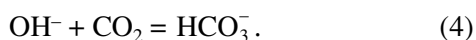
Sample	Sum of salts	pH	SO_4^{2-}	Cl^-	Degree of concentration, calculated for Cl^-	Cl/SO_4	Amount of SO_4^{2-} due to evaporation,	
							mg/l	%
2	3279	7.81	552	518	42.1	0.93	547	99
29	4412	7.83	668	803	65.3	1.20	848	126
31	1824	7.87	321	128	10.4	0.39	135	42
32	2528	8.02	292	277	22.5	0.94	292	100
33	2822	8.83	331	305	24.8	0.92	322	97
34	2138	8.43	318	106	8.61	0.33	112	35
35	2909	8.35	446	348	28.3	0.78	368	82
36	3023	8.02	442	330	26.8	0.74	348	78
Average	2867	8.14	421	352	28.3	0.83	372	88

where n pertains to variable atomic ratios, o and t correspond to octahedral and tetrahedral sites, respectively, and M denotes cations of metals. The last term of the reaction, $(M, H)Al^oSi^tAl^oO_n$, includes at least three possible compounds: a clay mineral, zeolite, and silicate fragments.

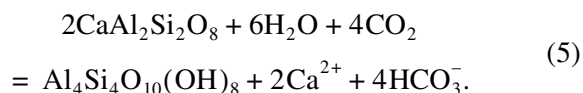
An example of a hydrolysis reaction is the incongruent dissolution of anorthite with the formation of kaolinite:



As can be readily seen, the cation charge is here counterbalanced by that of the hydroxyl group OH^- , which is also produced from water during hydrolysis. At cation concentrations analogous to those commonly contained in the waters (from 10^{-2} to 10^{-3} mol/l), the pH of these waters should be 9–11 [9], which is, however, not the case with either our waters or other commonly occurring water types. The reason for this is the interaction of the OH^- anion with CO_2 and its neutralization by the reaction



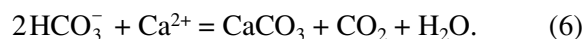
The constant of this reaction is equal to $10^{6.2}$ at $25^\circ C$, $10^{4.1}$ at $50^\circ C$, and $10^{1.6}$ at $100^\circ C$. It can be seen that, at the partial pressures of carbon dioxide commonly occurring in groundwaters ($10^{1.0}$ – $10^{2.5}$ Pa), the alkalinity produced during weathering is continuously neutralized by carbon dioxide and various organic acids. As a result, one of the hydrolysis products is constantly modified, and groundwaters of carbonate type are formed. Correspondingly, reaction (3) can be rewritten in the form



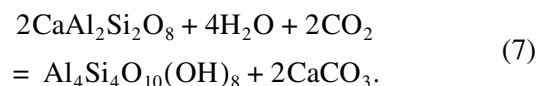
It follows that, along with the formation of secondary products, the system water–aluminosilicates is also characterized by the participation of some of the hydrolysis products in the neutralization reactions, which facilitate the maintaining of a nonequilibrium state in the system water–aluminosilicates. These neutralization reactions proceed only in the presence of organic, carbonic, and, more rarely, some other inorganic acids. Because of this, the hydrolysis of aluminosilicates should be regarded in close relation with the origin of acidic products in groundwaters. The source of the latter is, in our situation, the organic matter contained in the soils and rocks or, at deeper levels, metamorphic and magmatic processes.

The preservation of the nonequilibrium state of the water–rock system and the continuing dissolution of aluminosilicates result in a gradual increase in the concentrations of cations and HCO_3^- as hydrolysis prod-

ucts, so that equilibrium with calcite is eventually reached, and this mineral starts to precipitate from the solution according to the reaction

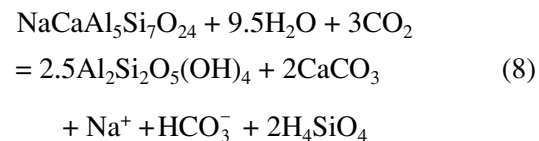


The onset of calcite crystallization significantly modifies the processes that determine the composition of groundwaters because Ca concentration in the solution cannot increase any more (if all other factors remain the same). Correspondingly, reaction (4) can be rewritten in the form

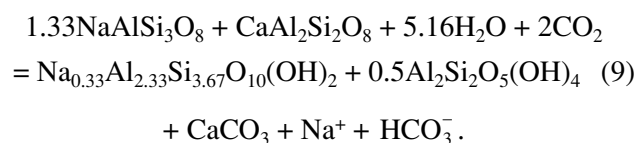


However, equilibrium between water and primary aluminosilicates still cannot be established, and these minerals continue to dissolve with the passage of all of their chemical elements into solution. During this interaction stage, various montmorillonite and illite varieties are formed instead of kaolinite, with these minerals accommodating K, Mg, and, partly, also Ca and Na. However, solutions usually acquire much more Na than can be incorporated into the secondary products, and, thus, the balance of this element in water is positive, Na accumulates in the water, forming sodic waters.

Inasmuch as the primary aluminosilicates dissolved in waters are diverse, as also are their hydrolysis reactions, it is impossible to write all of them. The process of water interactions with aluminosilicates during this stage can, in essence, be expressed by the reaction



or in a more complicated form



It is important that all of these reactions proceed with the formation of certain clay minerals and calcite with the enrichment of the solution in Na and HCO_3^- , i.e., sodium bicarbonate. If these reactions proceed for a long time, soda continues enriching the solution, and its concentration can become sufficient for the precipitation of sodic minerals. Although this stage of water interaction with aluminosilicates has not been reached in our situation, this is possible theoretically.

Hence, *the formation of sodium bicarbonate waters is a natural evolutionary stage of the system water–aluminosilicates, and this stage begins when the water reaches equilibrium with calcite.* It takes a certain time for the interaction process to reach this stage. This time

has not been evaluated as of yet, which is a task for future research. It is, however, quite obvious now that this time is determined by the intensity of water exchange that controls these stages of interaction between waters and rocks, with each type of water exchange characterized by certain interaction types [13].

Water exchange is, thus, one of the most important factors controlling the origin of sodic waters. Other factors controlling these processes include the type of the rock, because, at other equal factors, the richer the rock in Na, the more active water exchange is needed to produce sodic waters. The same also pertains to Mg: if its amount transferred into solution is greater than that incorporated into the secondary minerals, this element is enriched in the groundwaters. The latter situation is typical of the Datong Basin, whose waters are dominated with Na and Mg (they are richer in Na) and, thus, often belong to the Na–Mg type (Table 2).

Another factor that affects the soda-forming process is the degree of the evaporative concentration of salts. Water evaporation results in an increase in the salinity of the water, more rapid enrichment of chemical elements in it, and, correspondingly, the precipitation of carbonates, clay minerals, and, during a certain stage, sodium bicarbonate also. As is illustrated by the example of the Datong Basin, the degree of salt concentration equal to a few tens does not negatively affect the soda-producing process, because it is not active enough. At higher degrees of salt concentration (perhaps, more than 100), the solutions are dominated by sulfates and chlorides, and the contents of soda are insignificant. This dependence of soda formation on the degree of the evaporative concentration of salts was documented by Bazilevich in the Barabinskaya steppe in western Siberia [5].

The aforementioned examples of soda formation make it possible to understand as to why the soda-forming process at the Earth's surface is spatially restricted mostly to the boundaries of forest and steppe or forest-steppe catenae [4, 6], which are characterized by relatively sluggish water exchange and whose degrees of the evaporative concentration of salts are not high enough. The formation of sodic waters proceeds independently of the rock types. At the same time, sodic waters occur at some depths, regardless of the catena types [22].

The Datong Basin is most suitable for the formation of soda waters, because this is an intermountain depression with an arid or semiarid climate and with forest catenae (in the mountainous part) adjoining forest-steppe and steppe catenae. The insufficient atmospheric precipitation and active evaporation are favorable for sluggish water exchange, which predetermines the possibility of the relatively long-lasting interaction of the waters with aluminosilicate rocks and the establishment of equilibrium with calcite. Under these conditions, the latter mineral does not dissolve but precipi-

tates. The relatively low intensity of water evaporation is also favorable for the formation of sodium bicarbonate, because Na^+ and HCO_3^- (CO_3^{2-}) have no geochemical barriers.

The materials presented above on the sodic waters of the Datong Basin, which evolved in continental environments for hundreds of millions of years, provide convincing evidence in support of the geological hypothesis of the genesis of these waters, if this hypothesis is considered from the modern standpoint of the evolutionary stages of the water–rock system as a consequence of its equilibrium–unequilibrium state. This provides support for the conclusion, which was drawn by one of the authors in 1978, that *the formation of sodic waters is a natural consequence of water interaction with aluminosilicate rocks and is related to a certain evolutionary stage of the system, when the water becomes saturated with respect to carbonates. The latter is possible only at slow water exchange, elevated mineralization of the waters, and their alkaline compositions.* [9, p. 252].

PRINCIPAL CONCLUSIONS

(1) The Datong intermountain basin in China contains predominantly sodic waters with overall mineralization from 0.6 to 4.5 g/l and pH from 7.8 to 8.8, which are locally affected by the process of continental salinization.

(2) Thermodynamic simulations indicate that most of these waters (except only those at two sampling sites) are in equilibrium with calcite, and all of them are in equilibrium with one or more clay minerals (kaolinite, montmorillonite, and illite) and, at a few sampling sites, with analcime while, at one site, with Mg-chlorite. At the same time, all of the waters are not in equilibrium with endogenic aluminosilicates: anorthite, albite, forsterite, microcline, muscovite, and others. The water–rock system has a clearly pronounced equilibrium–unequilibrium character.

(3) The study area includes mostly leaching waters with low degrees of the evaporative concentration of salts, with the latter only locally reaching a few tens. In these situations, the elevated chlorine concentrations and 90% of the sulfate-ion concentrations caused by the evaporative concentration, and no more than 10% SO_4^{2-} , are acquired from the host rocks via the oxidation of their sulfide minerals. The contribution of anthropogenic sources is insignificant.

(4) Sodic waters are produced by the dissolution of endogenic aluminosilicates of sedimentary, metamorphic, and magmatic rocks, which are not in equilibrium with the groundwaters, and the water–rock system occurs at an interaction stage at which weathering is associated with the origin of secondary products in the form of clay minerals and carbonates (calcite).

(5) The formation of sodic waters is a natural stage of the evolution of water–aluminosilicates systems. This stage begins when the aqueous solution reaches equilibrium with calcite.

(6) Water exchange is the leading factor of soda formation. Other, subordinate, factors of these processes are the types of the rocks (and their Na concentrations) and the degree of the evaporative concentration of salts. The latter should not exceed a few tens.

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