

# Geochemistry of Fresh Groundwater in the Main Landscape Zones of the Earth

S. L. Shvartsev

*Institute of Oil and Gas Geology (Tomsk Branch), Siberian Division, Russian Academy of Sciences,  
Akademicheskii pr. 3, Tomsk 634021 Russia*

*e-mail: tf@igng.tsc.ru*

Received

DOI: 10.1134/S0016702908130016

## CONTENTS

### INTRODUCTION

#### CHAPTER 1. AVERAGE ABUNDANCES OF CHEMICAL ELEMENTS IN THE GROUNDWATERS OF THE SUPERGENE ZONE

- 1.1. *Method of Calculation of Clarke Values*
- 1.2. *Groundwaters of the Permafrost Province*
- 1.3. *Groundwaters of the Province of Tropical and Subtropical Climate*
- 1.4. *Groundwaters of the Province of Temperate Humid Climate*
- 1.5. *Groundwaters of Mountain Regions*
- 1.6. *Groundwaters of the Province of Arid Climate*

#### CHAPTER 2. COMPARATIVE GEOCHEMISTRY OF GROUNDWATERS FROM VARIOUS PROVINCES AND THEIR RELATION WITH RIVER WATER AND SEAWATER

- 2.1. *Comparative Analysis and Average Composition of Groundwaters from the Supergene Zone*
- 2.2. *Individuality and Stability of Groundwater Composition in Various Provinces*
- 2.3. *Comparative Analysis of the Compositions of Groundwater, River Water, and Seawater*

#### CHAPTER 3. EQUILIBRIUM–NONEQUILIBRIUM CHARACTER OF THE WATER–CO<sub>2</sub>–ROCK SYSTEM

- 3.1. *Equilibrium of Groundwater with Carbonate Minerals*
- 3.2. *Equilibrium of Groundwater with Aluminosilicate Minerals*
- 3.3. *Nature of Nonequilibrium in the Water–Primary Aluminosilicate System*
- 3.4. *Factors Controlling the Character of the Geochemical Environment*

#### 3.5. *Direction and Hydrogeochemical Role of Organic Matter Decomposition*

#### CHAPTER 4. MAGNITUDE AND COMPONENTS OF SUBSURFACE CHEMICAL EFFLUX

- 4.1. *Quantitative Characteristics of the Components of Subsurface Chemical Efflux*
- 4.2. *Mechanisms of Aluminosilicate Interaction with Aqueous Solutions*
- 4.3. *Relations between the Removal of Chemical Elements and the Magnitude of Rock Dissolution*

#### CHAPTER 5. GEOCHEMICAL LINK BETWEEN WEATHERING AND DEVELOPMENT OF GROUNDWATER COMPOSITION

- 5.1. *Main Geochemical Types of Weathering*
- 5.2. *Mechanisms and Stages of Weathering*
- 5.3. *Geochemical Types of Groundwater*
- 5.4. *Factors Controlling the Formation of Geochemical Types of Water and Weathering*
- 5.5. *Formation of the Chemical Composition of Groundwater*
  - 5.5.1. *Atmogenic stage*
  - 5.5.2. *Biogenic stage*
  - 5.5.3. *Lithogenic stage*
  - 5.5.4. *Evaporative stage*
  - 5.5.5. *Cryogenic metamorphism of groundwater*
- 5.6. *Relation between the Compositions of Groundwaters and Rocks*
- 5.7. *Geologic Evolution and Self-Organization of the Water–Rock System*

## FINAL REMARKS

## REFERENCES

## INTRODUCTION

The eminent Russian scientist V.I. Vernadsky wrote: "The geochemistry of waters is among vital geologic problems because it deals with water and water controls the main structural features of the biosphere, the environment with which all living systems are intimately connected in a regular way" [1, p. 665]. This problem is especially important nowadays, with the demand for clean fresh water ever increasing as its resources rapidly decrease due to continuous pollution. This gave rise to the formidable challenge of clean water supply, which is closely related to the problems of human health and the ecological state of the environment.

The clean water problem has become one of the most important global issues and is already more significant than such main concerns of humankind as climate change, destruction of the ozone layer, soil salinization and erosion, protection of the atmosphere and ocean from pollution, etc. This is related to the special role of water in geologic processes, the origin of the biosphere, the evolution of life, and the formation of the environment.

Fresh groundwater occurs mainly in the supergene zone and is significant not only as a source of drinking water for the population. It controls the chemistry of all supergene processes, the genesis of the majority of minerals and many mineral deposits, the formation of weathering zones, soil genesis, mechanisms of dissemination and concentration of chemical elements, the development of relief and the landscape in general, the environment of life, the types of ecosystems, etc.

A special problem is the study of the interaction of water with rocks, gases, and organic matter. It is important not only to describe the character of this interaction but also to unravel its nature and search, following G.W.F. Hegel, for the general source of process movement and development. This can be done only if the interaction itself is considered as part of a more complex system involving mass and energy exchange with the external environment in time.

The geochemistry of fresh groundwater is actively developing both in Russia and in other countries. The main theoretical and practical aspects of this relatively young discipline were discussed in [2–28]. There are still many unsolved problems. One of the most important among them is the problem of the formation of the chemical composition of groundwater because it is controlled by many factors and processes. As to the upper zone, the most widely recognized factors are climate, relief, rock type, organic matter, and their derivatives (precipitation, evaporation, temperature, permeability, water exchange, etc.) and the main processes are dissolution, leaching, exchange reaction, evaporative concentration, sorption, mixing, hydrolysis, etc. However, it is evident that the essence of the problem of the formation of groundwater chemistry cannot be determined by investigating only factors and processes because the time of activity of particular factors or pro-

cesses remains unconstrained in such a case. For instance, dissolution as a chemical process may occur during the initial stages of water–rock interaction, but it may cease as the solution becomes saturated in corresponding compounds. The same is true of leaching, cation exchange, and other processes.

Consequently, the problem is to determine whether water can interact with rocks over the whole time period of contact or only during part of this time. In other words, is the time of interaction equivalent to the time of water–rock contact? What factors control this interaction, what is the direction of its development, and how does it affect the composition of groundwater? Of course, the solution of all these problems is possible only through establishment of the character of water–rock equilibrium and the direction of rock alteration. If such equilibrium is possible, what are the time scales and conditions of its attainment? If not, what are the reasons? Therefore, the elucidation of the nature of equilibrium with rocks is one of the most fundamental problems.

In addition to rocks, groundwaters interact with organic matter and various gases during their migration. Therefore, all of the aforementioned problems concern also the water–organic matter–gas system. It is important to identify the stage of water formation during which it interacts with these important constituents of the upper part of the Earth's crust, determine the consequences of this interaction, and estimate its influence on the evolution of water composition during its movement from sources to discharge areas.

Thus, in addition to determining main factors and processes affecting the composition of groundwaters, it is essential to track the effect of each of them during the whole period of interaction. This requires the analysis of water–rock–organic matter interaction mechanisms and coupled effects of factors and processes.

The diversity of water interaction with rocks and organic matter should also be kept in mind: rocks may dissolve either congruently or incongruently; interaction may be accompanied by dissolution, leaching, oxidation, or reduction; and organic matter may be remineralized, humified, or transformed into various new organic compounds of complex structures and compositions. Of course, each of these processes does not occur separately but is coupled with other processes, which further complicates diverse natural reactions.

New fundamental data have been obtained in recent years on the character of the geologic evolution and self-organization of the water–rock system, and the essential role of this system in the structure and evolution of the environment in general was demonstrated. These results and the urgency of environmental problems, which concern mostly the upper layers of the Earth's crust, emphasize the special role of this global shell and pose a number of fundamental problems. Some of these are (1) calculation of the average abundances of chemical elements in groundwaters from various landscape and climatic zones, especially under

conditions of limited anthropogenic activity; (2) determination of particular sources of chemical elements in groundwaters; (3) investigation of the mechanisms of water–rock interaction; (4) assessment of the degree of water–rock equilibration; (5) determination of mechanisms, factors, directions, and sequences of secondary mineral formation under the influence of groundwater; (6) analysis of geologic self-organization in the water–rock system; (7) unraveling of the mechanisms of ore-forming processes in the water–rock system; (8) analysis of the relations between the compositions of water and rocks, including weathering products; (9) investigation of the stages and mechanisms of development of groundwater composition; and (10) estimation of the ecological and geochemical state of the aquatic environment.

Even this cursory listing of scientific problems to be solved illustrates the importance of the investigation of the geochemistry of groundwater from the upper hydrodynamic zone under various landscape conditions differing in the character of water exchange and, consequently, the time of water–rock interaction. In this connection, the goal of this contribution is to consider new aspects of the geochemistry of groundwater and the scales of its changes and evolution during interaction with rocks and organic matter.

## CHAPTER 1. AVERAGE ABUNDANCES OF CHEMICAL ELEMENTS IN THE GROUNDWATERS OF THE SUPERGENE ZONE

The distinguished American geochemist F.W. Clarke more than a hundred years ago pioneered the investigation of the average abundances of chemical elements in geologic objects (rocks, soils, waters, etc.), which were subsequently named clarkes in his honor. This direction of research has been fostered by many illustrious researchers, including A.G.W. Cameron, A.E. Fersman, F. Heide, J.D. Hem, H. Lange, D.A. Livingston, B. Mason, A.I. Perel'man, K.K. Rankama, A.B. Ronov, H.J. Rössler, W.W. Rybey, T. Sahama, S.R. Taylor, K.K. Turekian, H.C. Urey, V.I. Vernadsky, A.P. Vinogradov, H.S. Washington, K.H. Wedepohl, D.E. White, and many others. As a result, clarkes have been determined for all types of rocks, soils, plants, seawater, river water, lakes, etc. However, groundwaters are still poorly studied in this respect, probably because of their high complexity. There is hardly any reason to doubt the importance of clarkes: it has been proved by the history of geochemistry. The lack of such data for groundwaters hampers the solution of many global problems in hydrogeology, hydrochemistry, and related disciplines (geochemistry, lithology, etc.) and prevents the evaluation of the fundamental geochemical features of the subsurface hydrosphere.

Vernadsky was the first to substantiate the concept of the unity of all natural waters. He distinguished 485 mineralogical types of natural waters and quantitatively characterized the abundances of chemical elements in each

type. However, the estimation of the average concentrations of chemical elements in groundwaters turned out to be a very complex problem because of the diversity of their composition and salinity. Suffice it to say that the total dissolved solids in natural waters range from 0.02 to 700 g/l. Therefore, we proposed [6] to calculate average element abundances separately for each genetic type comprising waters of relatively similar compositions and geologic conditions. In this study, the previous Clarke values for chemical elements in the groundwaters of the supergene zone, i.e., the zone dominated by fresh waters, were significantly refined and extended.

With respect to the mode of occurrence, the waters of the supergene zone are mainly groundwaters and occasionally perched waters drained by local river networks. Their temperature is only slightly different from the mean annual air temperature and does not extend beyond the range of surface temperatures. The continuous replenishment of groundwater resources leads to the formation of a zone of active water exchange within the area of local drainage of rocks. The supergene zone is the part of the Earth's crust where the geochemical role of groundwater is especially clearly manifested in the processes of soil formation, weathering, epigenesis, decomposition of ore bodies, salinization, etc. Thus, it is believed that this zone is a peculiar hydrochemical system controlling the geologic evolution and self-organization of the geologic environment and the origin and development of life.

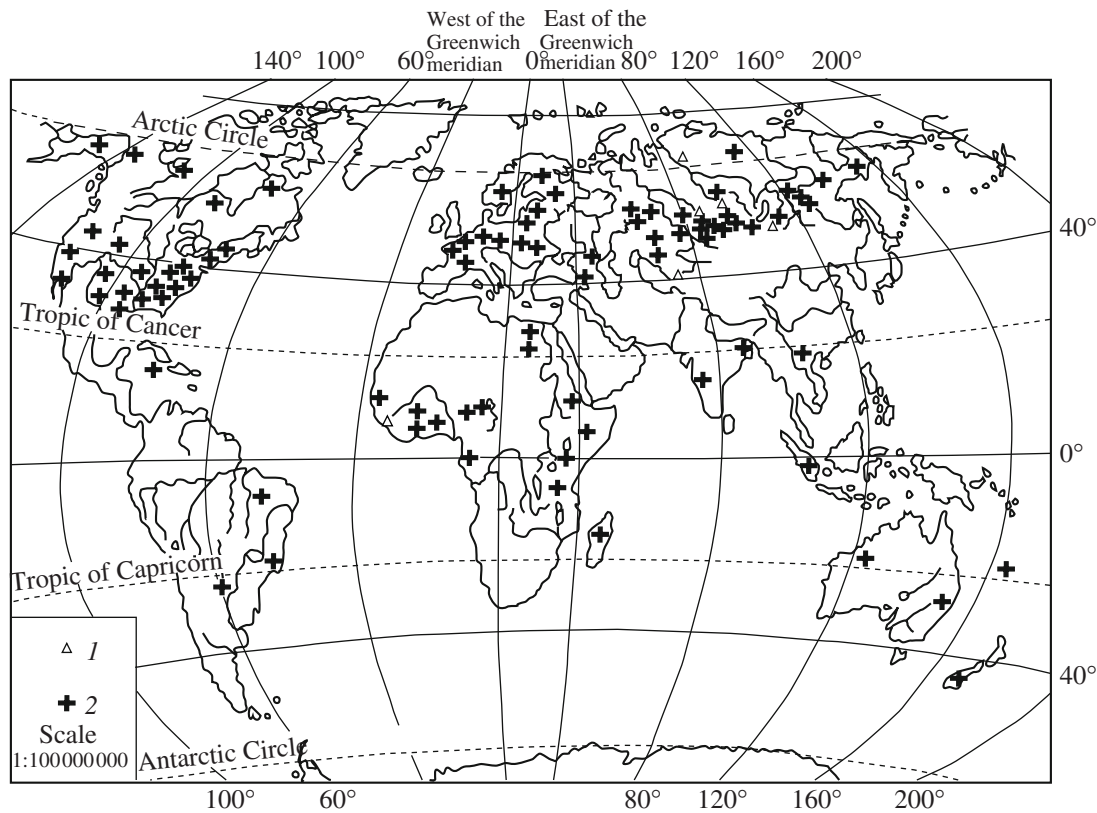
Nowadays, the geochemical activity of groundwater is increasing considerably under the influence of anthropogenic activity, which is becoming a geological force. Anthropogenic factors control the state of the environment, and this makes acute the problem of the rational use of the geologic medium as a habitat for humans and aggravates the problem of natural catastrophes. The influence of anthropogenic factors on groundwaters has become global; large-scale pollution of groundwaters can be observed, and their compositions and geochemical signatures are changing. Under such conditions, the determination of the composition of uncontaminated groundwater is especially important for the subsequent estimation of the extent of its modification.

The average abundances of more than 50 chemical elements in the groundwaters of the supergene zone were first calculated by us in 1978 [6]. After 20 years, in 1998, they were recalculated using an extended database [29]. In this study, they are reported with minor modifications based on the most recent data.

### *1.1. Method of Calculation of Clarke Values*

It is known that groundwaters from the supergene zone are strongly affected by main climatic factors and show a latitudinal zoning, which was used by us as a basis for the systematization of the numerous data. In such a way, we excluded the dominating influence of





**Fig. 1.** Map showing the regions whose groundwater compositions were used in this study, including (1) regions investigated by the author and (2) regions interpreted on the basis of literature data.

hydrochemically well studied types of groundwater of limited distribution.

In accordance with the principle of zoning, Clarke values were calculated for groundwaters from five main hydrogeological provinces: (1) permafrost, (2) temperate humid climate, (3) tropical climate, (4) arid climate, and (5) mountain regions with a vertical zoning. The waters of each province were systematized on the basis of main landscape types. For instance, wetland, mixed forest, southern taiga, forest steppe, and steppe terrains were distinguished within the province of temperate humid climate; forest (humid and moderately humid), savanna (humid and arid), and subtropical terrains were distinguished in the province of tropical and subtropical climate; and high mountain, mountain meadow, mountain taiga, and mountain steppe terrains were distinguished in the mountain province. All waters showing evidence of continental salinization, including waters from mountain steppes, poorly drained intermontane depressions, tropical steppes, American prairies, etc., were classed with the waters of the arid climate province.

In order to avoid accidental errors, the groundwaters of each landscape zone were represented by at least three and more often six to eight or even ten regions of the world (Fig. 1). Overall, we considered 34300 analyses of groundwater from 91 regions (Table 1) of all continents, except Antarctica, and large islands (Mada-

gascar, Cuba, New Caledonia, Hawaii, etc.). The contents of individual chemical elements in waters were taken into account in the same fashion.

The composition of groundwater from a particular small region was systematized on the basis of aquifer lithology. The general procedure of data processing and determination of mean values for the composition of waters from individual areas, regions, landscape zones, etc., was the following: particular water analyses for the area under study with certain landscape conditions → average for the water from a certain type of aquifer rocks → average for the water of the region → average for the landscape zone → average for the hydrogeological province → average for the water of the supergene zone. Taking into account that the regions of arid climate occupy approximately 20% of the total area of continents, the proportion between the waters of continental salinization and leaching was taken to be 1 : 4.

### 1.2. Groundwaters of the Permafrost Province

The permafrost zone occupies considerable land areas, including Antarctica, northeastern Europe, a major portion of Siberia, almost all of Alaska, much of Canada, Arctic islands, and Greenland. There are frozen zones in the high mountain regions of all continents, including those of the tropical belt.

**Table 1.** Distribution of data on the composition of groundwaters in the section of hydrogeological provinces and landscape zones

No.	Hydrogeological province	Landscape zone	Number of regions studied	Number of water analyses used
1	Permafrost	1.1. Swamp	2	415
		1.2. Tundra	4	1583
		1.3. Northern taiga	7	5638
2	Temperate climate	2.1. Swamp	4	983
		2.2. Mixed forest	10	2840
		2.3. Southern taiga	6	4366
		2.4. Steppe and forest steppe	7	3721
3	Tropical climate	3.1. Wet savanna	4	370
		3.2. Tropical forests	5	517
		3.3. Subtropics	3	615
		3.4. Dry savanna	4	339
4	Arid climate	4.1. Dry steppes of the temperate belt	9	3192
		4.2. Dry steppes of the tropical belt	5	529
5	Mountain regions	5.1. High mountains	5	945
		5.2. Mountain forests	9	4290
		5.3. Mountain steppes	9	2995
	Total	16	91	34338

Within the world's land areas, the permafrost zone accounts for  $35 \times 10^6$  km<sup>2</sup>, or approximately 24%, including  $22 \times 10^6$  km<sup>2</sup> in the northern hemisphere and  $13 \times 10^6$  km<sup>2</sup> in the southern hemisphere [30]. If the ice-covered areas of continents are excluded ( $2.17 \times 10^6$  km<sup>2</sup> in Greenland and  $12.98 \times 10^6$  km<sup>2</sup> in Antarctica), the percentage of land areas underlain by permafrost decreases to 13.7%. Within the territory of the former USSR, only the subaerial cryolithic zone occupies  $10.98 \times 10^6$  km<sup>2</sup>, or 49.1%. However, the area of the permafrost proper without taliks is much smaller,  $7.66 \times 10^6$  km<sup>2</sup>, or 34.1% of the whole territory. Therefore, taliks occupy  $3.32 \times 10^6$  km<sup>2</sup> in the cryolithic zone. Permafrost islands occur sporadically far to the south of Russia, in particular, within 40% of northern Mongolia [31].

The average contents of chemical elements in the groundwaters of the cryolithic zone were calculated using data for the northern and western Siberian Platform [32–36], Transbaikalia [37–41], Yakutia [42–49], Alaska [50], Canada [51–57], and the Kola Peninsula [58, 59], as well as compilations [60–62] and many other publications, which cannot all be listed here.

The collected data on the composition of groundwater from the permafrost zone is summarized in Table 2, which indicates that ultrafresh and fresh waters are most common. They are mainly calcium–sodium bicarbonate in composition and have a total salinity of less than 0.5 g/l. Minor variations in their composition between regions are controlled by the intensity of water exchange; the composition of aquifer rocks; regional metallogenic characteristics; the intensity of biological processes; types of soils; and the influence of cryogenic processes, for instance, periodic freezing and thawing of the active layer, freezing of water at discharge sites during the winter period, migration of moisture in the

upper part of the permafrost, and other processes. Various combinations of these factors and processes under local conditions produce particular compositions and salinities of groundwaters.

Among the aforementioned factors, the intensity of water exchange is of special importance. It controls total dissolved solids: the higher the water exchange (Baltic shield, Canadian shield, Yenisei Range), the lower the salinity of groundwater. For given water exchange conditions and rock types, total dissolved solids are controlled by the time of water–rock contact or the depth of water migration. This is the reason for the regular increase in the salinity of groundwaters in the course of their movement from a drainage divide to the base of slopes observed by many researchers.

Another important feature of water from northern regions is the high content of organic acids. According to Nikitina [47], organic compounds account for 10–75% of total dissolved solids in wetland areas; i.e., the concentration of organic acids in the water is higher than that of mineral matter and reaches 25–40 mg/l recalculated to C<sub>org</sub>. Also important is the great role of fulvic acids among the nonvolatile components of organic matter. The contribution of fulvic acids to the total amount of organic acids is up to 80% and five to ten times higher than that of humic compounds. This is a consequence of specific climatic conditions (low temperatures), relatively weak water exchange, close connection of water with soils, and (most importantly) relatively weak and short-term water–rock interaction owing to the small thickness of the active layer and, consequently, short paths of water migration in rocks.

Minor variations in the contents of dissolved solids and particular elements in the groundwaters of the permafrost province allowed us to calculate their average compositions separately for wetland, tundra, and northern taiga ter-

**Table 2.** Chemical composition of groundwater from the zone of intense water exchange in the permafrost province

Component	Unit	Siberian Platform	Yenisei Range	Transbaikalia	Maya R. basin	Olenek R. basin	Aldan	Alaska	Yukon, Canada
1	2	3	4	5	6	7	8	9	10
pH	–	6.9	6.8	7.0	6.8	8.0	6.3	6.8	6.9
HCO <sub>3</sub> <sup>-</sup>	mg/l	118	96.3	125	176	160	52.9	108	33.8
SO <sub>4</sub> <sup>2-</sup>	"	8.3	2.5	4.6	6.5	8.3	1.2	13.3	5.9
Cl <sup>-</sup>	"	10.9	6.8	4.0	1.0	5.6	1.4	11.4	3.5
F <sup>-</sup>	"	0.1	0.12	0.46	0.1	0.3	0.22	0.1	0.08
Ca <sup>2+</sup>	"	16.9	20.1	20	39.0	35.8	9.1	28.9	10.2
Na <sup>+</sup>	"	6.1	9.9	13.6	2.4	27.9	0.7	9.1	5.1
Mg <sup>2+</sup>	"	9.9	5.3	9.3	16.0	6.4	4.9	7.4	2.3
K <sup>+</sup>	"	0.7	1.2	1.7	–	–	0.2	1.4	0.6
SiO <sub>2</sub>	"	9.2	10.3	17.5	6.6	6.5	6.6	12.8	6.2
Al	"	0.29	0.13	0.30	0.03	1.26	0.15	–	0.08
Fe	"	0.38	0.35	0.18	0.3	0.4	0.23	0.34	0.06
Total	"	182	147	179	241	242	83.4	187	64
C <sub>org</sub>	"	9.2	–	12.0	10.8	–	6.8	–	8.0
CO <sub>2</sub>	"	14.0	–	12.1	–	–	5.5	–	6.1
Zn	μg/l	8.5	7.5	13.7	70.0	4.0	22.1	40	18.5
P	"	–	10.6	7.0	–	–	2.6	4.4	30.5
Sr	"	15.0	28.0	–	40.0	16.0	16.5	–	–
Mn	"	12.7	8.9	7.3	46.0	3.0	3.0	26.0	9.0
Ba	"	15.9	6.6	2.1	20	–	18.7	–	–
Li	"	–	9.1	0.2	12.5	–	0.3	–	–
Ti	"	9.7	6.6	2.5	3.0	2.0	5.1	–	1.3
Cu	"	2.5	0.9	4.4	7.0	2.0	1.7	1.0	3.5
Cr	"	3.4	1.7	0.9	–	2.33	5.9	–	0.6
Sb	"	1.4	0.1	0.5	0.37	–	–	–	5.1
Ni	"	2.2	1.0	2.9	2.0	1.5	1.0	–	0.9
Pb	"	0.4	0.7	2.7	3.0	0.2	1.8	–	0.5
Zr	"	2.1	0.5	–	0.7	1.07	1.2	–	0.3
As	"	0.3	0.4	0.3	1.0	0.5	–	–	–
Mo	"	0.1	0.5	1.9	0.5	0.25	0.6	0.3	1.0
V	"	1.2	0.7	0.2	0.1	2.0	0.6	–	–
Ga	"	0.27	–	0.5	0.5	0.4	0.05	–	–
Sn	"	0.6	0.1	0.1	0.4	–	0.7	–	–
U	"	0.08	–	–	0.47	0.22	–	–	0.12
Co	"	0.2	0.1	0.5	0.1	–	0.2	–	0.15
Ag	"	0.13	0.08	0.09	0.7	0.3	0.02	–	0.5
Be	"	0.04	0.01	0.01	0.07	–	0.05	–	–
Au	ng/l	–	–	3.0	12	–	–	–	6.0
Number of analyses		415	8000	360	180	56	43	22	61

rains ignoring the areas of occurrence of particular types (Table 3).

The obtained data indicate that the regional groundwaters of the permafrost province are weakly acidic, ultrafresh, mainly calcium–magnesium bicarbonate, and rich in organic matter. The latter is especially characteristic of palustrine waters, which are distinguished by low total salinities; low pH values; and high contents of various organic compounds, including acids and nitrogen compounds [47, 48].

The inclusion of palustrine waters into the database for the calculation of average abundances resulted in an average salinity of groundwater from the permafrost province somewhat lower compared with previous estimates, but this does not lead to a fundamental revision. On average, the salinity of waters from tundra terrains is 2 times lower than that of northern taiga water and the salinity of palustrine waters is 1.5 times lower than that of tundra water. Correspondingly, palustrine waters are most acidic and contain lower amounts of almost all major and many trace components compared with other types. The waters of the tundra zone are intermediate in composition and more similar to the palustrine waters than to the waters of northern taiga terrains.

The same can be said of trace components in each landscape zone. For instance, the waters of the tundra zone differ from those of the northern taiga zone in higher contents of phosphorus, nickel, lead, rubidium, and cobalt only. The difference between the palustrine and tundra waters in trace components is even smaller: the former show higher concentrations of only iron, phosphorus, iodine, zirconium, and cobalt. The concentration ratios of the majority of elements in the waters of the landscapes considered are not proportional to the content of total dissolved solids, which suggests that the relationships between these parameters are more complex than a simple dependence of concentration on the amount of dissolved rock.

It should also be taken into account that, in addition to the overall low salinity of groundwaters, processes of continental salinization were observed in some cases (central Yakutia, Transbaikalia, Saskatchewan, etc.), where the salinity of waters above the permafrost table increased up to 1 g/l or higher. However, owing to their limited occurrence, such areas have only a small influence on the average salinity of waters from this province.

### 1.3. Groundwaters of the Province of Tropical and Subtropical Climate

Tropical regions extend over a wide band along the equator in Africa, South and Southeast Asia, Central and South America, Australia, and Oceania. In this zone, an abundance of heat is coupled with high precipitation, which intensifies the development of most geochemical processes. The climate is either humid equatorial or tropical with distinct dry and rainy seasons. The former type of climate is responsible for the

**Table 3.** Average chemical compositions of groundwaters from the permafrost province

Component	Unit	Landscape type			Average
		North- ern swamp	Tundra	North- ern taiga	
1	2	3	4	5	6
pH	–	6.23	6.54	6.82	6.53
HCO <sub>3</sub> <sup>–</sup>	mg/l	48.5	61.5	137	82.8
Cl <sup>–</sup>	"	4.13	4.03	5.91	4.67
SO <sub>4</sub> <sup>2–</sup>	"	1.91	4.84	5.26	4.05
NO <sub>3</sub> <sup>–</sup>	"	0.18	0.36	0.38	0.31
F <sup>–</sup>	"	0.16	0.17	0.21	0.19
NO <sub>2</sub> <sup>–</sup>	"	–	0.02	0.03	0.03
Ca <sup>2+</sup>	"	9.15	13.0	26.0	16.8
Na <sup>+</sup>	"	2.98	4.28	12.8	6.64
Mg <sup>2+</sup>	"	4.21	5.37	7.35	5.66
K <sup>+</sup>	"	0.46	0.84	1.22	0.83
NH <sub>4</sub> <sup>+</sup>	"	1.51	0.22	1.36	1.09
SiO <sub>2</sub>	"	6.65	7.60	11.7	8.63
Total	"	79.5	102	209	135
Free CO <sub>2</sub>	"	12.3	14.0	10.8	12.4
C <sub>org</sub>	"	17.6	10.1	9.3	12.3
Fe	μg/l	405	200	380	328
Al	"	150	160	340	216
P	"	26.3	19.1	21.7	22.6
Zn	"	12.4	23.0	31.8	22.4
Sr	"	16.5	21.3	26.3	20.8
Mn	"	11.0	12.3	15.1	12.7
Ba	"	7.12	10.0	10.2	9.09
Ti	"	3.18	3.34	5.64	4.09
Li	"	4.01	3.97	4.19	4.08
Cu	"	2.48	1.94	2.98	2.44
Cr	"	2.32	2.52	2.16	2.34
J	"	2.92	2.21	1.45	2.19
Ni	"	1.61	1.91	2.03	1.84
Pb	"	1.53	1.88	1.16	1.52
Rb	"	1.27	1.53	1.47	1.42
Zr	"	1.35	0.78	1.28	1.13
La	"	0.83	1.10	1.42	1.11
Sb	"	0.88	0.75	1.08	0.91
As	"	0.87	0.73	0.99	0.86
Mo	"	0.76	0.64	0.92	0.78
V	"	0.56	0.50	0.88	0.64
Nb	"	–	0.47	0.50	0.48
Sn	"	0.15	0.22	0.50	0.29
Co	"	0.34	0.30	0.24	0.29
Ga	"	0.14	0.30	0.38	0.27
U	"	0.18	0.25	0.34	0.25
Ag	"	0.20	0.21	0.29	0.24
Sc	"	0.18	0.06	0.05	0.10
Be	"	0.07	0.05	0.04	0.05
Au	ng/l	2.0	1.8	2.8	2.2
Number of regions		2	4	7	10



**Table 4.** Average compositions of groundwaters from various landscape zones of western Africa

Component	Unit	Wet savanna	Wet forest	Dry savanna	Steppe	Average (without steppe zone)
pH	–	5.3	6.1	6.8	7.0	6.1
HCO <sub>3</sub> <sup>–</sup>	mg/l	20.9	173	208	268	161
Cl <sup>–</sup>	"	5.9	6.5	4.8	65.3	5.6
SO <sub>4</sub> <sup>2–</sup>	"	3.7	6.4	3.6	48.5	5.1
NO <sub>3</sub> <sup>–</sup>	"	–	–	1.6	3.07	1.6
F <sup>–</sup>	"	0.08	0.09	0.24	0.3	0.14
NO <sub>2</sub> <sup>–</sup>	"	0.15	–	0.24	0.54	0.19
Ca <sup>2+</sup>	"	–	–	0.09	0.93	0.09
Na <sup>+</sup>	"	2.5	27.8	27.8	32.9	18.7
Mg <sup>2+</sup>	"	3.8	14.0	24.6	84.9	14.1
K <sup>+</sup>	"	0.5	15.3	18.4	14.7	11.4
NH <sub>4</sub> <sup>+</sup>	"	1.1	3.8	5.1	32.2	3.3
SiO <sub>2</sub>	"	–	–	0.07	1.1	0.07
pH	"	7.3	10	47.1	59.5	22.1
Total	"	45.7	259	329	612	243
C <sub>org</sub>	"	13.6	10.3	8.6	–	10.8
Free CO <sub>2</sub>	"	39.8	97	9.0	37.3	48.6
Fe	µg/l	71	280	365	723	239
Al	"	133	184	34	20	91.5
Mn	"	12.6	–	77.5	560	45.0
Sr	"	19.3	–	56	–	38.1
Zn	"	29.9	–	330	180	29.9
Ba	"	12.8	–	15	–	13.9
Pb	"	4.6	3.2	–	–	3.9
Rb	"	5.3	3.0	3	–	3.8
Li	"	2.2	–	5.0	–	3.6
Ti	"	2.4	–	4.0	–	3.2
Cu	"	2.4	2.6	2.7	70	2.6
Mo	"	1.6	–	2.0	–	1.8
Ni	"	1.2	–	2.0	–	1.6
Cr	"	1.2	–	2.0	–	1.6
V	"	0.5	0.7	–	–	0.6
Ag	"	0.19	0.13	–	–	0.16
Number of analyses		162	105	63	54	330

development of wet tropical forests, and the latter, grassy tropical savanna.

The groundwaters of the tropical zone were comprehensively studied by us in western Africa, where two types of climate were distinguished: (1) equatorial Guinean along the coast of the Gulf of Guinea and (2) tropical Sudanian in the interior continental areas of the region. The equatorial climate type is characterized by high amounts of precipitation (2000–4800 mm/yr), which falls almost year-round; persistently high humidity (80–100%); and moderate mean annual temperatures (24–27°C). The number of rainy days in an average year may be as high as 200 and never decreases below 120. Therefore, the dry season is short (1.5–2.0 months) and indistinct; rain also falls during this period, although less intensely. This is favorable for the development of humid tropical forests in a narrow band along almost the whole Gulf of Guinea coast. The abundance of moisture and heat results in the rapid growth of vegetation and, correspondingly, the extreme density of forests and the abundance of tree and grass species. These forests have the highest biological productivity on Earth, averaging 3250 t/(km<sup>2</sup> yr) [63].

The tropical type of climate is characterized by higher mean annual temperatures (27–29°C), greater annual temperature variations, lower humidity, and lower precipitation: 750–2000 mm/yr in the savanna zone and 200–750 mm/yr in the steppe zone. The average number of rainy days is 50–120 in the savanna zone and 20–50 in the steppe zone. The distribution of rainfall within the year is rather uneven, and there are, therefore, two distinct seasons: a wet season, lasting in the savanna zone from May to October, when the entire amount of rainfall falls, often as tropical showers, and a dry season, lasting from November to May, when precipitation is absent and the air temperature rises to 40°C or even higher. In the steppe zone, the dry season is even longer and hotter. During the wet period, savannas are covered by lush grassy vegetation, which is strongly dominated by elephant grass, reaching 5 m in height. During the dry season, the grass cover perishes and the savanna is transformed into a brown desert. The biological productivity of savannas is high, for instance, 1200 t/(km<sup>2</sup> yr) for the territory of Ghana [64].

The geochemical characterization of groundwaters from western Africa was based on our own data [65] and materials of other authors for Guinea [66, 67], Côte d'Ivoire [66, 68], Senegal [69], northern Nigeria [70], Ghana [71], etc.

The aforementioned and other publications on the chemistry of groundwater from the supergene zone of particular regions of western Africa (Table 4) indicate its considerable diversity, controlled by the annual amount and distribution of precipitation, the intensity of water exchange, the type of host rocks, and landscape conditions. The least saline and most acidic waters are formed in the savanna zone, where there is considerable precipitation and active water exchange, which is promoted, among other factors, by the existence of a hilly relief. With decreasing precipitation and,



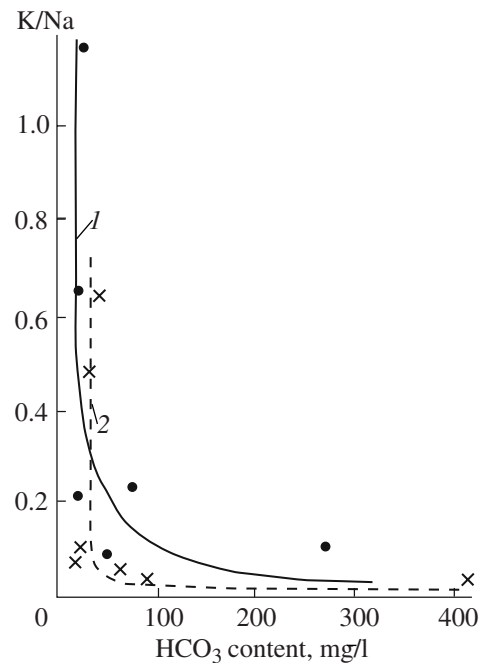
consequently, decreasing runoff, the salinity and pH of groundwater increase gradually owing to the carbonation weathering of silicates. It should be pointed out that the acidic pH of soils and high  $\text{CO}_2$  partial pressure promote the development of an acidic environment, which is favorable for the migration of most chemical elements, including the hydrolysate elements. The latter gradually precipitate from the solution below the soil horizon.

In the zone of humid tropical forests, perennially high humidity, a more uniform rainfall distribution within the year, and dense population reduce the intensity of runoff, which results in a somewhat higher total water salinity compared with the savanna zone. The less intense remineralization of organic matter under these conditions is related to the absence of a distinct dry season and promotes the formation of less acidic waters. At the same time, the abundance of dissolved organic substances in the waters promotes the formation of organomineral complexes, which enhances the migration of hydrolysate elements.

Under the conditions of flat topography and moisture deficit in the tropical steppe zone, groundwaters may undergo continental salinization, which leads to an increase in their total salinity. The increase in salinity in this case is connected not only with bicarbonate compounds, but mainly with chloride and sulfate salts. The latter play a minor role during the early stages of evaporative concentration but gradually become dominant in the salt composition under conditions of increasing salinization. However, the interaction of waters with host rocks continues, which is indicated by the observed uneven accumulation of particular elements.

In addition to western Africa, we used data on groundwater composition from Cuba [72, 73], New Caledonia [74, 75], North Vietnam [76], the Hawaiian Islands [77–80], southern France [68], the southern United States [81–85], California [81, 86, 87], Brazil [88], Madagascar [68], Guyana [89], Indonesia [89], Jamaica [90], Argentina [91], the Batumi coast of the Caucasus [92], etc.

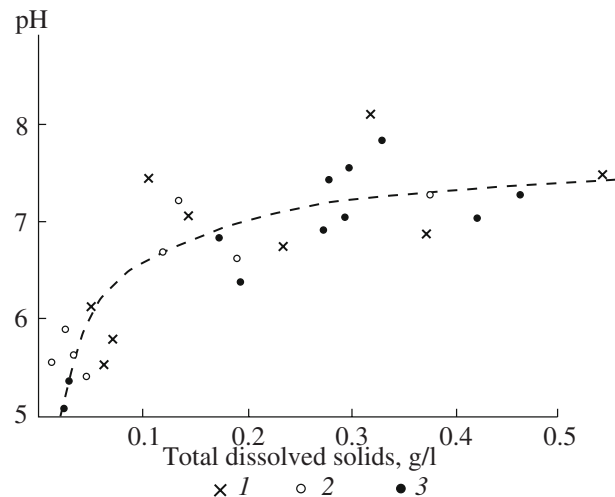
The extensive dataset on the composition of waters from the upper hydrodynamic zone of the tropical and equatorial belt of the Earth provides insight into their main characteristics and allows us to calculate the average abundances of chemical elements. First, it should be pointed out that ultrafresh and fresh waters with a total salinity of 0.1 g/l usually occur within these vast areas. Their salinity increases only under drier climatic conditions and may reach 1 g/l in arid savannas (Chad) (Table 4). The waters are bicarbonate with variable cation composition, which is controlled by the type of host rocks. The dependence of the cation composition on the chemistry of aluminosilicates is most clearly manifested in the ultrafresh waters. For instance, the waters of granites are usually sodic (southern France), sodic-calcic (Benin), or even potassic-sodic (Côte d'Ivoire); the waters of mafic-ultramafic rocks are magnesian (New Caledonia) or sodic-magnesian (Hawaiian



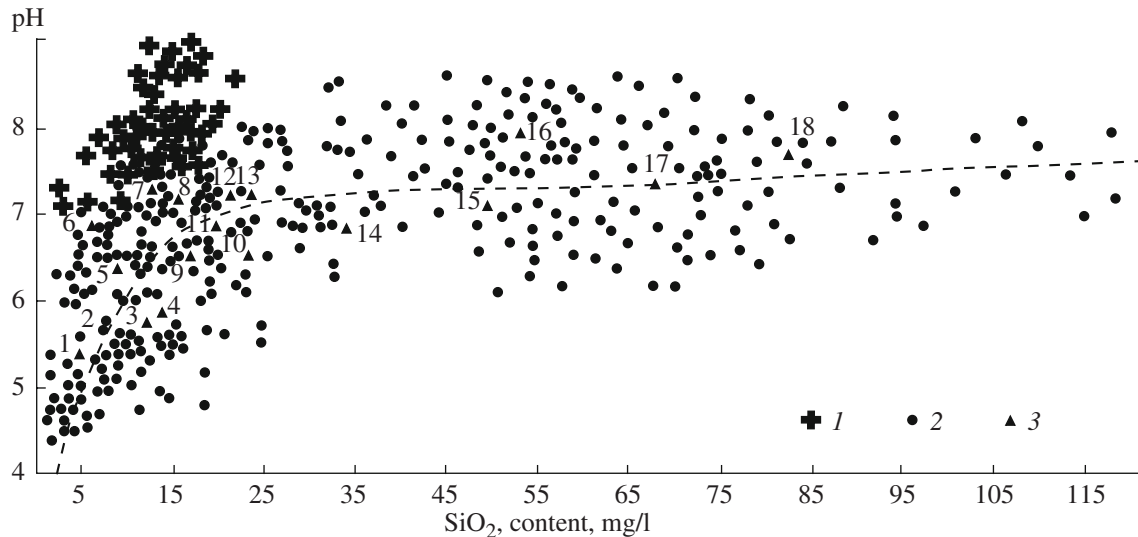
**Fig. 2.** Changes in the K/Na value of water with an increase in the concentration of bicarbonate ion for (1) waters from granites and granite gneisses and (2) waters from mafic rocks.

Islands). It is important that the freshest waters of granites are enriched in potassium, whereas the role of this element decreases dramatically with an increase in total salinity, while the fraction of sodium increases; as a result, the K/Na ratio decreases with increasing salinity (Fig. 2).

Another characteristic feature of groundwater geochemistry is that the pH value increases with increasing total salinity (Fig. 3). It is important that this



**Fig. 3.** Dependence of pH value on the total salinity of groundwaters from (1) basic and ultrabasic rocks, (2) granites and granite gneisses, and (3) various sedimentary rocks.



**Fig. 4.** Silica content in groundwater as a function of pH value. (1) Waters from carbonate rocks, (2) waters of carbonate-free rocks, and (3) average contents of  $\text{SiO}_2$  in waters from particular regions. Numbers in the diagram: 1, Guinea; 2, southern France; 3, Côte d'Ivoire; 4, Hawaiian Islands; 5, Gabon; 6, Jamaica; 7, New Caledonia; 8, Madagascar; 9, North Vietnam; 10, Batumi coast of the Caucasus; 11, Corsica; 12, southern United States; 13, Calcutta region; 14, northern Nigeria; 15, Cuba; 16, California; 17, Senegal and 18, Chad.

tendency is observed in waters from almost any type of aluminosilicate rocks: the rank correlation coefficient between these parameters is 0.80 at an acceptable significance level of 0.52.

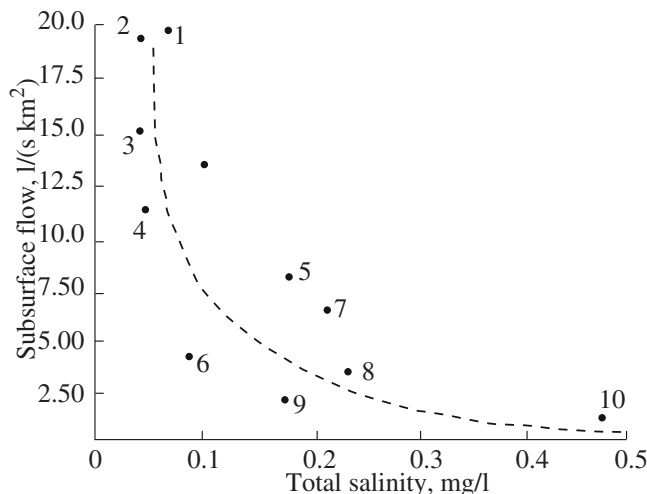
An increase in the pH value of water is accompanied by a sharp increase (especially within the pH range from 5.0 to 7.0) in water silica content (Fig. 4), which is almost independent of the type of host rocks. The only exception is carbonate rocks, which host waters

with rather low  $\text{SiO}_2$  contents at relatively high pH values. Because of this, the waters of this type are shown by a special symbol in Fig. 4.

Despite the increase in the absolute content of silica in waters with increasing salinity and pH, its relative concentration decreases continuously. This can be especially clearly seen from a comparison of silica content with the total of other cations (Table 5). For instance, this ratio is higher than 2.0 in the ultrafresh waters of southern France and Côte d'Ivoire and decreases to 0.36 in the fresh waters of Chad. This is the third important feature that needs to be addressed.

Finally, it should be emphasized that the analysis of spatial variations in the total salinity of groundwater reveals primarily its correlation with the intensity of water exchange: the lower the water exchange, the higher the water salinity. This is clearly observed in the regions of western Africa, Cuba, the southern United States, etc. For instance, according to the data of Bugel'skii [73], the contents of magnesium and silica in waters from ultrabasic rocks of Cuba increase dramatically with decreasing water exchange intensity (Table 6). The same tendency was established for the whole province (Fig. 5).

Consequently, regions with the most intense water exchange contain the freshest and most acidic waters. With decreasing water exchange intensity, both the pH values and the total salinity of waters from the same rocks increase. The proportions of elements concentrated in the solution change, which indicates different trends of water–rock interaction in different geochemical environments.



**Fig. 5.** Dependence of the total salinity of groundwater on the intensity of water exchange for (1) Guinea, (2) southern France, (3) the Korhogo region, (4) Madagascar, (5) Côte d'Ivoire, (6) Benin, (7) North Vietnam; (8) Florida, (9) northern Nigeria, and (10) Senegal.

**Table 5.** Average geochemical characteristics of groundwaters from selected regions of the tropical and subtropical belts

Geochemical parameter	Unit	Southern France	Côte d'Ivoire	Guinea	Brazil	Hawaiian Islands	New Caledonia	Northern Nigeria	Southern United States	California	Senegal
1	2	3	4	5	6	7	8	9	10	11	12
pH	–	5.9	5.6	5.4	6.7	5.8	7.4	6.8	7.2	8.0	7.4
HCO <sub>3</sub> <sup>-</sup>	mg/l	6.5	10.9	14.0	30.0	24.0	60.5	75.2	148	122	341
Cl <sup>-</sup>	"	2.5	2.7	6.3	0.8	14.8	8.3	4.6	8.7	22.3	5.0
SO <sub>4</sub> <sup>2-</sup>	"	1.2	0.6	0.3	0.4	9.3	0.6	4.8	5.8	37.5	2.4
NO <sub>3</sub> <sup>-</sup>	"	–	–	–	1.9	0.9	–	1.6	2.1	3.4	–
F <sup>-</sup>	"	–	–	–	0.21	0.12	–	0.24	0.31	0.97	–
PO <sub>4</sub> <sup>3-</sup>	"	–	–	–	–	0.09	–	0.08	0.20	0.12	0.6
Na <sup>+</sup>	"	2.4	1.3	6.2	2.1	12.4	3.2	16.2	19.4	45.9	33.6
Ca <sup>2+</sup>	"	0.8	1.7	0.9	5.4	3.8	1.4	17.6	21.3	17.2	38.0
K <sup>+</sup>	"	0.5	1.5	1.3	1.2	1.1	0.2	6.9	2.1	2.8	3.2
Mg <sup>2+</sup>	"	0.3	0.2	0.3	2.0	3.4	7.8	3.2	4.8	9.8	33.2
NH <sub>4</sub> <sup>+</sup>	"	–	–	–	–	0.02	–	0.07	–	–	–
SiO <sub>2</sub>	"	8.2	11.0	3.7	26.8	11.7	11.7	28.3	19.6	28.0	66.0
Total	"	22.4	30.2	33.0	70.9	93.4	93.7	169	232	291	423
Fe	µg/l	72	53	90	88	36	100	650	185	92	79
Al	"	23	6.8	26	17	79	33	20	129	96	48
Sr	"	8.8	19	–	–	–	4.3	–	138	100	56
B	"	–	–	–	–	35	–	–	–	41	–
Ba	"	5.2	17	6.8	–	–	3.0	–	–	–	15
Zn	"	–	–	30	–	–	–	330*	48.5	46	–
Cr	"	3.1	1.2	–	–	–	5.6	–	–	–	2.6
Ti	"	1.7	2.2	2.5	–	–	2.5	–	–	0.6	4.1
Mn	"	1.5	23	1.8	–	154	2.9	140*	27.6	67	15
Rb	"	1.5	5.3	–	–	–	0.5	–	–	–	3.5
Cu	"	1.2	3.5	1.3	–	–	6.1	110*	14.5	8.6	3.4
Li	"	1.2	2.2	–	–	–	0.5	–	–	–	5.2
V	"	<1.0	<0.5	–	–	–	0.5	–	–	–	4.3
Ni	"	<1.0	1.1	1.4	–	1.8	6.7	–	–	–	2.7
Mo	"	<1.0	0.5	2.7	–	–	1.2	–	–	–	2.1
Pb	"	<1.0	4.6	–	–	–	3.0	–	–	0.4	–
Co	"	<0.3	–	–	–	–	1.0	–	–	0.3	–
U	"	–	–	–	–	–	–	–	0.65	1.1	–
Ra	pg/l	–	–	–	–	–	–	–	0.47	0.1	–
K/Na	–	0.24	1.15	0.2	0.55	0.05	0.05	0.42	0.11	0.06	0.09
SiO <sub>2</sub> /ΣCations	–	2.05	2.34	0.42	0.40	0.50	0.94	0.65	0.42	0.36	0.60
Number of analyses		171	123	44	42	28	37	46	92	25	17

\* Values are evidently overestimated.

**Table 6.** Characteristics of silica and magnesium removal in various hydrogeological zones of Cuba

Type of water exchange	Subsurface flow rate, l/(s km <sup>2</sup> )	Median concentration in water, mg/l		Subsurface ion flow, g/(s km <sup>2</sup> )		Outflow with groundwaters, t/(yr km <sup>2</sup> )	
		Mg <sup>2+</sup>	SiO <sub>2</sub>	Mg <sup>2+</sup>	SiO <sub>2</sub>	Mg <sup>2+</sup>	SiO <sub>2</sub>
Retarded	0.44	73	80	0.032	0.035	1.01	1.11
Medium intensity	14.47	33	48	0.477	0.694	15.0	21.9
Intense	17.17	10	16	0.172	0.274	5.41	8.65
Very intense	28.73	8	12	0.229	0.344	7.24	10.9

The calculated average abundances of chemical elements in groundwaters for the whole province of the tropical belt are given in Table 6. In addition to the results of the aforementioned publications, these estimates also included data for Madagascar, Corsica [68], Brazil [93, 95], the islands of the Vietnamese shelf [96],

and New Zealand [97]; unpublished results of Shi Wei-Tsung for eastern China; etc.

Analysis of the data from Table 7 shows that the freshest waters occur in humid savannas, under the conditions of the highest water exchange. This can be exemplified by the territory of Guinea, where ultrafresh

**Table 7.** Average chemical compositions of groundwaters from the province of tropical and subtropical climate

Component	Unit	Landscape zone				Overall average	Component	Unit	Landscape zone				Overall average
		Wet savanna	Tropical forests	Sub-tropical forests	Dry savanna and steppe				Wet savanna	Tropical forests	Sub-tropical forests	Dry savanna and steppe	
pH	—	5.3	6.1	6.9	7.2	6.4	Mn	"	59.7	33.3	24	52.6	42.4
HCO <sub>3</sub> <sup>-</sup>	mg/l	21.6	103	119	194	109	B	"	35.0	—	40.5	—	37.7
Cl <sup>-</sup>	"	4.6	6.0	8.2	10.6	7.35	Zn	"	29.9	36.5	47.2	—	37.6
SO <sub>4</sub> <sup>2-</sup>	"	3.5	3.7	6.2	15	7.10	J	"	4.0	—	20.0	—	12.0
NO <sub>3</sub> <sup>-</sup>	"	1.2	1.3	2.4	1.6	1.52	Ba	"	11.7	13.0	5.2	9.0	9.11
F <sup>-</sup>	"	0.15	0.22	0.37	0.24	0.22	Ni	"	1.2	4.0	4.9	7.6	4.92
PO <sub>4</sub> <sup>3-</sup>	"	0.09	0.20	0.18	0.39	0.22	Cu	"	2.4	3.4	6.6	4.5	4.63
NO <sub>2</sub> <sup>-</sup>	"	0.05	—	—	0.09	0.07	Ti	"	2.3	3.6	3.8	3.2	3.35
Ca <sup>2+</sup>	"	3.8	16.1	19.8	28.1	16.6	Cr	"	1.1	—	2.2	3.8	2.25
Na <sup>+</sup>	"	4.7	8.9	12.5	17.8	10.9	Li	"	3.8	—	1.2	2.7	2.22
Mg <sup>2+</sup>	"	1.4	8.2	9.31	19.1	8.07	Rb	"	5.3	—	1.5	1.7	2.21
K <sup>+</sup>	"	2.9	2.7	2.4	1.7	2.25	Pb	"	4.6	2.1	0.6	2.5	2.05
NH <sub>4</sub> <sup>+</sup>	"	0.02	0.13	0.14	0.07	0.09	Mo	"	1.6	—	1.6	1.4	1.55
SiO <sub>2</sub>	"	10.3	17.6	23.1	31.6	20.9	Co	"	—	1.9	1.2	1.0	1.41
Total	"	56	170	203	318	185	V	"	2.2	—	1.0	0.5	1.23
Free CO <sub>2</sub>	"	44.8	97	—	—	63.1	U	"	—	—	0.7	1.24	0.97
C <sub>org</sub>	"	3.3	10.9	8.16	4.12	6.62	Ag	"	0.19	—	—	—	0.19
Fe	μg/l	60.8	396	185	362	251	Se	"	—	—	—	0.13	0.13
Al	"	83.7	369	82.3	32.2	147	Au	ng/l	—	1.3	3.0	—	2.1
Sr	"	19.3	26.8	82	30.2	47.5	Ra	pg/l	—	—	0.47	0.1	0.29
							Number of regions		4	5	3	4	10



waters are formed under very intense water exchange. Unfortunately, the rate of subsurface flow is not known for the majority of regions and thus this problem cannot yet be considered in full detail. Nonetheless, it is evident that water salinity increases with decreasing water exchange. For instance, in terms of total water salinity, humid savanna is followed by tropical and equatorial forests; subtropical forests; and, finally, dry savanna and steppe, where the most saline and alkaline waters occur, although their absolute values of both salinity and alkalinity are not high. It should be pointed out that the total salinity of groundwater increases primarily at the expense of bicarbonate ions and equivalent amounts of cations. The proportions of cations (but not their contents) are controlled mainly by the composition of the host rocks.

A characteristic feature of waters from this province is a relatively high content of silica and free CO<sub>2</sub> and low content of organic carbon. The latter fact requires additional explanation. It is generally believed that the waters of the tropics are very rich in organic matter. However, this problem is not fully understood, and, to our knowledge, there are no special studies on the hydrochemistry of organic matter. The only exception is the study of Lenheer et al. [98], who systematized the abundance of the nonvolatile part of C<sub>org</sub> in waters from 27 states of the United States, including some southern regions with tropical (Florida) and subtropical (California, Alabama, Arkansas, New Mexico, etc.) climates.

Lenheer et al. [98] reported C<sub>org</sub> contents for nine samples from Florida showing that the maximum value is 15 mg/l and the average is 3.12 mg/l. The waters of other states showed even lower average C<sub>org</sub> contents: 1.3 mg/l for California, 0.19 mg/l for Alabama, 1.2 mg/l for Arkansas, etc. Thus, the average concentrations obtained by us on the basis of a limited analytical database probably adequately reflect the following general relation: the highest contents of C<sub>org</sub> are characteristic of waters from tropical and equatorial forests, and the lowest contents are typical of dry savanna and steppe.

We emphasize again that the waters of the humid tropics are acidic rather than alkaline as was previously thought. The most acidic waters are observed not in the zone of tropical forests but under the conditions of well-drained humid savanna, which is characterized by prolonged dry seasons. This fact leads to the very important conclusion that the acidity of savanna waters is related mainly to carbonic acid rather than to organic acids. The role of organic acids increases drastically only in the forest zone, where high and almost year-round humidity is favorable for the humification of organic matter. In other climatic (drier) zones, the major portion of organic matter is not humified.

#### 1.4. Groundwaters of the Province of Temperate Humid Climate

The zone of a temperate humid climate includes considerable areas of the boreal belt (almost all of Europe and most of North America and Asia) and part of the southern belt (Australia and the southern regions of Africa and South America). This vast zone has diverse natural conditions and includes taiga, forest steppe, and partly steppe and broadleaf forest landscapes. Summer in this province is usually relatively wet, and winter is characterized by a considerable amount of snow. This prevents the formation of liquid surface runoff during part of the year and promotes its increase in the spring season, which results in the predominance of surface runoff over subsurface flow.

The geochemistry of groundwaters from the temperate humid climate zone was studied by the example of the southern part of Krasnoyarsk krai (Kansk–Taseevskaya and Rybinskaya troughs), the Tomsk region, Salair, the Kuznetsk Basin, Khakassia, wetland areas in the southeastern part of West Siberia, the Kolyvan'–Tom' folded zone, the basin of the Tom' River, and other localities.

In terms of orography, the region is a strongly peneplaned flatland with average absolute altitudes of 200–300 m above sea level (ASL). The relief is usually relatively flat and hilly and, in general, inclined from the mountain massifs of the Kuznetsk Alatau and the Salair Range toward the West Siberian lowland. The climate of this region is sharply continental; the mean annual temperature ranges from –0.6 (Tomsk) to +1.0°C (Barnaul). The amount of precipitation is 300–550 mm/yr and decreases slightly from north to south. In the same direction, landscape conditions change from the zone of southern taiga in the north to typical forest steppes and steppes in the south, and gray forest podzolic soils give way to leached chernozems. The coefficient of river runoff varies widely, from 10 to 65%, usually being between 25 and 50%; the rate of subsurface flow ranges from 0.2 to 9.6 l/(s km<sup>2</sup>) and averages 1.9 for the taiga zone and 1.6 l/(s km<sup>2</sup>) for the forest steppe zone. The rate of surface runoff is on average three times higher and equals 5.7 l/(s km<sup>2</sup>).

The most important geologic feature is the existence of two structural units: a lower level composed of Paleozoic complexes strongly dislocated in the late Hercynian phase of tectogenesis and an upper level of unconsolidated, mainly sandy–clayey sediments of Mesozoic–Cenozoic age, 0–40 m thick (occasionally up to 100 m). Loess-like carbonate loams and clays underlain by fine-grained sands occur among Middle and Late Quaternary rocks, which are rather widespread in water divides. Ancient weathering mantles, mainly of kaolinite–illite composition, and subordinate bauxite-bearing clays lie on the surface of Paleozoic complexes [29, 99].

The waters of the upper structural level are assigned to the interstitial formation type, and the waters of the lower level to the fracture type owing to the presence of

**Table 8.** Average chemical compositions of groundwaters from the main landscapes of the southern part of West Siberia

Chemical component	Unit	Main landscapes			
		Swamps	Forests	Forest steppes	Steppes*
pH	–	5.33	7.21	7.36	7.74
HCO <sub>3</sub> <sup>–</sup>	mg/l	38.4	315	396	542
Cl <sup>–</sup>	"	11.0	6.4	14.1	61
SO <sub>4</sub> <sup>2–</sup>	"	2.6	4.1	16.3	51
NO <sub>3</sub> <sup>–</sup>	"	1.3	1.8	2.6	1.8
F <sup>–</sup>	"	0.15	0.23	0.37	0.41
PO <sub>4</sub> <sup>3–</sup>	"	0.26	0.13	0.29	0.37
Ca <sup>2+</sup>	"	10.1	66	75	68
Mg <sup>2+</sup>	"	3.7	21	28	29
Na <sup>+</sup>	"	2.1	38	41	87
K <sup>+</sup>	"	1.2	2.6	2.9	5.3
NH <sub>4</sub> <sup>+</sup>	"	3.8	0.3	0.42	0.57
SiO <sub>2</sub>	"	–	14.1	17.3	19.4
Total	"	74.3	469	594	865
C <sub>org</sub>	"	53.9	5.8	6.9	7.1
Free CO <sub>2</sub>	"	17.6	22.3	24.2	29.3
Fe	"	1.91	1.1	0.8	0.7
Al	µg/l	124	221	260	319
Sr	"	87	77	153	511
Mn	"	75	46	38	83
Br	"	–	340	570	626
Ba	"	11	6.3	8.9	13.6
B	"	–	–	3.1	4.6
Zn	"	13	28	34	63
Ti	"	2.8	7.3	5.0	16.2
Li	"	–	7.4	8.3	10.5
Cu	"	1.9	2.1	2.4	4.6
Ni	"	0.7	2.2	1.8	4.1
I	"	–	2.7	3.1	3.7
Pb	"	1.3	1.8	1.9	1.9
As	"	–	1.5	1.7	0.9
V	"	0.6	0.5	0.9	2.3
Zr	"	–	0.6	0.8	1.2
Cr	"	1.9	4.2	2.3	4.8
Mo	"	–	0.4	0.35	0.81
Sn	"	–	0.2	0.31	0.43
Ag	"	–	0.18	0.24	0.43
U	"	–	0.17	0.53	0.61
Sb	"	–	0.08	0.21	0.44
Cd	"	–	0.13	0.16	0.21
Co	"	–	0.11	0.32	0.36
Be	"	–	0.09	0.15	0.27
Ga	"	–	0.25	0.36	0.63
Hg	ng/l	–	24	33	36
Au	"	–	2.0	2.8	3.3
Number of analyses		93	941	1740	345

\* Waters showing no apparent signs of continental salinization.

a thick fractured zone in the upper layer of bedrocks. In accordance with lithological characteristics, the lower level may contain aquifers of sandy–shale, volcanosedimentary, limestone, and granite complexes.

The northern part of this large region comprises extended wetland areas, which are formed owing to the high amount of precipitation, weak evaporation related to the deficit of heat, flat relief, and presence of confining beds. With respect to the scale of wetland areas, this region is a phenomenon unique in the world [100].

In addition to our own data, the analysis of the chemical composition of groundwaters from this vast territory was based on results reported by Udodov et al. [101], Rogov and Popov [102], Pokatilov [103], Kopylova et al. [104, 105], Rasskazov et al. [99, 106–108], Inisheva and Inishev [109], Ermashova [110], Zuev et al. [111], Dutova and Pokrovskii [112], and Parnachev et al. [113, 114]. The average compositions of waters from the main landscape zones of the southern part of West Siberia are given in Table 8.

It can be easily seen from these data that the most acidic and freshest waters occur in the wetland areas. Their chemistry is strongly dependent on the local geomorphology: the most acidic (pH 3.5–5.0) and ultrafresh (in most cases, total dissolved solids <30 mg/l) waters occur in smoothed water divides. The alkalinity and salinity of palustrine water increase toward river valleys. The content of metals in waters increases in the same direction.

The behavior of organic substances is different: their contents are highest in the waters of raised bogs and decrease dramatically toward valleys [100, 115]. It should be pointed out that the contents of organic substances in raised bogs are much higher than the contents of dissolved mineral components, which indicates the unique composition of this water type.

The salinity of waters from all other landscape zones of the southern part of West Siberia is much higher and increases gradually from the forest zone toward the steppe zone. The waters of the taiga zone are usually fresh and mainly of calcium or calcium–magnesium bicarbonate composition with a salinity of 300–600 mg/l. Their salinity increases considerably and may reach 1 g/l under the conditions of open steppes, which results in the formation of sodium–calcium bicarbonate waters. With depth, the salinity of water increases and may often be higher than 1 g/l, while the pH values increase up to 9.0. As a result, the content of Ca decreases owing to calcite saturation and precipitation.

The analysis of the behavior of major cations in groundwaters with increasing total salinity (Fig. 6) reveals a gradual transition from sodic to calcic waters. The maximum increase in Ca content in waters is observed within the salinity range 0.2–0.6 g/l; at higher salinities the increase of Ca ceases and it gives way to Na. The increase in Na content is retarded at a salinity of 0.4–0.5 g/l, at which magnesium content increases more rapidly; the opposite tendency is observed at

water salinities higher than 0.7 g/l. Groundwaters with a salinity of more than 0.7 g/l are mostly calcite-saturated, and, therefore, these waters are sodic if their total salinity is higher than 1 g/l.

An important feature of groundwaters from the region considered is, thus, their elevated salinity and transition at a certain depth (0.3–1.0 km) from Ca–Na bicarbonate to Na–Ca and then Na waters. Consequently, sodic waters are formed there at a certain salinity and, thus, a certain stage of water–rock interaction.

The distribution of organic matter in fresh waters was studied by us in detail in a taiga region in the Kuznetsk Basin (Krapivinskii) [106]. The waters of this region contain various organic compounds, including humic substances (humic acids, fulvic acids, etc.), petroleum series hydrocarbons, fatty acids, nitrogen-bearing organic compounds, and (sporadically) polychlorinated biphenyls and polycyclic aromatic hydrocarbons. At the same time, the contents of such compounds as chlorinated organic pesticides are lower than the sensitivity levels of the analytical methods. The total organic carbon content ( $C_{org}$ ) in the groundwaters varies considerably, from 0.4 to 18.6 mg/l; nonvolatile petroleum hydrocarbons, from <0.02 to 0.5 mg/l; fatty acids, from traces to 0.24 mg/l; and fulvic acids, from <0.1 to 0.3 mg/l. The concentration of humic  $C_{org}$  reaches 12 mg/l, and the average concentrations of organic compounds in the waters are moderate: the total  $C_{org}$  is no higher than 5.7 mg/l; humic  $C_{org}$ , 4.1 mg/l;  $C_{org}$  of petroleum substances, 0.13 mg/l; and of fatty acids, 0.16 mg/l.

Analyses of groundwater from the upper hydrodynamic zone of temperate climate regions are available for a number of localities worldwide, including Finland [116–121], Sweden [122–125], Lithuania [126], Poland [16, 127, 128], Germany [9, 20, 129], France [68, 130, 131], the Czech Republic [12, 132–135], Slovakia [136], Ireland [137], Scotland [138], England [139], Belarus [140–145], the United States [81–83, 146–150], Kazakhstan [151, 152], and many areas in Russia [153–161]. The average compositions of groundwaters from some of these regions are given in Table 9.

The analysis of these data showed that the waters of the temperate humid climate province are diverse in composition and salinity: their pH values (5.0–8.5) are weakly acidic, near neutral, or weakly alkalic, and their total salinities (0.05–0.9 g/l) correspond to ultrafresh, moderately fresh, and fresh waters. The freshest and most acidic waters were reported from regions with active water exchange and shallow bedrock occurrence, which is favorable for rapid water migration (Scandinavia, France, Iceland, etc.). Waters with a total salinity of more than 0.5 g/l occur in regions with relatively low precipitation in steppe and forest steppe terrains at sites where thick unconsolidated sequences (usually, more than 100 m) isolate bedrocks from direct interaction with precipitation and suppress water exchange (the

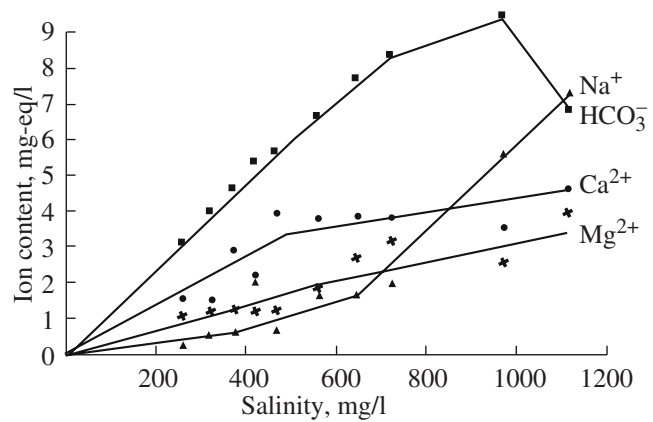


Fig. 6. Dependence of the cation composition of waters from southern West Siberia on their salinity.

Great Plains of the United States, the Baltic countries, Kazakhstan, etc.). It should be noted that most common are bicarbonate waters with diverse (most frequently, Ca–Na) cation compositions, whose pH and concentrations of most elements (including trace elements) increase with increasing total salinity. The concentrations of dissolved organic matter are usually not high, except for the wetland and soil water types.

The calculated average abundances of chemical elements in the waters of the whole province are given in Table 10. In addition to the above-cited studies, additional data for the calculation of these values were taken from [162–192].

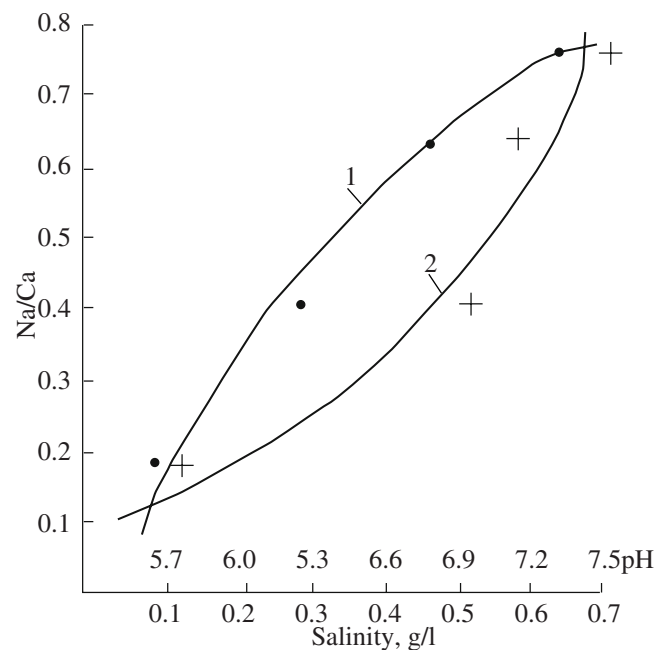


Fig. 7. Dependence of the Na/Ca ratio of groundwater on (1) total salinity and (2) pH value.

**Table 9.** Chemical compositions of groundwaters from selected countries with a temperate humid climate

Component	Unit	France	Finland	Sweden	Poland	Czech Republic	Northeastern United States	Belarus	Texas, United States	Lithuania	Kazakhstan
1	2	3	4	5	6	7	8	9	10	11	12
pH	–	6.82	6.16	6.98	6.44	6.18	7.48	7.23	7.56	7.33	7.07
HCO <sub>3</sub> <sup>-</sup>	mg/l	23.6	34.1	27.5	67.6	113	156	226	287	360	266
SO <sub>4</sub> <sup>2-</sup>	"	11.6	11.0	23.1	18.8	53.8	38.0	17.5	25.8	26.1	91.4
Cl <sup>-</sup>	"	7.4	9.2	10.7	19.9	4.5	10.8	20.7	24.6	19.7	65.9
NO <sub>3</sub> <sup>-</sup>	"	3.9	4.1	1.2	7.2	2.7	3.2	7.4	6.3	0.7	2.4
NO <sub>2</sub> <sup>-</sup>	"	–	–	0.01	–	0.02	–	–	–	0.01	–
PO <sub>4</sub> <sup>3-</sup>	"	0.07	0.02	0.10	0.22	0.07	0.09	0.23	0.13	–	–
F <sup>-</sup>	"	0.31	0.21	–	0.26	0.28	0.36	0.45	1.05	0.48	–
Ca <sup>2+</sup>	"	8.6	10.4	14.5	18.4	36.3	35.6	56.1	55.6	66.8	49.0
Mg <sup>2+</sup>	"	3.4	3.2	6.6	4.9	10.2	10.4	13.8	26.1	24.2	54.5
Na <sup>+</sup>	"	7.2	5.1	10.6	19.1	6.4	21.4	19.9	25.6	35.1	73.6
K <sup>+</sup>	"	2.3	1.8	1.3	3.9	3.2	2.8	3.4	6.0	3.6	8.2
NH <sub>4</sub> <sup>+</sup>	"	–	–	0.17	0.85	1.1	–	–	–	0.45	0.14
SiO <sub>2</sub>	"	16.5	15.8	8.0	10.4	16.5	24.9	11.1	32.6	–	–
Total	"	75.3	94.9	103	170	244	304	376	493	536	611
Free CO <sub>2</sub>	"	–	18.5	16.7	–	13.3	–	6.8	–	50.8	–
C <sub>org</sub>	"	–	6.9	–	–	–	–	5.1	2.2	2.9	–
Fe	µg/l	469	150	826	770	396	390	941	10.9	1125	–
Al	"	178	110	–	93.4	203	110	180	95.3	186	–
Mn	"	4.7	19.3	147	48.3	101	48.0	14.7	–	49	181
Sr	"	30.9	45.0	32.1	100	–	172	185	940	–	–
Br	"	–	90	11.4	–	–	–	12.6	–	200	127
Ba	"	20.7	13.0	11.0	15.0	–	–	22.7	–	269	45.8
Zn	"	–	10.0	134	15.1	91.0	77.5	24.4	–	40	37.9
Li	"	4.6	2.6	5.5	–	34.0	–	2.7	–	–	–
Rb	"	14.1	2.7	3.5	1.5	–	–	2.8	–	–	–
B	"	–	7.8	–	36.1	5.7	–	39.5	–	162	35
Cu	"	2.7	2.7	6.3	5.3	4.9	5.7	1.8	–	2.2	6.9
Ni	"	2.8	1.4	–	4.0	–	–	4.9	–	–	9.0
Co	"	0.8	0.8	0.2	0.03	–	–	0.6	–	1.5	0.4
Cr	"	4.3	1.8	1.4	1.0	–	–	0.2	–	12.5	7.0
Pb	"	–	1.2	3.5	3.6	6.3	–	0.24	–	3.1	5.4
V	"	1.5	0.6	–	–	1.6	–	0.5	–	–	2.9
Mo	"	1.6	0.2	1.0	–	–	–	0.7	–	1.5	4.1
Ti	"	5.2	–	3.0	–	2.2	–	2.3	–	–	12.7
As	"	–	0.34	4.3	–	–	–	4.7	–	–	1.4
Cd	"	–	0.02	–	–	0.94	–	–	–	–	–
U	"	–	0.46	0.12	–	0.27	0.72	–	1.3	–	–
Cs	"	–	–	2.9	–	–	–	–	–	–	–
Sb	"	0.2	<0.02	0.9	0.13	–	–	0.09	–	–	–
Se	"	–	0.3	0.37	0.05	–	–	0.4	–	3.8	–
Be	ng/l	–	–	–	–	–	–	10	–	27	–
Sc	"	–	–	16	70	–	–	–	–	–	–
Au	"	14.0	–	3.0	–	–	–	–	–	–	–
Ra	pg/l	–	–	–	–	–	0.34	–	0.26	–	–
Number of analyses		92	7506	25	40	418	284	216	66	362	1035



**Table 10.** Average chemical compositions of groundwater from the province of temperate humid climate

Component	Unit	Landscape type				Overall average
		Wetland	Mixed forest	Southern taiga	Forest steppe and steppe	
1	2	3	4	5	6	7
pH	–	5.73	6.88	7.12	7.45	6.82
HCO <sub>3</sub> <sup>-</sup>	mg/l	44.8	129	312	398	222
SO <sub>4</sub> <sup>2-</sup>	"	10.9	13.0	8.04	40.7	18.2
Cl <sup>-</sup>	"	6.11	13.3	12.4	29.8	15.9
NO <sub>3</sub> <sup>-</sup>	"	0.36	5.32	1.09	1.87	2.13
F <sup>-</sup>	"	0.04	0.29	0.35	0.38	0.26
NO <sub>2</sub> <sup>-</sup>	"	–	0.10	0.08	0.12	0.10
Ca <sup>2+</sup>	"	11.9	26.7	49.8	65.3	38.3
Na <sup>+</sup>	"	2.10	16.1	32.3	51.2	23.8
Mg <sup>2+</sup>	"	4.22	8.67	22.1	30.5	16.5
K <sup>+</sup>	"	0.68	3.02	3.38	4.04	2.74
NH <sub>4</sub> <sup>+</sup>	"	1.19	0.37	0.41	0.23	0.52
SiO <sub>2</sub>	"	7.19	14.9	15.1	15.5	13.3
Total	"	89.5	231	457	638	354
Free CO <sub>2</sub>	"	22.8	14.7	24.4	21.0	20.7
C <sub>org</sub>	"	22.2	5.56	5.06	6.58	9.86
Fe	µg/l	860	469	855	583	689
Sr	"	145	104	152	321	185
Al	"	101	202	185	178	165
P	"	191	59.5	57.1	75.8	98.2
Br	"	15.7	64.2	102	270	85.6
Mn	"	39.9	57.3	66.9	75.6	59.2
B	"	17.9	80.7	55.0	70.3	55.9
Zn	"	49.9	36.4	37.4	40.8	42.8
Ba	"	27.7	27.4	19.6	22.5	25.3
Li	"	7.67	11.0	10.3	13.7	10.7
Ti	"	2.07	7.36	7.46	18.4	8.82
J	"	3.06	7.67	4.86	6.78	5.59
Cu	"	5.08	4.29	3.88	5.41	4.85
Ni	"	2.37	4.11	3.42	3.69	3.45
Pb	"	4.68	4.12	1.65	1.98	3.10
Cr	"	1.25	4.02	3.24	3.62	2.83
Rb	"	0.36	4.76	2.48	2.83	2.55
As	"	0.75	2.46	1.74	1.52	1.64
Zr	"	3.0	1.18	0.71	1.24	1.51
Nb	"	–	1.16	–	1.62	<1.40
V	"	0.68	1.45	0.87	2.11	1.28
Mo	"	0.56	1.08	0.65	1.28	0.89
Se	"	0.39	0.37	0.44	1.36	0.64
Sb	"	0.53	0.39	0.55	0.74	0.55
Ga	"	0.21	0.63	0.38	0.87	0.52
U	"	0.38	0.42	0.51	0.75	0.51
Sn	"	0.10	0.57	0.31	0.76	0.44
Co	"	0.15	0.37	0.28	0.52	0.34
Be	"	0.01	0.13	0.21	0.60	0.24
Ag	"	0.26	0.21	0.17	0.32	0.24
Cd	"	0.08	0.15	0.21	0.19	0.15
Th	"	0.09	0.06	0.08	0.21	0.11
Hg	ng/l	58	23	26	68	44
Au	"	2.1	5.8	4.3	12.0	6.1
Ra	pg/l	0.05	0.13	0.08	0.34	0.20
Number of regions		4	10	6	7	17

The obtained data show that, in accordance with the general climatic and landscape zoning, the freshest and most acidic waters are formed in the zones of northern and waterlogged taiga and the most saline and alkaline waters occur in the zones of southern taiga and forest steppes. The zone of mixed forests is intermediate in this respect. Consequently, the salinity of groundwater increases with decreasing water exchange intensity from north to south. This fact was recognized by V.S. Il'in and P.V. Ototskii. This is accompanied by changes in the macro- and microcomponent composition of waters.

On average, groundwaters from all landscape zones show bicarbonate anion compositions, whereas their cation composition is strongly variable. In particular, Ca–Mg waters occur in wetlands, Ca–Na waters occur in mixed forests, and Ca–Mg–Na waters occur in the southern taiga and forest steppes. The contents of almost all of the major components, silica, and some trace components (F, Br, Mn, Ti, U, Sb, Be, and Se) increase with increasing total salinity. The contents of iron, aluminum, and most other trace elements show much more complex relations. In addition, there is a group of elements concentrating in palustrine environments, i.e., in low-salinity waters. Among them are K, Fe, P, Zn, Cu, Zr, Pb, and N, as well as, to a lesser extent, Ba, Sb, Hg, Ag, and Th. The most salient feature of wetland waters is the high content of organic matter, which decreases rapidly with an increase in pH and total salinity. For instance, the concentration of  $C_{\text{org}}$  in waters from wetlands averages 22.2 mg/l, which is three times higher than that of waters from the forest steppe zone (6.58 mg/l). The abundance of organic substances in waters from wetlands is accompanied by high concentrations of many metals.

During the early stages of formation of the chemical compositions, waters are enriched mainly in biogenic elements in the soil horizon and waterlogged areas and in lithogenic elements in the subsoil. During the early stages of lithogenic evolution, their composition is controlled by the type of host rocks and the direction of their weathering, whereas selective sodium accumulation becomes possible during subsequent stages, when the total salinity becomes higher than 0.6–0.8 g/l and the waters equilibrate with calcite (Fig. 6). This results in the formation of sodic waters with a salinity of 0.8–5.0 g/l. The latter is supported by an increase in the Na/Ca ratio of waters with an increase in their total salinity and pH (Fig. 7).

It should be pointed out that each landscape zone is characterized by a specific geochemical type of water and a certain geochemical environment with particular values of total salinity, pH, and Eh and contents of  $O_2$ ,  $C_{\text{org}}$ ,  $N_{\text{org}}$ ,  $SiO_2$ , etc. Another important geochemical parameter is the partial pressure of  $CO_2$ , which controls the state of carbonate equilibrium, the direction of organic matter transformation, water–aluminosilicate interaction, etc. In this respect, it is noteworthy that,

according to the data of Harmon et al. [193], the values of  $P_{CO_2}$  in carbonate rocks are connected with the water temperature  $T$  by the following expression:

$$\log P_{CO_2} = -3.16 + 0.07T \quad (1.1)$$

This implies that an increase in the water temperature by 1°C leads to an increase in  $P_{CO_2}$  by 0.07 atm, or  $7 \times 10^3$  Pa. At 25°C,  $P_{CO_2}$  is  $10^{-1.41}$  atm, or  $10^{3.59}$  Pa.

### 1.5. Groundwaters of Mountain Regions

In terms of general geography, mountain regions, occupying vast areas on Earth, are azonal phenomena, and their hydrogeology therefore deserves special attention. Diversity of natural conditions, intense water exchange, dissected topography, and relatively low mean annual air temperatures are the main factors controlling the hydrogeological features of mountain massifs.

The hydrogeochemistry of the Altai–Sayan folded region is rather well known owing to the many years of research undertaken there by the Laboratory of Hydrogeochemical Problems of Tomsk Polytechnical University and other organizations [6, 37, 99, 104, 194–201].

The Altai–Sayan folded region, occupying considerable areas in southern Central Siberia, is a system of deeply eroded ranges, mostly covered with taiga, with elevations up to 4000 m ASL and even higher (Western and Eastern Sayan, Gornyi Altai, Kuznetsk Alatau, etc.), which are separated by intermontane depressions (Kuznetsk, Tuva, Minusinsk, etc.). The mountain massifs sequentially give way westward and northward to hilly highlands (Salair and Rudnyi Altai), high flatlands (Kuznetsk Basin, Kolyvan'–Tom' highland), and the plains of West and East Siberia.

The mountain massifs are made up of strongly metamorphosed sedimentary and volcanogenic rocks of the Archean, Proterozoic, and Early to Middle Paleozoic, which are assembled into compressed and occasionally overturned folds, fragmented by numerous faults and cut by intrusions of various compositions. The intermontane depressions are filled with Paleozoic and, in part, Mesozoic rocks assembled into relatively gentle folds.

The mountain massifs are characterized by a sharply continental climate, excessive moistening, elevated subsurface flow rate values (3–6 or, occasionally, up to 6–8 l/(s km<sup>2</sup>)), negative mean annual temperatures, and the presence of permafrost and permanent glaciers in the highest areas. The annual precipitation varies widely, from 100–200 mm/yr in intermontane steppes to 400–600 mm/yr in piedmont zones and 1000 mm/yr in the most humid mountain massifs. The major portion of precipitation falls in the autumn–summer period. The variability of hydrologic and climatic conditions leads to the diversity of landscape zones, from mountain tundra to mountain steppes. This region is, there-

fore, one of the most interesting for the investigation of genetic aspects of groundwater chemistry.

The hydrogeological peculiarities of this region are related to the abundance of fracture waters, which occur mainly in the upper fractured zones of bedrocks, and, in part, fracture–formation waters, confined to superimposed structures. The main aquifers are confined to Cambrian–Proterozoic carbonate rocks and Early–Middle Paleozoic volcanosedimentary complexes. The recharge of groundwaters is usually local and related to precipitation. The considerable amount of precipitation, prolonged periods of snow melting, and strongly dissected topography are, in general, favorable for groundwater recharge and development of intense water exchange. The latter factor is responsible for the low salinity of groundwaters, from 0.1 g/l in water divides to 0.5 g/l in the transitional areas near intermontane depressions. In the same direction, Na–Ca bicarbonate waters give way to waters with more complex compositions.

The Altai is a typical mountain range of the region. Table 11 gives the average compositions of groundwaters from this area. It can be seen that the composition of waters displays a clear belt zoning. For instance, the main geochemical features of waters from mountain meadow terrains are their extremely low salinity (about 100 mg/l), weakly acidic pH values (outside carbonate rock complexes), Na–Ca bicarbonate compositions, and low concentrations of trace components. Waters from the areas of carbonate rock occurrence are weakly alkaline and somewhat more saline, although the concentrations of the majority of trace components in them are even lower.

The groundwaters of mountain forest terrains have a more alkaline, mainly Ca–Mg bicarbonate composition and relatively high salinity. From the forest to the steppe zone, the composition of groundwater changes from Ca–Mg bicarbonate to Ca–Na and the average salinity increases from 360 to 750 mg/l. There are indications of continental salinization in the waters of the steppe zone, including the accumulation of sulfates and chlorides in the solution. The pH values increase rather significantly in the same direction.

Consequently, the total salinity of groundwater increases with decreasing absolute altitude; decreasing degree of relief ruggedness; and a change in landscape conditions from mountain tundra and alpine meadows (high mountains), through the moderately humid forest zone (middle mountains), to forest steppe terrains with chernozem soils. However, the contents of most chemical elements increase unevenly and show complex patterns, suggesting the existence of geochemical barriers for many of the chemical elements. This is a consequence of a variable character of water–rock interaction.

Table 12 summarizes data on the composition of groundwater from the whole mountain part of the Sayan–Altai region. The analysis of this evidence reveals some general relations in the formation of the

**Table 11.** Average chemical compositions of groundwaters from the Altai

Component	Unit	Landscape			Average
		Mountain meadow	Mountain taiga	Mountain steppe	
pH	–	6.9	7.55	7.90	7.43
HCO <sub>3</sub> <sup>–</sup>	mg/l	72.5	248	355	226
Cl <sup>–</sup>	"	3.55	5.07	94.8	34.5
SO <sub>4</sub> <sup>2–</sup>	"	2.75	12.1	85.0	32.6
Ca <sup>2+</sup>	"	13.9	54.7	83.8	52.2
Na <sup>+</sup>	"	5.9	12.1	78.3	32.4
Mg <sup>2+</sup>	"	5.45	15.6	38.5	17.6
K <sup>+</sup>	"	1.15	1.26	5.61	2.67
SiO <sub>2</sub>	"	9.61	11.4	9.12	10.1
Total	"	104	364	750	408
Free CO <sub>2</sub>	"	4.40	9.25	13.5	8.82
O <sub>2</sub>	"	7.0	6.4	4.63	6.02
C <sub>org</sub>	"	4.8	5.11	5.24	5.05
Fe	μg/l	353	389	776	506
Al	"	86.5	327	522	312
F	"	131	195	316	214
Sr	"	98	127	348	191
Mn	"	8.5	15.4	185	64.6
Ti	"	1.81	2.65	33.2	16.7
Zn	"	8.35	15.6	17.6	13.9
Ba	"	6.9	15.2	16.4	12.4
Cu	"	1.93	3.15	7.25	4.11
Cr	"	0.95	2.15	3.75	2.26
Pb	"	0.35	2.85	4.71	2.64
Ni	"	0.32	0.85	2.45	1.23
V	"	0.12	0.65	1.75	0.89
U	"	0.53	0.93	1.18	0.88
As	"	1.07	0.48	0.55	0.72
Be	"	0.05	0.35	0.91	0.44
Sb	"	0.23	0.38	0.56	0.39
Mo	"	0.05	0.37	0.43	0.28
Zr	"	0.50	0.14	0.09	0.24
Cd	"	0.15	0.19	0.31	0.22
Sn	"	0.13	0.31	0.13	0.19
Co	"	0.03	0.19	0.31	0.17
Ag	"	0.10	0.15	0.24	0.16
Ga	"	0.02	0.08	0.18	0.09
Hg	"	0.009	0.032	0.059	0.033
Number of analyses		122	338	146	606

**Table 12.** Chemical compositions of groundwaters from the Sayan–Altai region

Component	Unit	Landscape zone			
		Mountain tundra and alpine meadows	Mountain taiga	Mountain steppe	Average
1	2	3	4	5	6
pH	–	6.82	7.20	7.63	7.22
HCO <sub>3</sub> <sup>-</sup>	mg/l	65.6	189	357	209
SO <sub>4</sub> <sup>2-</sup>	"	2.21	5.34	47.2	18.6
Cl <sup>-</sup>	"	4.55	6.12	39.9	16.9
NO <sub>3</sub> <sup>-</sup>	"	–	1.74	1.24	1.82
NO <sub>2</sub> <sup>-</sup>	"	–	0.19	0.11	0.15
Ca <sup>2+</sup>	"	11.5	38.4	69.7	39.9
Na <sup>+</sup>	"	6.52	14.1	47.8	22.4
Mg <sup>2+</sup>	"	5.32	12.7	32.1	17.3
K <sup>+</sup>	"	0.63	0.87	3.12	1.62
NH <sub>4</sub> <sup>+</sup>	"	–	0.41	0.38	0.39
SiO <sub>2</sub>	"	7.86	11.3	15.0	11.6
Total	"	104	279	641	339
Free CO <sub>2</sub>	"	4.63	8.72	12.3	8.55
O <sub>2</sub>	"	7.22	6.26	2.92	5.47
C <sub>org</sub>	"	4.81	6.22	5.04	5.36
Fe	μg/l	320	425	538	423
F	"	131	195	398	241
Al	"	166	243	308	238
Sr	"	68.3	75.1	302	147
B	"	–	37.2	50.0	43.6
Br	"	–	9.69	73.5	41.5
P	"	–	40.2	40.8	40.5
Mn	"	10.9	21.8	62.6	36.8
Zn	"	9.06	13.8	35.1	19.8
Ba	"	5.82	10.3	29.2	16.0
Ti	"	3.11	21.6	21.8	15.5
Li	"	–	8.03	17.4	12.7
J	"	1.63	2.89	10.3	4.94
Cu	"	2.06	2.52	5.65	3.38
Cr	"	1.21	2.45	2.54	2.31
Ni	"	1.18	1.46	2.79	1.89
Pb	"	1.13	1.65	2.55	1.77
As	"	0.77	0.72	1.72	1.06
Zr	"	0.62	0.84	1.40	0.93
U	"	–	0.53	1.03	0.78
Sb	"	0.31	0.37	0.88	0.52
V	"	0.36	0.83	0.49	0.51
Mo	"	0.35	0.53	0.66	0.46
Sn	"	0.29	0.36	0.55	0.40
Ga	"	0.09	0.12	0.66	0.30
Be	"	0.15	0.18	0.37	0.23
Co	"	0.15	0.15	0.32	0.22
Cd	"	–	0.21	0.23	0.22
Ag	"	0.12	0.22	0.28	0.21
Bi	"	–	0.16	0.17	0.16
Y	"	0.06	0.08	0.12	0.08
Hg	ng/l	10	30	70	40
Au	"	–	6.0	4.0	5.0
Number of analyses		248	4227	693	228

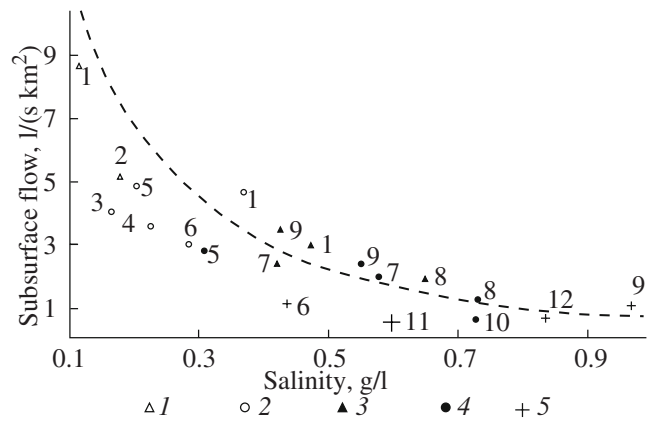


chemical composition of waters in mountain regions. First of all, there is an evident regular correlation between the total salinity of water and the intensity of water exchange: the freshest waters are formed under the conditions of the most intense water exchange (strongly dissected high mountain regions). In those areas where water exchange is depressed, waters with elevated salinity are formed even in high mountain regions (Chuya Steppe). In the direction from high mountain terrains, through middle mountains, and toward low mountains and plains, the salinity of groundwater increases monotonously and in forest steppe terrains may be as high as 1.0 g/l even in the absence of distinct indications of continental salinization. The inverse dependence of groundwater salinity on the intensity of water exchange, which is quantified by the rate of subsurface flow, is clearly seen in Fig. 8, which shows data for intermontane (Kuznetsk Basin) and low mountain (Kolyvan'-Tom' folded zone) regions.

The waters of the region considered are mostly Ca or Ca-Mg bicarbonate in composition, including low-salinity varieties from high mountain regions. With increasing salinity, the fraction of Na and, especially, Mg increases and the waters of low mountain terrains are almost ubiquitously Ca-Mg and sometimes even Mg-Na in composition (the piedmont of the Gornyi Altai), which is related to their high alkalinity, preventing Ca accumulation in the solution. In the forest steppe and, especially, steppe regions, the role of magnesium and sodium further increases and the water composition becomes Mg-Ca (Baitak Range) or, in a highly alkaline environment, Na-Mg (Chuya Steppe); i.e., soda waters occur there. The concentrations of most trace components in the groundwaters increase with increasing total salinity, although the enrichment factors are different for different elements.

Groundwater geochemistry was also studied by us in the Kurama Mountains (spurs of the Tien Shan, Uzbekistan), which are characterized by a dissected relief with elevations from 500 to 3700 m ASL [6, 29]. The climate is sharply continental, with precipitation being from 300 (low mountains) to 1000 mm/yr (high mountains). The considerable precipitation results in a relatively high subsurface flow ranging from 1–2 (low mountains) to 3–4 l/(s km<sup>2</sup>) (high mountains).

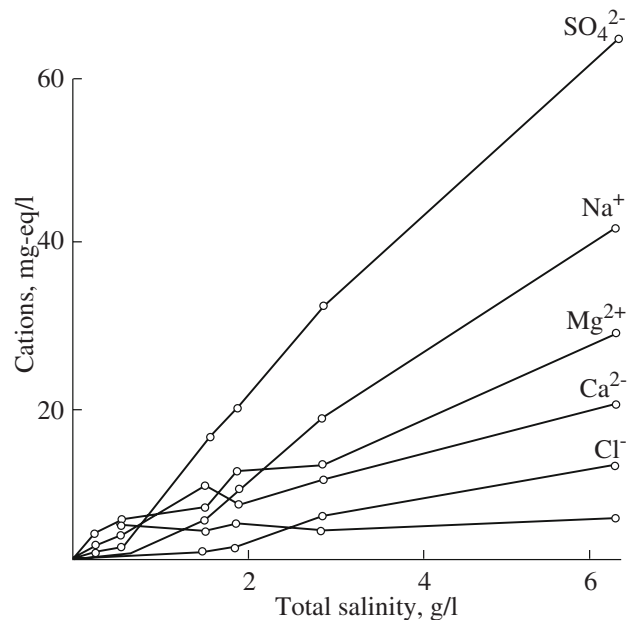
The intense water exchange in the medium and high mountain areas of the Kuramas leads to the formation of fresh Ca-Na bicarbonate waters with a total salinity of less than 1 g/l. In the low mountain zone, the prevalence of evaporation over precipitation promotes the early development of sulfate salinization with an increase in groundwater salinity up to 8 g/l. Owing to this, a distinct vertical geochemical zoning is observed in the region: fresh bicarbonate waters of high mountain areas are gradually replaced at decreasing altitudes by brackish sulfate waters with a variable cation composition. It is important that this relation has a regional character and is independent of the composition of the



**Fig. 8.** Total salinity of groundwaters as a function of the magnitude of subsurface flow. (1–5) Landscapes: (1) high mountains, (2) middle mountain taiga, (3) low mountain taiga, (4) low mountain forest steppe, and (5) mountain steppe. Numbers in the diagram: 1, Gornyi Altai; 2, Tannu Ola-Sangilen region; 3, Western Sayan; 4, Eastern Sayan; 5, Kuznetsk Alatau; 6, Rudnyi Altai; 7, Salair; 8, Tom'-Kolyvan'; 9, Kuznetsk Basin; 10, Baitak Range; 11, Tuva Depression; and 12, Chuya Steppe.

underlying rocks. The composition of waters changes regularly with increasing salinity.

The freshest waters are Ca-Mg bicarbonate-sulfate ones (Fig. 9). Such water compositions are observed at salinities of 0.1–0.7 g/l. In some cases, Na or Mg dominates in the solution instead of Ca. The salinity of the Mg waters ranges from 0.3 to 0.6 g/l, and that of the Na waters is from 0.5 to 0.8 g/l; i.e., the Na waters show the highest salinity among the bicarbonate-sulfate waters. The average concentrations of chemical elements in the waters of this type are shown in Table 13.



**Fig. 9.** Ion composition of groundwaters from the Kurama Range as a function of their salinity.

**Table 13.** Average abundances of chemical elements in the groundwaters of selected regions of the mountain province

Chemical component	Unit	Sangre de Cristo, United States	Sierra Nevada, United States	Norway	Sikhote Alin, Russia	Kurama Mountains, Uzbekistan	Bol'shoi Karatau, Kazakhstan
pH	–	7.23	6.75	8.07	6.96	7.52	7.26
HCO <sub>3</sub> <sup>-</sup>	mg/l	35.7	41.7	32.7	10.6	170	291
SO <sub>4</sub> <sup>2-</sup>	"	7.65	1.78	5.39	6.82	34.8	75.3
Cl <sup>-</sup>	"	0.14	0.97	4.91	10.1	5.88	18.5
NO <sub>3</sub> <sup>-</sup>	"	0.16	0.24	0.46	1.32	4.5	4.3
PO <sub>4</sub> <sup>3-</sup>	"	–	0.03	0.05	0.09	–	–
F <sup>-</sup>	"	–	0.07	0.28	0.41	–	–
Ca <sup>2+</sup>	"	11.7	7.12	16.6	13.1	43.0	47.4
Na <sup>+</sup>	"	1.28	4.32	6.31	16.3	14.6	18.7
Mg <sup>2+</sup>	"	1.06	2.11	2.23	11.4	10.8	15.8
K <sup>+</sup>	"	0.46	1.30	1.66	0.9	2.5	π1.7
NH <sub>4</sub> <sup>+</sup>	"	–	–	–	–	0.37	0.16
SiO <sub>2</sub>	"	5.77	20.3	10.2	16.6	18.8	–
Total	"	53.9	79.9	81.8	172	301	444
Free CO <sub>2</sub>	"	–	–	–	16.9	11.2	–
C <sub>org</sub>	"	–	–	–	2.8	1.6	–
Fe	µg/l	47.7	25.6	18.6	48.7	–	227
Sr	"	23.7	65.0	122	106	44.6	414
Br	"	–	38.1	30.6	26.3	–	–
Al	"	20.7	29.2	13.0	108	–	402
Ba	"	14.0	–	15.6	7.7	21.1	11.8
Zn	"	–	–	14.0	19.5	10.3	40.1
Cr	"	8.7	–	0.14	1.3	1.8	4.1
B	"	5.0	–	14.0	11.6	15.7	–
Cu	"	1.8	–	16.1	1.3	1.5	2.1
Mn	"	2.4	5.6	–	18.5	17.1	20.3
Ni	"	1.6	–	0.53	0.9	1.6	1.5
Pb	"	1.3	–	0.36	0.4	1.7	3.8
V	"	–	–	0.24	1.3	0.4	1.6
Ti	"	1.2	–	0.59	0.09	8.8	20.5
As	"	–	–	0.18	2.2	3.7	–
Li	"	0.8	–	2.9	12.1	–	–
J	"	–	3.6	0.6	4.5	–	–
Ga	"	–	–	0.013	<0.07	–	0.3
Mo	"	0.3	–	1.4	1.6	0.7	1.7
Rb	"	0.1	–	2.6	0.7	–	–
U	"	0.6	0.9	2.5	0.6	–	–
Sb	"	–	–	0.03	0.2	0.6	0.4
Co	ng/l	50	–	65	66	410	450
Be	"	40	–	12	46	–	–
Ag	"	20	–	2.0	<100	70	70
Au	""	–	–	–	4.1	4.5	–
Sn	"	–	–	8.0	–	190	120
Cd	"	–	–	17	<50	–	–
Ra	pg/l	0.1	0.13	–	–	–	–
Number of analyses		23	102	1604	84	598	707

**Table 14.** Variations in element ratios accompanying an increase in the total salinity of water

Total salinity, g/l	Cl/SO <sub>4</sub>	Na/Ca	Na/Mg	Cl/Na	Cl/Ca	Cl/Mg
0.27	0.17	0.18	1.06	0.69	0.12	0.73
1.50	0.09	0.64	2.02	0.53	0.34	1.06
1.86	0.10	1.28	1.53	0.47	0.61	0.73
2.84	0.12	1.93	2.91	0.47	0.92	1.38
6.18	0.13	2.29	2.75	0.46	1.06	1.27

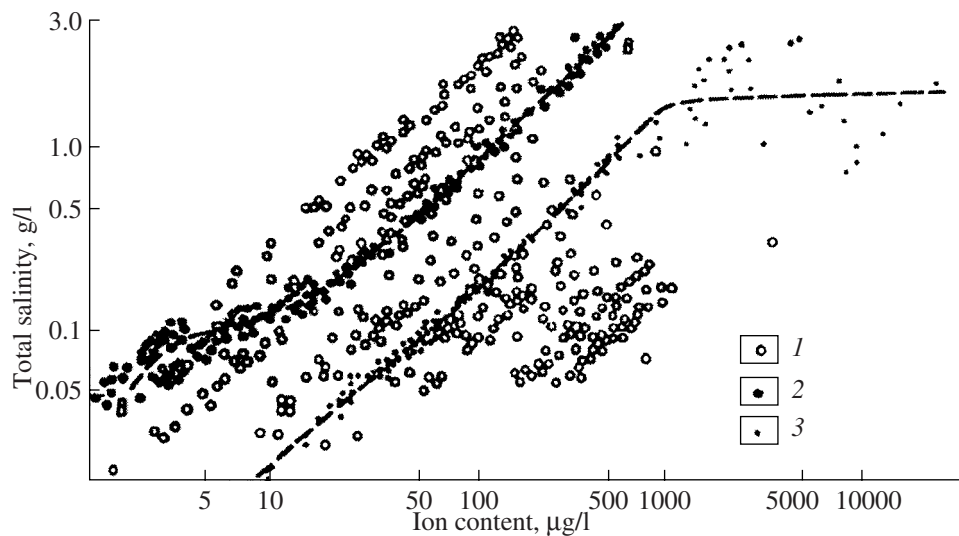
The total salinity of sulfate-type waters is higher than 0.8 g/l. As in the case of the bicarbonate type, the least mineralized are calcic and the most mineralized are sodic waters. A transition between these subtypes is usually observed at a salinity of 1.5–2.0 g/l. Magnesium may be the dominating cation in some cases, at salinities of 1.6–2.5 g/l. Waters with a salinity of higher than 2.5 g/l are always sodium sulfate in composition. In atomic units, magnesium is more abundant than calcium.

Thus, even a cursory survey of the behavior of the main elements in the composition of groundwaters from the Kurama Range indicates a variable degree of their concentration with an increase in the content of total dissolved solids. This is supported by the data of Table 14.

The nonuniform enrichment of solutions in individual elements during their concentration indicates the existence of geochemical barriers preventing the accumulation of some elements in the solution. In particular, the considerable increase in Na/Ca and Cl/Ca values suggests that the behavior of calcium is controlled by a barrier related to saturation of the solution with calcite and gypsum.

It should also be noted that the silica concentration in waters remains practically invariant with increasing total salinity. This indicates that, in addition to calcite and gypsum, clay minerals also precipitate from the solution. They fix magnesium, potassium, and to a lesser extent sodium and calcium. This is the reason for the increase in Na/Ca and Na/Mg in waters (Table 14). In contrast, the Cl/Na ratio decreases with increasing salinity, which indicates that Na is more rapidly accumulated in saline waters compared with Cl. This fact can only be attributed to continuous Na input into the groundwaters from primary aluminosilicates.

Thus, the analysis of the available material suggests that the sulfate waters of the Kurama Range owe their existence to both continental salinization and more complex processes of the decomposition of primary aluminosilicates and sulfides with the formation of clays, carbonates, and occasional gypsum. Some of the chemical elements are intensely accumulated in the solution (Na, Cl, S, Mg, Sr, and B) (Fig. 10), and other elements less so (Ca, K, Mn, Ti, As, Cr, and Mo); the concentration of yet others may increase to a certain level and then decrease (N, Ba, Zn, Sb, V, and Au) or show only a negligible increase (Si, Pb, Ni, Cu, Co, Cd, Sn, Be, Ag, and Sr).

**Fig. 10.** Dependence of the contents of (1) barium, (2) boron, and (3) strontium on the salinity of groundwaters from the Kurama Range.

**Table 15.** Average chemical compositions of groundwaters from mountain regions

Chemical component	Unit	Landscape type			Average	Chemical component	Unit	Landscape type			Average
		High mountain and mountain meadow	Mountain forest and mountain taiga	Mountain steppe				High mountain and mountain meadow	Mountain forest and mountain taiga	Mountain steppe	
1	2	3	4	5	6	1	2	3	4	5	6
pH	–	6.98	7.09	7.56	7.23	Ni	"	2.17	2.36	2.13	2.22
HCO <sub>3</sub> <sup>-</sup>	mg/l	61.1	154	292	169	Pb	"	1.53	2.11	2.34	2.04
SO <sub>4</sub> <sup>2-</sup>	"	3.81	10.7	46.8	20.3	As	"	1.47	1.21	1.86	1.51
Cl <sup>-</sup>	"	2.21	8.43	17.8	12.7	Mo	"	0.78	1.38	1.66	1.34
NO <sub>3</sub> <sup>-</sup>	"	0.91	2.36	3.42	2.26	Rb	"	0.87	1.41	1.06	1.06
NO <sub>2</sub> <sup>-</sup>	"	–	0.19	0.21	0.20	V	"	0.33	1.01	1.37	0.91
F <sup>-</sup>	"	0.14	0.22	0.40	0.25	Ce	"	–	0.83	0.98	0.90
Ca <sup>2+</sup>	"	14.5	28.6	69.6	37.8	Zr	"	0.72	0.95	0.88	0.85
Mg <sup>2+</sup>	"	6.02	11.6	25.3	14.5	Ge	"	0.31	0.53	1.04	0.62
Na <sup>+</sup>	"	3.84	13.5	22.2	13.8	U	"	0.10	0.61	1.08	0.57
K <sup>+</sup>	"	0.68	0.87	3.11	1.55	Se	"	0.33	0.51	0.82	0.57
NH <sub>4</sub> <sup>+</sup>	"	–	0.41	0.39	0.37	Cs	"	0.35	0.57	0.5	0.48
SiO <sub>2</sub>	"	10.5	16.2	18.3	15.2	Sb	"	0.31	0.37	0.57	0.45
Total	"	103	246	481	288	Nb	"	–	0.36	0.50	0.43
Free CO <sub>2</sub>	"	4.52	8.72	11.2	8.11	Sn	"	0.23	0.37	0.35	0.32
C <sub>org</sub>	"	3.77	4.25	3.25	3.72	Co	"	0.11	0.31	0.41	0.28
Fe	µg/l	181	538	573	429	Cd	"	–	0.18	0.32	0.25
Al	"	96.2	341	270	236	La	"	–	0.15	0.29	0.24
Sr	"	61.6	76.8	176	102	Ag	"	0.14	0.21	0.25	0.20
Br	"	–	42.5	73.5	58.1	Be	"	0.14	0.15	0.32	0.19
P	"	18.0	40.1	46.8	34.9	Ga	"	0.11	0.18	0.23	0.17
B	"	6.5	35.6	42.7	27.9	Bi	"	–	0.13	0.17	0.15
Mn	"	8.57	25.2	34.1	22.7	Th	"	–	0.19	0.08	0.14
Zn	"	9.88	16.3	30.1	18.4	Y	"	0.10	0.18	0.15	0.14
Ba	"	9.24	11.3	20.8	14.1	Sc	"	–	0.08	0.03	0.05
Ti	"	2.67	16.6	15.4	11.6	Hg	ng/l	10	30	75	38.3
Li	"	1.48	8.01	13.7	7.73	Au	"	2.2	3.5	4.5	3.4
J	"	1.63	4.95	6.15	4.25	Ra	pg/l	–	–	0.6	<0.5
Cu	"	2.76	4.61	4.73	4.06	Number of regions		5	9	9	16
Cr	"	4.44	3.80	2.84	3.71						



In addition to our data, there are many published data on the composition of groundwater from mountain terrains in many regions worldwide. In this study, we used data for mountain massifs of the United States (Sierra Nevada [202], Sangre de Cristo [203], and Appalachian [204]), Slovakia (Low Tatras) [136], Norway [139, 205–207], and Scotland [138]; Bol'shoi Karatau in Kazakhstan [151]; Sikhote Alin [154, 161]; the Urals [160, 208]; and the Ukrainian Carpathians [209] and from compilations [13, 37, 83, 185, 210–217]. Average compositions for individual mountain massifs are shown in Table 13, and those for the whole province of mountain regions are shown in Table 15.

The available data support the relation deduced for the Sayan–Altai region regarding an increase in the salinity of groundwater with decreasing absolute altitude and, correspondingly, decreasing intensity of water exchange. This relation is valid for individual mountain systems and also for particular slopes; i.e., the longer the path of water migration through rocks, the higher its salinity. In this respect, data for Transbaikalia (Fig. 11) reported by Stepanov [218] are especially instructive. He presented compelling evidence that the groundwaters of free water exchange in mountain systems show a zonal (belt) distribution: the least saline waters of Mg and Ca bicarbonate compositions occur in the highest parts of mountain systems near water divides, a transitional zone of ultrafresh and fresh waters of middle mountain structures is located below them, and bicarbonate–sulfate waters of elevated salinity occur in low mountain and piedmont regions. These inferences by Stepanov have a regional rather than local significance.

The initial stages of water metamorphism related to the accumulation of salts result in an increase in the content of most elements, including such low-mobility elements as Al, Fe, Ti, V, etc. Subsequently, the concentrations of many of them cease to increase. For example, Kolotov [213] noted that the contents of hydrolysate elements in the waters of Primorye are interrelated and their enrichments are proportional to each other and especially to those of Al and Ti. Of course, this relation is observed only within a certain salinity range. For instance, the contents of Al, Ti, Rb, Cs, Sn, Y, Sc, and Th do not increase in the waters of mountain steppe terrains relative to the waters of mountain taiga terrains, although the total salinity of the former is only 0.48 g/l. The same applies to the content of organic matter.

In general, the groundwaters of mountain regions have low salinities even under the conditions of steppe and forest steppe landscapes. Their salinity increases considerably only in response to processes of continental salinization. This is explained by active water exchange in mountain regions. On the other hand, the groundwaters of this province are usually neutral or slightly alkaline. Acid waters are formed only in the cases of oxidation of sulfide minerals. This indicates specific conditions of the formation of the chemical

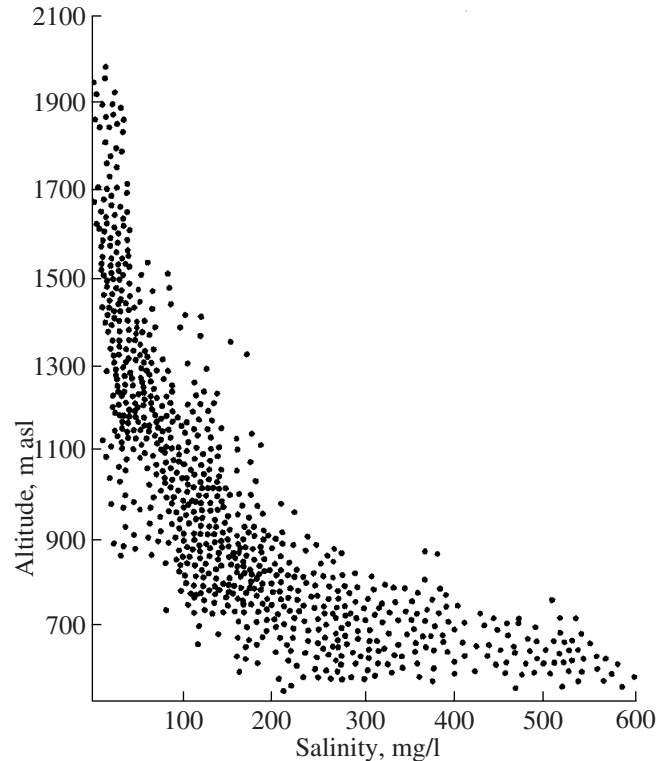


Fig. 11. Dependence of the salinity of fissure groundwaters from the mountain structures of Transbaikalia on relief.

composition of groundwaters in mountain regions. In very general terms, this is related to the prevalence of low temperatures under these conditions and the low acidifying influence of organic substances, which cannot neutralize the forming alkalinity of even low-saline waters. This is in complete agreement with the facts of relatively low contents of organic acids and free  $\text{CO}_2$  in the waters.

#### 1.6. Groundwaters of the Province of Arid Climate

In terms of hydrogeology, the province of arid climate associates with the widespread areas of salinization in continental and coastal environments. Geographically, they are related to large poorly drained depressions, troughs, lowlands, and river valleys characterized by the prevalence of evaporation over precipitation. Such depressions may be situated on high plateaus or uplands, as in Central Asia, Iran, East Africa, and Mexico. Some of them are confined to lowlands, which is the case in the West Siberian, Aral–Caspian, and Hungarian basins.

The province of continental salinization is characterized by the evaporation regime of groundwaters, which occur at shallow levels in poorly permeable deposits. The regime and balance of groundwaters is compensated under such conditions by evaporation

and, in part, transpiration. The role of capillary rise and evaporation increases with the increasing aridity of the terrain and decreasing depth of the water table.

The evaporation regime of groundwater leads to the progressive accumulation of salts in solutions. According to Kovda [219], the salinity of groundwater increases through the following stages (g/l): silicate (0.02–0.1), calcium bicarbonate (0.2–0.5), soda (0.5–3.0), sulfate (5–20), and chloride (more than 20). During the wet season, precipitation dilutes the saline waters and dissolves part of deposited salts, but this circumstance cannot change the general trend of salt concentration in solutions.

The analysis of the extensive hydrogeological literature on arid regions shows that, even under such conditions, highly saline chloride waters are rather rare and restricted to small local areas with an extremely high degree of evaporation, a small amount of precipitation, and low rock permeability. The waters of this type are rather exotic and have no regional distribution. Therefore, during the calculation of average concentrations, saline waters and brines with concentrations of more than 20 g/l were ignored, being used only for the elucidation of general tendencies in compositional variations during the evaporative concentration of groundwaters.

The chemical composition of groundwaters from some arid regions, in particular, the Kurama piedmonts, was considered in the previous section. This section presents some additional data, and the available information is analyzed.

Steppe terrains and related waters of continental salinization are widespread in the southern part of West Siberia in Russia and Kazakhstan. Salt occurrences have been observed there in all landscape components: soils; grounds; peats; waters of underground, lacustrine, palustrine, riverine, and soil systems; and plants. The processes of salinization also affect a thick zone of deeper geologic sequences. According to available data [219], most of the salts owe their existence to input from the surrounding mountain systems and accumulation in unconsolidated continental deposits. The accumulation of salts accompanies rock weathering and soil formation. Soda, sulfate, and chloride salinization is observed there. For instance, the Baraba Plain is part of the large West Siberian province of soda accumulation and, correspondingly, the development of soda waters, whose formation is still controversial.

The Baraba lowland is a peculiar forest–meadow–steppe terrain, where forest plant communities associate with meadow–steppe, meadow, and wetland ones. However, soda occurrences are most common in the undrained areas of the forest steppe zone. According to Bazilevich [220], the role of soda in the soils, surface

water, and groundwaters definitely decreases both northward (in the zone of broadleaf forests) and southward (in the zone of forest steppe with birch groves). Bicarbonates of alkali earth elements become predominant in the north, whereas the concentrations of sulfates and chlorides increase in the south, although in both cases soda remains an active component of salt solutions. The moderately warm forest steppe zone is characterized by unstable moistening, and the possible evaporation is 1.3–1.5 times higher than the precipitation. The mean annual precipitation is 300–400 mm, and significant variations may be observed in individual years.

The geochemistry of Baraba groundwaters is highly variable owing to the influence of continental salinization of varying intensity depending on particular geomorphologic, landscape, and hydrogeological conditions. Each geochemical water type shows specific total salinity values.

The lowest salinity is observed in bicarbonate waters, which reflect the initial phases of their metamorphism, and the highest salinity is typical of soda-free chloride and chloride–sulfate waters, which were produced by the most extensive metamorphism. The salinity of soda waters varies rather widely and reaches its maximum value in the uppermost aquifers confined to young geological complexes. Based on this observation, Bazilevich convincingly argued that soda is actively formed nowadays and has been formed during the whole Quaternary period. She placed the beginning of soda formation at the second half of the Tertiary period.

The highest stability of soda solutions is observed in waters with salinities of 1–4 g/l, which are most common in the region. It should be noted that all of these waters were formed owing to the processes of continental salinization and contain, therefore, elevated amounts of chlorides and sulfates (Table 16).

It is also noteworthy that the soda waters, as was shown by Bazilevich, are transitional between sulfate and chloride waters. This implies that evaporative concentration causes initially extensive accumulation of sulfate salts because part of  $\text{Na}^+$  and  $\text{Ca}^{2+}$  and, consequently,  $\text{CO}_3^{2-}$  is fixed by clays and carbonates developing under these conditions. The role of chloride solutions increases after the attainment of equilibrium with gypsum and its precipitation. This is additionally assisted by sulfate reduction, which occurs under reducing (wetland) conditions. The soda and sulfate waters are closely related, which is also reflected in their average compositions: the former are sodium bicarbonate and the latter are sodium–magnesium sulfate–bicarbonate (Table 16).

**Table 16.** Chemical compositions of groundwaters from the Baraba lowland, mg/l

Component	Soda waters				Sulfate waters	Chloride waters
	Sandy–clayey unconsolidated deposits		Perched waters	Average		
	Neogene–Paleogene	Quaternary				
pH	7.72	7.76	–	7.74	–	–
Cl <sup>–</sup>	263	117	186	168	79.1	1617
SO <sub>4</sub> <sup>2–</sup>	206	171	436	269	389	706
HCO <sub>3</sub> <sup>–</sup> + CO <sub>3</sub> <sup>2–</sup>	654	618	687	654	387	469
NO <sub>3</sub> <sup>–</sup>	3.54	6.41	–	4.98	–	–
NO <sub>2</sub> <sup>–</sup>	0.08	0.08	–	0.08	–	–
Na <sup>+</sup> + K <sup>+</sup>	355	181	434	323	176	981
Mg <sup>2+</sup>	47.7	58.9	59.2	51.6	67.6	194
Ca <sup>2+</sup>	60.0	83.1	33.3	52.1	68.2	182
NH <sub>4</sub> <sup>+</sup>	2.15	1.47	–	1.84	–	–
SiO <sub>2</sub>	31.1	26.8	30.5	29.5	–	–
Total	1623	1267	1865	1559	1167	4149
CO <sub>2</sub>	14.5	18.7	–	16.6	–	–
C <sub>org</sub>	11.3	17.2	–	14.3	–	–
O <sub>2</sub>	5.52	3.42	–	4.45	–	–
Al <sup>3+</sup>	1.65	1.93	–	1.79	–	–
Fe <sup>3+</sup>	0.77	1.12	–	0.95	–	–
Fe <sup>2+</sup>	0.33	0.42	–	0.37	–	–
Number of analyses	173	48	60	282	35	28

Thus, the following sequence of transformations of groundwater composition with increasing total salinity can be established: fresh calcium bicarbonate waters transform at a salinity of 0.6–1.0 g/l into sodium sulfate–bicarbonate or bicarbonate (soda) waters with elevated contents of sulfate ion, and a further increase in salinity leads to the appearance of sodium–magnesium or sodium chloride–sulfate waters. This general scheme may be complicated by some deviations under particular conditions but is always observed at a slight excess of evaporation over precipitation. Consequently, the soda waters are transitional between the waters of leaching and typical waters of continental salinization.

In addition to the regions of soda salinization of southern West Siberia, we used data on groundwaters

from the steppe terrains of the Kuznetsk Basin [102, 106], the Nazarovskaya Depression (Krasnoyarsk krai) [103], the Republic of Khakassia [113, 114], the southern Urals [151, 160], northern Kazakhstan [151], the southern United States [81–83, 221, 222], etc. The average compositions of groundwaters from some of these regions are shown in Table 17. It is readily seen that the waters show a considerable scatter in average total salinity (from 0.8 to 2.0 g/l), small variations in average pH values (from 7.3 to 7.8), and elevated contents of sulfate and chloride ions. In general, they are fresh and brackish waters showing variable degrees of evaporative concentration. At the same time, the influence of rocks, responsible for different proportions of

**Table 17.** Chemical compositions of groundwaters from selected regions of the province of continental salinization

Component	Unit	Jordan	Southern steppes, United States	Steppes, Kuznetsk Basin	Coal-bearing deposits, southern United States	Steppes, southern Krasnoyarsk krai	Steppes, Kazakhstan	Steppes, southern Urals	Steppes, Kurama Mountains
1	2	3	4	5	6	7	8	9	10
pH	–	7.39	7.63	7.72	7.77	7.77	7.31	7.46	7.51
HCO <sub>3</sub> <sup>-</sup>	mg/l	331	295	573	614	429	309	271	243
SO <sub>4</sub> <sup>2-</sup>	"	30.1	184	84.3	202	267	441	393	1047
Cl <sup>-</sup>	"	59.9	74.7	79.8	12.2	108	162	558	115
F <sup>-</sup>	"	0.24	0.74	–	0.56	0.31	0.46	0.35	–
NO <sub>3</sub> <sup>-</sup>	"	48.8	3.37	0.82	–	–	3.13	3.05	9.96
PO <sub>4</sub> <sup>3-</sup>	"	0.04	0.05	–	0.12	0.04	0.19	0.13	–
NO <sub>2</sub>	"	0.49	–	–	–	0.03	–	0.07	–
Na <sup>+</sup>	"	43.1	105	128	167	156	214	512	236
Ca <sup>2+</sup>	"	90.2	94.2	69.8	32.7	91.2	109	85.1	210
Mg <sup>2+</sup>	"	28.3	27.1	30.5	16.0	47.1	51.6	57.9	97.8
K <sub>+</sub>	"	4.3	6.0	6.31	5.10	7.3	19.5	12.6	24.4
NH <sub>4</sub> <sup>+</sup>	"	6.75	–	0.96	–	0.03	0.08	0.06	0.44
SiO <sub>2</sub>	"	–	21.0	18.0	26.4	7.92	20.3	–	21.9
Total	"	643	819	990	1075	1114	1335	1893	2000
Free CO <sub>2</sub>	"	–	–	26.8	–	–	38.3	–	20.2
C <sub>org</sub>	"	0.48	–	8.35	5.40	–	–	–	2.36
Fe	"	0.03	0.25	0.30	0.43	–	–	–	–
Al	"	–	0.24	–	0.02	–	–	–	–
Sr	"	–	0.91	0.14	0.49	–	0.48	0.12	0.66
Br	"	0.49	0.22	–	0.19	–	–	0.09	–
B	µg/l	–	–	–	468	–	35.9	24.5	99.3
Mn	"	–	22.0	41.5	31.0	91.4	64.2	120	34.4
Zn	"	4.82	–	105	45.3	103	38.3	47.5	13.7
Ti	"	–	–	27.0	–	4.3	57.8	18.9	19.7
Li	"	–	–	–	42.5	–	27.5	5.8	–
Ba	"	–	–	25.2	32.3	–	31.1	21.4	18.4
Cu	"	2.1	–	–	–	10.5	6.7	8.9	3.4
I	"	–	–	5.6	14.3	1.4	6.3	7.9	–
Pb	"	2.8	–	2.7	–	1.6	3.2	2.1	1.7
Ni	"	–	–	6.1	–	2.8	2.7	7.6	2.6
U	"	–	6.0	–	0.9	–	–	–	–
Mo	"	–	–	0.51	–	1.9	1.4	1.7	2.3
Cr	"	0.88	–	7.4	–	5.1	3.8	1.2	5.0
V	"	–	–	2.6	–	3.0	3.5	1.9	0.75
Rb	"	–	–	–	–	–	–	0.96	–
As	"	–	–	0.36	0.85	–	0.79	1.2	7.3
Zr	"	–	–	1.4	–	–	1.9	1.5	0.53
Sb	"	–	–	–	–	–	0.71	0.12	2.5
Co	"	–	–	0.31	–	0.10	0.55	0.73	0.44
Ga	"	–	–	0.72	–	–	0.36	0.19	–
Sn	"	–	–	0.15	–	–	0.26	0.81	0.24
Ag	"	–	–	0.67	–	0.29	0.47	1.14	0.10
Cd	"	0.49	–	–	–	–	–	0.16	–
Be	"	–	–	0.87	–	–	–	0.23	0.09
Ra	pg/l	–	1.4	–	–	–	6.9	–	–
Number of analyses		56	85	46	88	29	455	347	642



chemical elements in waters with identical degrees of concentration, is also evident [29].

Before we proceed to the estimation of the average abundances of elements in the groundwaters of the arid climate province, note that, in addition to the aforementioned data, other materials were used, especially for regions of the tropical belt, including Egypt [223]; Ethiopia, Uganda, and Kenya [224]; western Australia [225, 226]; India [227, 228]; northern Nigeria [70]; Jordan [234]; etc.

For instance, weakly alkaline and alkaline fresh waters with a total salinity of 0.2–0.7 g/l occur at depths of 80–100 m in the desert area of northern Egypt. They have sodium bicarbonate compositions and are enriched in sulfate and chloride ions. Such waters are rather common in the supergene zone of steppe and desert terrains, and this circumstance should be taken into account during the calculation of the average concentrations of elements in groundwaters.

Chemically peculiar waters occur in Ethiopia, Uganda, and Kenya, where 40 groundwater springs were investigated in different geologic complexes extending more than 2500 km along the rift zones of East Africa. All of them are cold, and their salinity and composition suggest a meteoric origin, except for a few saline springs that have a more complex origin and are not further considered here. Compositionally diverse waters occur in this vast region. There is a large group of alkaline soda waters with an average salinity of about 2.0 g/l. They show very low sulfate and chloride contents and low calcium and magnesium but are very rich in fluorine and relatively rich in potassium. The fraction of soda in these waters is on average 65.8% of the total salts and may be as high as 85% at some sites.

The sulfate waters of this region are low-saline (0.5–0.8 g/l) but also alkaline; i.e., as in the above case, they were formed ahead of the appearance of soda waters in terms of salt accumulation. In fact, these two water types develop in somewhat different geologic and hydrogeological environments.

Fresher waters occur in the semiarid climate of western Maharashtra (India), which receives an average annual precipitation of 750 mm. The aquifer investigated by us is made up of Eocene–Cretaceous basalts. Groundwater occurs at depths of 10–20 m and occasionally up to 100 m. The pH value of water ranges from 7.8 to 8.5 (8.2 on average) in the dry period and from 7.0 to 7.6 (7.3 on average) in the wet period. The average total salinity is 606 and 549 mg/l, respectively; i.e., it does not vary significantly. Despite the high content of sulfate ion (on average, 45.1 mg/l in the dry season and 83.5 mg/l in the wet season) and chlorine (on

average, 54.3 and 49.7 mg/l, respectively), the waters are, on average, magnesium bicarbonate in composition. Magnesium–calcium bicarbonate–sulfate waters were reported only from a few sites.

The data presented here on the composition of various groundwaters from many regions of the continental salinization province can be used with confidence to calculate the average abundances of chemical elements in groundwaters from this climate zone (Table 18). The calculations were performed separately for the steppe terrains of temperate continental and dry tropical climates. In the former case, the waters were subdivided according to chemical composition, whereas the available data were insufficient for such partitioning in the latter case.

It can be readily seen that the waters of regions with arid climatic conditions are on average weakly alkaline, brackish, and compositionally variable. We believe that the data of Table 18 need not be analyzed in more detail because they are generally consistent with the well-known model of the evaporative concentration of salts accounting for their continuous interaction with rocks. It should only be pointed out that soda water with a salinity of higher than 5 g/l is very rare in the supergene zone owing to the selective concentration of sodium chlorides and sulfates. During early stages, the formation of soda waters is closely related to an increase in the concentration of sulfate ions, but the two processes are subsequently decoupled. The contents of some trace components and silica in the waters increase somewhat with increasing solution concentration and alkalinity, but these parameters are not exactly proportional to each other in most cases, which can be explained by the coprecipitation of trace elements with salts and clay minerals crystallizing from the solution during its concentration. Only such mobile elements as bromine, boron, iodine, sulfur, molybdenum, lithium, strontium, etc., can be significantly concentrated together with sodium and chlorine in brackish waters. Thus, as the solution salinity increases, the number of chemical elements that can be retained and concentrated in the liquid phase decreases continuously. This results in the unification and qualitative impoverishment of the spectrum of chemical elements in brackish waters. It should also be emphasized that the waters of the steppe terrains of the tropical zone are much fresher and less alkaline than the waters of temperate steppe regions. We believe that this is not an accidental phenomenon related to a paucity of data but an objective regularity related to much higher precipitation under the conditions of tropical climate and to more extensive decomposition and oxidation of organic matter.

**Table 18.** Average chemical compositions of groundwaters from the province of arid climate

Component	Unit	Temperate continental zone				Dry tropical zone	Average
		Soda waters	Sulfate waters	Chloride waters	Average		
1	2	3	4	5	6	7	8
pH	–	7.87	7.44	7.42	7.58	7.41	7.50
HCO <sub>3</sub> <sup>-</sup>	mg/l	663	355	353	444	254	349
SO <sub>4</sub> <sup>2-</sup>	"	250	586	512	455	154	304
Cl <sup>-</sup>	"	100	160	876	340	176	258
NO <sub>3</sub> <sup>-</sup>	"	4.12	3.87	3.23	5.98	5.58	5.78
NO <sub>2</sub> <sup>-</sup>	"	0.05	0.46	0.07	0.21	0.83	0.53
Na <sup>+</sup>	"	319	275	772	392	175	260
Ca <sup>2+</sup>	"	54.5	118	145	111	61.8	86.4
Mg <sup>2+</sup>	"	39.2	60.3	92.3	67.5	25.0	46.2
K <sup>+</sup>	"	18.3	15.8	24.1	17.3	19.6	18.4
NH <sub>4</sub> <sup>+</sup>	"	0.94	0.24	0.14	0.61	1.10	0.85
SiO <sub>2</sub>	"	39.2	21.3	28.3	27.0	35.7	31.3
Total	"	1487	1595	2805	1860	910	1360
Free CO <sub>2</sub>	"	16.6	29.2	–	20.4	37.2	28.8
C <sup>org</sup>	"	9.83	10.3	12.1	10.6	7.31	8.95
F	"	0.86	0.76	0.68	0.77	2.18	1.47
Fe	"	1.98	0.52	0.27	0.93	0.49	0.71
Al	"	0.99	0.28	0.24	0.47	0.28	0.37
Sr	µg/l	505	340	553	421	700	560
Br	"	210	180	439	276	349	313
B	"	627	173	606	350	146	248
Mn	"	189	48.2	65.0	88.0	182	135
Zn	"	73.0	30.7	52.2	45.2	96	70.6
P	"	20.6	63.3	21.7	48.5	76.7	62.6
Ti	"	83.0	49.7	45.0	101	–	59.1
Li	"	49.0	29.0	15.8	33.5	46.0	39.7
Ba	"	36.5	24.3	23.7	33.6	–	33.6
Cu	"	10.4	8.98	11.3	9.98	12.7	10.9
J	"	12.7	9.08	7.93	9.95	–	9.95
Pb	"	1.69	4.43	5.29	3.62	5.64	4.53
Ni	"	3.12	5.60	8.63	5.47	3.47	4.47
U	"	2.31	1.76	4.40	2.83	5.82	4.32
Mo	"	1.33	5.55	5.01	4.12	–	4.12
Cr	"	3.83	4.33	2.67	4.03	0.77	2.40
V	"	3.25	2.21	2.16	2.65	–	2.65
Rb	"	2.15	2.06	1.96	2.05	–	2.05
As	"	–	2.15	1.16	1.93	–	1.93
Se	"	–	–	–	1.78	–	1.78
Zr	"	–	1.24	1.46	1.37	–	1.37
Sb	"	–	1.60	0.12	0.86	–	0.86
Th	"	–	–	–	0.80	–	0.80
Co	"	0.13	0.52	0.65	0.62	–	0.62
Cs	"	0.80	0.65	0.35	0.60	–	0.60
Ga	"	–	0.66	0.51	0.58	–	0.58
Sn	"	–	0.41	0.77	0.54	–	0.54
Ag	"	0.36	0.27	0.68	0.44	–	0.44
Cd	"	–	0.62	0.16	0.42	0.39	0.40
Be	"	–	0.09	0.23	0.33	–	0.33
Bi	"	–	0.05	0.08	0.06	–	0.06
Au	ng/l	–	11.0	14.0	13.0	–	13.0
Ra	pg/l	0.97	2.16	0.73	1.28	–	1.28
Number of regions		5	7	5	9	5	13

## CHAPTER 2. COMPARATIVE GEOCHEMISTRY OF GROUNDWATERS FROM VARIOUS PROVINCES AND THEIR RELATION WITH RIVER WATER AND SEAWATER

The previous chapter presented the compositions of various groundwaters from main hydrogeological provinces and landscape zones. These data can be used to perform a comparative analysis, calculate the average abundances of chemical elements in the waters of the supergene zone, and track variations in their composition with an increase in total salinity.

### 2.1. Comparative Analysis and Average Composition of Groundwaters from the Supergene Zone

It is evident from Table 19 that groundwaters from the permafrost province are on average the freshest among the waters of all provinces. This could be expected because the presence of frozen rocks significantly suppresses the infiltration of precipitation into deep levels of the supergene zone and, thus, predetermines short travel distances of groundwaters and short times of their interaction with rocks. The low-temperature conditions of this zone are also unfavorable for active water-rock interaction. On the other hand, the groundwaters of this province show moderate acidity and extremely high contents of dissolved organic matter, which is often dominated by fulvic acids, and  $\text{NH}_4^+$ .

There is a widespread opinion that silica-rich waters are common in northern latitudes, but it is not supported by the available data because the contents of  $\text{SiO}_2$  in these waters turn out to be the lowest. Thus, the most significant features distinguishing groundwaters from this province from other waters are the lowest contents of most chemical elements, abundance of organic matter, and moderate acidity.

Rather fresh waters are formed under tropical and subtropical conditions, which show the highest intensity of water exchange. This province is characterized by the highest water acidity, high mean annual temperature, and the prevalence of subsurface flow above surface runoff. An important chemical feature of groundwaters from tropical regions is a very high silica content, the highest among all of the provinces of leaching groundwater. This, in particular, supports the suggestion that the most typical silica-rich waters are formed in hot tropical regions rather than in cold northern ones. This results from the highest acidity and temperatures of these waters. The rather intense removal of silica relative to the sum of major cations by the waters of tropical and subtropical regions is in good agreement with the phenomena of extensive laterization observed under these conditions. This factor is also responsible for the maximum K/Na ratio observed in the waters of the province of tropical climate. The high mean annual temperatures lead to a high degree of organic matter remineralization under these conditions, which is reflected in high concentrations of free  $\text{CO}_2$  and high

$\text{CO}_2$  partial pressures at relatively low contents of  $\text{C}_{\text{org}}$  and hydrolysate elements (Al, Fe, and Ti). This is an important difference between the waters of tropical regions and lower temperature landscapes.

In the sequence of increasing groundwater salinity, the next province is that of mountain massifs, which also show rather intense water exchange and produce fresh waters. A characteristic feature of these waters is their relatively high alkalinity owing to the insufficient neutralizing influence of organic matter. Compared with other provinces, the groundwaters of mountain regions have the lowest contents of dissolved ( $\text{C}_{\text{org}}$ ) and remineralized (free  $\text{CO}_2$ ) organic matter. An increase in the total salinity of groundwaters under these conditions is related to more active accumulation of almost all major cations and anions in the solution. Exceptions are K,  $\text{NH}_4^+$ , and  $\text{SiO}_2$ . The increase in total salinity is accompanied by enrichment in many trace components, although not all of them. The elements that are accumulated in the waters of the mountain province include Fe, Al, Sr, Br, Ba, Li, Ti, Cr, As, Se, Au, and Ra. It is intriguing that the commonly immobile hydrolysate elements are also among the accumulated components. On the other hand, the contents of many trace elements (P, Mn, B, Zn, I, Cu, U, Ni, Rb, etc.) in these waters are much lower than in the waters of tropical regions, which are less saline but much more acidic and rich in organic matter. Consequently, the hydrogeochemical environment controls the ability of waters to be enriched in particular elements. The salinity of water is but one particular parameter of this environment.

The most saline among the leach waters are groundwaters from the regions of temperate climate in plateaus; shields; and, occasionally, ancient folded structures. The relatively limited water exchange results in the formation of near neutral groundwaters with a total salinity of 354 mg/l. An increase in total dissolved solids compared with other provinces is mainly related to bicarbonates of all the major cations; i.e., it is formed from the products of organic matter remineralization ( $\text{CO}_2$ ) and rock decomposition (cations). On the other hand, these waters do not exhibit any significant silica accumulation, which results in a considerable decrease in the  $\text{SiO}_2/\Sigma\text{cations}$  value compared with other provinces (Table 20). Consequently, even during this stage of the development of groundwater chemistry, the chemical elements are not accumulated proportionally and their behavior is controlled by the character of the geochemical environment. This is additionally supported by the analysis of trace component behavior. Although the waters of this province show the highest concentrations of many elements, the rate of their accumulation with increasing total salinity is different for different elements. As can be seen from Fig. 10, the maximum increase is characteristic of Sr and Ba, which are followed by P, Mn, and K. In contrast, the concentrations of  $\text{C}_{\text{org}}$ , Al, and Sb decrease rapidly.

**Table 19.** Average chemical compositions of groundwaters from the supergene zone

Component	Unit	Groundwaters of provinces of leaching					Groundwaters of the province of continental salinization	Average for waters of the supergene zone
		Tropical and sub-tropical climate	Permafrost	Temperate climate	Mountain regions	Average		
1	2	3	4	5	6	7	8	9
pH	–	6.40	6.53	6.82	7.23	6.75	7.50	6.90
HCO <sub>3</sub> <sup>-</sup>	mg/l	109	82.8	222	169	146	349	187
SO <sub>4</sub> <sup>2-</sup>	"	7.10	4.05	18.2	20.3	12.4	304	70.7
Cl <sup>-</sup>	"	7.35	4.67	15.9	12.7	10.1	258	59.7
NO <sub>3</sub> <sup>-</sup>	"	1.52	0.31	2.13	2.26	1.56	5.78	2.40
F <sup>-</sup>	"	0.22	0.19	0.26	0.25	0.23	1.47	0.48
NO <sub>2</sub> <sup>-</sup>	"	0.07	0.03	0.10	0.20	0.10	0.53	0.19
Na <sup>+</sup>	"	10.9	6.64	23.8	13.8	13.8	260	67.6
Ca <sup>2+</sup>	"	16.6	16.8	38.3	37.8	27.4	86.4	39.2
Mg <sup>2+</sup>	"	8.07	5.56	16.5	14.5	11.2	46.2	18.2
K <sup>+</sup>	"	2.25	0.83	2.74	1.55	1.84	18.4	5.15
NH <sub>4</sub> <sup>+</sup>	"	0.09	1.09	0.52	0.37	0.52	0.85	0.59
SiO <sub>2</sub>	"	20.9	8.63	13.3	15.2	14.5	31.3	17.9
Total	"	185	135	354	288	239	1360	469
Free CO <sub>2</sub>	"	63.1	12.4	20.7	8.11	26.1	28.8	26.6
C <sub>org</sub>	"	6.62	12.3	9.86	3.72	8.12	8.95	8.29
Fe	µg/l	251	328	689	429	424	710	481
Al	"	147	216	165	236	190	370	226
Sr	"	47.5	20.8	185	102	88.7	560	183
Br	"	10.9	8.46	85.6	58.1	40.8	313	103
B	"	37.7	20.2	55.9	27.9	35.4	248	77.9
P	"	71.8	22.6	98.2	34.9	56.9	62.6	58.0
Mn	"	42.4	12.7	59.2	22.7	34.3	135	54.5
Zn	"	37.6	22.4	42.8	18.4	30.3	70.6	38.4
Ba	"	9.11	9.09	25.3	14.1	14.4	33.6	18.3
Ti	"	3.35	4.09	8.82	11.6	6.96	59.1	17.4
Li	"	2.21	4.08	10.7	7.73	6.20	39.7	13.0
J	"	12.0	2.19	5.59	4.25	6.00	9.95	8.02
Cu	"	4.63	2.44	4.85	4.06	4.00	10.9	5.38
Ni	"	4.92	1.84	3.45	2.22	3.11	4.47	3.38
Cr	"	2.25	2.34	2.83	3.71	2.78	2.40	2.70
Pb	"	2.05	1.52	3.10	2.04	2.18	4.53	2.65
Rb	"	2.22	1.42	2.55	1.06	1.81	2.05	1.86
Mo	"	1.55	0.78	0.89	1.34	1.16	4.12	1.75
As	"	<2.0	0.86	1.64	1.51	1.34	1.93	1.46
V	"	1.23	0.64	1.28	0.91	1.01	2.65	1.34
U	"	0.90	0.25	0.51	0.57	0.56	4.32	1.31
Zr	"	–	1.13	1.51	0.85	1.16	1.37	1.20



Таблица 19. (Contd.)

Component	Unit	Groundwaters of provinces of leaching					Groundwaters of the province of continental salinization	Average for waters of the supergene zone
		Tropical and subtropical climate	Permafrost	Temperate climate	Mountain regions	Average		
1	2	3	4	5	6	7	8	9
Se	"	0.13	–	0.64	0.57	0.45	1.78	0.72
Sb	"	–	0.91	0.55	0.45	0.64	0.86	0.68
La	"	–	1.11		0.24	0.67	–	0.67
Nb	"	–	0.48	<1.40	0.43	0.45	–	0.45
Co	"	0.41	0.29	0.34	0.28	0.33	0.62	0.39
Sn	"	<0.5	0.29	0.44	0.32	0.35	0.54	0.39
Ga	"	<1.0	0.27	0.52	0.17	0.32	0.58	0.37
Ag	"	0.19	0.24	0.24	0.20	0.22	0.44	0.26
Cs	"	–	–	–	0.48	0.18	0.60	0.26
Cd	"	<0.3	–	0.15	0.25	0.20	0.40	0.24
Th	"	–	0.07	0.11	0.14	0.10	0.80	0.24
Be	"	<0.1	0.05	0.24	0.19	0.16	0.33	0.19
Sc	"	–	0.10		0.05	0.07	–	0.07
Hg	ng/l	–	–	44.0	38.3	41.1	–	41.1
Au	"	2.1	2.2	6.1	3.4	3.4	13.0	5.32
Ra	pg/l	0.29	–	0.20	<0.5	0.25	1.28	0.46
Number of regions		10	10	17	16	53	13	66

Table 20. Selected characteristic parameters of the composition of groundwaters from the supergene zone

Element ratio	Provinces of leaching-related groundwaters				Waters of continental salinization
	Tropical climate	Permafrost	Mountain regions	Temperate climate	
SiO <sub>2</sub> /ΣCations	0.55	0.29	0.22	0.16	0.076
K/Na	0.21	0.12	0.11	0.11	0.071

Thus, the leach waters of each hydrogeological province are characterized by specific compositional features, which have to be explained. It should also be pointed out that the relative fraction of silica in the aqueous solution decreases monotonously with increasing total salinity (Table 20). This feature of groundwaters from the supergene zone is very important and, as will be shown below, is of fundamental significance.

Compared with our previous publications, the calculated average composition of leaching-related

groundwaters remained almost unchanged. A decrease in the average concentrations by more than a factor of 2 was observed only for Br, U, and Ra because of the increase in the number of analyses and the wider range of regions, as well as for Sb, Hg, and Au owing to the use of new and more accurate analytical techniques. The total salinity and concentrations of major components remained identical within the analytical errors.

The average composition of leaching-related groundwaters is given in Table 19 and can be represented by the following Kurlov formula:

$$M0.24 \frac{HCO_3 80.7 C 19.4 SO_4 8.8 NO_3 1.0 F 0.3}{Ca 46.4 Mg 31.5 Na 20.3 K 1.7} pH 6.75, \quad (2.1)$$

i.e., these waters are moderately fresh, slightly acidic, and calcium–magnesium bicarbonate in composition.

In contrast to the leaching-related groundwaters, the average composition of groundwaters of conti-

mental salinization classifies them as brackish, slightly alkaline, sodium chloride–sulfate–bicar-

bonate waters described by the following Kurlov formula:

$$M1.36 \frac{Cl37.3SO_432.5HCO_329.3NO_30.5F0.4}{Na56.7Ca21.7Mg19.3K2.3} pH7.50. \quad (2.2)$$

It should be emphasized that the contents of chemical elements in the waters of continental salinization do not increase proportionally to one another or to the total water salinity in general. For instance, a salinity increase by a factor of 5.7 relative to the leaching-related waters (Table 19) is accompanied by an increase in the concentration of particular elements by a factor of 4.1 for magnesium, 25.5 for chlorine, 18.8 for sodium, 3.2 for calcium, 1.7 for iron, 3.9 for manganese, 3.0 for copper, 1.1 for phosphorus, 6.4 for bromine, etc. The nonproportional enrichment in chemical elements is fully relevant to trace components. The maximum degree of accumulation is characteristic of Br, Sr, Mn, Li, B, Zn, Ti, U, Au, Se, Th, Ra, Pb, and Mo. This indicates a fundamental rearrangement in the chemical composition of waters owing to their evaporation and interaction with the host rocks. During this process, some elements precipitate from solutions as secondary clays and carbonates (Ca, Mg, and Si), whereas other elements actively accumulate in the solution practically proportionally to the increase in total salinity (Cl, S, Na, Br, B, and Sr). Owing to these processes, the proportions of particular elements and element groups change dramatically (Table 19).

The average composition of groundwaters from the supergene zone was calculated on the basis of the following considerations. The area of arid regions on Earth is much smaller than that of humid regions; therefore, before calculating the average composition of fresh and brackish groundwaters, it is necessary to determine the areal proportions of these zones. In this context, it should be recalled that permafrost regions alone occupy about 24% of the total area of continents.

$$M0.47 \frac{HCO_348.9Cl26.7SO_423.4NO_30.6F0.3}{Na44.9Ca29.9Mg23.2K2.0} pH6.9, \quad (2.3)$$

i.e., the waters are moderately fresh, near neutral, and sodium–calcium bicarbonate–chloride in composition.

## 2.2. Individuality and Stability of Groundwater Composition in Various Provinces

The above comparative analysis of the compositions of groundwaters from various hydrogeological provinces and landscape zones highlighted their specific geochemical features, primarily their different salinities and distinctive chemical compositions, associations of chemical elements, and environmental charac-

Similar fractions of the total land area are represented by the regions of tropical and subtropical climate and the regions of temperate climate and mountains. In addition, it should be kept in mind that fresh waters not significantly affected by continental salinization are widespread within the province of arid lithogenesis. With these considerations in mind, it was assumed that the relative proportion of waters related to leaching and continental salinization is about 4 : 1, and this estimate was used to calculate the average concentrations of elements in the groundwaters of the supergene zone on the whole (Table 19). The average concentrations of individual elements reported by various authors [6, 8, 9, 11–17, 20–22, 24, 29, 84, 97, 167, 184, 185, 188, 230, 231, etc.] were also used in these calculations.

Thus, the average abundances (clarkes) of chemical elements in the groundwaters of the upper hydrodynamic zone were estimated for the first time. Although the obtained values are approximate, their significance can hardly be overestimated because these data are useful for solving important problems of global hydrochemistry, for instance, the mobilization and transportation of chemical elements by groundwaters, the scales of chemical denudation, the direction of rock weathering, etc. A.E. Fersman noted that vast fields of natural sciences are still concealed in the laws of clarkes, and considerable research efforts are needed to refine these estimates and determine clarkes values for various areas of the world.

The Kurlov formula for the average chemical composition of groundwaters from the supergene zone is the following:

ter. The significance of differences was quantified by Student's *t* test:

$$t = \frac{x_1 - x_2}{\sqrt{\frac{\sigma_1^2}{n} + \frac{\sigma_2^2}{n}}}, \quad (2.4)$$

where  $x_1$  and  $x_2$  are the average concentrations of elements in the waters of each province,  $\sigma_1$  and  $\sigma_2$  are the standard deviations, and  $n$  is the number of analyses. Differences between average values were considered significant at a confidence level of 5% if the respective *t* value was higher than 1.96.

The significance of relations was calculated for the following 11 parameters of water composition: total salinity (M), pH,  $\text{HCO}_3^-$ ,  $\text{SO}_4$ , Cl, Ca, Mg, Na, K,  $\text{C}_{\text{org}}$ , and  $\text{SiO}_2$ . It turned out that, among the 55 calculated cases, the relations were significant only in 4 cases (7.3%): between mountain regions and the temperate zone for  $\text{SO}_4$ , Ca, and Mg, and between the zones of temperate and continental climate for  $\text{C}_{\text{org}}$ . In all other cases, the hydrogeological provinces differed significantly from each other.

The maximum difference was observed between the provinces of continental salinization and all other provinces for almost all of the parameters, especially for pH, M,  $\text{HCO}_3^-$ ,  $\text{SO}_4$ , Cl, Ca, and Mg, which is understandable. In addition, the mountain regions are significantly different from the tropical regions in pH, Ca, K, and M; the tropical regions from the temperate regions in pH,  $\text{HCO}_3^-$ , Ca, and M; the permafrost regions from the temperate regions in K,  $\text{SO}_4$ , Na, Cl, Ca, Mg, and M; etc.

Thus, the waters of various provinces differ from each other in a number of parameters, which form the following descending sequence of significance of difference (Student's *t* values are shown in parentheses): pH (36.8) →  $\text{HCO}_3^-$  (27.2) →  $\text{SO}_4$  (19.7) → Ca (17.7) → M (16.6) → Mg (15.2) → Cl (13.1) → K (12.7) → Na (9.7) →  $\text{SiO}_2$  (7.5) →  $\text{C}_{\text{org}}$  (6.0).

A comparative analysis on the basis of Student's *t* test was carried out for the average contents of macro-components (Tables 3, 7, 10, 15, 18) and indicated that the waters of each province display specific (individual) characteristics, which supports the well-known principle of the zoning of groundwater composition on Earth. On the other hand, it is also known that the composition of waters shows seasonal variations and is modified during migration from the catchment to the discharge area or in response to an increase in the time of their interaction with components of the geologic environment. In other words, the composition of water changes continuously and systematically both in space and time, which is consistent with the principle of variability. How can these two seemingly contradictory principles be reconciled?

In order to answer this question, we first briefly consider the results of the investigation of seasonal variations in the composition of waters from some landscape zones. Let us begin from tropical regions.

According to the results of seasonal observations in western Africa, the compositions of waters show only minor variations even between the dry and wet seasons. Throughout the year, the waters remain acidic or weakly acidic and ultrafresh and have relatively high  $\text{SiO}_2$  concentrations (compared with other cations), high K/Na ratios, low contents of trace components, etc.; i.e., throughout the whole period, they display the features of waters from wet savannas. Moreover, the seasonal variations in water composition are less significant than the differences between different sites of this region. For instance, according to monitoring measure-

**Table 21.** Comparative characteristics of the average compositions of groundwaters for the dry and wet seasons of Brazil and India, mg/l

Component	Brazil		India	
	Dry season	Wet season	End of the dry season	End of the wet season
pH	6.89	6.75	8.20	7.30
$\text{HCO}_3^-$	38.7	35.3	353	249
$\text{SO}_4^{2-}$	0.48	0.29	45.1	83.5
Cl <sup>-</sup>	0.67	0.85	54.3	49.7
$\text{NO}_3^-$	2.29	1.49	–	–
F <sup>-</sup>	1.52	1.01	–	–
Na <sup>+</sup>	2.18	2.12	52.7	49.7
Ca <sup>2+</sup>	5.24	5.48	31.6	43.2
Mg <sup>2+</sup>	1.94	2.04	67.0	71.5
K <sup>+</sup>	1.44	1.13	1.56	1.17
$\text{SiO}_2$	32.3	21.3	–	11.1
Total	86.8	70.9	606	558
Fe	0.064	0.112	–	–
Al	0.017	0.015	–	0.027
Number of analyses	22	20	29	29

ments, the pH values of waters from Guinea vary within 4.9–6.3, whereas they range from 4.5 to 6.5 in various springs of this region. Similar relationships are characteristic of total salinity and contents of particular elements [65].

Relatively minor seasonal variations in water composition were also documented in other regions with a tropical or subtropical climate: Caledonia, southern France, southwestern India, and Brazil (Table 21). The climate is humid equatorial in the former case and semiarid in the latter case. In both cases, insignificant variations in water composition were observed.

The established relations are also characteristic of other landscape zones. For instance, the composition of waters from the Tomsk region (southern taiga) shows very minor variations throughout the year: from 482 to 524 mg/l in total salinity, from 7.1 to 7.3 in pH, from 342 to 366 mg/l  $\text{HCO}_3^-$ , from 19.3 to 30 mg/l  $\text{SiO}_2$ , etc. The concentrations of trace components show more significant variations (by factors of 2–5), but these variations do not change the chemical type of water or the character of the geochemical environment. Similarly small variations in the composition of waters from the Kolyvan'–Tom' zone were reported by Udodov et al. [37].

Relatively small variations in the concentrations of major components in the waters of the temperate zone

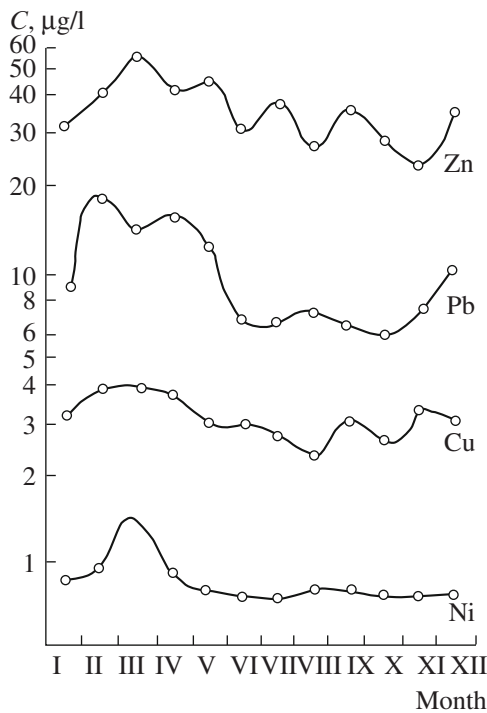


Fig. 12. Variations in metal contents for the water of a spring in the Baltic shield [212].

are also suggested by the data of Kiryukhin et al. [212] for the Russian Far East (Table 22).

As was noted by these authors, the salinity of water increases in the winter period by all of 20–30% at the expense of enrichment in chloride and sulfate ions and all cations. Similar observations were reported by Elpat'evskii [154] for the waters of the Ussuri taiga. Of course, this concerns only waters of atmospheric origin because, in other cases, the picture may be dramatically

different. For instance, Kiryukhin et al. reported data on the regime of a spring in the Baltic shield. The concentration of chlorine in the water increased strongly in the winter period owing to the influx of deep saline waters. Of course, such cases are beyond our present scope.

The trace component composition of waters usually shows significant variations, although in this case as well their ranges are not very large. Waters from a particular spring in the Baltic shield show variations by a factor of 1.5 for Ni, 1.8 for Cu, 3.0 for Pb, and 2.2 for Zn (Fig. 12).

Somewhat higher variations in water composition were observed in permafrost regions, owing to the shallow occurrence of groundwater, but the waters of unfrozen areas also have very minor compositional variations. For instance, under the severe climatic conditions of the Chukchi Peninsula, the lowest water salinity in the unfrozen layers is observed in the spring–summer period, when groundwaters are diluted by ultrafresh supraperafrost waters produced by the thawing of frozen rocks. Low salinities are retained until the end of the year or, more accurately, until the complete freezing of the active layer (Fig. 13). The maximum salinity is observed in the late winter period, when there is practically no water recharge from the surrounding slopes and the main supply is related to deeper sources, where water interacts with rocks for a longer time. The annual variations in total salinity do not extend beyond the range 50–200 mg/l. The variations are mainly due to  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$ , contents and, to a lesser extent,  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Cl}^-$  [232]. Similar relations were observed in the regions of continental salinization.

The groundwater regime in the Altai Mountains (basin of the Katun' River) was investigated by V.S. Kuskovskii from 1989 to 2001 in 16 springs and 12 wells. The results of his observations for one spring and

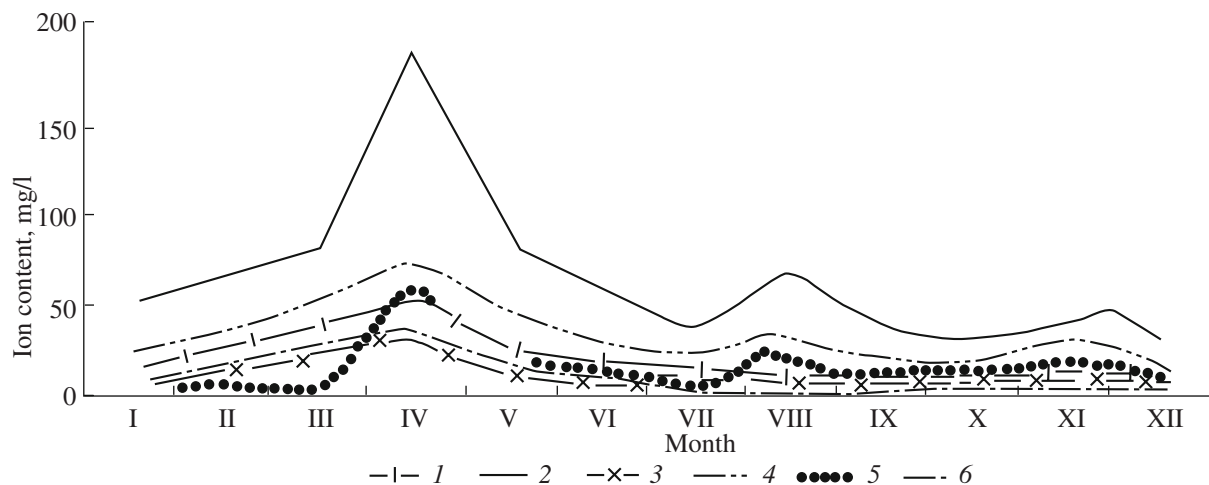


Fig. 13. Seasonal variations in the chemical composition of groundwaters from permafrost regions. (1)  $\text{Na}^+ + \text{K}^+$ , (2) dry residue, (3)  $\text{Cl}^-$ , (4)  $\text{HCO}_3^-$ , (5)  $\text{SO}_4^{2-}$  and (6)  $\text{Ca}^{2+}$ .



**Table 22.** Variations in the concentration of major components in fissure groundwaters according to data collected over many years, mg/l

Observation region	Years of observation	Na <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup>
Knyazevo-Volkonskoe village	1961–1966	44–49	23–28	23–27	3–7	0–2.5	322–350
Teploe Ozero station	1953–1958	5–20	2.4–11	52–62	4–10	0–24	152–195
Sovetskaya Gavan	1964–1967	5–7	4–6	6–9	4–7	0–2	46–60

**Table 23.** Compositional variations of groundwaters from the Gornyi Altai

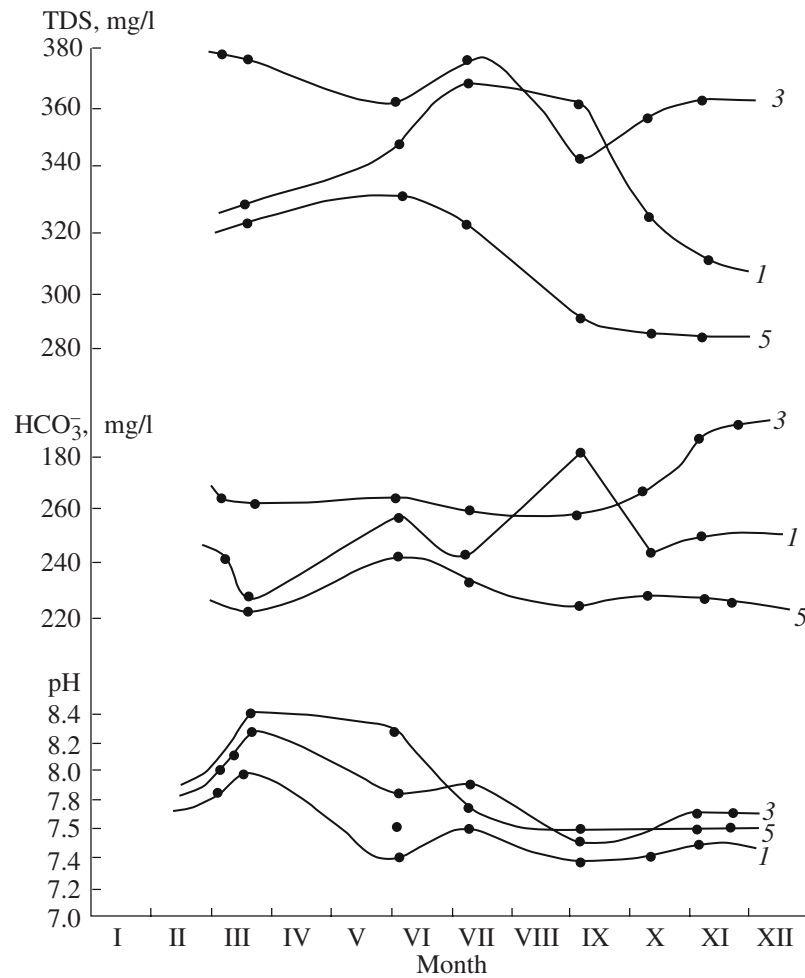
Parameter	Unit	Spring 2					Well 4					
		16.03.89	12.07.89	03.09.90	12.10.89	02.11.90	17.03.89	30.05.90	28.07.89	04.09.90	15.10.89	31.11.90
Discharge	l/s	1.10	10.1	1.20	3.53	1.64	–	–	–	–	–	–
pH	–	8.0	7.8	7.6	7.7	7.5	7.8	7.3	7.9	7.3	7.7	7.6
HCO <sub>3</sub> <sup>-</sup>	mg/l	215	223	215	215	207	200	217	188	217	188	176
SO <sub>4</sub> <sup>2-</sup>	"	31.9	27.0	25.0	23.3	23.0	29.8	5.90	22.5	5.00	36.0	4.48
Cl <sup>-</sup>	"	0.46	0.55	0.46	0.81	0.36	3.50	2.00	1.58	0.35	1.86	3.60
F <sup>-</sup>	"	0.19	0.22	–	0.20	–	0.21	–	0.18	–	0.18	–
Ca <sup>2+</sup>	"	51.1	56.0	54.7	31.5	46.7	29.0	28.7	31.6	29.4	18.1	20.3
Mg <sup>2+</sup>	"	15.2	10.7	10.4	17.2	6.90	19.8	13.3	13.4	11.6	21.3	8.50
Na <sup>+</sup>	"	3.8	2.6	7.9	5.1	3.8	14.4	10.0	8.90	13.8	9.10	9.10
K <sup>+</sup>	"	0.8	1.7	0.9	0.6	0.7	1.4	2.8	1.2	1.5	1.1	1.7
SiO <sub>2</sub>	"	10.1	10.7	–	10.1	–	3.64	–	3.86	–	3.10	–
Total	"	328	334	314	303	289	302	280	272	280	275	225
Fe	µg/l	<10	<10	30	50	20	60	920	500	1300	600	340
Al	"	38	12	–	8.0	–	70	–	40	–	8.0	–
Hg	ng/l	90	30	30	10	<10	10	<10	30	40	<10	10

one well are given in Table 23. As can be seen from these data, the composition of groundwater shows only minor seasonal variations, despite an almost tenfold variation in spring discharge. The water of well 4 showed somewhat higher variations in sulfate ion content. Perhaps this is due to the nonuniform oxidation of sulfide minerals over the year, which results from the variability of the water table depth and the related regime of oxygen input into the system. This factor is probably also responsible for the relatively large variations in iron content. In other springs and wells, the character of variations is in principle the same, although the regime of each spring has specific features (Fig. 14).

The above observations allow us to conclude that seasonal variations in groundwater composition may be significant but not high enough to change the geochemical type and characteristic parameters of waters (pH, Eh, total dissolved solids, chemical type, proportions of major elements, content and type of organic matter, silica content, etc.). For instance, the waters of tropical regions are acidic and have elevated SiO<sub>2</sub> and K con-

tents, with these compositional features being observed throughout the year. If waters are alkaline and saline, these characteristic features remain so both in different seasons and over many years. The same is observed, for instance, in wetland waters, which retain their main parameters (pH, Eh, salinity, C<sub>org</sub>, etc.) during the whole period of the existence of the given wetland type. If, for example, the water of a mountain spring is fresh and contains little Fe, Si, P, and Al, these qualitative features are always observed despite certain annual compositional variations. Many more examples can be found. For instance, the waters of the active layer of tundra terrains always show some features similar to those of wetland waters.

Thus, the parameters of groundwaters from the supergene zone certainly vary with time and their composition changes continuously to some extent, but these changes are smooth and involve all components, which are coupled with each other. Although each of the components shows its own fluctuations, the relations between them are not disturbed. Moreover, these varia-



**Fig. 14.** Variations in some parameters of the composition of groundwaters from the Gornyi Altai. Numerals in the diagram show spring numbers.

tions are limited and do not change the geochemical type of water.

At least three important conclusions can be drawn from the above considerations. (1) Temporal variations in the composition of water in any landscape zone usually do not cause a change in the main (dominant) features characterizing its geochemical type. (2) In contrast to a simplistic model, the geochemical type of groundwater is not fully controlled by the regime of its recharge but is related to its numerous fundamental connections with all landscape components. Seasonal changes in recharge conditions are only one of these parameters, which cannot disturb other connections. (3) The parameters of the geochemical type of water in different landscape and climatic zones are not necessarily the same.

We consider now the problem of spatial variations in groundwater composition, focusing on variations along the infiltration flow path from recharge to discharge areas. It should be kept in mind that, within the supergene zone, recharge areas usually coincide with occur-

rence areas and often with discharge areas. Of course, these factors complicate the relationships between the compositions of groundwaters in recharge and discharge areas. Nonetheless, the general characteristics of such variations need to be determined.

Let us begin from permafrost regions. We investigated the composition of waters along a profile from the water divide to the river valley almost 2 km long in the basin of the Kureika River under northern taiga conditions (Fig. 15). It can be seen that the concentrations of individual elements increase severalfold along the infiltration flow: by factors of 3.5 for HCO<sub>3</sub><sup>-</sup>, 5.1 for Na<sup>+</sup>, 2.8 for Ca<sup>2+</sup>, and 2.2 for SiO<sub>2</sub>. However, the concentrations increase more or less synchronously, although not proportionally. During the last stage (river valley), more complicated changes in water composition are related to mixing with the stream waters of the valley.

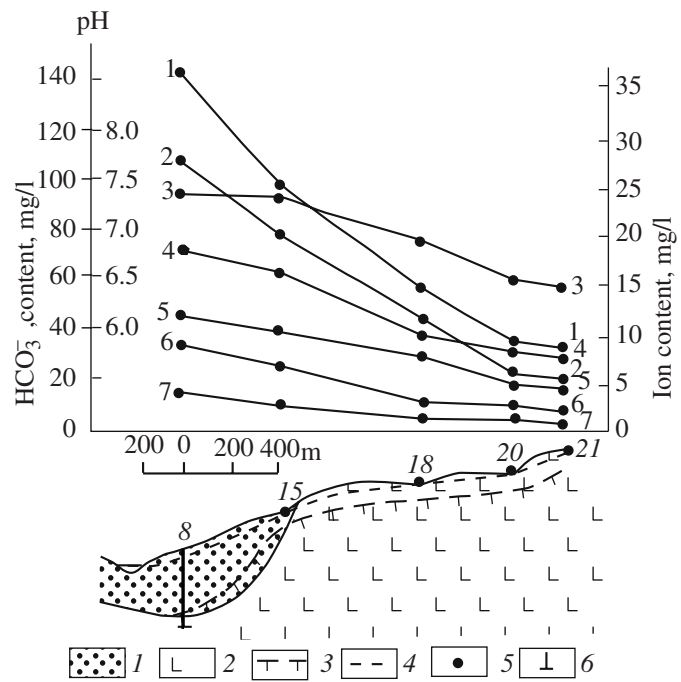
It is important to note that the total salinity increases along the infiltration flow but the composition remains almost unchanged or changes within certain limits that are characteristic of waters from the given province in

general. Among the parameters that reflect the specific character of waters of the given province are pH values and contents of Na, K, SiO<sub>2</sub>, etc. This specific character is manifested already in water divides, i.e., from the first contact of rainwater with rocks or soils. The specific character of groundwater from the province is manifested already in the soil horizon. This circumstance is very important.

As to the humid tropical conditions, the composition of waters within the small catchment of Korhogo (Côte d'Ivoire) was studied by Tardy [68]. As was noted above, he showed that the concentrations of mobile components (HCO<sub>3</sub><sup>-</sup>, SiO<sub>2</sub>, Na, K, Mg, Rb, Li, Ba, and Sr) in waters increase with increasing travel distance. In contrast, the concentration of poorly mobile elements (Fe, Al, and Mn) decreases in the same direction. However, these variations are small (Table 24) and do not affect the geochemical type of water. It is important that, over the whole catchment and geologic section and all the seasons, the waters are ultrafresh, acidic or weakly acidic, and rich in SiO<sub>2</sub> compared with cations and also show low Na/K ratios; i.e., both in the recharge area and in the discharge area, they display the characteristic features of the particular landscape and climate zone. The pH values increase only at great depths in wells.

The groundwaters of wooded terrains in the temperate climate zone are almost ubiquitously, starting from the soil horizons, weakly alkaline and have a total salinity of 0.3–0.5 g/l and low contents of chloride and sulfate ions but elevated contents of organic matter. The concentration of SiO<sub>2</sub> is elevated in absolute value but low compared with the sum of major cations. This can be exemplified by the groundwaters of the Kolyvan'–Tom' folded zone, which in soils already show the same geochemical signature as in the underlying rocks. Less alkaline groundwaters are formed only in the regions of occurrence of podzolic soils, whose waters are pronouncedly acidic [29].

Except for the most extensively drained high areas, in mountain regions the groundwaters are usually weakly alkaline and show low salinities and low contents of organic matter along the whole infiltration path. Under such conditions, the elements are concentrated nonuniformly but sympathetically (Fig. 16). At the very beginning of groundwater–rock contact, the waters acquire features typical of mountain regions (Table 13), which are not observed in tropical regions (Tables 4, 5, 7), the permafrost province (Tables 2, 3), the province of temperate climate (Tables 8–10), or, especially, the



**Fig. 15.** Changes in the composition of groundwaters in the permafrost province from source to discharge regions (basin of the Kureika River, Siberian Platform). (1) Quaternary unconsolidated deposits, (2) bedrocks (traps), (3) permafrost boundary, (4) groundwater table, (5) spring and its number, and (6) well and its number. Numbers in the diagram: 1, HCO<sub>3</sub><sup>-</sup>; 2, Na<sup>+</sup>; 3, pH; 4, Ca<sup>2+</sup>; 5, SiO<sub>2</sub>; 6, Mg<sup>2+</sup>; and 7, K<sup>+</sup>.

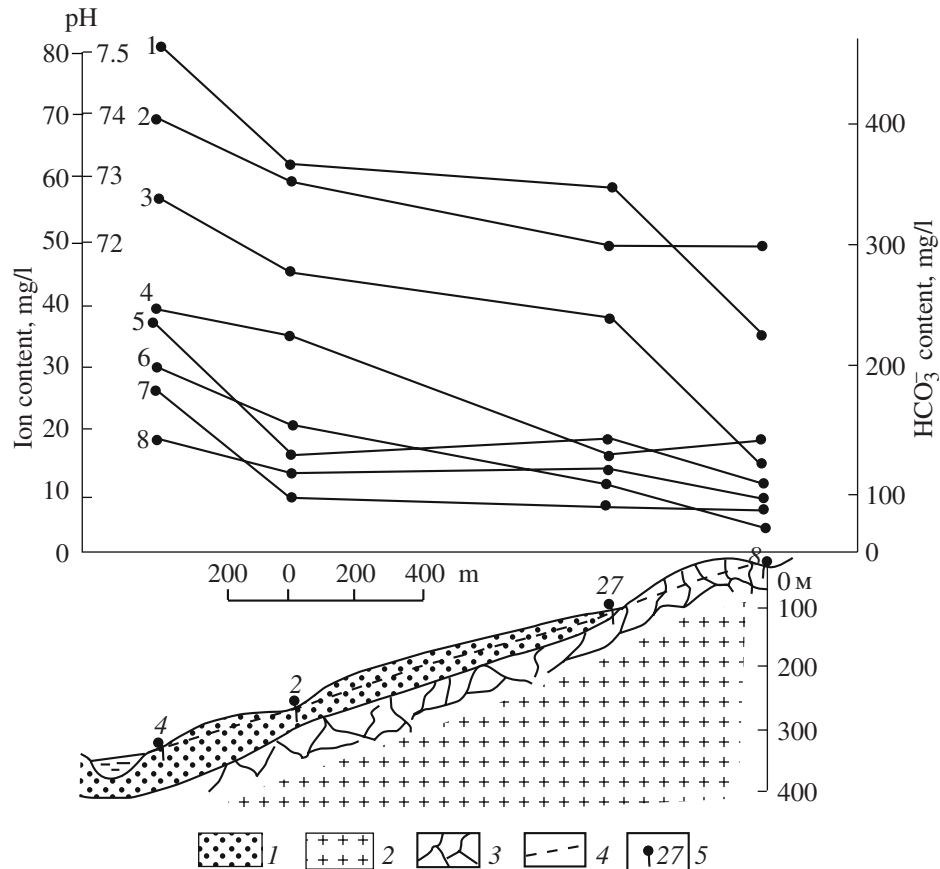
province of continental salinization (Tables 16, 17). Needless to say, the waters of the latter province have a very specific composition.

Consequently, the groundwater composition of all landscape zones and provinces changes regularly along the infiltration path. However, these variations are insufficient to change the geochemical type or migration class of water. This leads us to the important conclusion that *the specific geochemical character of groundwater is generated in the catchment and is continuously enhanced along the infiltration path.* The most important parameters reflecting this specific character are total salinity, pH, O<sub>2</sub>, CO<sub>2</sub>, SiO<sub>2</sub>, Fe, Al, K, P, S, the chemical type of water, and ratios of individual elements.

It is interesting that, in addition to the specific geochemical features of groundwaters from each prov-

**Table 24.** Average contents of chemical elements in the waters of recharge and discharge areas, mg/l

Wells	pH	HCO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	SiO <sub>2</sub>	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	SiO <sub>2</sub> /Na	Na/K
in water divide	5.8	4.0	0.4	9.8	1.2	1.7	1.7	0.2	8.12	0.71
in river valley	5.2	15.6	0.6	20	2.1	1.7	1.4	0.4	9.52	1.23



**Fig. 16.** Changes in the composition of groundwaters in the Gornyi Altai from the water divide to the river valley (forest terrains). (1) Granites, (2) unconsolidated coarse sediments, (3) fractured rocks, (4) groundwater table, and (5) spring and its number. Numbers in the diagram: 1,  $\text{Ca}^{2+}$ ; 2, pH; 3,  $\text{HCO}_3^-$ ; 4,  $\text{Na}^+$ ; 5,  $\text{SO}_4^{2-}$ ; 6,  $\text{Mg}^{2+}$ ; 7,  $\text{Cl}^-$ ; and 8,  $\text{SiO}_2$ .

ince, there are additional differences between waters from the provinces of cold and temperate climate, on the one hand, and the waters of tropical provinces, on the other hand. In particular, this concerns the relations of pH and total salinity. In all of the provinces, the freshest waters are simultaneously the most acidic and, vice versa, the higher the salinity, the higher the pH value. This relationship holds for both particular regions and the waters of the provinces as a whole (Tables 3, 7, 10, 13, 18). However, at the same salinity, waters of the tropical zone are almost always more acidic than waters of temperate climate areas (Fig. 17). This correlation is especially pronounced for ultrafresh and fresh waters; it weakens with increasing total salinity and probably vanishes above 1.5 g/l.

In connection with the above considerations, it is pertinent to recall a brilliant empirical conclusion of Vernadsky, who was disappointed that *the concept of the constancy of the chemical composition of natural waters within certain ranges of variations* was never expressed in a definite and clear-cut general form, although it is, in fact, a cornerstone of our knowledge. He proposed the following formulation of this concept: *“the chemical composition of any particular natural*

*water can be specified for each chemical element by boundary minimum and maximum values, which do not shift during the short period of historical time. The average chemical characteristics deduced in this context are constant values in historical time”* [1, p. 256]. This profound idea is fully confirmed by our data.

The above considerations allow us to draw several important conclusions: (1) the geochemical set of elements in the aqueous solution of the supergene zone is a fairly stable system, whose spatial and temporal variations do not affect its main (basic) parameters; (2) a stable individual hydrogeochemical system is formed in each type of landscape and hydrogeological province on the whole; it has many degrees of freedom, which allow variations in its parameters within stringent limits, and can be characterized by average values of these parameters; (3) the individuality and stability of a hydrogeochemical system is due to the existence of fundamental relations with all landscape (rocks, soils, vegetation, relief, secondary mineral products, and organic matter) and environmental components (temperature; the amount, regime, and composition of precipitation; etc.); and (4) the mechanisms of formation of the composition of water and the origin of the stabil-



ity of a hydrogeochemical system cannot be understood without taking into account its complex relationships with the environmental components.

Let us consider the problem of variations in the composition of water with an increase in total salinity, independent of the landscape characteristics of the region.

In analyzing the extensive obtained data, it was noted that some components (bicarbonate ion, calcium, magnesium, and sodium) show strictly regular behavior during the initial stages of an increase in water salinity; i.e., their contents rise proportionally to the total salinity. Other elements show more complicated relationships because their content depends on local factors, the influence of the ocean in the case of chlorine and the presence of sulfides in rocks in the case of sulfate ion. Still other elements (potassium and silica) are controlled by the composition of secondary phases, first of all, clay minerals. These factors complicate the relations between the contents of individual elements and the total salinity.

Despite these complications, we managed to show in Fig. 18 average data characterizing the behavior of individual elements in waters of different salinity and establish in this way the most general features of their compositional variations accompanying salt accumulation in the solution. The analysis of the obtained data allows us to distinguish at least four stages in the chemical evolution of fresh and brackish waters.

The earliest stage of evolution is most distinctly manifested under the conditions of humid savanna and includes the formation of acidic and weakly acidic ( $\text{pH} < 6.5$ ) waters with a total salinity of less than 0.1 g/l. A salient feature of these waters is the relative abundance of silica, which is second in absolute content only to  $\text{HCO}_3^-$ , and high concentrations of chlorine and potassium. This stage produces bicarbonate waters with a complex cation composition. Note that this feature of the formation of water composition during the earliest stage was not properly addressed before our studies, although it is of special importance, for instance, for the understanding of the mechanisms of rock laterization.

The second stage of evolution involves the salinity range from 0.1 to 0.6 g/l. During this stage, the contents of all elements in waters increase, but not uniformly. The concentrations of all of the major cations and anions increase especially rapidly, whereas the behavior of silica is less active, and an increase in iron and aluminum concentrations in waters either ceases or even changes to a decrease (for aluminum) at a salinity of more than 0.2 g/l. As a result, calcium becomes the second most abundant component instead of silica. The composition of waters remains calcium-sodium, calcium-sodium-magnesium, or even magnesium bicarbonate depending on the type of the host rock. The concentration of potassium is always low (Fig. 18).

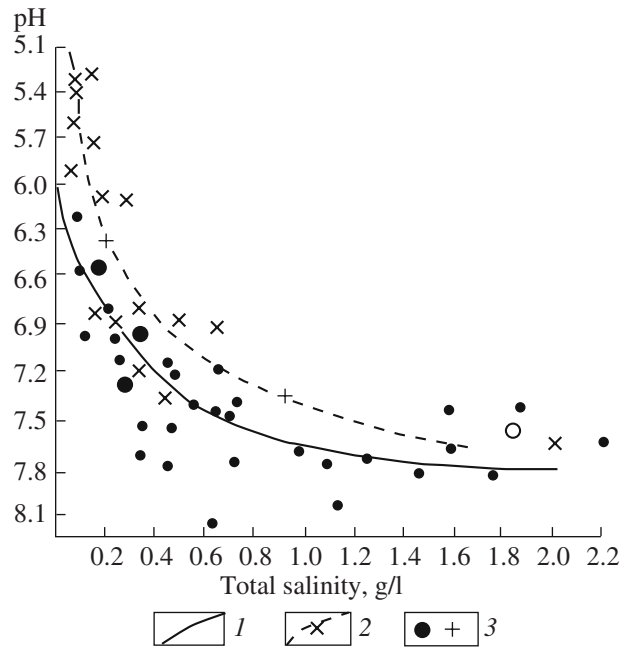


Fig. 17. Correlation between the pH value and the total salinity of groundwaters. (1) Regions of temperate climate, (2) regions of tropical climate, and (3) average for landscape zones.

The third stage of evolution corresponds to the salinity range from 0.5 to about 1.0 g/l. During this stage, the concentration of bicarbonate ion decreases rather than increases; the rates of calcium and silica concentration decline; and accumulation of chlorine, sulfate, and sodium is intensified. As a result, the waters transform gradually from bicarbonate to bicarbonate-chloride-sulfate or bicarbonate-sulfate-chloride compositions with  $\text{pH} > 7.0$ . The most abundant cation is sodium, and the waters become sodium-calcium, or soda in another nomenclature.

The fourth and final stage of evolution is characterized by solutions strongly dominated by sulfate and chloride anions and sodium and magnesium cations. The rate of accumulation of silica decreases further, whereas those of iron and aluminum increase. The content of bicarbonate ion varies only slightly depending on the particular pH value of the environment. Of course, the evolution of water composition does not terminate during this stage, but it involves mainly the processes of evaporative concentration, which have been thoroughly discussed in the literature.

Thus, starting from the very first stages of formation, groundwaters concentrate chemical elements non-uniformly (selectively). A particular stage of formation may be characterized by rapid accumulation of some elements and less extensive accumulation of others. These relations may change during the following stage.

The salinity variations are accompanied by changes in water composition. Leach waters from aluminosili-



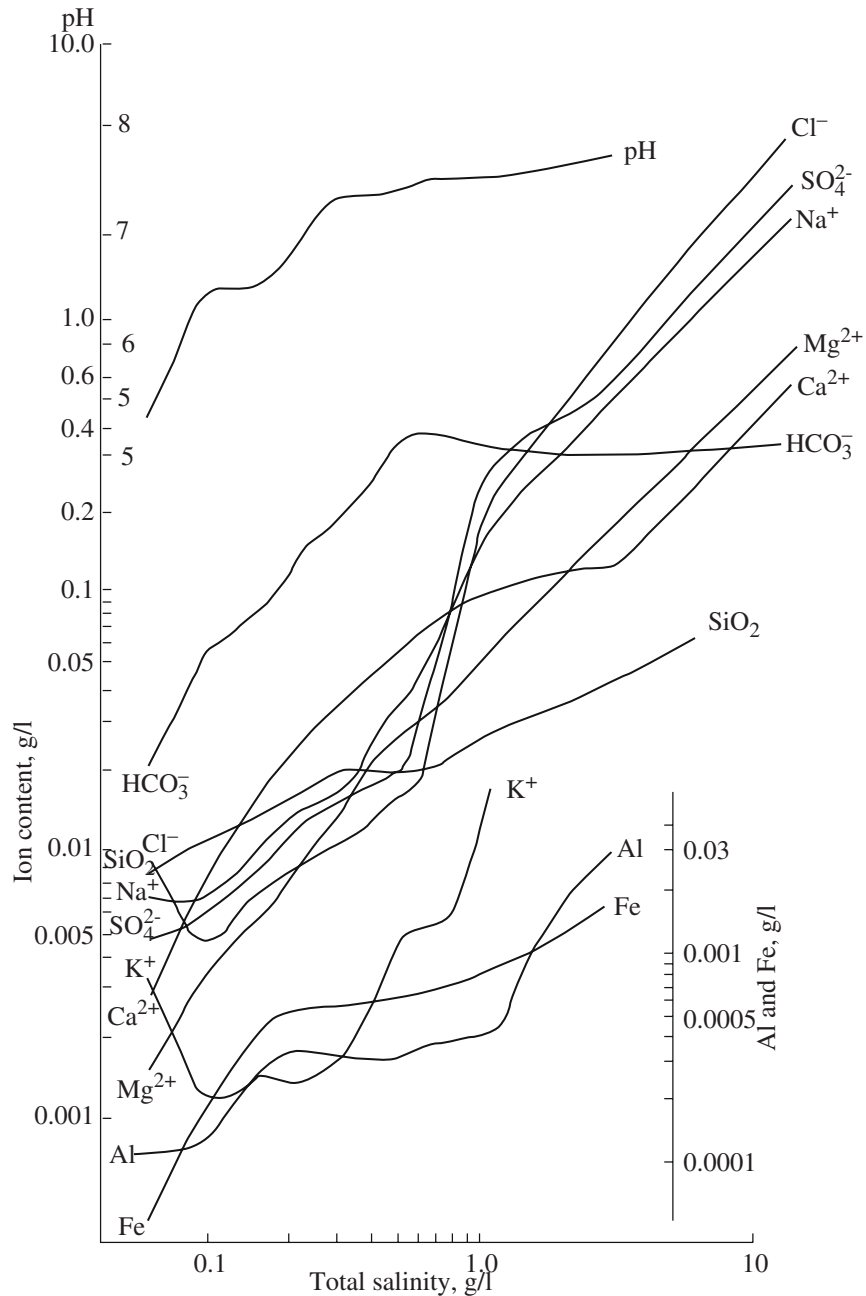


Fig. 18. Correlation of the average contents of major elements with the total salinity of groundwater.

cate rocks show a continuous change in cation composition from a multielement one controlled by the host rock composition to calcium–sodium and sodium–calcium to sodium types. The second type usually gives way to the third at a salinity of <1 g/l, and the latter gives way to soda waters at a salinity of >1 g/l. The waters of continental salinization are in most cases sodic, but their anion composition changes from bicarbonate to sulfate to chloride with all transitional subtypes (Fig. 18). This raises the problem of more sophisticated investigation of the conditions of concentration of each element in the solution depending on the char-

acter of the particular geochemical environment and secondary mineral formation.

### 2.3. Comparative Analysis of the Compositions of Groundwater, River Water, and Seawater

Table 25 shows the compositions of the natural water types of interest. The analysis of these data leads us to several interesting conclusions. Let us consider first the compositions of subsurface and surface fresh waters. It can be readily seen that, within this group, the subsurface variety is more saline: the total content of

**Table 25.** Average chemical compositions of natural waters

Component	Unit	Groundwaters of the supergene zone	Leach waters	River waters [233, 234]	River waters [235–237]	Seawater [234]	Concentration factor for seawater relative to groundwater
1	2	3	4	5	6	7	8
pH	–	6.90	6.75	–	–	8.2	–
HCO <sub>3</sub> <sup>–</sup>	mg/l	187	146	58.4	52.0	488	2.6
SO <sub>4</sub> <sup>2–</sup>	"	70.7	12.4	11.2	8.25	2712	35.3
Cl <sup>–</sup>	"	59.7	10.1	7.8	5.75	19400	325
NO <sub>3</sub> <sup>–</sup>	"	2.40	1.56	1.0	0.44	–	–
F <sup>–</sup>	"	0.48	0.23	0.10	0.10	1.3	2.7
NO <sub>2</sub> <sup>–</sup>	"	0.19	0.10	–	0.03	–	–
Na <sup>+</sup>	"	67.6	13.8	6.3	5.15	10800	160
Ca <sup>2+</sup>	"	39.2	27.4	15	13.4	411	10.5
Mg <sup>2+</sup>	"	18.2	11.2	4.1	3.35	1290	70.9
K <sup>+</sup>	"	5.15	1.84	2.3	1.30	392	76.1
NH <sub>4</sub> <sup>+</sup>	"	0.59	0.52	–	0.02	–	–
SiO <sub>2</sub>	"	17.9	14.5	13.1	10.4	6.2	0.35
Total	"	469	239	120	100	35500	75.7
Free CO <sub>2</sub>	"	26.6	26.1	–	–	–	–
C <sub>org</sub>	"	8.29	8.12	6.9	–	0.5	0.06
N <sub>org</sub>	"	0.98	–	0.7	–	0.5	0.51
Fe	µg/l	481	424	670	40	3.4	0.007
Al	"	226	190	400	50	1.0	0.004
Sr	"	183	88.7	50	60	8100	44.3
Br	"	103	40.8	20	–	67300	790
B	"	77.9	35.4	10	–	4450	57.1
P	"	58.0	56.9	20	10	88	1.52
Mn	"	54.5	34.3	7.0	8.2	0.4	0.007
Zn	"	38.4	30.3	20	–	5.0	0.12
Ba	"	18.3	14.4	10	–	21	1.15
Ti	"	17.4	6.96	3.0	10.0	1.0	0.06
Li	"	13.0	6.20	3.0	–	170	13.1
J	"	8.02	6.00	7.0	–	64	7.98
Cu	"	5.38	4.00	7.0	–	0.9	0.16
Ni	"	3.38	3.11	0.3	–	6.6	1.84
Cr	"	2.70	2.78	1.0	–	0.2	0.07
Pb	"	2.65	2.18	3.0	–	0.03	0.01
Rb	"	1.86	1.81	1.0	–	120	64.1
Mo	"	1.75	1.16	1.0	–	10	5.71
As	"	1.46	1.34	2.0	–	2.6	1.78
V	"	1.34	1.01	0.9	–	1.9	1.42
U	"	1.31	0.56	0.04	–	3.3	2.52
Zr	"	1.20	1.16	–	–	0.026	0.02
Se	"	0.72	0.45	0.2	–	0.09	0.12

Таблица 25. (Contd.)

Component	Unit	Groundwaters of the supergene zone	Leach waters	River waters [233, 234]	River waters [235–237]	Seawater [234]	Concentration factor for seawater relative to groundwater
1	2	3	4	5	6	7	8
Sb	"	0.68	0.64	1.0	–	0.33	0.48
La	"	0.67	0.67	0.2	–	0.0034	0.005
Nb	"	0.45	0.45	–	–	0.015	0.002
Co	"	0.39	0.33	0.2	–	0.39	1.00
Sn	"	0.39	0.35	0.5	–	0.81	2.08
Ga	"	0.37	0.32	0.09	–	0.03	0.08
Cs	"	0.26	0.18	0.02	–	0.3	1.15
Ag	"	0.26	0.22	0.3	–	0.28	1.08
Th	"	0.24	0.10	0.1	–	0.0004	0.002
Cd	"	0.24	0.20	–	–	0.11	0.46
Be	"	0.19	0.16	–	–	0.0006	0.003
Sc	"	0.07	0.07	0.004	–	<0.004	0.06
Hg	ng/l	41.1	41.1	70	–	150	3.65
Au	"	5.32	3.40	2.0	–	11.0	2.07
Ra	pg/l	0.46	0.25	0.35	–	0.1	0.22

salts in the groundwater of the supergene zone is in general four times higher than that in river waters. The same holds for many trace components. Only the relations of Fe and Al contents remain obscure because various authors have reported contradictory values for these elements in river waters.

A comparison of leach waters with river waters, which is especially interesting because the former are the main sources of the latter, shows that the groundwaters are again almost two times more saline than the river waters. This relation is consistent and logical because river waters are mixtures of groundwaters and fresher surface waters.

The groundwaters are relatively enriched in both the major components and most of the trace elements. The only exceptions are Cu, Pb, Sb, Hg, Sn, and Ag. However, even in this case, the observed differences are minor and probably stem mainly from the uncertainties in the obtained average values rather than from the influence of some natural factors. On the other hand, the river waters are strongly depleted (by a factor of 4 or more) relative to the groundwaters in a number of chemical elements, including Br, Mn, B, Li, Ti, U, Ni, Cs, and Sc. The reason for this phenomenon is still unclear and requires special analysis.

Many chemical elements are concentrated in groundwater more extensively relative not only to river waters but even to seawater, although the total dissolved solids in seawater are 80 times higher than in groundwater. This is indicative of a peculiar character of the geochemical environment that develops in

groundwaters, which should not therefore be identified with the environment of marine basins.

Table 26 lists the elements whose concentrations in groundwaters differ from those in seawater by more than an order of magnitude. It can be seen that among the elements that are most intensely concentrated in the ocean are primarily elements showing elevated mobility under supergene conditions. The only exceptions are potassium and rubidium, whose mobility in groundwaters is not high. In turn, the groundwaters are enriched relative to seawater primarily in hydrolysate elements, which are rather immobile under supergene zone conditions. Consequently, groundwaters rather than seawater are most favorable for the migration of hydrolysate elements. This is probably related to the fact that groundwaters are more acidic and contain more organic matter, which can form complex compounds with poorly mobile elements.

The observed difference in geochemical conditions between fresh groundwaters and seawater results in significant narrowing of the concentration interval within which the elements occur in solution in the former case and its extension in the latter case. This circumstance creates a certain disharmony between groundwaters and seawater and leads to the accumulation of poorly mobile elements in marine bottom sediments.

Thus, there are certain differences between the compositions of groundwaters from the supergene zone and seawater: the ocean concentrates primarily mobile elements, whereas groundwaters concentrate both mobile and relatively immobile elements. The concentrations of the latter in groundwaters are, therefore, higher than

**Table 26.** Concentration factor (CF) of selected chemical elements in seawater

Elements with a higher content in seawater relative to groundwaters		Elements with a lower content in seawater relative to groundwaters			
Element	CF	Element	CF	Element	CF
Bromine	653	Thorium	0.002		
Chlorine	325	Niobium	0.002	Titanium	0.06
Sodium	160	Beryllium	0.003	Chromium	0.07
Potassium	76.1	Aluminum	0.004	Gallium	0.08
Magnesium	70.9	Lanthanum	0.005	Selenium	0.12
Rubidium	64.1	Scandium	0.006		
Boron	57.1	Iron	0.007		
Strontium	44.3	Manganese	0.007		
Sulfur	35.3	Lead	0.01		
Lithium	13.1	Zirconium	0.02		
Calcium	10.5	Organic carbon	0.06		

in seawater. However, this holds true only for a small number of elements (10–15), whereas the concentration of all other elements in groundwaters is much lower than in the ocean (Table 26). Therefore, we cannot agree with the statement of Belyakova et al. [238, p. 23] that a comparison of element concentrations determined in the natural waters of known ore-bearing regions with those in seawater shows that even the lowest among the former are one to two orders of magnitude higher than the latter. This inference is grossly misleading because these authors compared the concentrations of chemical elements in the dry residue of groundwaters with their percentages in seawater relative to the weight of water with mineral salts, i.e., in the units that were recommended by Vernadsky and used by A.P. Vinogradov, whose work was cited by Belyakova et al.

Finally, let us note some characteristic features of groundwater chemistry compared with the compositions of the lithosphere and biosphere (Table 27). First, the contents of chemical elements in the waters are several orders of magnitude lower than those in rocks and living matter. Except for oxygen, which is the basis of all the materials of the Earth's crust, only the concentrations of chlorine, sodium, magnesium, sulfur, and nitrogen in seawater are comparable with or even higher than those in rocks (chlorine) and living matter (chlorine, sodium, magnesium, and bromine). Consequently, the hydrosphere shows specific geochemical characteristics that distinguish it from both the lithosphere and the biosphere. The hydrosphere concentrates most extensively those elements that do not tend to form a stable crystal lattice under the thermodynamic conditions of the Earth's upper crust. Among them are

either elements with large ionic radii (chlorine, bromine, potassium, etc.) or elements with small ionic radii (sulfur, carbon, nitrogen, etc.) which can form complex compounds with large radii ( $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$ ,  $\text{NO}_3^-$  etc.). This is one of the most important differences between the compositions of the hydrosphere and the lithosphere.

Among the elements that show the highest concentrations in the hydrosphere are mainly either lithophile elements with an 8-electron structure of the atomic shell (sodium, magnesium, chlorine, potassium, calcium, strontium, and barium) or chalcophile elements with 8- and 18-electron structures of the atomic shell (sulfur, bromine, iodine, and mercury). On the other hand, elements with the completing type of electron shell and inert gases show the lowest concentrations.

We believe that the material briefly presented here demonstrates that the distribution of chemical elements in the hydrosphere is different from that in the lithosphere, which emphasizes the specific composition of the water shell of the Earth.

### CHAPTER 3. EQUILIBRIUM–NONEQUILIBRIUM CHARACTER OF THE WATER– $\text{CO}_2$ –ROCK SYSTEM

The above-described empirical dependence of groundwater salinity on the intensity of water exchange and, hence, indirectly, on the time of water–rock contact needs to be explained. This, in turn, poses the problem of the determination of the degree of groundwater saturation relative to the host rocks.

**Table 27.** Comparison of the abundances of chemical elements in low-salinity groundwaters, seawater, living matter, and rocks

Decade	Wt %	Fresh groundwater	Seawater	Living matter [239]	Lithosphere [240]
I	>10 <sup>1</sup>	O, H	O, H	O, C, H	O, Si
II	10 <sup>1</sup> –10 <sup>0</sup>	–	Cl, Na	–	Al, Fe, Ca, Na, K, Mg
III	10 <sup>0</sup> –10 <sup>-1</sup>	–	Mg	N, Ca, K, Si	Ti, Mn
IV	10 <sup>-1</sup> –10 <sup>-2</sup>	–	S, Ca, K	Mg, P, S, Na, Cl, Fe	P, F, Ba, S, Sr, C, Cl, Zr, Rb
V	10 <sup>-2</sup> –10 <sup>-3</sup>	C, Cl, Na, Ca, S, Mg	Br, C, N	Al, Ba, Sr, Mn, B, TR	V, Cr, Zn, Ce, Ni, Cu, Nd, Li, Y, La, Nb, Ga, N, Co, Pb, Th, B, Sc
VI	10 <sup>-3</sup> –10 <sup>-4</sup>	Si, K, N	Sr, B, Si, F	Ti, F, Zn, Rb, Cu, V, Cr, Br, Ge	Pr, Sm, Gd, Dy, Tb, Be, Cs, Er, Sn, U, Ta, Br, As, Ho, Ge, W, Eu, Mo, Hf, Tl
VII	10 <sup>-4</sup> –10 <sup>-5</sup>	Fe, Al, Sr, Br	Li, Rb	Ni, Pb, Sn, As, Co	Lu, Sb, J, Yb, Jn, Cd
VIII	10 <sup>-5</sup> –10 <sup>-6</sup>	P, Mn, B, Zn, Ba, J, Li, Ti	J, Ba, Mo	Li, Mo, Y, Cs	Hg, Ag, Se, Pd
IX	10 <sup>-6</sup> –10 <sup>-7</sup>	Cu, U, Ni, Cr, Rb, Pb, As, Mo, V, Sb, Zr	Ni, Zn, Fe, U, As, V, Al, Ti	Se, U, Hg	Bi, Au, Te
X	10 <sup>-7</sup> –10 <sup>-8</sup>	Hg, Se, Co, Ga, Cs, Th, Sn, Cd, Ag, Be, La, Y, Nb, Ge	Cu, Sn, Mn, Co, Sb, Cs, Ag, Cr, Hg, Cd	–	Re
XI	10 <sup>-8</sup> –10 <sup>-9</sup>	Au, Sc, Bi, W	Se, Ge, Pb, Ga, Zr, Bi, Nb, Y, Au	–	–
XII	10 <sup>-9</sup> –10 <sup>-10</sup>	Ce, In, Yb	La, Sc, Ce	–	–
XIII	10 <sup>-10</sup> –10 <sup>-11</sup>	–	Yb, Be, Th, W	–	–
XIV	10 <sup>-11</sup> –10 <sup>-12</sup>	–	–	Ra	–
XV	10 <sup>-12</sup> –10 <sup>-13</sup>	Ra	–	–	–
XVI	10 <sup>-13</sup> –10 <sup>-14</sup>	–	Ra	–	–

### 3.1. Equilibrium of Groundwater with Carbonate Minerals

The diversity of aquifer rocks calls for a flexible approach to the problem of their interaction with aqueous solutions. The most common in the supergene zone are aluminosilicate and carbonate rocks, which play the main role in the enrichment of groundwaters in chemical elements and deserve, therefore, special attention. It should be emphasized that the rock types considered here show different mechanisms of interaction with solutions: carbonates dissolve congruently in water, and aluminosilicates, incongruently. Consequently, different approaches must be used to describe their equilibrium with aqueous solutions.

In order to estimate the extent of variations in groundwater saturation with respect to calcite as a function of salinity and alkalinity, we used the nonequilibrium index [132], or, after Zverev, the *A* coefficient [155]:

$$A = \log \frac{K}{Q}, \quad (3.1)$$

where *K* is the constant of the reaction and *Q* is the reaction quotient [241]. As the water approaches satu-

ration with respect to a certain compound, the nonequilibrium index decreases toward zero; its value becomes negative when the water is oversaturated, and a zero value corresponds to the equilibrium state.

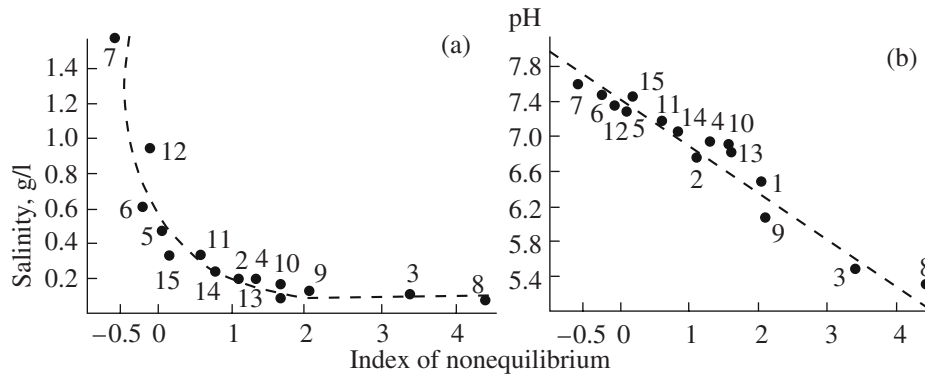
In the case of calcite, the water–mineral equilibrium is controlled by the reaction



the constant of which at 25°C is 10<sup>-5.8</sup>, whereas the average value of the reaction quotient in various landscape zones ranges from 10<sup>-5.1</sup> to 10<sup>-10.1</sup> and the nonequilibrium index ranges from -0.5 to +4.5 (Fig. 19). The highest values of the nonequilibrium index were detected in the waters of wet savannas and wetlands of the temperate zone; i.e., these waters are undersaturated to the highest extent with respect to calcite. Negative values of the nonequilibrium index, indicating solution oversaturation with calcium carbonate, were observed in the waters of forest steppe and steppe terrains. The waters of southern taiga and mountain steppe terrains are close to saturation, but, on average, do not reach equilibrium with calcite.

It is important to point out that there is a distinct inverse proportionality between the nonequilibrium





**Fig. 19.** Dependence of the index of nonequilibrium on the (a) total salinity and (b) pH of groundwater from various landscapes: 1, tundra; 2, northern taiga; 3, wetlands of the temperate zone; 4, mixed forests; 5, southern taiga; 6, forest steppe; 7, steppes of the temperate zone; 8, humid savanna; 9, tropical equatorial forests; 10, subtropical forests; 11, arid savanna; 12, steppes of the tropical zone; 13, high mountain zone; 14, medium mountain forests; and 15, mountain steppe.

index and the total salinity of water (Fig. 19a): with increasing salinity, the degree of solution saturation with calcite increases, and the nonequilibrium index becomes zero at a salinity of 0.6 g/l; i.e., equilibrium is reached. A similar relation was detected between the nonequilibrium index and the pH value (Fig. 19b): with increasing solution alkalinity, the nonequilibrium index decreases, approaching zero at pH 7.4, when equilibrium between calcite and water is reached.

Thus, groundwaters with a salinity of more than 0.6 g/l and pH higher than 7.4 are usually saturated in calcium carbonate, which, therefore, does not dissolve under these conditions but precipitates from the solution. Such carbonate-saturated waters occur under the conditions of forest steppe, steppe, semidesert, and desert terrains. In all other cases, calcite-equilibrated waters may, of course, also occur, but their distribution is limited and related to the influence of local rather than regional factors.

Among the latter, of special significance are carbonate rocks themselves because waters within them can be potentially completely saturated in the corresponding salts. Such facts have been documented in many landscape zones. The role of local factors must, therefore, always be taken into account, but here we focus on a more general problem related to evaluating the influence of regional factors.

Consequently, the carbonate saturation of groundwater shows a zoned character, which is eventually controlled by climatic rather than lithological factors. That is, during a certain stage of water evolution, when the total salt content is 0.6 g/l and the pH is 7.4, groundwaters become saturated in carbonates not only within carbonate sequences but also in aluminosilicate rocks owing to the decomposition of the latter. This is supported by the results of special studies. For instance, Pawar [228] investigated the equilibrium state of basalt-hosted groundwaters in the steppe terrains of India and demonstrated that most of these waters were in equilibrium with calcite and dolomite at a  $\text{CO}_2$  par-

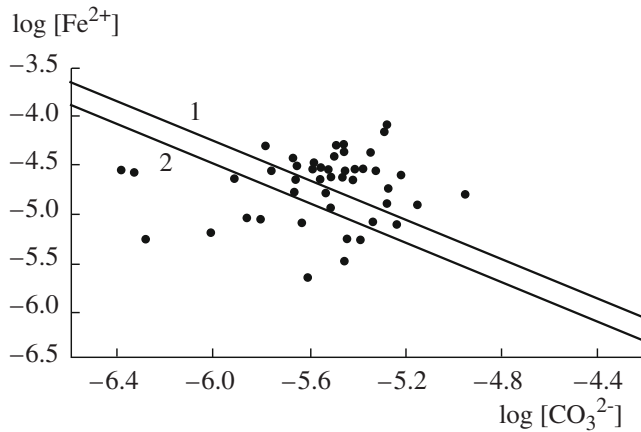
tial pressure of  $10^{2.0}$ – $10^{3.3}$  Pa. Identical relations were observed in brackish and saline groundwaters from the Yucatán region (Mexico), which are ubiquitously saturated in calcite, aragonite, and dolomite [242]. Many other similar examples can be found.

Thus, despite the low solubility of aluminosilicates, under favorable conditions (weak water exchange), they may supply groundwaters with such amounts of salts that they are precipitated from solution as secondary carbonates. Owing to the zoned character of water exchange in the supergene zone, *the phenomenon of water saturation with respect to carbonates is also zoned and is controlled by the time of water interaction with rocks, primarily, with aluminosilicate rocks.*

A somewhat different situation is typical of the equilibrium state between groundwater and siderite. The supergene zone is dominated by oxidizing geochemical conditions, which prevent  $\text{Fe}^{2+}$  accumulation in waters; correspondingly, equilibrium with siderite is not attained. However, at depths of 100–200 m in confined aquifers isolated from the direct influence of atmospheric precipitation or even on the surface (wetlands), anoxic environments are often formed. They are favorable for iron accumulation, which eventually produces siderite-saturated groundwaters. This can be exemplified by the Tomsk water supply system, whose sites mostly occur above the line of siderite saturation at temperatures of 7 and 25°C, although there are, of course, waters not equilibrated with siderite (Fig. 20).

The same relationships are characteristic of many other fresh waters from artesian basins. Krainov and Shvets [19] convincingly demonstrated that oxygen- and sulfide-free fresh waters are formed in the upper levels of many artesian basins, weathering mantles, zones of tectonic faults in crystalline massifs, and other localities. Such waters contain tens of milligrams of iron per liter and are usually equilibrated with siderite, which controls the extent of iron accumulation in them.

Consequently, the degree of groundwater–siderite equilibrium is controlled by vertical rather than latitu-



**Fig. 20.** Degree of groundwater saturation in iron carbonates for the Paleogene horizon of the Tomsk water intake. Saturation levels are shown for (1) 7 and (2) 25°C.

dinal zoning and is related to the redox state of the geochemical environment.

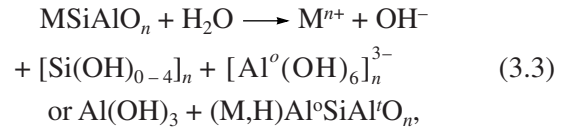
### 3.2. Equilibrium of Groundwater with Aluminosilicate Minerals

Before consideration of the problem of groundwater–aluminosilicate equilibrium, it should be emphasized that, although this problem was formulated long ago, it had never been systematically explored in terms of chemistry and thermodynamics before the pioneering studies of Garrels and Christ [241]. Based on the well-known facts of extensive aluminosilicate weathering under supergene zone conditions, the nonequilibrium state of this system has long been recognized. Related issues were considered from this viewpoint in well-known studies by B.B. Polynov, V.I. Vernadsky, A.E. Fersman, A.I. Perel'man, I.I. Ginzburg, and many other researchers. However, the recognition of nonequilibrium does not reveal its nature and the degree of its manifestation in particular cases. For instance, it remains unclear whether water equilibrium with primary aluminosilicates can be reached, and, if so, under which conditions, or, if not, why and what factors control this nonequilibrium state.

Statements that processes occurring on the Earth's surface are generally nonequilibrium ones, the system is open, the cycles are open, etc., are now commonplace; however, little attention is given to the investigation of the nature of these nonequilibrium processes, which can be illustrated by the very poor knowledge of water–aluminosilicate equilibria.

Leaving aside for the moment the detailed mechanisms of the incongruent dissolution of aluminosilicates, which will be considered in Section 4.2, we note only that the dissolution, despite its complexity, is

related mainly to phenomena of hydrolysis. The reaction of hydrolysis was presented by Keller [248] as



where  $n$  refers to indefinite atomic proportions; the superscripts  $o$  and  $t$  indicate the octahedral and tetrahedral coordinations, respectively;  $M$  refers to metal cations; and the last component of the reaction,  $(\text{M,H})\text{Al}^o\text{SiAl}^t\text{O}_n$ , corresponds to at least three possible substances: clay mineral, zeolite, and silicate fragments.

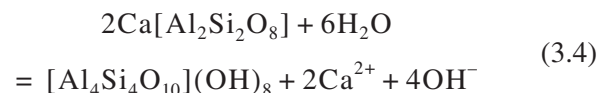
Hydrolysis includes coupled chemical decomposition of a solid substance and water. Unfortunately, accepting current geological concepts on the hydrolysis of aluminosilicates, researchers often overlook the accompanying chemical decomposition of water molecules. In this connection, it is pertinent to remember the opinion of Keller [248, p. 100] that water has mostly dissociated to  $\text{H}$  and  $\text{OH}$  ions since the onset of chemical weathering, and that the  $\text{OH}$  ions have been transported together with metal cations to the ocean and caused an increase in its alkalinity, while the  $\text{H}$  ions have bonded to aluminosilicate anions to form clay minerals, which are chemically characterized as poorly soluble and weakly dissociating (weak) acids.

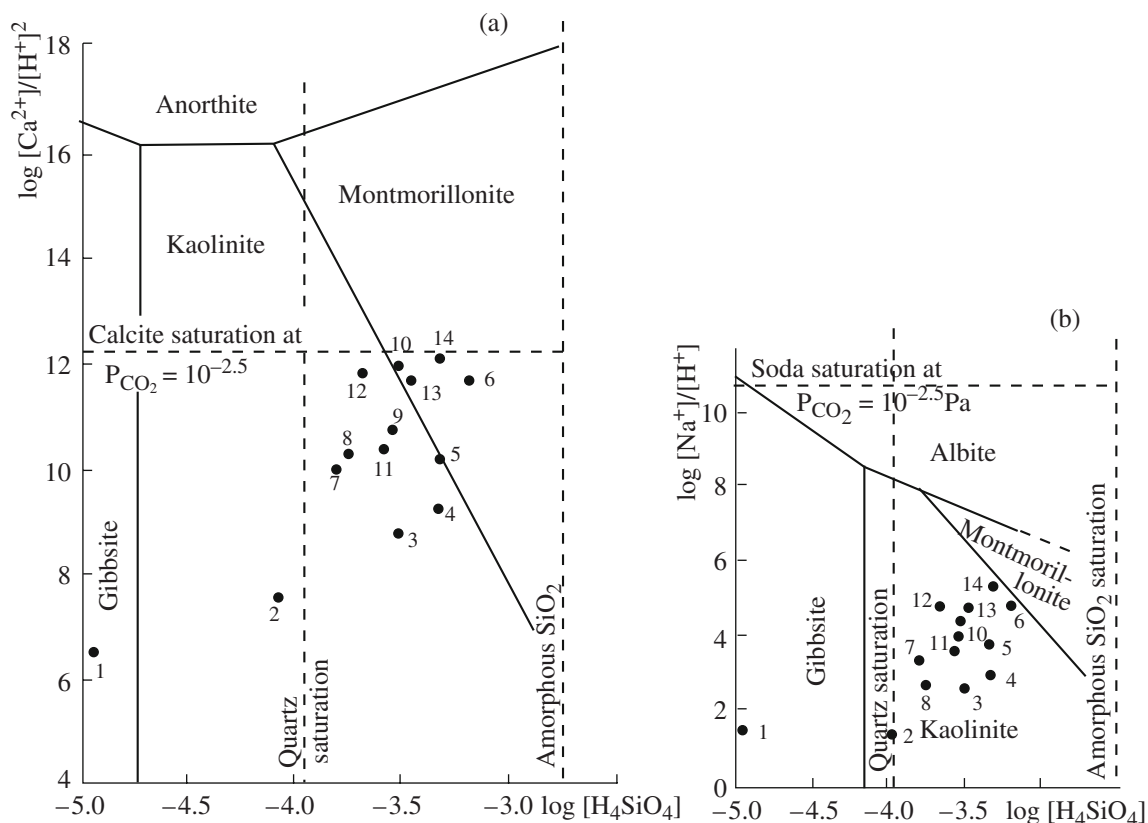
The analysis of the available experimental data on aluminosilicate decomposition under the influence of water suggests that, in most cases, the hydrolysis of aluminosilicates involves the *complete transfer of chemical elements into solution and their subsequent precipitation as newly formed secondary mineral phases* [249]. Consequently, the geochemical environment rather than the chemistry of the initial mineral controls the composition of the produced secondary minerals.

Experimental data indicate that even minor concentrations of aluminum and silicon may lead to the saturation of low-temperature waters in clay minerals and high-temperature waters in zeolites and other compounds. Therefore, the dissolution of aluminosilicates is always accompanied by the formation of some secondary product with simultaneous transfer of mobile cations and part of silica into the solution.

Thus, the interaction between aluminosilicates and water results in the formation of secondary products, whose solubility is lower than that of the initial substances. This is a very important circumstance implying persistent water undersaturation with respect to the initial minerals, which, therefore, can be dissolved during the whole time of their interaction with groundwaters.

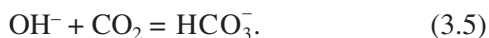
Another important process accompanying hydrolysis is the neutralization of the produced alkalinity. Indeed, as can be seen from generalized hydrolysis reaction (3.3) and particular reactions of the type





**Fig. 21.** Systems (a) HCl-H<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-CaO-CO<sub>2</sub>-SiO<sub>2</sub> and (b) HCl-H<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-Na<sub>2</sub>O-Ca-SiO<sub>2</sub> at 25°C with data on the average composition of groundwaters from various landscape zones. (1) Precipitation, (2) wetlands of the forest zone, (3) tropical forests, (4) savanna, (5) subtropical forests, (6) tropical steppes, (7) permafrost taiga terrains, (8) high mountains, (9) mountain forests, (10) mountain steppes, (11) mixed forests, (12) southern taiga, (13) forest steppes, and (14) steppes of temperate climate.

the charge of mobile cations in the solution is compensated by the OH<sup>-</sup> group that is formed during hydrolysis. When CO<sub>2</sub> is present in water, most of the produced alkalinity is neutralized via the reaction



The constant of this reaction is 10<sup>6.2</sup> at 25°C. It can be easily shown that, under CO<sub>2</sub> partial pressures characteristic of natural groundwaters (10<sup>1.0</sup>-10<sup>2.5</sup> Pa), the alkalinity produced during weathering is continuously neutralized by carbonic acid and various organic acids. This mechanism results in continuous transformation of one of the products of the hydrolysis reaction and formation of bicarbonate groundwaters.

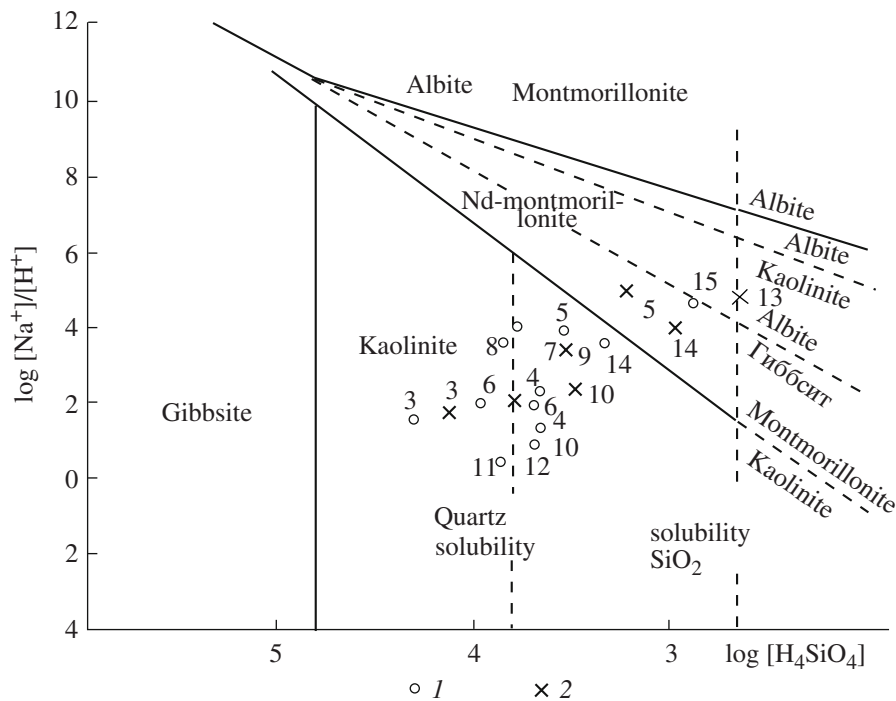
Thus, the second (after the formation of secondary products) characteristic feature of the water-aluminosilicate system is that part of the hydrolysis products participate in the neutralization reaction, which maintains the nonequilibrium state of the water-primary aluminosilicate system. The neutralization reaction in turn occurs only under the influence of organic, carbonic, and occasionally other mineral acids. Therefore, the hydrolysis of aluminosilicates should be considered in connection with the formation of acidic products in groundwaters. The source of acidic products is often

organic matter or metamorphic and magmatic processes in deep levels of the Earth's crust. This raises the problem of the correlation between the intensity of hydrolysis reactions and the scale of acid formation.

Finally, the phenomenon of ion removal from the zone of the hydrolysis reaction should be taken into account because it also disturbs the water-rock equilibrium. Intense water exchange in the upper crust leads to the rapid removal of the products of dissolution, which decreases with depth and probably reaches the minimum values in the case of sedimentation waters in the lower parts of artesian basins. All these factors affect the character of development, scales of occurrence, and kinetics of hydrolysis reactions in various parts of the Earth's crust.

Before we proceed to the calculation of groundwater equilibrium with aluminosilicate rocks, note that this problem was first considered in detail by Garrels and Christ [241], who developed methods for its solution.

The analysis of the data presented in Chapter 1 showed that waters from all landscape zones are undersaturated with respect to primary aluminosilicates. This is additionally supported by the summary diagram based on average data (Fig. 21a), which clearly shows



**Fig. 22.** Diagram of albite–montmorillonite–kaolinite–gibbsite equilibria showing the compositions of waters from (1) granites and (2) waters of some regions [68] (denoted by numbers): 3, Norway; 4, Vosges, France; 5, French Massif Central; 6, Alrance, France; 7, Bretagne, France; 8, Corsica; 9, Sahara; 10, Madagascar; 11, Korhogo, Côte d'Ivoire, wet season; 12, Korhogo, dry season; 13, Côte d'Ivoire; 14, Senegal; and 15, Chad.

that all of the water compositions plot within the stability field of clay minerals rather than primary aluminosilicates. This is also reflected in Fig. 21b, which was constructed in different coordinates, and Fig. 22, adopted from Tardy [68].

In order to confirm this, let us consider data on the equilibrium of cold waters with aluminosilicates in Iceland. This region contains abundant low-salinity but strongly alkaline cold waters, which are formed in summer at the expense of firn field melting [245]. The pH values of these waters are, with rare exceptions, 8.1–9.2 and occasionally even up to 9.45. But, even in this case, they are not in equilibrium with primary aluminosilicates (Fig. 23). As was noted by Gislason et al. [245], the coldest ultrafresh waters, formed directly during the melting of firn fields, are in equilibrium with gibbsite, whereas the waters of springs, which have resided in rocks for 40–400 days, are always in equilibrium with Mg- and Ca-smectites, kaolinite, and occasionally laumontite and illite. Consequently, the neutralizing influence of carbonic acid is in this case less significant than the influence of alkalinity produced by aluminosilicate dissolution, and this circumstance results in the high pH values of cold waters.

As can be seen from Fig. 21, the highest degree of nonequilibrium is characteristic of wetland waters, which are the least saline and most acidic. In order of decreasing degree of nonequilibrium, they are followed

by the waters of tropical forests, tropical savannas, subtropical forests, permafrost taiga landscapes, mountain regions, and the forest zone of temperate climate. The lowest degree of nonequilibrium is observed in the weakly alkaline and relatively highly saline waters of forest steppe and steppe terrains. However, even in the latter case, the degree of nonequilibrium is very high and the waters are far from saturation.

It is interesting that the carbonate barrier hampers the equilibration of waters with primary aluminosilicates (Fig. 21a); i.e., as the concentration of calcium in the solution and the pH value increase, the waters are saturated in carbonates and calcite begins to precipitate from the solution. This phenomenon is widespread in the forest steppe and steppe zones. The precipitation of carbonates decreases the concentrations of corresponding elements in the solution and contributes to the retention of the nonequilibrium state in the water–host aluminosilicate system.

Thus, even after the attainment of carbonate equilibrium in the solution, water remains out of equilibrium with primary aluminosilicates and continues to decompose them; however, during this process, calcium is not accumulated in the solution but precipitates as carbonates, other cations, including sodium, whose compounds are characterized by low degrees of water saturation (Fig. 21b), continue to accumulate in the solution. This is why sodium becomes dominant in

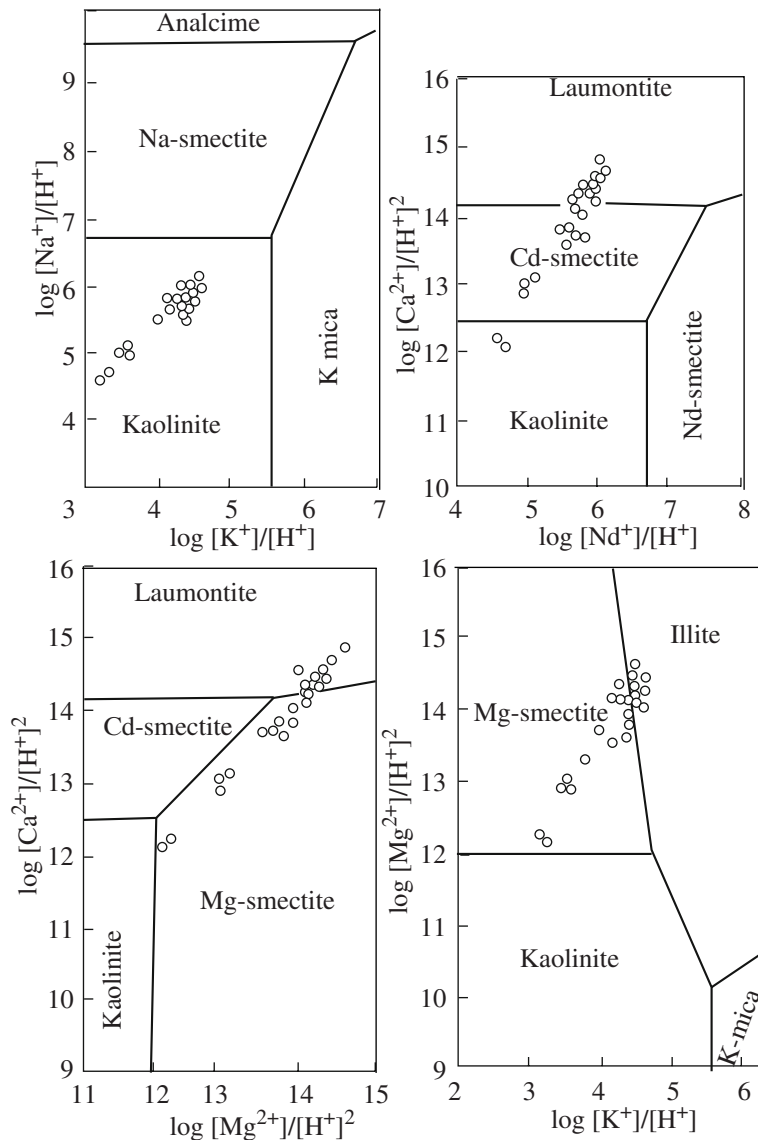


Fig. 23. System CaO–MgO–Na<sub>2</sub>O–K<sub>2</sub>O–SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub>–H<sub>2</sub>O at 25°C and  $\log[H_4SiO_4] = -3.60$  with data on springs of Iceland.

the solution instead of calcium at a certain stage of natural water evolution (Fig. 18).

Thus, *the primary aluminosilicate–groundwater system of the supergene zone is out of equilibrium in all landscapes without exception*, and this predetermines the continuous decomposition of bedrocks by water with the formation of weathering products, which are stable under the given geochemical conditions and, very importantly, are in equilibrium with groundwaters. *Consequently, the equilibrium of waters with rocks has a dual character: the water–rock system is out of equilibrium relative to primary aluminosilicates but may be in equilibrium with secondary minerals under certain geochemical conditions.* The latter factor controls the compositions of the resulting weathering products. In other words, only those compounds are formed during weathering that are in equilibrium with water and,

therefore, resistant to the aggressive influence of groundwaters.

Among the phases equilibrated with water are kaolinite and, occasionally, gibbsite under the acidic conditions of tropical regions; illite and kaolinite in the weakly acidic and neutral environments of northern and mountain regions; and montmorillonite and calcite under the weakly alkaline conditions of forest steppes and steppes (Figs. 21, 22).

Thus, owing to the nonequilibrium character of the water–primary aluminosilicate system, groundwaters continuously destroy igneous and metamorphic rocks, producing some weathering products. Most of the chemical elements migrate into groundwaters, whose salinity increases with increasing time of water–rock interaction. The latter parameter is in turn controlled by the intensity of water exchange.



Does the conclusion on the equilibrium of water with weathering products contradict its mobility and continuous washing of the supergene zone? Indeed, secondary minerals are in equilibrium only with those solutions in which they were formed, and a change of water should disturb this equilibrium. How should the equilibrium of water with secondary products be understood?

In order to resolve this apparent contradiction, several points must be taken into consideration. First, the produced clay minerals bind considerable amounts of interlayer water in their structure, which protects their crystal lattice from the destructive activity of aggressive gravitational waters. Second, owing to their extremely fine-grained texture and the presence of bonded water, clay minerals show a very low permeability, which additionally hinders their interaction with gravitational waters. Third, clay minerals are very poorly soluble and, therefore, they are equilibrated with precipitation in the soil horizon (Fig. 24). This is the most important factor. Fourth, the stability field of clay minerals is very wide, and thus even considerable variations in the activities of ions of major elements in the solution will not always lead to their decomposition.

Thus, clays are exceptional among all secondary minerals: their texture, composition, and structure ensure their resistance to the destructive action of the environment in which they were formed. In this case, we witness the amazing capacity of inanimate nature to preserve what it has created itself. Clays, formed owing to the development of a nonequilibrium water–primary aluminosilicate system, not only turn out to be the most suited to their environment but also acquire a certain safety factor in the case of changes in environmental characteristics.

Of course, the conclusion on the stability of clay minerals starting from soil horizons does not exclude the possibility of their destruction by groundwaters during some seasons or leaching of some chemical elements from them. We fully agree with the assertion of Ogilvy [246] that, in terms of chemistry, clay minerals should be considered as salts of aluminosilicic acids. They dissociate in a water medium, producing large crystalline anions (colloidal micelles) and cations [246, p. 87]. Such dissociation and cation exchange result in the enrichment of solutions in chemical elements, but the degree of this enrichment under equilibrium conditions remains very low and may increase significantly only in the case of an abrupt change in the geochemical environment and a disturbance of the thermodynamic equilibrium, when clay minerals become unstable. Therefore, the main sources of chemical elements in waters from aluminosilicate rocks are primary minerals rather than the products of their decomposition.

Thus, the equilibrium–nonequilibrium character of the water–CO<sub>2</sub>–aluminosilicate system predetermines, on the one hand, the general possibility of primary alu-

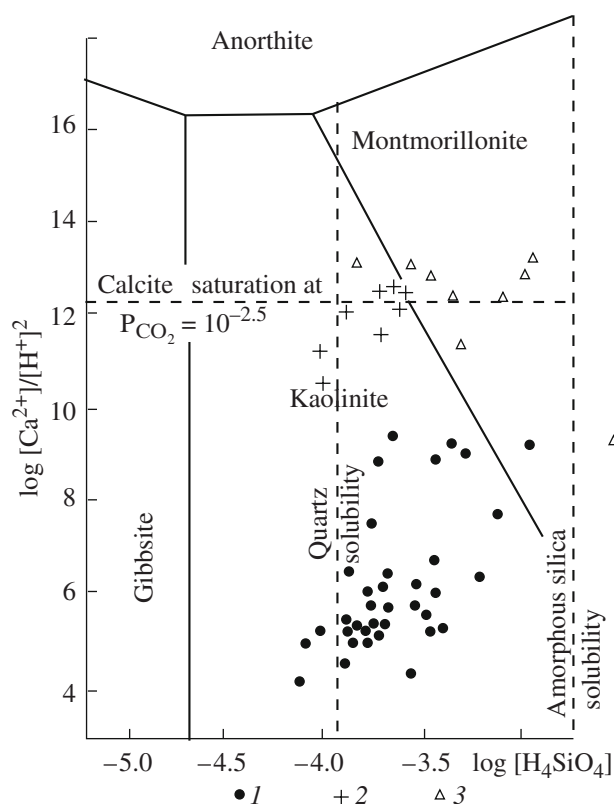
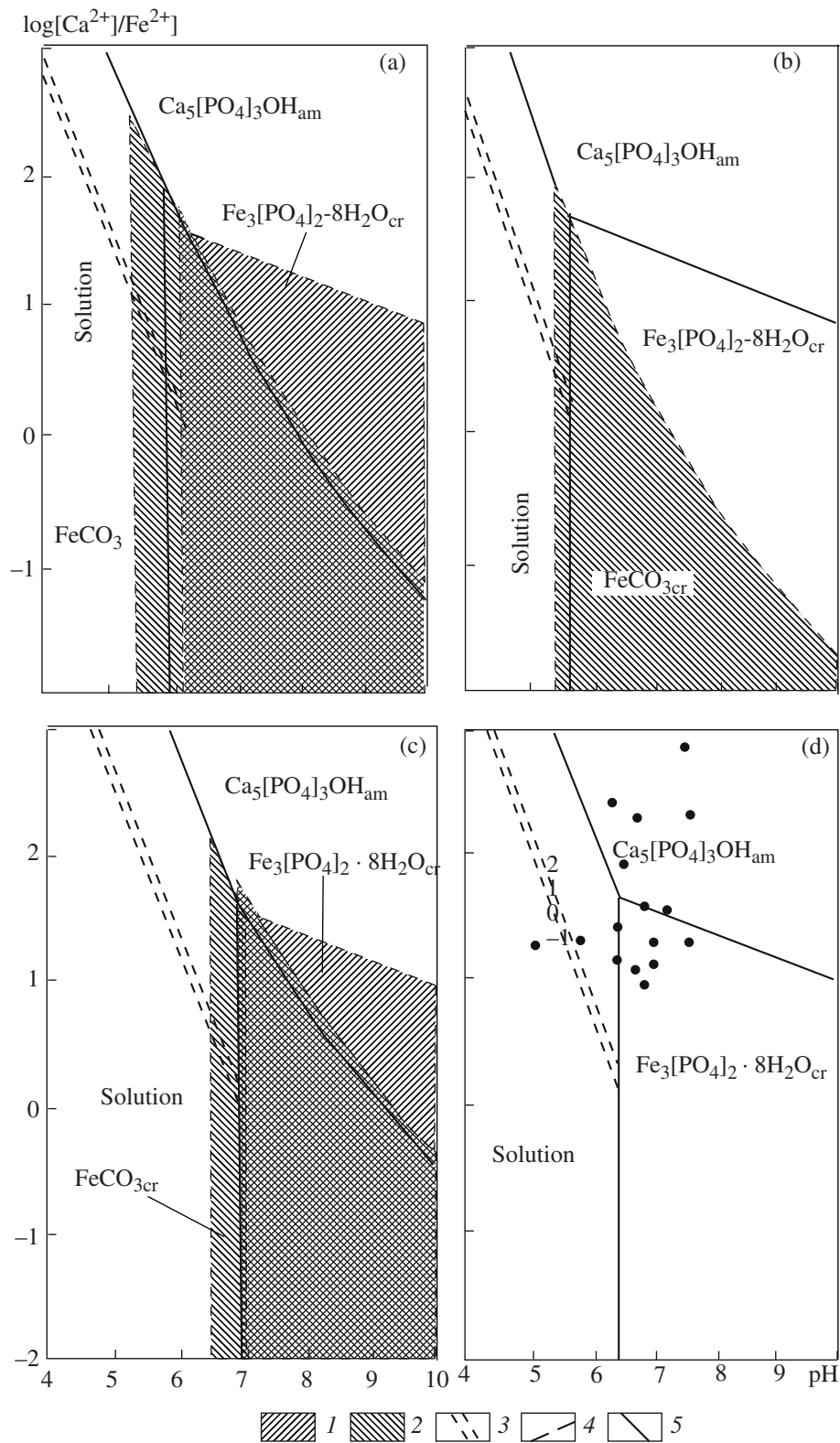


Fig. 24. System HCl–H<sub>2</sub>O–Al<sub>2</sub>O<sub>3</sub>–CO<sub>2</sub>–CaO–SiO<sub>2</sub> at 25°C with data on the composition of soil waters from (1) podzolic soils, (2) grey forest soils, and (3) soils with soda salinization.

minosilicate dissolution during the whole period of residence of water in the rock and, on the other hand, the continuous formation of secondary minerals, whose compositions must change in response to the chemical evolution of the aqueous solution.

In conclusion, we will consider briefly the equilibrium of groundwater with phosphate minerals. As was previously shown, the highest phosphorus contents are characteristic of wetland waters (Table 10), which often associate with vivianite aggregates. Phosphate–iron–calcium equilibria in the wetland waters of Belarus were studied in detail by Kovalev and Zhukhovitskaya [142]. The equilibrium state of this system is depicted in Fig. 25. It is clearly seen that the compositional points of wetland waters are confined to the boundary with vivianite, siderite, and amorphous apatite, which can be formed under such conditions. At low P and high Fe contents in the solution, only equilibrium with siderite is attained. When the concentration of P reaches hundreds of micrograms per liter, which is typical of wetland waters, and pH values range from 5.5 to 6.5, equilibrium with vivianite is established.

Consequently, in wetland environments, equilibrium with both siderite and vivianite is often attained



**Fig. 25.** Water–mineral equilibria in the calcium–iron–phosphate system at  $[\text{HCO}_3^-] = 10^{-2.5}$ ,  $[\text{Fe}^{2+}]$  of (a, b)  $10^{-3.85}$  and (c, d)  $10^{-4.85}$ , and  $[\Sigma\text{P}]$  of (a, c)  $10^{-4.85}$  and (b, d)  $10^{-4}$  with data for the composition of wetland waters from Belarus. (1) Field of crystalline vivianite, (2) field of siderite, (3) xylapatite–solution boundary, and boundaries at (4)  $[\text{HCO}_3^-] = 10^{-3}$  and (5)  $[\text{HCO}_3^-] = 10^{-2}$ .

under reduced (gley) geochemical conditions, relatively low pH, and elevated  $\text{PO}_4^{3-}$  contents. This is another piece of evidence for the equilibrium–nonequilibrium state of the water–gas–mineral system.

### 3.3. Nature of Nonequilibrium in the Water–Primary Aluminosilicate System

It is commonly believed that the nonequilibrium of groundwaters with rocks in the supergene zone is related mainly to the mechanical removal of hydrolysis products from the weathering zone as a result of its continuous flushing. This opinion was most comprehensively formulated by W.D. Keller, who noted that hydrolysis occurs not through the saturation of a rock with stagnant water but rather through the multiple renewal of waters, which pass through rocks and leach the soluble products of hydrolysis reactions. Thus, geological observations support the geochemical principle that is implied by the general reaction of hydrolysis; namely, the progress of the reaction to the right (increasing weathering) requires that the dissolved products of hydrolysis be eliminated from the active system [243, p. 101].

Keller mentioned the following among processes resulting in the removal of hydrolysis products:

- (1) repeated leaching by fresh rain- or snow waters;
- (2) addition of  $\text{H}^+$  ions, which (a) react with  $\text{OH}^-$  groups and are eliminated as water or (b) substitute for metal cations in compounds of these metals;
- (3) precipitation of ions as relatively insoluble compounds;
- (4) removal of ions via complexation;
- (5) absorption and assimilation of products by living plants and animals; and
- (6) absorption of products by colloidal substances.

We do not deny the importance of all these processes, but, in our opinion, the most significant process is missing from this list, namely, the chemical interaction of  $\text{OH}^-$  group with carbon dioxide. Let us consider this point in more detail.

It was already noted above that reaction (3.5) results under natural conditions in almost complete neutralization of the solution alkalinity by carbon dioxide with the formation of bicarbonate ion. This is proved by the fact that the amount of bicarbonate ion in solutions is similar (in equivalent units) to the amount of cations leached from rocks. If the alkalinity is neutralized by other acids, their anion groups should be present and partly compensate for the cations. This is observed only in rare cases, for instance, in wetland waters enriched in organic acids, and is, therefore, an exception rather than a rule.

The scales of the processes of alkalinity neutralization can be assessed from the relations of the theoretical and real values of groundwater pH in aluminosilicate rocks. The fact is that, given the contents of cations in a

solution forming in aluminosilicate rocks, the theoretical pH value of water can be calculated for weathering processes, and this value can be compared with observations. Such a comparative analysis (Table 28) showed that the observed pH values of waters from the supergene zone are lower than the calculated values by four to five units; i.e., the alkalinity formed during weathering is practically completely neutralized by simultaneously formed acidic products, primarily carbon dioxide. This leads to the chemical transformation of the product of the hydrolysis reaction and, correspondingly, the disturbance of thermodynamic equilibrium.

*Consequently, rather than the removal of hydrolysis products from the zone of weathering by groundwaters, the neutralization of alkalinity by carbon dioxide is the main reason why the water is not saturated with respect to primary aluminosilicates.*

What is the source of carbon dioxide in groundwaters? It is obvious that the atmosphere cannot serve as such a source because the partial pressure of  $\text{CO}_2$  in it is  $10^{1.5}$  Pa, which is much lower than the groundwater  $P_{\text{CO}_2}$ , averaging  $10^{2.8}$ – $10^{3.2}$  Pa [Eq. (1.1)]. These values are higher than the  $P_{\text{CO}_2}$  of river waters, which averages  $10^{2.5}$  Pa. Garrels and Mackenzie [247, p. 105] rightly noted that  $\text{CO}_2$  pressure in water flows probably reflects the conditions of dynamic equilibrium in the process of  $\text{CO}_2$  formation by the oxidation of organic matter in waters and its continuous release into the atmosphere owing to diffusion from the surface of flows.

A deep  $\text{CO}_2$  source also cannot play a significant role on a regional scale. Therefore, the main source of  $\text{CO}_2$  in the waters of the supergene zone is the processes of oxidation of organic matter in the soil and subsoil horizons.

Of course, it should be taken into account that, in some cases, free carbon dioxide can be formed as a result of current processes of exogenic metamorphism in the zones of active oxidation of sulfide minerals and decomposition of carbonate rocks. However, these processes also do not occur on a regional scale.

Hence, organic matter prevents the equilibration of waters with rocks. It decreases the pH values of waters and, in addition, participates in hydrolysis reactions, formation of complex compounds, etc. All these factors eventually promote the dissolution of aluminosilicates. Therefore, *organic matter and related microorganisms must also be considered as a very important geochemical barrier preventing the equilibration of waters with aluminosilicates.*

Thus, the nonequilibrium of waters with endogenous aluminosilicates has a complex chemical nature related to the influence of hydrolysis products on various subsequent chemical processes. The mechanical removal of elements from the reaction zone plays an important role but is not the crucial factor.

**Table 28.** Comparison of the theoretical and real pH values of groundwaters

Region	Water-bearing rock	pH <sub>meas.</sub>	pH <sub>calc</sub> <sup>-</sup>	Ca <sup>+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>	HCO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Fe	SiO <sub>2</sub>	Al	Total of salts
Guinea	Nepheline syenites	5.3	10.4	0.5	0.47	7.9*	–	19.4	5.5	0.7	0.070	4.0	0.29	38.6
Same	Granite gneisses	5.5	10.6	0.7	0.15	14.6*	–	33.5	4.2	0.0	0.030	–	–	53.2
Côte d'Ivoire	Granites	5.5	9.9	1.0	0.1	0.5	0.8	6.1	3.0	0.5	0.032	9.4	0.007	21.4
Southern France	"	5.9	10.2	0.8	0.3	2.4	0.5	6.5	3.0	1.2	0.072	8.2	0.023	23.0
Vosges, France	"	6.1	10.5	5.8	2.4	3.3	1.2	15.9	3.4	10.9	0.200	11.5	0.122	54.7
Corsica	"	6.7	10.7	8.1	4.0	16.5	1.4	40.3	22.0	8.6	0.166	13.2	0.058	115
North Vietnam	Granites and schists	6.7	11.2	29.4	6.2	9.4*	–	110	7.3	4.8	0.620	17.4	0.860	186
Yenisei Range	Granite gneisses	6.8	11.0	20.1	5.3	8.9	1.6	96.3	6.8	2.5	0.350	10.3	0.130	147
Sierra Nevada Mountains	Granites	6.9	10.9	9.3	1.6	4.9	1.5	50.0	0.54	1.8	0.046	20.8	0.026	90.4
Southern United States	Granite gneisses	7.2	11.0	16.2	2.6	8.3	1.9	69.5	5.0	6.0	0.415	22.1	0.060	134
Senegal	Granites	7.3	11.5	30.4	18.0	36.9	4.2	274	7.0	4.0	0.118	58.0	0.087	433
Kurama Range	Grano-diorites	7.4	11.1	35.4	5.4	6.0	1.4	129	5.1	12.5	–	12.4	–	207

\* Na<sup>+</sup> + K<sup>+</sup>.

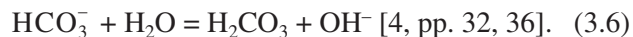
### 3.4. Factors Controlling the Character of the Geochemical Environment

The chemical nature of water–rock nonequilibrium, which was established above, provides insight into the regional features of variations in acid–base and redox properties of solutions, i.e., the reasons for changes in the geochemical environment. Let us consider first acid–base conditions, i.e., pH values.

The zoned distribution of groundwater acidity in the territory of the former Soviet Union was most comprehensively demonstrated by Perel'man [248], who compiled a map of the geochemical types of groundwater aquifers. He also pointed out that this phenomenon is related to the zoning of climate elements, which may be locally obliterated by the influence of geologic factors.

However, many researchers still advocate the leading role of geologic factors. For instance, E.V. Posokhov arguably noted that the pH value in most natural waters is mainly controlled by the relations between the concentrations of carbonic acid and its ions but suggested that changes in this relation are due to the influence of carbonate rocks only. He wrote that “it is universally accepted that the sources of HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup> are various carbonate rocks (limestones, dolomites,

marls, etc.) and carbonate cement of many sedimentary rocks” [4, p. 32] and “HCO<sub>3</sub><sup>-</sup> groups are formed in considerable amounts in natural water by the dissociation of bicarbonates Ca(HCO<sub>3</sub>)<sub>2</sub> and Mg(HCO<sub>3</sub>)<sub>2</sub>, which increase the concentration of HCO<sub>3</sub><sup>-</sup> and lead to a decrease in H<sup>+</sup> (increase in pH) toward alkaline solutions, i.e., the appearance of OH<sup>-</sup> groups, in accordance with the hydrolysis reaction



Thus, Posokhov's concept is the following: an alkaline environment is formed in carbonate rocks, but in some cases (presumably, outside carbonate rocks), under the conditions of high CO<sub>2</sub> partial pressure and a high content of organic acids, a weakly acidic environment can be generated. However, it is not clear, then, why the pH value of waters varies considerably in aluminosilicate rocks (Table 28).

Keller proposed a different explanation for variations in the pH value of waters. Taking into account that the interaction of water with aluminosilicates produces alkalinity, which, in his opinion, is removed by groundwaters, he concluded that the more abundant precipitation, the closer the chemical properties of the weather-



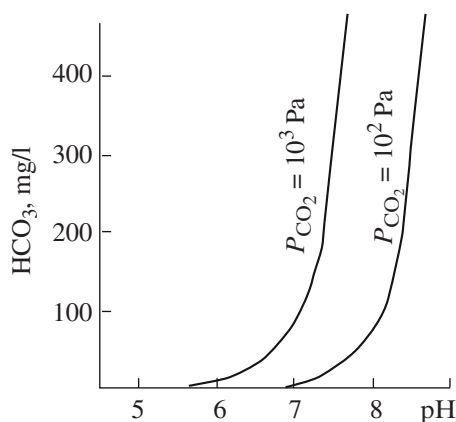


Fig. 26. Correlation between the  $\text{HCO}_3^-$  content and the pH value of solution.

ing system to neutral water and, furthermore, the volume of waters participating in leaching controls the pH of the weathering system [243, p. 102].

A different opinion was expressed by Krainov and Shvets [19], who argued that the main reasons for the phenomenon considered are the dissociation of acids and bases and the hydrolysis of anions and cations. Unfortunately, these authors, first, did not present quantitative estimates supporting their statements and, second, did not consider the sources of acids and alkalis as well as cations and anions for these phenomena. Therefore, the nature of the pH of groundwaters was not determined by these authors. Our model presented in 1978 in [6] has not been discussed by Krainov and Shvets.

Thus, the reasons for pH variations in groundwaters of regional distribution that contain no strong acids, such as hydrochloric, sulfuric, nitric, etc., are differently interpreted by researchers and require, therefore, a more detailed analysis.

As was shown above, the dissolution of carbonate and aluminosilicate rocks is accompanied by the formation of alkalinity [Eqs. (3.3) and (3.4)], which is neutralized by the concurrent process of  $\text{CO}_2$  formation and, to a lesser extent, by organic acids. Therefore, *if the rate of alkalinity formation is higher than the rate of formation of  $\text{CO}_2$  and organic acids, the environment should remain alkaline, whereas an acid environment should develop in the case of the opposite relations.*

It should be pointed out that the formation of acids and alkalis is an independent process controlled by various natural factors: the amount of produced acid depends on the intensity of the biological productivity of the terrain, as well as the direction and intensity of decomposition and remineralization of organic matter, and, consequently, the mean annual atmospheric temperature and humidity; the amount of alkalis depends on the intensity of water exchange and, consequently, on the amount of precipitation, evaporation, and the permeability and type of rocks.

It can be easily seen that all of the aforementioned factors, except for the permeability and type of rocks, show a zonal character defined by climatic characteristics, and this is the main factor in the formation of the phenomenon of zoning in water composition and pH value.

However, the identification of the main factors controlling water zoning does not reveal the reasons for the universal increase in the pH value of water with increasing total salinity (Figs. 3, 17). This empirical observation can be explained on the basis of Eq. (3.5), which suggests that, at a certain  $\text{CO}_2$  partial pressure, an increase in  $\text{HCO}_3^-$  content in solution is accompanied by an increase in the pH value. This is most clearly seen in Fig. 26.

The amount of  $\text{HCO}_3^-$  in solution is controlled by the sum of cations of bicarbonate salts, the content of which in low-salinity waters determines their total mineralization; in other words, water salinity increases owing to an increase in the content of cations leached from carbonate and silicate rocks and the practically equivalent amount of  $\text{HCO}_3^-$  groups formed during this process (more precisely, the sum of  $\text{OH}^-$  and  $\text{HCO}_3^-$ ).

The partial pressure of  $\text{CO}_2$  is also not constant but changes depending on the climatic features of the terrain and temperature [Eq. (1.1)]. This dependence was evaluated by Drake and Wigley [249], who presented the following relation for calcite-saturated waters:

$$\log P_{\text{CO}_2} = -3.42 + 0.077T. \quad (3.7)$$

A comparison of these equations leads to the very important conclusion that  $\text{CO}_2$  partial pressure decreases with increasing water salinity. This is supported by the data of Table 28. Thus, there are two reasons for the increase in pH with increasing groundwater salinity: (1) an increase in the content of  $\text{HCO}_3^-$  and (2) a decrease in  $P_{\text{CO}_2}$ .

Consequently, there is a complex relation between the content of  $\text{HCO}_3^-$  (and, consequently, the sum of salts) and the pH value, which is controlled by the  $\text{CO}_2$  partial pressure. *At a given  $\text{CO}_2$  partial pressure, the higher the content of  $\text{HCO}_3^-$  in the solution, the higher its pH value; alternatively, at a given  $\text{HCO}_3^-$  content (and, consequently, salinity), the higher the  $\text{CO}_2$  partial pressure, the lower the pH value.*

Thus, it can be reasonably explained why, first, an increase in the salinity of groundwater is accompanied by an increase in its alkalinity and, second, at a given salinity, the groundwaters of tropical areas are more acidic compared with the waters of the temperate zone (Fig. 17).

As to the redox properties of groundwaters, they are controlled by the quantitative relations of electron-accepting oxidizing elements, on the one hand, and electron-donating reducing elements, on the other



hand. Under the conditions of the supergene zone, oxygen is the most important oxidizer in groundwaters and organic matter is the most important reducer. Under the conditions of active water exchange, free oxygen usually occurs in waters and the geochemical environment is oxidizing, whereas weak water exchange results in oxygen consumption due to the oxidation of organic matter and variable-valence elements, with gley geochemical environments developing. Consequently, the main factor is again the process of neutralization of oxidizers by reducers and vice versa. If more reducers are formed in the system or introduced from an external source, a reducing environment is formed. If the rate of oxidizer formation and/or input is relatively high, an oxidizing environment is formed.

Note also that, in recent years, instead of the traditional indicator of redox conditions, Eh, the parameter  $pe$  has been widely used in geochemistry. It is defined as the negative logarithm of the concentration of electrons in the solution,

$$pe = -\log[e^-]. \quad (3.8)$$

High  $pe$  values (low activity of electrons) are characteristic of an oxidizing environment, whereas negative  $pe$  values correspond to strongly reducing conditions. The  $pe$  value is connected with Eh by the following expression [17]:

$$pe = \frac{F}{2.3RT} Eh, \quad (3.9)$$

where  $F$  is the Faraday constant,  $R$  is the gas constant, and  $T$  is the absolute temperature.

At 25°C,

$$pe = 16.9Eh \text{ or } Eh = 0.059pe. \quad (3.10)$$

Thus, similar to acidity–alkalinity, the redox state of an environment is controlled by the intensity of water exchange, the direction of transformation of organic matter, the composition of rocks, and other factors. On the other hand, it is important to note that, in clay deposits, usually the Eh of groundwater decreases and more reducing conditions develop. In our opinion, the reasons for this phenomenon are related to the fact that clays contain considerable amounts of chemically bonded water showing peculiar physicochemical properties, which shifts the redox potential of water toward low Eh values [10].

### 3.5. Direction and Hydrogeochemical Role of Organic Matter Decomposition

As was shown above, the nature of nonequilibrium in the water–endogenous aluminosilicates system and the character of the geochemical environment are controlled by the very active influence of the organic matter of landscapes as the main source of acid components in dissolved products. Therefore, let us briefly consider

the main mechanisms of organic matter decomposition in soil and subsoil horizons.

The tremendous masses of organic matter formed every year as a result of photosynthesis are affected after dying off by various kinds of biochemical transformations with the formation of soil humus and various organic acids and, eventually, complete remineralization with the generation of the initial products of photosynthesis, water and carbon dioxide. Currently, four types of organic matter decomposition are distinguished, reflecting the combination of various climatic conditions in particular provinces [219].

(1) *Peat formation*, involving the conservation of slightly altered organic plant remains with the formation of acidic and sterilizing compounds under waterlogged conditions and low contents of microorganisms.

(2) *Decay of organic compounds* under the conditions of insufficient air influx and high humidity, which form an anaerobic environment. Playing an important role in these processes are peculiar bacteria (anaerobic bacteria) facilitating the occurrence of reducing processes. The latter are accompanied by the formation of amines; phenols; hydrogen sulfide; hydrogen; methane; and reduced compounds of iron, manganese, and other elements. In this environment, nitrates are reduced to ammonium and gaseous nitrogen. These phenomena are typical of wetland and waterlogged terrains.

(3) *Humification of organic compounds* (aerobic decomposition) is characteristic of conditions of simultaneous moistening and aeration. It is related to sequential and repeated alternation of decomposition and resynthesis of organic compounds in soil by animals, fungi, and microorganisms. The decomposition of proteins is accompanied by ammonification and nitrification with the formation of nitric acid and its salts. Simultaneously, the sulfur and phosphorus of proteins are oxidized to sulfates and phosphates. Carbon is mostly oxidized to carbon dioxide. The mineral components of organic remains are either transformed to simple salts or accumulated in the composition of humus. Processes of aerobic humification are characteristic of most soils showing high humus contents: chernozems, soils of prairies, black soils of tropical areas, meadow soils, brown forest soils, etc.

(4) *Dry “smoldering” (combustion) of organic matter* occurs under the conditions of an especially dry climate, considerable oxygen influx, low humidity, active washing, and low activity of soil organisms. Soil animals mechanically and biochemically destroy organic matter. Fungi and bacteria complete the oxidizing processes, producing simple oxidized mineral salts, gases (especially carbon dioxide), and water. The resynthesis of humus is relatively limited. Therefore, the soils usually contain little humus and are light-colored. These phenomena are especially characteristic of dry and wet savannas and deserts, including areas of rock laterization.

Even a cursory examination of the directions of transformation of organic compounds indicates a con-

**Table 29.** Productivity of plants in various landscapes, 100 kg/ha [64]

Landscape	Region	Biomass	Annual production	Annual litter
Arctic tundra	–	50	10	9.5
Shrubby tundra	–	280	23.8	22.7
Hypnum bog	West Siberia	150	41	32
Coniferous forests	Russian Plain	1969	54	41
Leaf forests	West Siberia	2133	126	72
Broadleaf forests	Central Europe	3700	130	90
Meadow steppes	West Siberia	230	137	130
Dry steppes	Kazakhstan	100	42	36
Deserts	Syria	61	25	24
Tropical forests	China	5160	342	275
Subtropical forests	–	4100	245	213
Dry savanna	India	268	73	72

siderable role of diverse microbiological activity in these processes. Where organic matter is present, there are practically always various species of microorganisms whose life activity exerts a significant influence far beyond their sphere of residence and controls in many respects the composition of weathering products, the atmosphere, and groundwater and the geochemistry of such elements as carbon, nitrogen, sulfur, phosphorus, oxygen, potassium, iron, etc. According to the data of Kovda, “the main mass of microorganisms is confined to root-hosting soil horizons, especially to the uppermost 10–20 cm. The total wet mass of various microorganisms in the uppermost 25-cm-thick soil layer may be as high as 10 t/ha. The mass of microorganisms is 0.5–2.5% of the mass of humus in soils” [219, p. 240]. The amount of microorganisms decreases with depth. Their content is lower in surface waters and, especially, in groundwaters and air. However, even in these environments, they continue to decompose organic compounds, producing water and carbon dioxide.

The most important products of the biochemical transformation of plant remains are fulvic and humic acids, which almost always dissolve to some extent in soil solutions and are transported by them into subsoil (ground) waters. The amount of humic compounds in soil waters depends on the soil type and the stage and degree of organic matter decomposition. According to the data of Skrynnikova [250], unsaturated humic acids, including the most active group, fulvic acids, may appear in soil solutions in regions with a humid climate during the formation of acidic forest soils. Humic and fulvic acids may cause a decrease in the pH value of soil solutions to 3.0–3.5. In some cases, other organic acids, including acetic, oxalic, citric, etc., have been documented. Their formation is related to the decomposition of plant litter, excretions of roots and insects, and life activity of fungi and bacteria. When these acids enter groundwaters, they are rapidly neu-

tralized by the alkalinity produced by water–rock interaction.

It should be kept in mind that we are concerned with the tremendous scales of transformation of matter on the planet. According to Kovda, every year about 55 Gt of plant organic matter are formed and decomposed on land alone. More than 90% of this amount every year enters the gas phase, while the remainder is incorporated in intermediate organic compounds, humus, and mineral salts. Organic matter is synthesized from water, carbon dioxide, and other compounds and scavenges tremendous amounts of various elements from the lithosphere. The average content of ash material in the dry weight of plants is 5–8%, ranging from 1 to 45% (in halophytes). During decomposition and remineralization, all of these compounds migrate into soil or groundwater.

It is also important that the amount and quality of synthesized organic matter are very different in different climate zones. For instance, the cold conditions of tundra and the dryness of desert minimize plant growth and, correspondingly, the biomass of these landscapes (Table 29); in contrast, the forest terrains of tropical and subtropical regions are characterized by the maximum amount of biomass and its growth rate. The chemical composition of organic matter from particular plant types is also very variable. According to the data of Kovda, lower plants (fungi and bacteria) are rich in proteins, mosses and wood are rich in lignin, and grasses and mosses are rich in hemicelluloses and water-soluble organic compounds.

Highly acidic soluble organic compounds constitute almost half of the dry mass of lichens (45.84%). The concentrations of mineral matter in plants are also very variable. The lowest ash contents (1.5–2.5%) are characteristic of plants from tundra, forest tundra, and coniferous and broadleaf forests; medium contents

(2.5–5.0%) were detected in plants from alpine meadows, steppes, subtropical and tropical forests, thin forests, and savannas; high contents (8–15%) were measured in plants from subtropical, tropical, and subboreal deserts; and the highest contents (20–50%) are characteristic of plants from saline soils.

In general, the annual biomass production is higher, although only slightly, than the plant litter (Table 29). This leads to the important conclusion that, *on average, the weight of chemical elements fixed by organic matter is always higher than their amount released owing to the decomposition of organic matter*; i.e., the continental biosphere continuously sequesters part of elements from rocks, water, and air (except for oxygen, which is produced during this process). This synthesized and undecomposed part of organic matter is eventually dispersed in rocks, forming sapropels, peat, coal, oil, etc.

The continuous large-scale synthesis and decomposition of organic matter result in the entrainment of a considerable number of atoms into the biological cycle. The concept of atom cycling was considered by Perel'man as one of the most important laws of the geochemistry of the biosphere. He formulated this law as follows: "In the biosphere, atoms participate in biological cycles, during which they are absorbed by living matter and charged with energy and then leave the living matter, releasing the accumulated energy into the environment. Many chemical reactions occur at the expense of this biogenic energy. The main carriers of energy are natural waters" [239, p. 27].

For an understanding of the formation conditions of water composition, it is important to keep in mind that the atom cycle is not closed and part of elements is continuously eliminated from it, migrates into waters, and is carried into the ocean or intracontinental catchments.

Another important role of biological cycles is the concentration of elements from a dispersed state. Owing to this factor, the proportions of many chemical elements entering aqueous solutions during the decomposition of organic matter are fundamentally different from those of rocks and the atmosphere, which strongly enhances the compositional diversity of the hydrosphere. In particular, organic substances form complex compounds with many metals, which greatly increases their migration capacity. This primarily concerns the hydrolysate elements, especially iron and aluminum. In addition, organic acids play a significant role in the chemical decomposition of rocks, especially, aluminosilicates.

All these considerations illustrate the extremely diverse influence of organic matter on the properties of the geochemical environment and the mechanisms of various hydrogeochemical processes, which stems from the character of the development of the water-organic matter system. This is due to the (1) general nonequilibrium of the system, (2) different directions of organic matter decomposition in an aquatic environment, (3) high degree of dissolution and remineraliza-

tion of organic compounds, and (4) diversity of the composition of dissolved organic matter depending on particular landscape and geochemical conditions.

Note finally that it is necessary to distinguish two geochemical aspects of water interaction with dead organic matter. (1) On a global scale, organic matter cannot serve as a source of chemical elements for groundwaters, except for air migrants, because, first, the amount of chemical elements fixed during the formation of organic matter in the supergene zone is greater on average than the amount released as a result of its decomposition (Table 29) and, second, the dead part is not completely decomposed in situ, but is partly removed together with accompanying elements from the landscape owing to mechanical and chemical erosion into seas, lakes, and swamps. (2) A major portion of chemical elements participates in the biological cycle before entering gravitation groundwaters and is often fixed in complex organic or organomineral compounds, increasing the stability and migration capacity of many elements, which promotes their penetration into deep aquifers.

Summarizing the material presented in this chapter, it should be emphasized that the water-rock-gas-organic matter system is capable of continuous internal interaction owing to its nonequilibrium character, and this is the main factor controlling the character of the environment. Owing to the numerous quantitative relations between the main components of the system, the diversity of their compositions, geologic conditions of their occurrence, *PT*-parameters, etc., the resulting geochemical environment is very heterogeneous, which leads to the diversity of secondary mineral and organic phases. Consequently, the character of the geochemical environment is a resultant parameter of the direction and scale of the evolution of the system and, in this sense, an integral part of it. Therefore, the geochemical environment cannot be considered as something external, imposed from outside. In contrast, *the environment is a product of the evolution of the system, which, however, exerts a direct influence on the development of the system*. The mechanism of this influence operates through the secondary mineral and organic phases that form during the interaction of the main components of the system. The environment controls the character of the secondary phases and influences itself through their formation. This, in turn, changes the composition of the secondary phases and influences the environment. This is the main contradiction in the system considered here, which makes possible its continuous physicochemical and, ultimately, geologic evolution.

#### CHAPTER 4. MAGNITUDE AND COMPONENTS OF SUBSURFACE CHEMICAL EFFLUX

Using the material presented above, the dynamics of modern hydrochemical processes can be evaluated, which is very important for the solution of problems of modern weathering of rocks, scales of chemical and



mechanical erosion, formation of relief and soils, etc. It is also necessary for the elucidation of the formation conditions of groundwater composition and estimation of particular sources of chemical elements in waters. Such estimates can be quantified using the magnitude of subsurface chemical efflux.

The magnitude of subsurface and surface chemical efflux has been investigated by F.P. Savarenskii, F.A. Makarenko, G.A. Maksimovich, N.M. Strakhov, O.A. Alekin, L.V. Brazhnikova, V.P. Zvereva, and others. Fundamental studies were carried out by Garrels and Mackenzie [247]. All these investigations focused on the total chemical efflux. Its lithogenic, biogenic, and atmogenic components were first estimated in our studies [6]. These estimates established the relations between the components and contributed to the development of the concept of underground chemical denudation and mechanisms of formation of groundwater composition.

#### 4.1. *Quantitative Characteristics of the Components of Subsurface Chemical Efflux*

The subsurface chemical component of efflux is usually estimated from the composition and output of river water during the low-water period; i.e., it is assumed that rivers are mostly supplied by groundwater during that time. Without denying the feasibility of such a method of tackling the problem, we employed another approach, using the average compositions of groundwaters from the main landscape zones and provinces presented above and data on the rate of subsurface flow. This method is widely used by foreign researchers [251, 252].

The analysis of data on the rate of subsurface chemical flow and its components summarized in Table 30 allows us to draw a number of interesting conclusions. First of all, there is a conspicuously wide interval of values of subsurface chemical efflux, related to the diversity of natural conditions: from 1.9 (northern wetlands) to 190 t/(yr km<sup>2</sup>) (wet savanna), or 0.063 to 6.251 g/(s km<sup>2</sup>). The highest values were measured in tropical and subtropical forests (Fig. 27), which are characterized by extremely intense water exchange, high biological productivity, and high mean annual temperatures. High values of this parameter were also observed in the temperate climate zone (forest steppe, mixed forest, and southern taiga) and mountain regions. It is important that, in all of the three cases, the increase in subsurface chemical flow is related mainly to its biogenic component, which is especially high under such conditions.

The lowest rate of efflux is characteristic of wetlands and tundras owing to very weak water exchange and of the steppes of the tropical and temperate belt, which also show low water exchange rates. On the other hand, the rate of chemical efflux is an independent variable, which does not correlate with the rate of subsurface flow, total salinity, pH, temperature, and the type of rocks, or, more precisely, correlates in a com-

plex way. In order to elucidate the reasons for this phenomenon, it is necessary to consider the behavior of each efflux component separately.

The atmogenic component of chemical efflux is controlled by the amount of precipitation and the degree of evaporation. The maximum values of absolute efflux are observed either in the humid terrains of the tropical belt, where the amount of precipitation is especially high, or in the regions of intense evaporation (forest steppes and steppes), and the minimum values are confined to regions with relatively low precipitation and weak evaporation (tundra, northern taiga, and wetlands) or intensely washed regions far from seas and oceans (high mountains), which contain low-salinity groundwaters. The relative role of the atmospheric component of efflux in the total chemical sink is rather high, 15–30% for the leach waters of the temperate and mountain zones, 40–70% for the waters of continental salinization (steppes and arid savannas), and probably even 80–85% for deserts. Intensely washed tropical and equatorial regions show relatively low fractions of the removal of atmogenic salts (less than 15%), although their absolute amounts are practically no lower than those of arid zones (Fig. 27).

The lithogenic component of chemical efflux is also strongly variable (by a factor of more than 50), from 0.006 (northern wetlands) to 0.498 g/(s km<sup>2</sup>) (tropical forests), and connected in a complex manner with the rate of subsurface flow, total salinity, and pH value of groundwaters (Table 30, Fig. 27). Under the conditions of temperate climate, a close correlation is observed between the lithogenic component of efflux and the rate of subsurface flow. However, the maximum values of efflux are observed in the zone of southern taiga, which shows intermediate rates of subsurface flow, rather than in mixed forest terranes, having the highest rate of subsurface flow.

A similar relation between these parameters was also detected under the conditions of mountain, tropical, and equatorial landscapes: as the intensity of water exchange decreases, the efflux of chemical elements increases initially, reaches a maximum value, and then decreases. Because of this, the landscapes of the arid zone usually show relatively low effluxes of chemical elements.

Thus, there is a complex relationship between the intensity of water exchange and the efflux of chemical elements from rocks. This could be expected because, according to the principle of nonequilibrium formulated above, the degree of element enrichment in groundwaters from particular rocks is controlled by the time of water–rock interaction. The time of rock–water contact depends on the rate of subsurface flow in a complex fashion. Indeed, according to Darcy's law,

$$Q = KIF \quad (4.1)$$

or

$$V = KI, \quad (4.2)$$

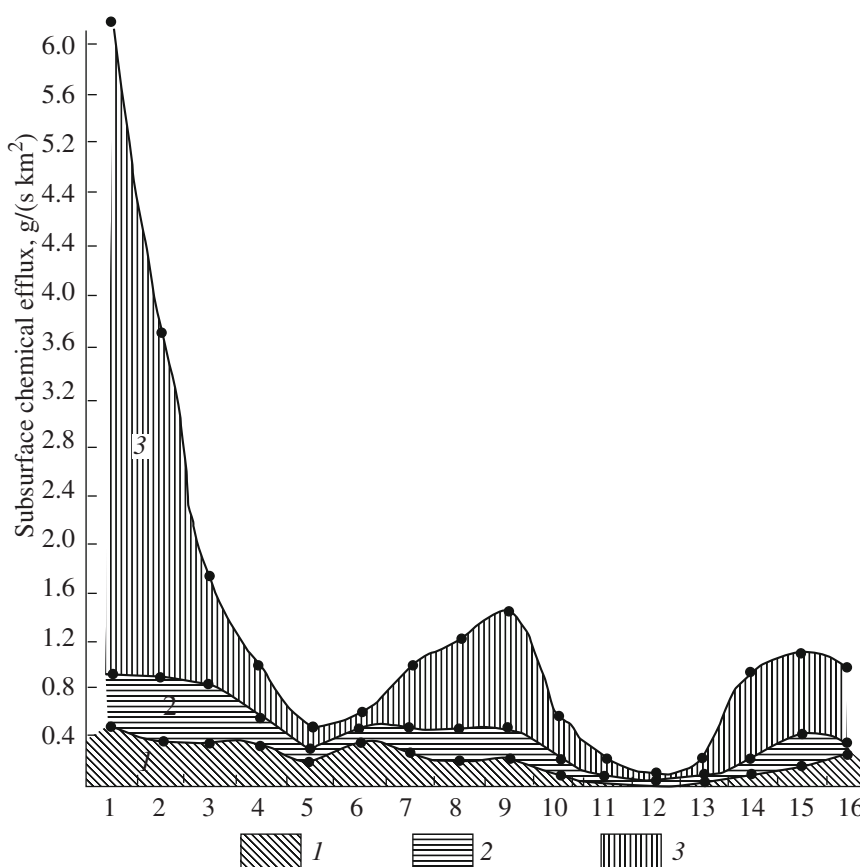
Table 30. Subsurface chemical efflux in the main landscape zones of the Earth

Landscape zone	Component of efflux, g/(s km <sup>2</sup> )			Total efflux		Chemical flow, g/(s km <sup>2</sup> ) [256]	Sum of lithogenic and part of biogenic efflux, g/(s km <sup>2</sup> )*	Efflux components, %			Rate of subsurface flow, l/(s km <sup>2</sup> )	Average salinity, g/l	Average pH
	lithogenic	biogenic	atmospheric	g/(s km <sup>2</sup> )	t/(yr km <sup>2</sup> )			lithogenic	biogenic	atmospheric			
1	2	3	4	5	6	7	8	9	10	11	12	13	14
<i>Temperate zone</i>													
Northern wetlands	0.006	0.039	0.018	0.063	1.9	—	0.019	9.6	61.9	28.5	0.1–0.5	0.08	6.2
Tundra	0.041	0.170	0.053	0.264	8.3	0.144	0.133	15.5	64.4	20.1	0.5–2.5	0.10	6.5
Northern taiga	0.105	0.400	0.113	0.618	18.8	0.389*	0.380	17.0	64.7	18.3	1.0–3.0	0.21	6.8
Wetlands of forest zone	0.013	0.138	0.054	0.205	6.3	—	0.036	6.4	67.3	26.3	0.3–0.7	0.09	5.7
Mixed forest	0.278	0.708	0.226	1.212	37.0	0.441	0.793	22.9	58.4	18.7	3.5–5.0	0.23	6.9
Southern taiga	0.319	0.977	0.223	1.519	46.3	—	1.129	21.0	64.3	14.7	1.5–3.5	0.46	7.1
Forest steppe	0.200	0.528	0.296	1.024	31.2	—	0.678	19.5	51.6	28.9	0.8–1.6	0.64	7.5
Steppe	0.053	0.144	0.412	0.610	18.6	0.472	0.187	8.7	23.6	67.7	0.1–0.5	1.86	7.6
Desert	—	—	—	—	—	0.525	—	—	—	—	—	—	—
Average	0.127	0.388	0.174	0.689	21.0	—	0.419	18.4	56.3	25.3	—	0.46	6.8
<i>Tropical and equatorial zones</i>													
Wet savanna	0.434	5.311	0.506	6.251	190.6	—	0.825	6.9	85.0	8.1	16–20	0.06	5.3
Tropical forests	0.498	2.852	0.385	3.735	113.9	—	1.426	13.3	76.4	10.3	8–10	0.17	6.1
Subtropical forests	0.468	0.892	0.395	1.755	53.5	2.03	1.028	26.7	50.8	22.5	6–8	0.20	6.9
Dry savanna	0.197	0.459	0.387	1.043	31.8	—	0.584	18.8	44.0	37.1	1–3	0.32	7.2
Steppe	0.061	0.151	0.275	0.487	14.9	—	0.189	12.5	31.0	56.5	0.2–0.8	0.91	7.4
Average	0.332	1.933	0.390	2.655	81.0	—	0.810	12.5	72.8	14.7	—	0.33	6.6
<i>Mountain zone</i>													
Meadow tundra	0.248	0.567	0.182	0.997	30.4	0.109	0.674	24.9	56.8	18.3	4–10	0.10	7.0
Mountain forest	0.283	0.761	0.199	1.243	37.9	0.317	0.899	22.8	61.2	16.0	3–5	0.25	7.1
Mountain steppe	0.152	0.567	0.319	1.038	31.7	0.649	0.675	14.7	54.6	30.7	0.6–1.6	0.48	7.6
Mountain desert	—	—	—	—	—	1.80	—	—	—	—	—	—	—
Average	0.228	0.631	0.233	1.092	33.3	—	0.749	20.8	57.5	21.7	—	0.28	7.2

Notes: \* For the taiga on the whole.

\*\*\* Biogenic component in the HCO<sub>3</sub><sup>-</sup> form only.





**Fig. 27.** Components of subsurface chemical efflux for various landscape zones: (1) atmospheric, (2) lithogenic, and (3) biogenic. Landscapes (numbers along the x axis): 1, wet savanna; 2, tropical forest; 3, subtropical forest; 4, arid savanna; 5, steppes of the tropical zone; 6, steppes of the temperate zone; 7, forest steppe; 8, mixed forest; 9, southern taiga; 10, northern taiga; 11, wetland; 12, northern wetland; 13, tundra; 14, meadow tundra; 15, mountain forest; and 16, mountain steppe.

which yields

$$\frac{S}{T} = KI. \quad (4.3)$$

The solution of Eq. (4.3) with respect to  $T$  and the substitution of  $Q$  and  $F$  for  $KI$  [Eq. (4.1)] give

$$T = \frac{SF}{Q}, \quad (4.4)$$

where  $Q$  is the water discharge, or the rate of subsurface flow in the case considered;  $K$  is the filtration coefficient;  $F$  is the cross-section area of the washed zone;  $V$  is the velocity of groundwater; and  $T$  is the time of movement (interaction) in the rocks.

Consequently, the time of water–rock interaction and the rate of subsurface flow are connected with each other through the thickness of the washed zone (in the case considered, the zone of intense water exchange) and the path of water movement between the catchment and the discharge region (spring or river), i.e., by the volume of rock washed by water. The latter parameter is not constant in different climate zones but varies within a wide range; because of this, there is no strict

inverse correlation between  $T$  and  $Q$  under natural conditions or, consequently, between the lithogenic component of chemical efflux and the rate of subsurface flow.<sup>1</sup>

There are currently no data on the volumes of water-washed rocks for various landscape zones, and the correlation between the removal of elements from rocks and the time of interaction with groundwaters cannot be quantified. This is a problem for future research. We note only that the total amount of elements transported by water flow depends on, among other factors, the volume of percolating water. Because of this, intense water exchange is accompanied by low chemical efflux owing to the short time of water–rock interaction, whereas weak water exchange is associated with low chemical efflux owing to the small volume of flowing water.

The maximum amounts of the lithogenic component in the subsurface efflux are, thus, related to landscapes showing intermediate and high rates of subsurface flow: southern taiga, tropical and subtropical for-

<sup>1</sup> Under arid conditions, the flow rate also depends on the intensity of water evaporation, which also disturbs the relation between  $T$  and  $Q$ .

ests, forest steppe, and mixed forests (Fig. 27). Other things being equal, the degree of element efflux is higher in the belt of tropical and equatorial climate than under the conditions of the temperate belt. This is explained by the higher water exchange rate and higher acidity, which results in a higher water reactivity in the tropical climate zone.

In the total amount of salts transported by groundwaters, the biogenic component plays a major role in all the landscapes of humid climate and especially in humid savanna, tropical and subtropical forests, northern taiga, and forest steppes, showing the maximum biological productivity (Table 29). Since the waters of these landscapes are rich in undissociated carbonic acid and, occasionally, organic acids, they are often weakly acidic or even acidic. Thus, there is a distinct correlation between the relative (absolute for tropical regions) fraction of biogenic product efflux and the pH value of waters (Table 30).

The rate of biogenic efflux is also controlled by the intensity and direction of transformation of soil organic matter, which depend not only on the general biological productivity of the terrain, but also on the mean annual temperature and intensity of water exchange [63, 64, 219]. Under the conditions of the temperate zone, as the mean annual temperature increases and the intensity of water exchange decreases (with some exceptions) from north to south, the absolute values of biogenic product efflux increase initially and then decrease toward arid regions owing to a sharp decrease in the amount of water discharge. Similar relations are characteristic of mountain regions (Fig. 27).

A different situation is observed in tropical and equatorial regions, where persistently high temperatures are favorable for a high degree of both microbiological transformation of organic matter and its remineralization. We believe that the major portion of the annual production of living matter in tropical regions is mineralized. This is especially characteristic of the savanna zone, which is distinguished by a prolonged dry and hot season when the temperature of the upper layers of rocks may reach 70°C.

This conclusion is also supported by the very low humus content in the group of allitic soils [219, 253]; the well-known high rate of the decomposition of green litter, which is higher than that in the forests of temperate zones by a factor of 5–7 [63, 76, 254]; the absence of evidence for peat formation in soils; and the low content of dissolved organic matter in the waters (Table 7).

Water exchange also plays a very important role in the formation of the biogenic component: the higher the water exchange, the higher the efflux of organic matter and products of its metamorphism. The maximum value of biogenic efflux is characteristic of humid savanna, where water exchange is the most intense, and the lowest value is observed in tropical steppes, with the minimum water exchange. Also noteworthy is the fact that the absolute values of the biogenic component

of efflux are higher than its lithogenic component by a factor of 2–3 (by a factor of 10–15 in the tropics) and, therefore, the behavior of the former rather than the latter component controls the total efflux of chemical elements.

It is interesting to compare the obtained values of the biogenic efflux of chemical elements with data on the total biological productivity of landscapes. As can be seen from the data of Table 31, only several percent of the total organic matter produced in a landscape take part in the subsurface flow. Even the highest value of this parameter, observed under the conditions of humid savanna, is no higher than 10%. In all other landscapes, the biogenic efflux is no higher than 3%, and it is even lower than 1% in steppe terrains. The obtained data are, in general, well consistent with the well-known facts of the relative closeness of the biological cycle, from which only small amounts of chemical elements are removed. For instance, according to the data of Remezov [255], which were considered by Kovda [219] as characteristic of all soils, only a small fraction of chemical elements (several percent) is removed by subsurface flow and surface runoff (Table 32). This was supported on a global scale by a study by Rodin and Bazilevich [64].

Given these considerations, we agree with the opinion of soil scientists and biologists, who showed that soil is an independent and relatively closed system where the decomposition of organic matter is accompanied by the participation of the released elements in a new biological cycle and in the synthesis of secondary clay minerals. And only a small fraction (a few percent) of them is removed outside the soil horizon by surface runoff and subsurface flow.

There is another important aspect of the problem of biogenic efflux related to the nature and dynamics of migration of inorganic and organic compounds. Tables 31 and 32 show that organic matter is an almost inexhaustible source of chemical elements in the supergene zone, but this potentiality is realized only to a small extent. Consequently, *the biogenic sink is limited not by a deficiency of organic matter but by the rate and direction of its decomposition*. This conclusion has fundamental significance for the understanding of the mechanisms of the development of supergene processes.

Thus, each component of the subsurface chemical efflux is an independent variable controlled by strictly defined factors. The total subsurface efflux depends on the net effect of all these factors and therefore varies within a wide range, which explains the absence of a linear correlation between its values and the intensity of water exchange, pH value, groundwater salinity, composition of precipitation, and other environmental parameters.

For comparison of the obtained values of the rate of subsurface chemical efflux with available data from the literature, Table 30 gives the sum of the lithogenic component of efflux and the part of the biogenic component

**Table 31.** Biogenic component of subsurface chemical efflux (B) and the total biological productivity (P) of main landscape zones, t/(yr km<sup>2</sup>)

Landscape type	B, t/(yr km <sup>2</sup> )	P*, t/(yr km <sup>2</sup> )	$\frac{B}{P}$ , %
Tundra	5.2	238	2.2
Northern taiga	12.2	560	2.2
Mixed forest	21.6	800	2.7
Southern taiga	29.8	1100	2.7
Forest steppe	16.1	700**	2.3
Steppe of temperate zone	4.4	500**	0.9
Wet savanna	162	1800	9.0
Tropical forest	87.0	3420	2.5
Subtropical forest	27.2	2450	1.1
Dry savanna	14.0	730	1.9
Tropical steppe	4.6	500**	0.9

Notes: \* After Rodin and Bazilevich [64].

\*\* After Bazilevich [223].

represented by  $\text{HCO}_3^-$ , i.e., that part of the total efflux which was calculated by Makarenko and Zverev [256] for the territory of the former Soviet Union. The data of these authors are given in the seventh column of Table 30.

A comparison of these data shows that, for the landscapes of humid temperate climate, the values obtained for the rate of subsurface chemical efflux are rather similar and differ by no more than a factor of 2. Given our current knowledge and the general deficiency of evidence for the composition of waters and rates of subsurface flow, the obtained values can be considered as satisfactorily consistent. Indeed, it should be kept in mind that these estimates were based on fundamentally different raw data (surface and subsurface waters), different calculation procedures, different spatial locations of objects studied, etc.

Larger discrepancies were obtained for mountain regions, especially for the meadow tundra zone (difference by a factor of 6.2). Since the total salinities of groundwaters from high mountain and tundra regions

are identical and the rate of subsurface flow is much higher in the mountain meadow zone, higher efflux rates should be expected in high mountain regions, which is confirmed by our results. Therefore, we believe that the data of Makarenko and Zverev for the mountain tundra and mountain forest zones are underestimated.

Different relations were observed in the regions of continental salinization. Our data show that the rate of subsurface chemical efflux decreases from humid to arid landscapes and this effect is related to a sharp decrease in the volume of water participating in the flow and the related process of continental salinization. In contrast, Makarenko and Zverev argued that a decrease in subsurface flow is accompanied by a continuous increase in the rate of chemical efflux to maximum values in deserts. In our opinion, such a relationship conflicts with the well-known low degree of washing in steppe and desert terrains and their extensive salinization. These authors probably underestimated

**Table 32.** Relations between the input of elements with litter and their removal by intrasoil outflow

Vegetation	Dynamics of elements	Si	Al	Ca	K	P	N
Oak forest	Input with litter, kg/ha	29.0	5.5	83.9	35.6	7.4	42.4
	Output with efflux, kg/ha	0.02	0.53	4.01	0.71	tr	0.75
	Output, % of input	0.07	9.6	4.78	1.96	–	1.78
Aspen grove	Input with litter, kg/ha	21.0	6.0	85.3	42.7	9.9	31.7
	Output with efflux, kg/ha	0.008	0.4	1.59	0.45	tr	0.64
	Output, % of input	0.04	6.67	1.86	1.05	–	2.02

the evaporative concentration of salts under these conditions. In this connection, it is interesting that our estimate of the total rate of subsurface chemical efflux for mountain steppe regions almost coincides with the value reported by Makarenko and Zverev for this zone, whereas the results for the steppe terrains of the temperate zone differ considerably. Consequently, the total amounts of elements removed by groundwaters are the same, but the contribution of atmospheric components is estimated differently.

In addition, it should be noted that Zverev et al. [257, p. 126] defined the sum of atmogenic ions as "the product of the concentrations of individual ions in atmospheric precipitation by the volume of water participating in subsurface flow in the territory of the USSR." Such an approach is appropriate for humid regions, where the contribution of evaporative concentration is small, but invalid for arid regions, where, as was noted by these authors, up to 85% of precipitation may evaporate. It seems likely that Zverev et al. underestimated the fraction of atmospheric components in the total flow and overestimated the rate of subsurface chemical efflux for arid regions, which they justifiably identified as "not the whole mass of salts migrating with groundwaters, but only the part that is removed by groundwaters from the Earth's crust per unit time" [257, p. 107]. These authors did not dispute our data in their subsequent publications.

#### *4.2. Mechanisms of Aluminosilicate Interaction with Aqueous Solutions*

Before considering the relations between the efflux of chemical elements and the magnitude of rock dissolution, it is necessary to evaluate the mechanisms of reactions between natural aqueous solutions and aluminosilicate minerals. The fact is that these mechanisms are still debatable, which hampers the correct interpretation of the results of hydrogeochemical investigations.

Two opinions have been most popular in the recent literature [244]. Some authors argue that weathering and hydrothermal alteration of minerals occur in a solid state. The main evidence presented in support of this model is the existence of pseudomorphs, such as chlorite after biotite, iddingsite after olivine, kaolinite after feldspar, limonite after pyrite, etc. In addition, these concepts are often supported by crystal chemical considerations regarding the similarity of structural motifs of framework and sheet silicates with clay minerals and by the preservation of structural features of initial rocks in the weathering profile [258, 259]. Proceeding from similar structural characteristics of initial rocks and weathering products, some authors considered weathering mantles as metasomatic structures and identified weathering as solid-state autocompensated metasomatism (V.A. Bronevoi, S.A. Kashik, R.A. Tsykin, and others).

The proponents of the second model have developed concepts on the transformation of minerals through a liquid-state transitional stage. This implies that the nature and composition of weathering products are controlled not by the initial material but by the characteristics of the solution, i.e., the geochemical and barothermodynamic environment [243, 260]. In this connection, of special significance is the well-founded conclusion of Correns [261] that the ultimate result of leaching is the complete dissolution of aluminosilicate rather than its solid-state sequential transformation to clay minerals. According to his respected opinion, the popular hypothesis that the dissolution of aluminosilicates is accompanied by simple exchange of alkali elements and hydrogen ions is incorrect because the crystal lattice is completely destroyed rather than merely transformed during this process.

Compelling evidence has been obtained recently that the transformation of aluminosilicates to clays occurs through a transitional liquid phase. In particular, Fin'ko et al. [270, p. 197] investigated clay minerals from kaolinite weathering zones by electron microscopy with vacuum decoration and concluded that "the growth features of newly formed clay minerals and their relations with the initial minerals allow us to conclude unambiguously that the clay minerals were formed from solution under the conditions of free crystallization in dissolution voids in the initial minerals" [270, p. 197]. During this process, "clay minerals epitaxially overgrow the surface of undissolved areas on the initial minerals and, crystallizing simultaneously with the dissolution of the initial minerals, form overgrowth pseudomorphs, preserving many features of the initial minerals (cleavage, jointing, and shape)" [262, p. 200].

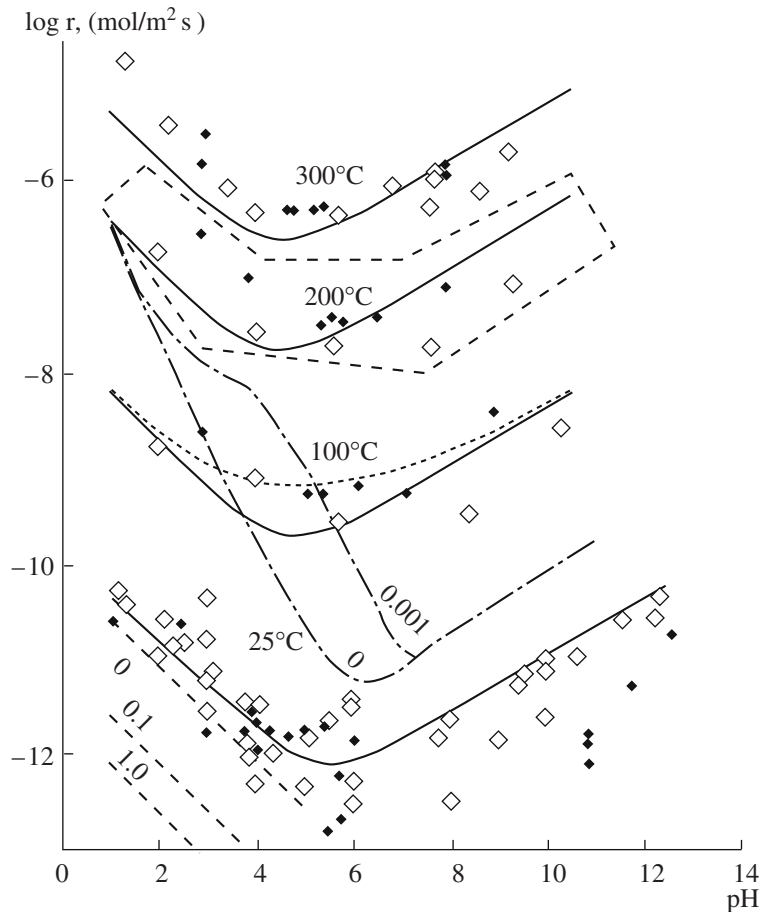
In recent decades, the formation of secondary products of aluminosilicate hydrolysis from aqueous solutions has been confirmed by numerous experiments and mineralogical data on newly formed secondary minerals. These studies were comprehensively reviewed in [251, 252, 263]. The main conclusions can be summarized as follows.

Three main stages of aluminosilicate dissolution were experimentally established.

(1) Cation exchange of Na, Ca, and Mg for  $H^+$  from an aqueous solution weakens the bonds of Al and Si atoms with the surface and facilitates their release into the solution. This is accompanied by the formation of a leached layer up to 1–2  $\mu m$  thick on the surface of the dissolving mineral. It is important that the formation of hydrogen feldspar was unambiguously established by modern methods of mineral surface analysis.

(2) The rapid cation exchange is followed by a stage of slow steady-state dissolution, which has a congruent character. The dependence of the logarithm of the dissolution rate is V-shaped for all feldspars, with a minimum in the near-neutral region (Fig. 28). This pattern is characteristic of both feldspars and other aluminosilicates and suggests the existence of two dissolution





**Fig. 28.** Dependence of the logarithm of dissolution rates of albite (unfilled symbols) and potassium feldspar (filled symbols) on the pH of solution [265].

mechanisms in acid and alkaline solutions, which correspond to the proton and hydroxyl forms.

(3) Incongruent dissolution and crystallization from the solution of a series of secondary minerals, whose compositions change sequentially. The gradual fixation of Al and Si by secondary mineral phases increases the time of attainment of equilibrium in the system and, correspondingly, the time of aqueous solution interaction with the dissolving mineral. This stage is characterized by the nonuniform nucleation of secondary minerals on the surface of primary phases. However, they do not form a continuous crust and do not prevent further interaction between the aqueous solution and the primary mineral and, correspondingly, its further dissolution.

It should also be pointed out that sanidine nuclei were found by means of nuclear ultrafilters in solutions from experiments on the pseudomorphic replacement of albite by K-feldspar at 300°C and pH = 9 [263]. In our opinion, this observation puts to rest the debate on a solid- versus liquid-phase mechanism of mineral transformation in favor of the latter.

In accordance with these concepts, there are two main approaches to the factors of secondary mineral

formation: crystal chemical (structurally inherited or transformational) and geochemical or synthetic, based on the assumption that secondary phases are synthesized by crystallization from solution and their composition is related to the parameters of the environment. The former approach does not disaffirm a certain influence of the character of the geochemical environment, during either chemical weathering, hydrothermal transformations, metasomatism, catagenesis, or mesogenesis. On the contrary, there are practically no researchers who would deny the influence of the environment as the most important factor of secondary mineral formation, even in the case of a solid-state mechanism of mineral transformation. Consequently, *the hydrolysis of aluminosilicates accompanied by the complete, although nonstoichiometric, dissolution of the initial rock results in the formation of diverse secondary mineral phases, whose composition is controlled mainly by the character of the geochemical environment.*

Based on these considerations, it can be suggested that, under the conditions of the supergene zone, even in the case of incongruent dissolution, all chemical elements pass into an aqueous solution, which produces subsequently or simultaneously with the dissolution all second-



ary mineral phases, including clay minerals. This is additionally supported by their equilibrium with groundwaters. Consequently, the knowledge of the composition of groundwater from a particular region, the composition of bedrocks (affected by weathering), and the composition of secondary products allows us to calculate the proportions of removed and concentrated elements.

#### 4.3. Relations between the Removal of Chemical Elements and the Magnitude of Rock Dissolution

It is clear from the data described above that groundwaters obtain chemical elements from precipitation, organic matter, and rocks. The contribution of the latter turns out to be relatively small, averaging only 18.4% for the temperate zone, 12.5% for the tropical zone, and 23.1% for mountain regions (Table 30). The maximum values are only 20–26% in some particular terrains. However, these data provide no insight into the magnitude of rock dissolution by groundwaters.

The fact is that the rock–water system shows both equilibrium and nonequilibrium properties; i.e., groundwaters ubiquitously dissolve some minerals but immediately form other minerals. Therefore, the real extent of rock dissolution includes two constituents: (1) the amounts of elements in aqueous solutions (lithogenic component of efflux) and (2) the amounts of elements forming a secondary mineral phase. This poses the important problem of searching for the relations between the lithogenic component of chemical efflux and the amount of newly formed mineral phases under particular conditions. In the former case, a chemical element is removed from the system (dispersed), and in the latter case, the element is concentrated. Therefore, we will consider below the quantitative relations *between the concentration and dispersion of chemical elements* accompanying the dissolution of rocks by groundwaters.

In the case of aluminosilicate rocks, the problem can be solved using well-known hydrolysis reactions (3.3). For instance, if anorthite is decomposed to form kaolinite, it can be easily calculated from reaction (3.4) that only 14.3% of the bulk rock is transferred into the solution, whereas the remaining 87.5% is fixed in kaolinite; i.e., the proportion of elements removed by water and concentrating in weathering products is 1 : 6.0. The corresponding ratio for albite weathering with montmorillonite formation is 1 : 1.5, that of mica alteration with gibbsite formation is 1 : 1.2, etc. According to the data of Alekin and Brazhnikova [264], the ratio of liquid and solid constituents during aluminosilicate decomposition varies from 1 : 2.3 to 1 : 7.8. However, these authors did not consider all possible reactions and the real ratio can be higher, especially during the laterization of rocks. For instance, during the decomposition of anorthite to gibbsite, this ratio increases to 1 : 0.6; i.e., in such a case, 62.5% of elements are released into the solution and only 37.5% remain in the precipitate. Under natural conditions, part of chemical elements

entering the solution (especially, silica) contributes to the synthesis of clay minerals, and calcium often participates to form carbonates and other phases, including clay minerals. All these factors will further decrease this ratio.

The real proportions of chemical elements removed with solutions and accumulated in weathering residues can be determined from data on the composition of groundwaters, or, more specifically, their lithogenic part. Indeed, the studies of B.B. Polynov showed the nonuniform character of leaching of chemical elements from aluminosilicates: calcium and sodium are removed first; then follow magnesium and potassium; and, finally, silicon, iron, and aluminum.

On the other hand, it is difficult to imagine the existence of a rock from which all cations have been leached, i.e., a rock composed of silicon, aluminum, and iron only, without its profound structural transformation. Consequently, the leaching of cations from the main rock-forming minerals is accompanied by their fundamental chemical transformation and migration of all of the chemical elements into solution; however, these elements are subsequently fixed in part by secondary minerals. Taking into account this circumstance, we calculated the proportions of removal and accumulation of chemical elements in weathering products for various landscape zones (Table 33), which led us to several interesting conclusions.

The first conspicuous feature is that this ratio varies within a wide range, from 1 : 0.9 (humid savanna) to 1 : 10.4 (steppe). An exception is carbonate rocks, which are dissolved congruently and do not produce large amounts of secondary minerals; correspondingly, this ratio for them increases to 1 : 0.2. In addition, the analysis of the available data suggests that, all other conditions being equal, the higher the pH of groundwater, the lower this ratio. For instance, in the acidic waters of humid savanna, almost half of the chemical elements of the dissolved rock pass into solution, whereas, in the alkaline waters of steppe and forest steppe terrains, the fraction of dissolved components decreases to 20% and in some cases to 10% or even lower. In an acid environment, in addition to all mobile cations, a considerable fraction of silicon is also removed from rocks; as a result, only iron and aluminum hydroxides are accumulated in the weathering products under such conditions (i.e., laterites are formed). In alkaline environments, the products of weathering retain not only most of the silicon but also considerable fractions of mobile cations, which are incorporated in montmorillonite and secondary calcite. Only sodium can be concentrated in solution under such conditions.

All these considerations lead us to the very important conclusion that *the character of water–rock interaction is not constant but changes continuously as chemical elements are accumulated in solutions and their alkalinity increases*. During the initial stages of

**Table 33.** Relationships of the removal and accumulation of elements during weathering of rocks under various landscape conditions

Landscape zone	Region	Type of weathered rocks	Average pH	Lithogenic component of chemical efflux, t/(yr km <sup>2</sup> )	Proportion of element removal and accumulation	Rate of chemical weathering, t/(yr km <sup>2</sup> )
1	2	3	4	5	6	7
Bald mountains	Sierra Nevada	Granites	6.7	3.7	1 : 3.0	14.8
Mountain taiga	Urals	Greenstones	6.8	6.4	1 : 2.8	24.3
	W. Sayan	Granites	–	8.0	1 : 3.0	34.6
Mountain steppe	Kurama Range	Granites	7.5	5.1	1 : 5.6	41.6
		Sandy–clayey deposits	7.5	6.5	1 : 5.4	48.0
Northern taiga (waterlogged)	Finland	Schists	6.7	1.0	1 : 2.2	3.2
Permafrost taiga	Siberian Platform	Traps	6.8	4.1	1 : 1.8	11.5
		Carbonates	7.4	14.0	1 : 0.2	16.8
	Yenisei Range	Schists	6.9	3.6	1 : 2.3	11.9
		Granites	6.7	4.1	1 : 2.0	12.3
Southern taiga	Tom'–Kolyvan'	Sandy–clayey	7.2	8.3	1 : 4.2	43.1
		Extrusive and sedimentary	7.1	8.1	1 : 4.0	40.5
Mixed forest	Northeastern United States	Basalts	7.8	8.3	1 : 4.2	43.2
		Granites	7.2	6.0	1 : 3.0	24.0
		Gneisses	7.1	3.5	1 : 2.5	12.3
		Sandstones	7.5	7.9	1 : 3.5	35.5
		Limestones	7.6	29.0	1 : 0.3	37.7
		Diorites	–	5.6	1 : 3.5	25.1
Forest steppe	Tom'–Kolyvan'	Extrusive and sedimentary	7.2	8.7	1 : 5.4	55.6
		Sandy–clayey	7.7	7.8	1 : 5.8	53.0
		Limestones	7.7	17.7	1 : 0.3	23.0
	Kansk–Taseevskaya Depression	Sandy coaliferous	7.2	7.4	1 : 4.9	43.6
		Sandstones	7.3	5.6	1 : 5.3	35.3
		Limestones	7.5	17.5	1 : 0.3	22.8
Steppe	Baraba lowland	Sandy–clayey	7.7	2.0	1 : 10.4	22.8
Wet savanna	Guinea	Dunites	5.6	12.6	1 : 0.9	24.0
		Nepheline syenites	5.3	7.2	1 : 1.1	15.1
		Quartz sandstones	5.4	6.4	1 : 1.1	13.4
	Korhogo	Granites	5.9	8.2	1 : 1.2	18.0
Tropical forest	Côte d'Ivoire	Granites	6.5	12.0	1 : 2.5	42.0
		Greenschists	6.5	15.6	1 : 2.1	48.5
		Tertiary sands	5.2	8.6	1 : 1.5	21.5
Dry savanna	Senegal	Granites	7.3	8.3	1 : 4.7	47.2
		Basic rocks	7.5	17.6	1 : 4.9	44.9

**Table 34.** Volumes and rates of rock decomposition by groundwaters

Landscape zone	Lithogenic component of efflux, t/(yr km <sup>2</sup> )	Proportion of element removal and accumulation	Volume of weathered rocks, t/(yr km <sup>2</sup> )	Rate of subsurface chemical weathering, cm/kyr	Rate of subsurface chemical denudation, cm/kyr	Total chemical denudation after Maksimovich [158], cm/kyr
<i>Temperate zone</i>						
Tundra	1.2	1 : 2.8	4.6	0.18	0.05	0.4
Northern taiga	3.2	1 : 3.0	12.8	0.51	0.13	–
Mixed forest	8.5	1 : 3.5	38.2	1.53	0.34	–
Southern taiga	9.7	1 : 3.8	46.6	1.86	0.39	1.3*
Forest steppe	6.1	1 : 6.0	42.7	1.71	0.24	–
Steppe	1.6	1 : 9.0	16.0	0.64	0.06	1.6
Average	5.1	1 : 4.7	26.8	1.08	0.20	–
<i>Tropical and equatorial zones</i>						
Wet savanna	13.2	1 : 1.1	27.7	1.11	0.53	–
Tropical forest	15.2	1 : 2.0	45.6	1.82	0.61	1.2**
Subtropical forest	14.2	1 : 3.0	56.8	2.27	0.57	–
Dry savanna	6.0	1 : 5.6	39.6	1.58	0.24	–
Steppe	1.9	1 : 7.0	15.2	0.61	0.08	–
Average	10.1	1 : 3.7	37.0	1.48	0.41	–
<i>Mountain zone</i>						
Meadow tundra	7.6	1 : 2.8	28.9	1.16	0.30	–
Mountain forest	8.6	1 : 3.5	38.7	1.55	0.34	–
Mountain steppe	4.6	1 : 6.0	32.2	1.29	0.18	–
Average	6.9	1 : 4.1	33.2	1.33	0.27	1.0

Notes: \* Forests and forest steppes.

\*\* Tropics and subtropics.

water–rock interaction, when the solution is still weakly saline and slightly acidic, the rock is dissolved relatively uniformly; i.e., the cation composition of water approaches that of the rock. The only exceptions are hydrolysate elements (Al, Fe, Ti, Mn, etc.), which cannot be accumulated in solutions owing to their high hydrolytic capacity and formation of secondary minerals. Such conditions are typical of tropical regions, which show intense water exchange resulting in rapid salt removal from the weathering profile. In this way, their slightly acidic character is maintained, which is favorable for rock laterization.

Under the conditions of retarded water exchange, when the removal of salts from the zone of water–rock interaction lags behind their accumulation in solution, the amount of chemical elements that can be concentrated in the solution becomes progressively smaller with increasing water salinity and alkalinity. Therefore, the difference between the compositions of water and host rocks increases with increasing pH and water chemistry becomes less diverse. This is commonly observed in forest steppe and steppe terrains, where the composition of water is only weakly dependent on the host rock composition. The processes of continental

salinization further decrease the diversity of groundwater chemistry.

Data on the relations of the removal and accumulation of chemical elements in the products of weathering from the main landscape zones of the Earth are summarized in Table 34. It can be easily seen that the removal-to-accumulation ratio declines continuously from north to south under the conditions of humid temperate climate; i.e., the fraction of elements concentrated in the solution relative to their amounts fixed in the products of weathering decreases monotonously. This occurs despite the increase in the total salinity of groundwaters in the same direction (Table 30). The same relation is observed in tropical and mountain regions. Consequently, variations in this ratio are not chaotic but show a zoned distribution and are strictly related to solution salinity: *the higher the total salinity of the water, the greater the fraction of chemical elements fixed in secondary products*. Correspondingly, there is a tremendous difference, up to an order of magnitude, between the lithogenic component of efflux and the volume of dissolved rock. On average, this ratio is highest in the temperate zone and lowest in the tropical zone, with the mountain regions being intermediate in this respect.

This could be expected because tropical regions are often affected by laterization, in which a considerable fraction of elements is removed. As can be seen from the average data given in Table 34, only 17–22% of elements are removed by groundwaters and 78–83% are incorporated in secondary phases. In particular landscape zones, this proportion may be either higher or lower. For instance, the average fraction of chemical elements removed by groundwaters is 48% in humid savanna and only 10% in the steppe regions of the temperate zone.

The total volume of rocks dissolved by groundwaters corresponds to the extent of chemical weathering, which also varies widely depending on landscape and climatic conditions. The minimum values are observed either in terrains with low-salinity groundwaters (tundra and northern taiga) or, in contrast, in regions with high water salinity but low water exchange rate (steppe). The highest values are characteristic of forest and forest steppe terrains; i.e., the magnitude of weathering shows a latitudinal zoning.

It should also be noted that the average volumes of weathering in the temperate and tropical zones differ only slightly, by a factor of less than 1.4. Therefore, the common belief that rock weathering in the zone of tropical forests is much more intense than in the temperate zone [265] is somewhat exaggerated. The reason is that, up to now, the difference in the proportions of removed and concentrated elements during weathering has not been accounted for and this factor reduces the difference in the scales of weathering between various climate zones. Under the conditions of tropical climate, the more acidic composition of solutions (Fig. 17) results in a higher fraction of chemical element removal compared with the temperate zone. Thus, the major portion of chemical elements is fixed by weathering products in the temperate zone. Moreover, the compositions of weathering products are also different. As a result, the magnitudes of weathering become similar.

Given the magnitudes of rock dissolution and the fraction of elements removed during this process, the rates of chemical weathering and chemical denudation can be readily calculated. The latter is the fraction of chemical elements transported by groundwaters from the weathering profile. As can be seen from Table 34, the rate of chemical weathering is two to ten times higher than the rate of chemical denudation. This creates conditions for the formation of weathering mantles, which are especially favorable in the temperate zone rather than in the tropics. Of course, the formed weathering residues are not always preserved because of the superimposed processes of mechanical erosion. For instance, the rates of formation of weathering residues in mixed forest, arid savanna, and mountain forest terrains are almost identical, but their preservation is different because of the difference in the amount and energy of precipitation, which control the extent of mechanical denudation. Consequently, chemical

weathering prepares a substrate for mechanical denudation and weathering mantles are formed when the rate of mechanical erosion is lower than the rate of chemical weathering.<sup>2</sup>

Thus, weathering products previously formed by chemical processes are more affected by mechanical denudation than bedrocks. Therefore, the fact that rivers transport more fine-grained suspended particles than dissolved salts does not necessarily mean that physical weathering predominates over chemical weathering, although this assumption can often be found in the literature.

Finally, Table 34 shows the rate of total chemical denudation of the land surface calculated by Maksimovich [158]. Similar values of this parameter were later reported by Zverev et al. [257]. It is easily seen that there is a considerable discrepancy with our data on the chemical denudation of land areas, although the results for the rate of chemical weathering of rocks are very similar. In this connection, it should be noted that, first, we estimated the chemical denudation using data on lithogenic efflux only, whereas the previous authors did not separate this contribution from the total efflux. Second, Maksimovich took into account both surface runoff and subsurface flow, whereas only the latter component was accounted for in our estimates.

The presented data allow us to draw some additional important conclusions. (1) It is necessary to distinguish between the *absolute and relative efflux of chemical elements* from rocks. The former is the sum of elements removed by waters from rocks, and therefore it increases with increasing time of water–rock interaction. The latter is the volume fraction of rocks dissolved in water, and it decreases owing to an increase in the extent of element concentration relative to removal. (2) Low-salinity waters produce weathering products with a small number of chemical elements. The spectrum and number of elements fixed in weathering products increase with increasing salinity and alkalinity of the solution. (3) The character of water–rock interaction is not constant and changes continuously with increasing salinity and alkalinity.

All these considerations refute the common assertion that the higher the content of an element in water, the lower its content in weathering products. Based on this simplistic concept, many researchers supposed, for example, that the laterization of rocks must be accompanied by silica-rich waters. It is evident that this suggestion is erroneous.

<sup>2</sup> Of course, the chemical and mechanical work of both subsurface flow and surface runoff must be taken into account.



## CHAPTER 5. GEOCHEMICAL LINK BETWEEN WEATHERING AND DEVELOPMENT OF GROUNDWATER COMPOSITION

The processes of rock weathering have long been studied. Considerable progress in the understanding of these processes was due to the studies of B.B. Polynov, I.I. Ginzburg, F.V. Chukhrov, A.V. Sidorenko, A.I. Perel'man, D.G. Sapozhnikov, V.P. Petrov, V.V. Dobrovolskii, N.M. Strakhov, A.B. Ronov, V.P. Kazarinov, K.I. Lukashev, B.M. Mikhailov, I.K. Karpov, Yu.P. Seliverstov, S.A. Kashik, W.D. Keller, C.W. Correns, M.L. Jackson, G. Pedro, G. Millot, C. Ollier, F.C. Loughnan, Y. Tardy, S.M. Colman, A.F. White, J. Déjou, E. Yatsu, S.L. Brantley, D. Nahon, and many others. However, only a few researchers (B.B. Polynov, A.I. Perel'man, Yu. Yu. Bugel'skii, G. Pedro, Y. Tardy, and V.P. Zverev) used hydrochemical data for deciphering the mechanisms of chemical weathering. Yet it is evident that the mechanisms and scales of rock weathering cannot be understood without the investigation of water geochemistry. On the other hand, the development of groundwater composition also cannot be evaluated without the geochemistry of weathering because both are related to a single process.

### 5.1. Main Geochemical Types of Weathering

Since the pioneering studies of V.V. Dokuchaev, who was the first to point out zoning in the mineral kingdom, including the subsoil horizons of the weathering zone, many researchers have greatly contributed to the investigation of supergene processes and their zoning (K.D. Glinka, P.A. Zemyatchenskii, A.B. Fersman, V.I. Vernadsky, B.B. Polynov, V.A. Kovda, A.I. Perel'man, K.I. Lukashev, A.G. Chernyakhovskii, C. Ollier, etc.). The studies of these authors unequivocally established the phenomenon of zoning in weathering mantles. Nonetheless, distinguishing zoned types of weathering mantles still involves certain difficulties related to the use of different criteria.

Based on the specific features of geochemical and soil processes in each landscape zone, Lukashev [266] distinguished the following geochemical types of weathering mantles: lithogenic (detrital) type of tundra, siallite-clay type of the taiga-forest zone, siallite-carbonate type of the steppe zone, siallite-chloride-sulfate type of the desert zone, and siallite-ferrite and allite (red-colored) types of humid subtropical and tropical regions. Perel'man [248] proposed a geochemical classification of weathering mantles on the basis of the principle of mobile components and the concept of typomorphic elements. He distinguished six types of weathering residues: (1) sulfate, (2) acid, (3) carbonate, (4) salt-bearing, (5) acid gley, and (6) carbonate gley. It should be recalled also that Polynov [267] distinguished carbonate, sulfate, and chloride types of weathering.

Pedro [268] proposed an interesting classification of weathering residues. He argued that the character of newly formed minerals is controlled by the intensity of removal of silica, aluminum, and bases during the decomposition of the initial rock. Based on this concept, he proposed to use the  $\text{SiO}_2/\Sigma$  bases values of waters ( $L$ ) and weathered rocks ( $R$ ) as a criterion for distinguishing four main types of rock weathering: allitization, monosiallitization, bisiallitization, and podzolization (Table 35).

Subsequently, Tardy [68] distinguished two additional types of weathering, (1) semisiallitization, in which amorphous products of weathering (allophanes) are formed with the molecular ratio  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 0.5-1.2$ , and (2) cryptic monosiallitization, producing three-layer clay minerals (vermiculite and montmorillonite) with excess  $\text{Al}_2\text{O}_3$  residing in the interlayer space of the clays. Tardy also proposed another more complicated coefficient for distinguishing geochemical types of weathering on the basis of the composition of drained waters. However, the method of Tardy is not fundamentally different from that of Pedro, and we will not consider it in detail.

The above classifications reflect the experience of studies in different climate zones, and, therefore, each of them has its advantages. For instance, Perel'man worked for many years in regions with an arid climate and reasonably distinguished carbonate and salt-bearing weathering residues. As an expert in laterite weathering, Pedro distinguished mono- and allite residues, which were considered by Perel'man as a single type (acid). More similar examples can be given because the classifications of different authors are based on different principles.

Using the experience of previous authors and the results of our own observations in various climate zones, we distinguished the following main geochemical types of rock weathering on the basis of a series of indicators.

(1) The *laterite* type is characterized by almost complete removal of silica and formation of aluminum and iron oxides and hydroxides. It develops under the conditions of active water exchange in an acid environment, where the magnitude of organic matter remineralization is much higher than that of rock weathering and ultrafresh waters are formed. Such conditions are most common in humid savanna terrains but have also been documented in tropical and subtropical forests.

(2) The *monosiallite* (kaolinite) type develops under the weakly acid conditions of tropical, subtropical, and temperate climate. Necessary conditions for the occurrence of kaolinization are a weakly acidic composition of waters, their low salinity, and a relatively low content of silica. These conditions are attained under the conditions of rather active water exchange and similar magnitudes of rock weathering and organic matter remineralization.



**Table 35.** Geochemical types of weathering

Geochemical characteristics of infiltration waters of the weathering zone	$q(\text{Al}_2\text{O}_3) < q(\text{SiO}_2)$			$q(\text{Al}_2\text{O}_3) > q(\text{SiO}_2)$
	$L R;$ $q(\text{SiO}_2)q(\text{bases})$	$0.64 L R;$ $0.64q$ (bases) $q(\text{SiO}_2) < q$ (bases)	$L < 0.64R;$ $q(\text{SiO}_2) < 0.64q(\text{bases})$	—
Mineral composition of residual products in the eluvial horizon	Al hydroxides (gibbsite and boehmite)	Clay minerals 1 : 1 (kaolinite)	Clay minerals 2 : 1 (illite and montmorillonite)	Free silica
Weathering processes	Allitization (lateritization)	Monosiallitization (kaolinization)	Bisiallitization (formation of three-layer minerals)	Podzol formation
Index of weathering type	I	II	III	IV

Note:  $q$  is the rate of element removal,  $L$  is the  $\text{SiO}_2/\Sigma\text{Bases}$  ratio in waters, and  $R$  is the same ratio in weathered rocks.

(3) The *bisiallite* type can be subdivided on the basis of its character into the montmorillonite and illite subtypes. The former occurs under the conditions of weakly alkaline and alkaline environments, relatively weak water exchange, elevated groundwater salinity, and high-silica solution composition. This subtype is confined to forest steppe, steppe, and southern taiga terrains and part of arid savanna terrains. The second subtype develops under less alkaline conditions, when solutions show relatively low contents of silica and other salts, and is observed mainly in the regions of cold temperate climate (northern forest zone both with and without permafrost), although it has also been described in other landscapes. A common feature of these two subtypes of weathering is that they develop under conditions where the magnitude of rock weathering is higher than the rate of organic matter remineralization, which results in the formation of a weakly alkaline or alkaline environment.

(4) The *podzol-forming* type develops under acidic gley conditions, favorable for active removal of both aluminum and iron. On the other hand, silica removal is somewhat depressed by low temperatures and insufficiently high water exchange rates. Gley geochemical conditions are maintained by high contents of organic matter, which can bind free oxygen transported by waters. This type of weathering is observed in the northern and middle parts of the forest zone, with thick forest litter. The products of this process are loose siliceous sand, illite, kaolinite, allophanes, and other clays.

(5) *Carbonate-type* weathering and *soda formation* are coupled processes occurring when water evaporation is somewhat higher than precipitation, the environment has an alkaline character, and water exchange is weak. Rapid salt accumulation in solutions owing to

both weathering and continental salinization results in the formation of an alkaline environment, a decrease in the solubility of calcium carbonates, and their precipitation from the solution. In turn, this leads to the relative accumulation of sodium carbonates (soda) in the solution. Carbonate formation develops as a zoned phenomenon under the conditions of forest steppe and steppe landscapes and is also possible in arid savanna terrains.

(6) The *sulfate–chloride* type is formed under conditions of much higher evaporation than precipitation (which is typical of the zone of arid steppe, semidesert, and desert), very slow water exchange, an alkaline character of the environment, and high groundwater salinity. Weathering of this type produces montmorillonite, carbonates, gypsum, and occasionally halite.

Thus, the geochemical type of weathering is a result of the coupled and interrelated development of the main components of landscapes—rocks, organic matter, and groundwaters—caused by their general nonequilibrium under supergene zone conditions and the influence of numerous zonal factors, among which water exchange is of special importance. Only such an approach to weathering phenomena can reveal the interplay of such seemingly disparate processes as lateritization and soda formation, kaolinization and podzol formation, etc. It becomes clear that the same mechanisms control the compositions of weathering products and groundwaters.

## 5.2. Mechanisms and Stages of Weathering

The distinguished geochemical types of weathering correspond to a certain stage of water–rock interaction. What mechanism controls the type of weathering? In

order to answer this question, it must be remembered that we are dealing with an equilibrium–nonequilibrium system, which provides the general possibility of continuous interaction in the water–rock system over geologically long time scales with the formation of a series of secondary mineral phases. The secondary minerals are closely controlled by the character of the geochemical environment, which also changes during the development of the interaction (see Chapter 3). These interrelated and interconnected simultaneous changes in the character of the geochemical environment and the composition of newly formed minerals are the essence of *the geochemical evolution of the water–primary aluminosilicate system*. Water migrating through rocks continuously dissolves them, extracts mobile elements into solution, and changes its composition and simultaneously the compositions of newly formed secondary minerals.

The problem of the formation of zoning in weathering residues and stages of secondary mineral formation was reviewed by Kashik and Karpov [269, 270]. Therefore, we note only some aspects of this problem important for our study.

Modern concepts on the geochemical essence of processes in the weathering zone were most vividly presented by I.I. Ginzburg. Summarizing information on this problem, he noted [271, p. 91]: “Theoretically, any residual weathering mantle should have a zoned profile because acidic and soil solutions percolating downward are gradually averaged or transform to weakly alkaline and alkaline solutions; i.e., the pH value of reacting waters increases with depth, and, eventually, they reach the pH value of fresh rock leaching. As a result of the increase in pH and changes with depth in the concentration of salts in water, the intensity of rock decomposition declines with increasing depth.”

This excerpt expresses the essence of a peculiar postulate that is acknowledged by most researchers and has long been used as a basis for the concept of the stage development of secondary mineral formation. The above considerations lead us to a number of inferences: (1) a weathering profile develops from top to bottom; (2) a weathering profile is zoned; (3) the composition of zones is controlled by the composition of the aqueous solution, which changes with depth; and (4) the transformation of minerals in the weathering profile occurs in several stages.

Ginzburg distinguished four main stages in the development of weathering residues: (1) the hydration of silicates and beginning of leaching; (2) the complete hydration of silicates, development of leaching, and beginning of oxidation (in iron-rich silicates); (3) final leaching, the development of hydrolysis, and weak oxidation (iron-poor rocks); and (4) extensive oxidation and complete hydrolysis. According to Ginzburg, each stage corresponds to a certain set of secondary minerals, which show a zoned distribution. Each zone of weathering residues was identified by him with a cer-

tain stage of weathering; i.e., each zone reflected a certain stage in the development of weathering processes.

Consequently, the concept of Ginzburg and his numerous students and followers is based on the idea of a transformation mechanism of weathering assuming that the composition of secondary mineral phases is controlled by the extent of removal of mobile elements, or, more precisely, by the fraction of mobile elements that is retained in the crystal lattice. The pH values of solutions are also controlled by the magnitudes of removal of alkaline and alkali earth elements. With increasing depth, the abundances of these elements in solutions increase, and the pH value of the solutions increases correspondingly. Eventually, they reach the pH of fresh rock leaching, at which the process supposedly ceases. Unfortunately, the concept of the pH of fresh rock leaching is not substantiated by theoretical, experimental, or field evidence. It is thought that the initial stages of weathering occur in all climate zones, whereas the final stages may occur only under tropical climate conditions, with high temperatures and considerable amounts of precipitation. Considerable efforts have been made by many researchers to determine the boundary conditions with respect to temperature and amount of precipitation above which laterization processes may develop, but with no success.

The idea of the transformation evolution of weathering products, which has been accepted by many Russian researchers (V.P. Petrov, I.P. Gerasimov, D.G. Sapozhnikov, Yu.Yu. Bugel'skii, I.V. Vitovskaya, K.K. Nikitin, and others) and which was developed before the studies of Ginzburg by I.I. Polynov, K.I. Lukashov, V.A. Kovda, and others, as well as by the school of Jackson [272], encountered considerable difficulties after the finding of compelling geological evidence for the formation of the final stages of weathering directly on bedrocks, i.e., without intermediate stages, which are necessary according to this theory. In particular, the finding of gibbsite developing directly after feldspars became a subject of heated debate.

In view of the accumulated new facts, Ginzburg's concept was revised. Nikitina et al. [273] substantiated the distinguishing of three types of weathering profiles: (1) a complete profile including all weathering zones; (2) a reduced profile with missing middle zones consisting of products of complete decomposition, which lie directly on fresh rocks; and (3) an incomplete profile, formed under peculiar weathering conditions, where only the lower zones are developed. However, the recognition of the different types of weathering profiles did not fundamentally change the interpretation of the stages and mechanisms of mineral transformations during weathering.

On the other hand, another opinion has long ago developed within the science of weathering that clay minerals can be synthesized from the components of an aqueous solution. Sedletskii [274] was, perhaps, the first to demonstrate experimentally that crystalline

**Table 36.** Calculated contents of minerals in the weathering profile after diorites (open system)

Zone	Thickness, cm	Goethite*	Gibbsite	Kaolinite	Montmorillonite	Chlorite	Silica
Goethite–gibbsite	$1.1 \times 10^{-4}$	$\frac{3.12 \times 10^{-5}}{28.8(18.8)}$	$\frac{7.72 \times 10^{-5}}{7.21(81.2)}$	–	–	–	–
Goethite–gibbsite–kaolinite	$3.5 \times 10^{-4}$	$\frac{9.86 \times 10^{-5}}{21.8(14.3)}$	$\frac{1 \times 10^{-4}}{22.9(26.3)}$	$\frac{2.5 \times 10^{-4}}{55.7(59.4)}$	–	–	–
Goethite–kaolinite	$3.5 \times 10^{-2}$	$\frac{9.86 \times 10^{-3}}{18.6(12.3)}$	–	$\frac{4.3 \times 10^{-2}}{81.4(87.7)}$	–	–	–
Chlorite–montmorillonite	1.1	–	–	–	$\frac{2.82}{97.9(98.2)}$	$\frac{6(2.5) \times 10^{-2}}{2.1(1.81)}$	–
Chlorite–montmorillonite with silica	35.2	–	–	–	$\frac{90.9}{97.7(97.6)}$	$\frac{0.6}{0.7(0.6)}$	$\frac{1.5}{1.6(1.8)}$

\* The nominator shows the amount of the newly formed mineral in grams, and the denominator shows its content in wt % (vol % in parentheses).

montmorillonite can be synthesized in 3–4 yr from an amorphous aluminosilicate gel at low temperatures. The idea of de novo synthesis of clay minerals in soils was also developed by Polynov.

Furthermore, French researchers demonstrated convincingly that the de novo synthesis of clay is widespread both in soils and throughout the whole section of weathering residues [260, 268, 275–277]. Using extensive experimental data, Pedro showed most comprehensively that the chemical elements migrating into solution during weathering produce not only carbonates and salts but also clay minerals, the process of formation of which was referred to as de novo synthesis.

The idea of clay formation from an aqueous solution via the mechanism of de novo synthesis has received comprehensive support in recent decades from structural mineralogy (see Section 4.2) and currently raises no objections. However, if this is the case, our concepts on the stages of secondary mineral formation during weathering change fundamentally. The fact is that the solid-state and liquid-phase mechanisms of secondary mineral formation are governed by different laws.

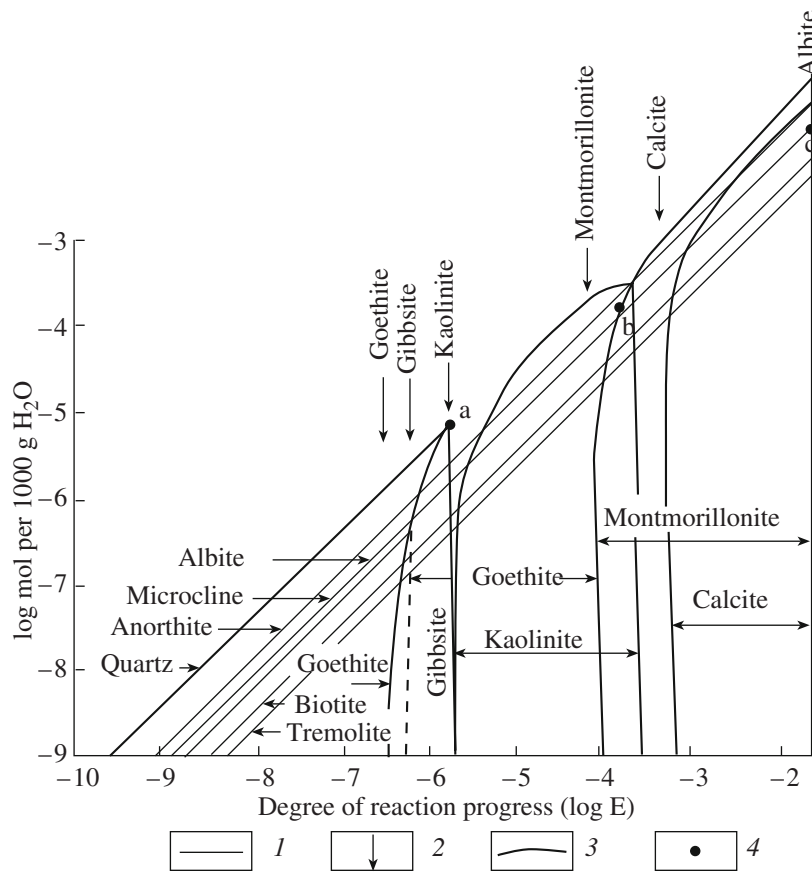
The de novo synthesis of clay from a solution is governed by the law of mass action, implying that the compounds precipitating from a solution must be the least soluble under the given conditions, or, more precisely, must show the lowest equilibrium constants of the corresponding dissolution reaction. The water–rock system tends toward the minimum free energy. This principle serves as a basis for the physicochemical and mathematical computer modeling of natural systems.

The simulation of weathering has been performed by many authors for various rock types under conditions ( $T$ ,  $P$ ,  $\text{CO}_2$ , pH, etc.) approaching natural ones. As an example, Fig. 29 shows the calculated sequence of mineral formation in the water–granite system at 25°C under open- and closed-system conditions. The estab-

lished sequence of secondary mineral formation (goethite, goethite + gibbsite, goethite + kaolinite, kaolinite + montmorillonite, montmorillonite + calcite) turned out to be strictly opposite to that proposed by the proponents of the transformation mechanism of secondary mineral formation.

The same sequence of mineral precipitation was obtained by the simulation of weathering processes in other rock types. Kashik [270] investigated this problem most comprehensively and determined both the sequence of secondary mineral formation and the possible thicknesses of weathering zones. Table 36 gives an example of a model profile produced by the open-system weathering of diorite. As in the case of other rock types, five sequential mineral zones of different thickness were distinguished: goethite–gibbsite, goethite–gibbsite–kaolinite, goethite–kaolinite, chlorite–montmorillonite, and chlorite–montmorillonite–silica.

Thus, independent of the rock type, the calculated sequence of secondary mineral formation is in general identical under both open- and closed-system conditions: gibbsite, boehmite, goethite  $\rightarrow$  kaolinite  $\rightarrow$  montmorillonite, chlorite, illite  $\rightarrow$  calcite. It can be seen that the sequence of stages of secondary mineral formation is the opposite of that developed by Ginzburg and many of his followers. Based on these observations, Kashik [270] and we [279] independently developed the concept that the first minerals formed during rock weathering are iron and aluminum oxides and hydroxides and the last minerals with respect to the front of water movement are three-layer clay aluminosilicates (illite and montmorillonite) and carbonates (calcite). Consequently, there are grounds for suggesting that, under the supergene zone conditions, the sequential development of secondary minerals is controlled by the parameters of the geochemical environment and the degree of solubility of particular mineral



**Fig. 29.** Sequence of secondary mineral formation during granite weathering at 25°C according to the results of computer modeling [278]. (1) Rate of mineral dissolution; (2) onset of precipitation of secondary minerals; (3) fields of formation of secondary minerals; and (4) points of saturation in (a) quartz, (b) microcline, and (c) albite.

compounds. The initial stages produce the most poorly soluble compounds, for instance, hydroxides of hydrolysate elements (Fe, Al, and more rarely Mn). Correspondingly, their contents in the solution do not increase and even decrease during the early stages of groundwater–rock interaction. This is supported by both physicochemical models and field observations.

As other elements are accumulated in the solution at the expense of dissolution of the parent rock, the compositions of water and secondary minerals change. In accordance with thermodynamic equilibrium, hydroxides are changed by clays, which fix not only Al and Fe but also SiO<sub>2</sub>, whose activity in the solution usually does not increase starting from this moment (Fig. 18). Similar to Fe and Al hydroxides, clays bind a relatively small fraction of major cations released during weathering (Na, Ca, Mg, and K), and their contents in the solution continue to increase. The corresponding salinity increase results in a pH increase. Therefore, at a certain stage of the evolution of the water–rock system, the solution becomes saturated in calcium carbonate and calcite is formed, which results in the development of carbonated weathering mantles and soils. Under favorable climatic (active evaporation) and hydrogeological

conditions (weak water exchange), sulfates, chlorides, phosphates, and other salts can be formed.

Consequently, the physicochemical parameters of the water–rock system can evolve continuously in various parts of the supergene zone. Under the influence of a variable solution, a single primary mineral can be sequentially transformed into a variety of secondary products associating with certain water types. The geochemical environment is formed by the same processes that result in the transformation of water–rock and water–organic matter systems. It becomes clear that *the solution composition (geochemical medium) and the geochemical type of weathering are two different products of the evolution of a single system*, and each type of geochemical medium corresponds to strictly predetermined compositions of weathering products.

### 5.3. Geochemical Types of Groundwater

The geochemical types of groundwater are usually distinguished in hydrogeology on the basis of dominant anions and cations, and a number of classifications have been proposed [4]. However, such an approach may be



unsatisfactory for the solution of many hydrogeochemical problems, especially in the case of bicarbonate-type fresh waters. For instance, the waters of the tropical and temperate zones are significantly different (Table 19), but their chemical types are identical; i.e., the existing chemical classifications ignore the specific geochemical features of waters from each landscape and climate zone.

This important shortcoming was clearly realized by Perel'man [63], who proposed to use classes of water migration instead of chemical types of water. These classes were distinguished on the basis of alkalinity–acidity (pH), redox conditions (Eh), typomorphic elements, and water salinity. Such an approach is certainly more promising and provides a solid basis for the development of a geochemical classification of groundwaters. However, even in this case, interrelations between water migration classes can be traced only indirectly. For instance, Perel'man distinguished three classes among weakly acidic waters: acidic, acidic in quartz sands, and acidic transitional to calcic. However, it remains unknown which of these classes is related to laterization and which to kaolinization and if there are differences between them. A similar situation is characteristic of the neutral and weakly alkaline classes, which also cannot be clearly assigned to particular weathering types. Therefore, it is unclear, for instance, which type of weathering (clay or carbonate) is related to the calcic class of water migration.

In accordance with the concepts developed in this contribution, the composition of groundwater is the difference between the dissolved rocks and those parts of elements that form secondary minerals. The fact that precipitation and organic matter are significant additional sources of elements has no fundamental importance. The reason is that a water solution of any stage of interaction with rocks forms a certain secondary phase, with which it is in chemical equilibrium. The input of elements into this system from another source results in their redistribution in certain proportions between the secondary phase or phases and the aqueous solution. The same occurs during the evaporative concentration of solution.

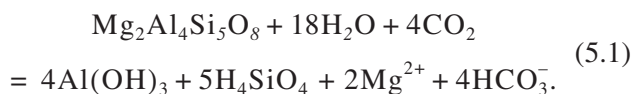
It is important to note that only a few of the great number of chemical elements available in the solution control secondary mineral formation at any given moment of interaction: Fe, pH, and Eh for goethite; Al and pH for gibbsite; Al, Si, and pH for kaolinite; Ca, HCO<sub>3</sub><sup>-</sup>, and pH for calcite; Si, Al, pH, and Mg for Mg-montmorillonite; Fe, HCO<sub>3</sub><sup>-</sup>, pH, and Eh for siderite; etc. During the evolution of the water–rock system, the number of controlling parameters increases in accordance with a strict sequence, which will be discussed below.

*Consequently, a transition from one geochemical type of weathering to another is controlled by the character of variations in the parameters of the geochemical environment and the composition of aqueous solu-*

*tion is governed by the mass action law.* The composition of water, or, more specifically, the product of the activities of a certain group of chemical components, including H<sup>+</sup> (pH) and e<sup>-</sup> (pe), is connected with the composition of weathering products by strict fundamental thermodynamic laws, and this relation must be used as a basis for the geochemical classification of waters. This is true of both the supergene zone and the Earth's crust in general [244].

As was shown above, even atmospheric precipitation is usually saturated in Al, Fe, and Ti hydroxides, which serve as a geochemical barrier preventing the concentration of these elements in groundwaters. Equilibrium with gibbsite is retained in small water channels, weathering residues, and soils [280, 281]. A possible example is the ultrafresh waters of Koloa Island (Hawaii), which are gibbsite-saturated, despite the very low content of Al (Table 5) and acidic character (Fig. 30) [285]. When Al from primary minerals that are not in equilibrium with groundwaters enters the aqueous solution, it is fixed in hydroxides, which prevent an increase in the content of this element in the solution and determine the beginning of component fractionation between the aqueous solution and the secondary mineral phase.

The above considerations reveal *a new important mechanism of chemical element redistribution among solid phases through an aqueous solution* and formation of geochemical types of water. Once the aqueous solution is saturated in Al, Fe, Ti, Mn, and other hydroxides, all of the dissolved elements are divided into two unequal groups: (1) mobile elements, which can be extensively concentrated in the solution and removed from the zone of the water–initial rock boundary, and (2) elements concentrated by the secondary phase and equilibrated with their hydroxides. Only part of the elements of the former group is incorporated in the solid phase as admixtures, whereas the second group fully controls the composition of the produced secondary phase. Thus, the first geochemical type of waters formed under such conditions can be referred to as *acidic iron–aluminum* and corresponds to the laterite type of weathering. The typical reaction of this type of weathering can be written as



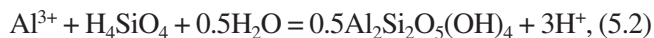
It is important that the primary aluminosilicate (cordierite) produces gibbsite during weathering; i.e., it fixes Al and Fe. Although the latter element is not explicitly present in this model, it is always available as an admixture. The solution is not saturated in Si and Mg, and these elements can be concentrated in the water phase. In addition to Mg, all other mobile cations that are not affected by geochemical barriers migrate into groundwaters under such conditions.



The characteristics of the acidic iron–aluminum geochemical type of water formed under such conditions are summarized in Table 37. Usually, these waters are acidic or weakly acidic (pH = 4.0–6.5) and occur in an oxidizing geochemical environment; they are ultrafresh (0.1–0.2 g/l) and show low SiO<sub>2</sub> contents (usually <5 mg/l). The low pH values of these waters are related to the high partial pressure of CO<sub>2</sub>, which is provided by the high degree of organic matter remineralization. The cation composition of such waters is usually controlled by the composition of the aquifer rocks and has relatively high K and Si concentrations. Such waters are formed under the conditions of the most intense water exchange in the landscape zones of humid savanna and, occasionally, tropical and subtropical forests. However, this geochemical type of waters can also be formed in other landscapes, including permafrost areas with active water exchange, if the time of water–rock interaction is limited. It is, therefore, not accidental that mineralogical findings of gibbsite, which associates with this water type, have been reported from Yakutia, the Kola Peninsula, and other similar regions.

Thus, on the one hand, the nonequilibrium between water and primary aluminosilicates leads to their continuous dissolution, while, on the other hand, the equilibrium between water and aluminum and iron hydroxides forces each new atom entering the solution to be fixed in these secondary phases. In such a way, an exchange system is formed and operates until a new chemical equilibrium is established in the solution in response to an increase in the contents of all elements but Fe and Al.

Among these elements, of special significance is Si, which contributes to the formation of clays. As was shown by Garrels and Christ [241] and confirmed by many experimental studies [283], Si and Al form kaolinite via the reaction



the constant of which is

$$K = [\text{H}^+]^3 / [\text{Al}^{3+}][\text{H}_4\text{SiO}_4] = 10^{-3.1}. \quad (5.3)$$

If the pH value of groundwater is 5.0 (tropics), which corresponds to an [Al<sup>3+</sup>] activity in equilibrium with gibbsite of 10<sup>-7.5</sup> (Fig. 31), the activity of H<sub>4</sub>SiO<sub>4</sub> is 10<sup>-4.4</sup>. Since the free energies of crystalline and amorphous gibbsite are different (Fig. 30), the activity of H<sub>4</sub>SiO<sub>4</sub> may increase up to 10<sup>-4.1</sup> according to the available data, which corresponds to about 5.0 mg/l SiO<sub>2</sub>. This SiO<sub>2</sub> concentration in groundwater is an approximate limit above which equilibrium with kaolinite is usually attained. Starting from this moment, kaolinite is formed in the weathering residue instead of gibbsite; i.e., the laterite type of weathering changes to the monosiallite type.

The characteristic reaction of this type of weathering can be written as

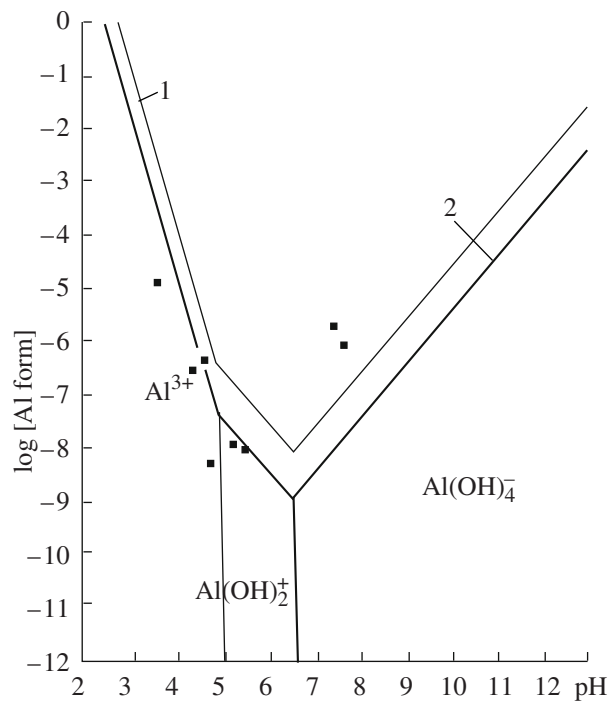


Fig. 30. Stability fields of (1) amorphous and (2) crystalline gibbsite and data on the composition of ultrafresh waters from Koloa.

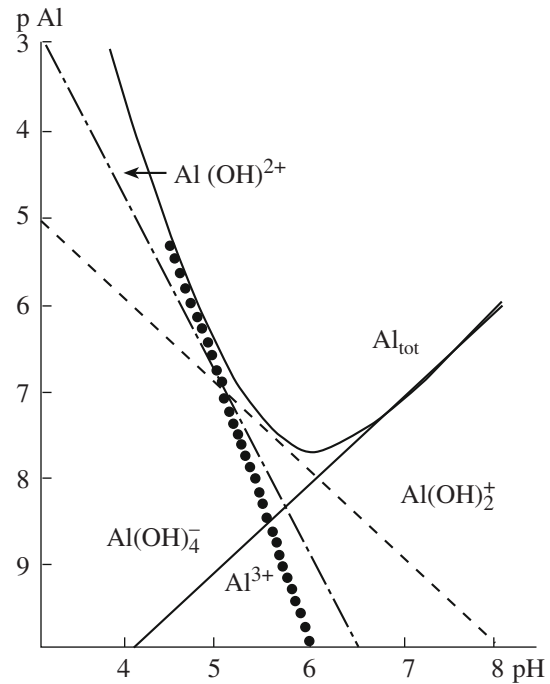
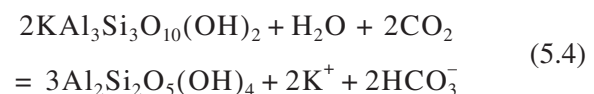


Fig. 31. Variations in concentration of species and solubility of Al in equilibrium with gibbsite [182].



**Table 37.** Geochemical types of groundwaters

No.	Water type	Geochemical type of weathering	Control parameters	Necessary chemical condition	Groundwater characteristics
1	Acidic iron–aluminum	Laterite	Al, Fe, Mn, pH, pe	Equilibrium with Al, Fe, and Mn hydroxides	Ultrafresh, acidic and weakly acidic, oxidizing, SiO <sub>2</sub> < 5 mg/l
2	Aluminum–silicon	Monosiallite	Al, Si, pH	Equilibrium with kaolinite	Fresh, weakly acidic and neutral, SiO <sub>2</sub> > 5 mg/l
3	Siliceous Na (Ca–Mg–K–Fe)	Bisiallite	Si, Na, Mg, Ca, K, pH	Equilibrium with illite- and montmorillonite-group minerals	Fresh and brackish, neutral and weakly alkaline, SiO <sub>2</sub> from 10 to 60 mg/l depending on pH and cation composition
4	Acidic siliceous–organic	Podzolization	Al, Si, C <sub>org</sub> , pH, pe	Removal of Al and Fe, equilibrium with kaolinite and, probably, SiO <sub>2</sub>	Fresh, acidic with high contents of organic acids and SiO <sub>2</sub>
5	Alkaline calcium–carbonate (sodic)	Carbonate formation	Ca, HCO <sub>3</sub> , pH	Equilibrium with calcite	Alkaline fresh and slightly brackish (0.6–1.5 g/l)
6	Brackish calcium–sulfate	Sulfate salinization	Ca and SO <sub>4</sub>	Equilibrium with gypsum	Brackish, alkaline with high contents of sulfate and chloride ions
7	Saline sodium–chloride	Chloride salinization	Na and Cl	Equilibrium with halite	Saline waters with high content of sodium chloride

In such a case, the weathering of potassium mica produces kaolinite, which binds Si and Al. Potassium migrates into the solution together with other cations and is concentrated there.

Starting from the moment of Si fixation by a secondary mineral phase, the increase in its content in the aqueous solution is depressed, which is favorable for the concentration of other elements and, consequently, a change in the geochemical character of groundwater to the *aluminum–silicon* type (Table 37). The onset of formation of the latter coincides with groundwater saturation in kaolinite.

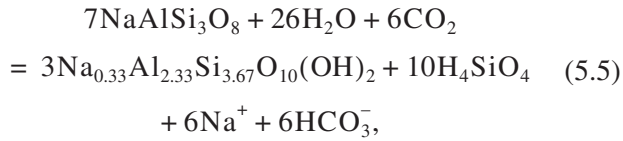
Aluminum–silicon waters differ from acidic iron–aluminum waters in slightly higher total dissolved solids (0.2–0.4 g/l); pH values (6.0–7.2); and contents of SiO<sub>2</sub> (>5 mg/l), other cations, and, occasionally, organic matter. Waters of this type occur not only under oxidizing conditions, but also in gley and reducing geochemical environments. Their cation composition is diverse and controlled by the type of aquifer rocks. The cation fraction of silicon is high. Aluminum–silicon waters are widespread under the conditions of active water exchange in all landscape types (tropical, subtropical, humid temperate, forest, northern high mountain taiga, and occasionally forest steppe and humid

savanna), where they are closely associated with the iron–aluminum type of water.

A peculiar geochemical type of water is formed in podzolic soils, which are widespread in taiga and mixed and broadleaf forest terrains, where the removal of Al prevails over the removal of Si. The reason is that tremendous amounts of various acids are formed from organic matter in soils under the conditions of high biological productivity coupled with relatively weak water exchange and poor aeration, which results in the development of acidic waters (pH 3.5–5.5) extremely enriched in organic compounds. Under such conditions, Fe and Al are rather mobile, whereas the migration of silica is suppressed. The resulting waters are usually equilibrated with kaolinite (Fig. 24) and, occasionally, with silica, which may form loose siliceous materials. This geochemical type of waters can be referred to as the *acidic silica–organic* type and is connected with podzolization.

The formation of kaolinite depresses but does not completely prevent silica concentration in the solution because the Si/Al ratio in the majority of weathered aluminosilicates is higher than that in kaolinite. Therefore, the concentrations of mobile cations and Si in the solution continue to increase under favorable hydrody-

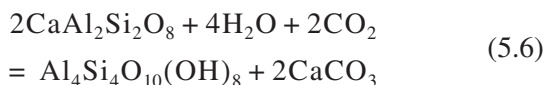
namic conditions. The pH values increase simultaneously. Eventually, this leads to the attainment of equilibrium with bisiallilite clay minerals (montmorillonite, illite, etc.), for instance, via the reaction



the constant of which depends on the activities of  $\text{H}_4\text{SiO}_4$ ,  $\text{Na}^+$ , and  $\text{HCO}_3^-$  and pH. As was shown above (Figs. 21, 22), considerable amounts of groundwater from various landscape zones are saturated in montmorillonite or illite, which bind both Al and Si and part of mobile cations (Ca, Na, Mg, and K). Consequently, after the equilibration of groundwaters with clay minerals of the illite and montmorillonite groups, the increase in the concentration of mobile cations decelerates somewhat, which suggests a transformation of the water composition into a new geochemical type associating with the bisiallilite type of weathering. Such waters can be referred to as *siliceous–sodium* and *siliceous–calcium* depending on the mobile element fixed by the secondary mineral phase.

The siliceous–sodium geochemical type of waters differs from the types considered above in a higher salinity (0.4–1.5 g/l), elevated pH values (7.0–8.0), and higher contents of mobile elements and  $\text{SiO}_2$  (usually, 10–30 mg/l). The main distinctive feature of this water type is equilibration with illite- and montmorillonite-group minerals (Table 37). This water type is rather common in regions with subdued water exchange and occurs over the main portion of taiga (including taiga permafrost), mixed forest, forest steppe, mountain taiga, mountain steppe, and desert steppe terrains. The aluminum–silicon and siliceous–calcium geochemical types of waters are closely associated in many landscape and climate zones.

The formation of illite- and montmorillonite-group clay minerals does not bind all mobile cations because their contents in the initial (subject to dissolution) rocks are much higher than in the resulting clays. Therefore, their concentrations in groundwaters increase owing to further water interaction with initial (parent) rocks. This process continues until equilibrium with calcite (the least soluble carbonate) is reached. In such a case, the process of weathering can be described by the following reaction:



i.e., a clay mineral and calcite are produced by weathering. Of course, this becomes possible only after the attainment of equilibrium between groundwater and Ca carbonate, i.e., normally, when the total salinity of groundwater is higher than 0.6 g/l and pH is higher than 7.4 (Section 3.1).

The appearance of calcite among the products of weathering changes dramatically the character of the water–rock system because an increase in calcium content in aqueous solution is strongly limited after this moment. Taking into account that the major portion of Mg and K is fixed in clay mineral products, it is evident that Na must be preferentially concentrated under such conditions. The Na content in water increases continuously (Fig. 18), and this leads eventually to the formation of sodium bicarbonate waters, which are commonly referred to as soda waters. Consequently, *carbonate formation and soda formation are two closely related and coupled phenomena associated with the overall process of rock weathering under the conditions of water saturation with respect to calcite.*

Using the criteria developed in this study, the geochemical type of water formed under these conditions should be termed *alkaline calcium–carbonate* (Table 37) because its formation is initially controlled by equilibrium with calcite, although such waters are usually referred to as soda waters on the basis of traditional criteria.

The alkaline calcium–carbonate geochemical type of waters is closely associated with the siliceous–Na type, but shows a higher salinity (0.6–1.5 g/l) and alkalinity (pH 7.4–8.6) and is often relatively enriched in sulfates and chlorides. It is widespread in forest steppe and steppe terrains, including arid tropical regions, where water exchange is subdued and initial stages of salinization are observed. In addition to calcite, this water type is associated with montmorillonite-group minerals.

When groundwater becomes saturated in calcite, its interaction with rocks does not cease, and many other chemical elements extracted from the rocks continue to accumulate in the solution. The most important among them are sodium, sulfate, and chloride ions. Under the conditions of arid climate, this process is enhanced by continental salinization. The precipitation of gypsum as the first salt depresses the increase in the concentration of sulfate ion, which could previously be monotonously concentrated in groundwaters. Correspondingly, the geochemical type of *brackish calcium–sulfate* waters is formed starting from this moment. This process requires that the activity product of  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  in the solution be higher than  $10^{-4.3}$ . During this stage, the total salinity of groundwater is usually higher than 6–8 and may even reach 10–12 g/l, especially in chloride-rich waters. Sodium is always strongly dominant among the cations of such waters. Brackish calcium–sulfate waters are widespread in the zones of arid steppes, semideserts, and deserts.

The subsequent stage of salt formation is related to the equilibration of groundwater with halite. This is possible only at a salinity of more than 300 g/l, which is rarely observed in the supergene zone. The geochemical type of waters formed there can be referred to as *saline sodium–chloride* (Table 37), which only locally

and sporadically occurs in desert and steppe zones at sites of intense evaporation and, consequently, salinization.

The geochemical diversity of groundwaters is not limited by the distinguished types. For instance, the iron-carbonate type of waters can be mentioned; it occurs in small artesian basins of intermontane and even platform types. Such basins contain fresh waters with high Fe contents, which are controlled by equilibrium with siderite (Fig. 20). Also widespread are wetland waters equilibrated with vivianite, apatite, and siderite (Fig. 25). Many other examples can be found.

The above considerations show that newly formed secondary minerals and the geochemical types of water are strictly connected by thermodynamic relations controlling the behavior of minerals and waters. Only some of the dissolved compounds in the aqueous solution take part in this control. Therefore, it is important to distinguish the elements and compounds that control equilibria in the solution rather than the most abundant components because the former serve as peculiar geochemical barriers preventing a proportional increase in all of the elements of a particular aqueous solution. Another important circumstance is that there is a strict correspondence between the amounts of secondary organomineral compounds and geochemical types of waters: *each type of secondary products corresponds to a certain geochemical type of water, and one cannot exist without the other.*

#### 5.4. Factors Controlling the Formation of Geochemical Types of Water and Weathering

Based on the above consideration, we can address the eternal question of the factors controlling the formation of various geochemical types of water and related types of weathering. It has long been recognized that both show zoning and, consequently, are controlled by climate, i.e., temperature and amount of precipitation. On the other hand, the main ultimate source of chemical elements, both during weathering and during the development of water chemistry, is rocks because most of the chemical elements of organic matter and precipitation also derive from rocks, except for the products of photosynthesis ( $C_{org}$  and  $O_2$ ) and, of course, water. The rocks of any region have different origins, compositions, structures, porosity, water permeability, etc., which influences the character of runoff distribution, its forms and intensity, and the velocity and paths of water movement.

The geologic history of a region is reflected in its geologic structure and the character of the relief. These factors affect not only the type and origin of rocks, but also the distribution of precipitation, the surface temperature, the intensity of runoff and water exchange, and thus the biological productivity of the terrain. Consequently, the geologic structure exerts a significant

influence on many parameters of zoned (climatic) factors.

Thus, there are two large groups of the most important factors, (1) zonal (climatic) and (2) azonal (structural geologic), which are relatively independent and have their own mechanisms of influence on the environment, including the composition of water and secondary products. The interaction of these two groups of factors gives rise to a long causal chain of phenomena and processes of transformation in rock materials (Fig. 32).

The geologically long interaction of climatic and azonal factors is sustained by the input of solar energy and led at the early stage of Earth's evolution to the development of two extremely important phenomena: (1) the water cycle and (2) photosynthesis. While the exceptional role of photosynthesis in the formation of the environment has been long and properly acknowledged by scientists, the water cycle has received less attention because it has been evaluated mostly in terms of the formation of renewable resources of fresh water and its role in the development of the environment is still not fully understood [23].

For our purposes, one of the most important consequences of photosynthesis is the formation of a strictly constrained amount of organic matter in a given area, which depends on the *biological productivity of the terrain*. The most important consequence of the water cycle is the formation of *water exchange of a certain intensity*. Both these parameters (biological productivity and water exchange) are unevenly distributed on Earth under the influence of structural geologic and climatic factors [63, 64, 284, etc.]. It should be emphasized that this distribution is *uneven on Earth but stable* within each climatic zone (landscape) and geologic structure; i.e., these parameters are important constants of the environment.

The established definite values of these parameters are controlled by the combination and relationships of various effects of groups of climatic and structural geologic (including topography) factors. In this respect, the *biological productivity and water exchange are integrated basic indicators* of the development of the environment on the whole, including the hydrosphere and the landscape zone. Let us consider in detail the role of water exchange, which is a less investigated problem.

Water exchange, which is formed under the influence of precipitation, temperature (degree of evaporation), relief (intensity and relations of subsurface flow and surface runoff), and the type of rocks (permeability and pathways and type of water migration), controls the volume and velocity of water movement in a particular geologic structure and, consequently, the time of water-rock interaction. These parameters play an important role in the development of this system. As was shown above (Section 4.1), the time of interaction controls not only the scales of chemical element removal from rocks but also the character of the geochemical environment, the proportions of removed



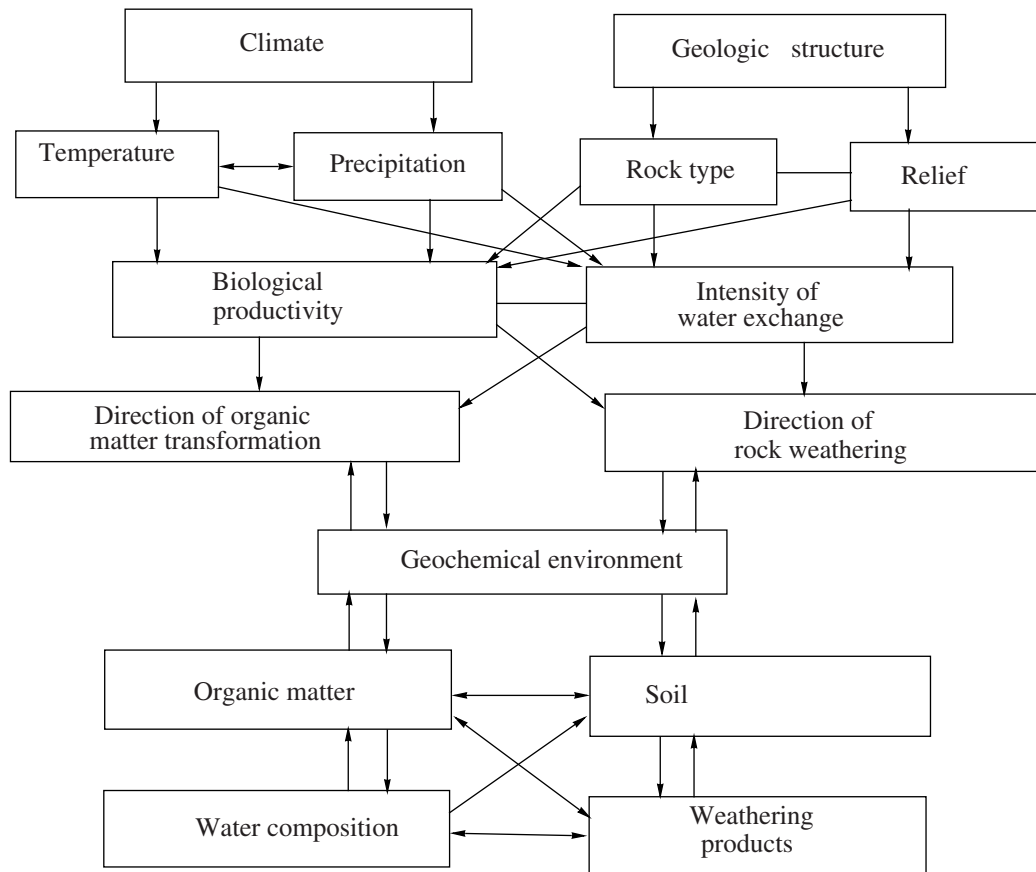


Fig. 32. Relationships of factors controlling the geochemical types of weathering and the composition of groundwaters.

and concentrated elements, and thus the geochemical type of weathering.

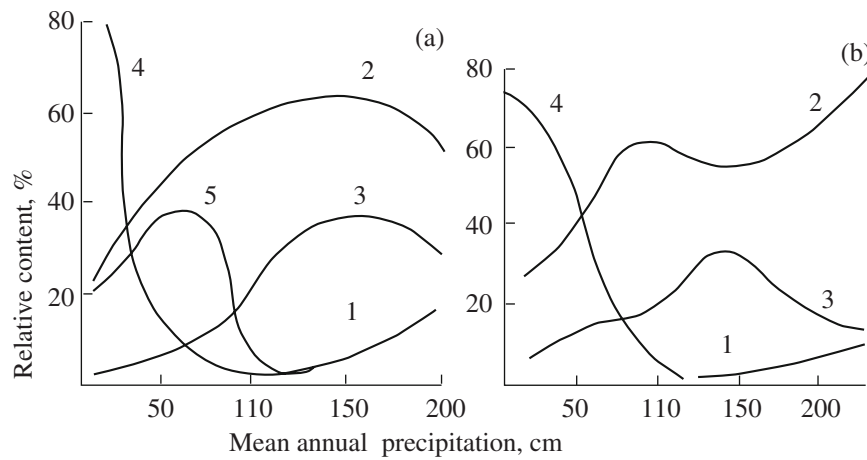
In fact, researchers have long intuitively recognized the considerable role of water exchange in the development of the types of weathering residues and searched for relationships between these two parameters, but they used for this purpose the amount of precipitation rather than the characteristics of water exchange, which is not the same. Nonetheless, some relationships between these parameters were established. For instance, Barshad [285] showed by the example of California (mean annual temperature 9–14°C) that an increase in the amount of precipitation is accompanied by significant changes in the composition of weathering products in soils (Fig. 33). Gibbsite, kaolinite, halloysite, and vermiculite are formed at a precipitation of >800 mm/yr, whereas illite and montmorillonite develop at a precipitation of <800 and even <500 mm/yr.

Conceptually similar results were reported for the products of weathering of basaltic tephra in Hawaii [79]. It is intriguing that the age of the tephra is only 10–17 ka; i.e., the products of the weathering are nearly modern. The amount of precipitation is 250–6350 mm/yr, which pre-determines a considerable diversity in the intensity of

water exchange. With increasing precipitation, the extent of silica removal increases (Fig. 34), which affects the composition of weathering products. Gibbsite and kaolinite were observed in the most extensively washed areas, whereas montmorillonite and calcite are confined to areas with minor precipitation. Similar data were also reported by other authors.

Thus, differences in water exchange within a single climatic zone and within a certain rock type result in the development of different geochemical types of groundwater and types of weathering zones. Under the conditions of very active water exchange and acidic media, a laterite weathering profile is formed, whereas, under the conditions of depressed water exchange and alkaline media, a carbonate–montmorillonite profile is formed, and evaporation gives rise to a salt-bearing profile. Other types of weathering occupy a transitional position.

Water exchange controls the geochemical direction of the development of both water–rock and water–organic matter systems. The biological productivity of a landscape, which was discussed above, forms the mass of organic matter, whereas temperature and water exchange define the subsequent type of its transformation (Section 3.5). It should be added that the geochem-



**Fig. 33.** Dependence of the composition of clays in residual soils on the (a) felsic and (b) mafic rocks of California on the amount of precipitation. (1) Gibbsite, (2) kaolinite and halloysite, (3) vermiculite, (4) montmorillonite, and (5) illite.

ical direction of organic matter transformation and the geochemical type of weathering, which are controlled by water exchange, also define the character of the geochemical environment (Section 3.4). Thus, it becomes evident that water exchange plays a special role in the development of the environment.

The above discussion leads us to the important conclusion that the rocks of a geologic structure and organic matter produced by photosynthesis are systematically transformed under the influence of integral regional and zonal factors (water exchange and biological productivity) and form interrelated secondary products, including geochemical types of water, secondary minerals, organic matter, soils, etc.

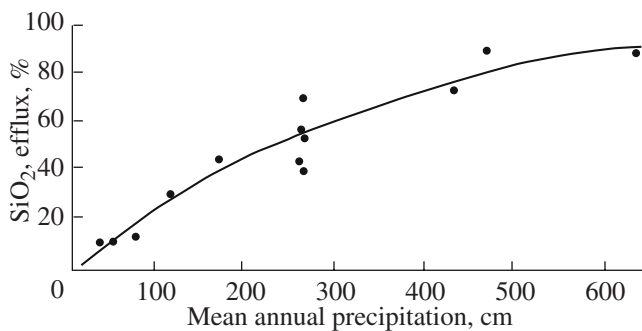
Biological productivity and water exchange, which determine the direction of organic matter transformation and the type of rock weathering, control the character of the geochemical environment *sensu lato*, which eventually determines the compositions of secondary solid and liquid products. Therefore, in Fig. 32, feedbacks reflecting their coupling appear starting from that moment. In this case, secondary products are soils, var-

ious kinds of organic matter, weathering residues, and geochemical types of water. All of them are derived from and simultaneously form the geochemical environment.

We arrive here at an important question. All of the aforementioned objects (water type, soils, minerals, and organic matter) are products of the same geochemical medium. Therefore, they are formed in equilibrium with this medium and, consequently, with each other. If this is the case, fundamental paragenetic relations must exist between them. And they do exist. Let us consider, for instance, the laterite process, which simultaneously produces laterite weathering residues, laterite soils with low contents of organic matter and silica, and acidic groundwaters also poor in silica and organic matter, which is remineralized to a considerable extent; i.e., all these secondary products show similar compositional characteristics.

Another example is the salt-bearing type of weathering. In this case, the waters are relatively rich in salts; the soils are affected by salinization; the weathering products contain much Ca, Mg, Na, and K and often sulfates and even chlorides; and the organic matter and even plants (steppe saltwort) are also rich in these elements [220]. Many other similar examples can be given.

The observations presented here are in conflict with a widely held, but erroneous, opinion that various chemical elements are mainly concentrated in a certain component of the environment (landscape). For instance, it is claimed that, if silicon is actively removed from soils, its content will be low in soils but high in soil waters. As a result, it is often assumed that the laterite process is accompanied by waters with high silica contents because the corresponding products of weathering are depleted in silica. If waters are rich in soda, its content in soils should be low, and vice versa, since wetland waters are rich in organic matter, the rocks are depleted in organic matter, etc.



**Fig. 34.** Fraction of silica efflux from the basaltic tephra of the Hawaiian Islands during their weathering as a function of the amount of precipitation.

However, the opposite is true. If one component of a landscape is enriched in any compound or element, its content must be high in all other components owing to fundamental thermodynamic laws. If groundwater is rich in silica or calcium, it will produce silica-rich calcic clays, which will gradually form weathering products, soils, and even plants and organic matter with similar compositional characteristics. In contrast, if water shows low contents of some elements, the same elements will be depleted in all other environmental components.

Based on the above considerations, the following fundamental law of the formation of supergene products can be formulated: *the nonequilibrium character of the system water–primary rocks–photosynthesis products results in their continuous dissolution and transformation with the development of new secondary products, including a geochemical type of water, concentrating chemical elements in accordance with the physicochemical equilibrium being established between them depending on the type of the geochemical environment.*

Let us consider again Fig. 32, noting that it presents not only the main factors of formation of secondary products, including water, in the supergene zone, but also their interrelations and interdependences. Thus, the problem is not only to determine the factors, but also to reveal their interrelations.

For instance, considering the relations between precipitation, water exchange, and water composition, it becomes obvious that neither water composition nor water exchange affects precipitation, but, in contrast, water exchange is a derivative of precipitation (of course, among other factors), and water composition is a derivative of water exchange. If this is the case, the sequence precipitation → water exchange → water composition can be envisaged, where each subsequent (after the first) factor is a derivative of the previous factor and simultaneously the controlling factor for each subsequent one.

The relationships between climate, soils, and water composition can be considered in a similar fashion. The existence of the sequence climate → soil → water composition, rather than vice versa, is obvious. Similarly, as a derivative of the geologic structure, the relief affects water exchange and, through this transitional step, water composition.

More complex relationships exist between the geochemical environment, type of weathering, character of organic matter transformation, and water composition because the environment is a complex function of the quantitative relations between all landscape components, which show both direct connections and feedbacks.

The above considerations allowed us to arrange the main factors controlling the composition of secondary supergene objects in a systematic sequence. For instance, as can be seen from Fig. 32, the composition

of groundwater is not directly connected with either the amount of precipitation, terrain topography, or rock type, although each of these factors exerts a certain influence on solution geochemistry. However, this influence operates through such parameters as the biological productivity of the terrain, the intensity of water exchange, the character of the geochemical environment, etc. Therefore, any attempt to search for a direct link between the composition of groundwaters and weathering products and the composition of rocks, the character of the relief, or the amount of precipitation is futile and does not help us to understand the essence of the phenomenon.

The recognition of the control relations between the main factors of secondary product formation allows us to better understand the connections between weathering products and groundwater compositions. Consider again the example of silicon with application to the tropical zone. It is commonly believed that laterites are formed under such conditions owing to intense silicon removal from the weathering profile by groundwater. However, this approach confuses the reasons and consequences of the natural phenomenon: the removal of silicon is the consequence of rather than the reason for laterization. Silicon is removed because it is not bound to weathering products. This is controlled by the geochemical environment, which is characterized by very low silica contents in waters, which are insufficient even for equilibration with kaolinite; i.e., silicate minerals cannot be formed and silicon can migrate freely under such conditions. Moreover, the development of laterization requires the maintenance of low silica concentrations in solutions, which is possible only under the conditions of active water exchange. As the intensity of water exchange decreases and the silica content in the solution increases, favorable conditions are created for silica fixation in clay minerals. This leads to a decrease in its removal from the weathering profile (although its concentrations in the solution increase) and the cessation of laterite-type weathering.

All of these considerations lead us to concur with Keller's opinion that it would be more correct and appropriate to refer to a product of the weathering environment [243, p. 155]. This is why it is incorrect to consider laterites as ultimate weathering products: they are ultimate products only under certain environmental conditions. Under other conditions, ultimate products may be kaolinite, montmorillonite, or carbonized weathering zones, and their transformation is possible only in response to changes in geochemical conditions.

Thus, the initial stages of interaction of ultrafresh waters with rocks produce laterites. As the time of this interaction increases, the salinity of waters increases, and, correspondingly, the character of weathering products changes sequentially through kaolinite and montmorillonite (illite) to calcite, gypsum, halite, etc. In such a case, the important question arises of why laterites are not ubiquitous and are formed only under trop-

ical condition (at least in economic concentrations), or, in other words, why the first stage of rock weathering (and often also the second, kaolinite stage) is missing in most landscape zones and the products of later stage weathering develop directly from the soil horizon.

The answer to this question is again connected with water exchange and the law of formation of secondary products formulated above: *each type of water exchange is associated with its own set of secondary mineral phases and geochemical types of water*. Water exchange of a certain intensity imposes strict relations between the amounts of removed and concentrated elements in weathering profiles. With time, secondary products consisting of concentrated elements occupy the whole weathering profile, soils, organic compounds, etc. Atmospheric precipitation passes initially through the soil horizon and the developing weathering zone, where it is equilibrated with the secondary phases. When these waters penetrate into bedrocks, they can form secondary products of the same composition only.

Thus, a concise answer to the above question can be formulated in the following way: *laterite products of weathering and soil formation are not developed in many climatic zones because water exchange in them is not sufficiently active*.

Finally, the reader's attention should be drawn to three important conclusions based on the considerations presented in this section: (1) water exchange plays a very important role in the transformation of mineral and organic matter in the supergene zone; unfortunately, this factor is ignored in the investigations of geoscientists; (2) the water-rock system includes a mechanism of geologic self-regulation, which will be discussed below; and (3) the formation of secondary phases occurs via repeated dissolution and precipitation. The produced secondary minerals are dissolved near the surface by a new portion of water, but they are formed again deeper in the section. These processes are especially active in soil horizons. This implies that a secondary product changes its spatial position with time and remains in essence always young or newly formed.

### 5.5. Formation of the Chemical Composition of Groundwater

The material presented above illustrates the complexity of groundwater chemistry, which is related to the contributions of diverse components from the atmosphere, biosphere, lithosphere, and even hydrosphere (products of water decomposition). The proportions of these constituents of the mineral residue vary considerably depending on the influence of particular factors (Fig. 32). However, if the contribution of precipitation is excluded, the cation composition of water is controlled primarily by the composition and character of transformation of the country rocks. More precisely,

*the cation composition of water is the difference between the compositions of dissolved and newly formed rocks; i.e., it has a lithogenic nature*.

The anion composition of waters from chemogenic and biogenic rocks (carbonates, sulfates, chlorides, phosphates, etc.) is defined by the composition of the host rocks. In aluminosilicate environments, the anion composition of water is independent of the rock type and is a product of water dissociation (hydroxyl group, OH<sup>-</sup>) chemically connected to the ultimate product of organic matter remineralization (CO<sub>2</sub>). Thus, in contrast to cations, the nature of anions is hydrogenous–biogenic rather than lithogenic.

Thus, the composition of water is, in general, heterogeneous and controlled by its interaction with all of the main components of the environment: rocks, organic matter, and gases. On the other hand, the influence of each of these components on groundwater depends not only on various factors, but also on the stages affecting the water under particular geologic and landscape conditions. As to the supergene zone, the formation of water composition begins in the atmosphere and continues in soils and rocks until the water enters the discharge zone and escapes from the rocks. In accordance with this, four stages can be distinguished in the formation cycle of groundwater composition: atmogenic, biogenic, lithogenic, and evaporative and/or cryogenic [10].

#### 5.5.1. Atmogenic stage

Despite a considerable diversity in chemical composition, rain and snow waters uncontaminated by industrial wastes usually show low salinity, no higher than 50 mg/l in the regions of humid climate and often even 20 mg/l (Table 38). The only exceptions are some seashore regions, where the salinity of rainwater may be higher than 100 mg/l in particular seasons owing to salt entrainment from the surface of the ocean and seas. Their total salinity increases especially significantly in the regions with an arid climate, where it may be as high as a few grams per liter during some seasons (in limited areas). Also important is the continuously increasing role of anthropogenic factors, which strongly modify the composition of precipitation. The emission of gases into the atmosphere, contamination of the atmosphere by dust, and pollution by various wastes produce various acids (H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub>) and, occasionally, alkalis and lead to water enrichment in various metals, organic compounds, and salts.

The chemical elements of precipitation are in part supplied from the ocean. The most important of them are sodium, chlorine, iodine, and bromine. For instance, Duce et al. [287] reported that precipitation on the island of Hawaii contained, on average, 7 mg/l Cl, 25 µg/l Br, and 10 µg/l I in the seashore zone and 0.3 mg/l Cl, 4.0 µg/l Br, and 2.0 µg/l I at an altitude of



**Table 38.** Average composition of precipitation for selected regions around the world, mg/l\*

Component	Regions of the former Soviet Union					Northwestern Europe	South-eastern Australia	United States	Japan	Northern Sweden	Belgium	California	Venezuela	Tasmania	Amsterdam Islands	Bermuda Islands
	with excessive moistening	with normal moistening	with low moistening	dry	weighted mean											
		Europe	Asia													
pH	5.8	5.9	6.0	6.3	7.1	5.47	3.0–7.2	4.1–5.8	–	–	4.4	4.4	4.8	6.0	4.7	4.7
Cl <sup>-</sup>	4.1	1.8	1.5	3.7	38.9	3.47	4.43	0.1–22.6	1.1	0.4	2.0	1.0	0.2	47.9	14.4	9.4
SO <sub>4</sub> <sup>2-</sup>	5.0	5.7	4.4	13.6	35.8	2.19	tr	0.03–5.3	4.5	2.0	6.0	1.9	0.2	7.6	2.5	2.3
HCO <sub>3</sub> <sup>-</sup>	5.0	5.7	5.6	16.0	53.0	–	–	–	–	1.3	–	–	–	–	–	–
NO <sub>3</sub> <sup>-</sup>	0.4	0.8	0.7	0.7	0.7	0.27	–	0.7–4.7	–	0.3	2.2	1.9	0.2	0.3	0.17	0.5
Ca <sup>2+</sup>	0.8	2.0	2.0	6.0	24.2	1.42	1.2	0.2–6.5	0.94	0.6	1.3	0.13	0.01	1.7	0.31	0.29
Mg <sup>2+</sup>	0.6	0.5	0.2	2.0	3.2	0.39	0.5	–	0.36	0.12	0.36	0.04	0.01	2.9	0.87	0.59
Na <sup>+</sup>	3.0	2.4	1.6	4.1	21.2**	2.05	2.46	0.1–22.3	1.1	0.30	0.97	0.55	0.06	29.0	7.68	5.08
K <sup>+</sup>	0.5	0.7	0.7	0.8	–	0.35	0.37	0.07–1.1	0.26	0.19	0.23	0.08	0.04	1.26	0.28	0.25
NH <sub>4</sub> <sup>+</sup>	0.5	0.6	0.8	0.8	0.6	0.41	–	0.05–2.2	–	0.13	0.55	0.46	0.37	0.04	0.11	0.1
Total	19.9	20.2	17.4	47.7	177.6	10.6	8.9	–	8.3	5.3	13.7	6.1	1.1	91.5	26.4	18.6

Notes: \* Data for the regions of the former Soviet Union, northwestern Europe, southeastern Australia, the United States, and Japan are after [10], and other data are after [286].

\*\* Na + K.

2.0–2.5 km. In the near-shore regions of Western Europe, the precipitation may contain up to 200–300 mg/l Cl.

Away from the seashore in continental areas, terrigenous materials play an increasing role in precipitation. They are introduced into the atmosphere as a result of the development and subsequent dissolution of dust particles of soils and rocks, as well as soluble salts under the conditions of arid climate. In the latter case, the precipitation has a sulfate or even chloride composition. In general, the salts dissolved in precipitation even under the conditions of humid climate have mostly a continental rather than marine origin related to the dissolution of eolian dust and products of anthropogenic activity [159, 286, 288–291].

It is important to emphasize that the contents of trace components in precipitation vary considerably (Table 39). This is attributed to both the influence of natural factors (dust content in the atmosphere, precipitation regime, its composition, pH value, etc.) and the significant role of anthropogenic factors. In this connection, of special interest are the results of the analysis of the ice cover of Greenland, which showed that the concentrations of all major and trace components, except for Fe and Al, in ancient ice are at least an order of magnitude lower.

In addition to salts, precipitation contains dissolved carbon dioxide, inert gases, nitrogen, and oxygen (Table 40). Owing to the different solubilities of individual gases, the proportions of gas components in the solution are different from those of air (Table 41). Part of gases chemically interacts to produce new compounds. For instance, CO<sub>2</sub> reacts with H<sub>2</sub>O to form carbonic acid, whose dissociation results in a pH decrease and enhancement of the aggressive properties of falling precipitation. Air gases penetrate with water into rocks and control to a large extent the composition of the subsurface hydrosphere. Chemically active gases take part in various reactions and produce diverse secondary compounds, whereas inert gases may penetrate to considerable depths without significant changes in their state and can be used, therefore, as indicators of groundwater genesis and pathways.

It should be pointed out that atmospheric precipitation is saturated in the hydroxides of the strongest hydrolyzate elements (aluminum, titanium, vanadium, iron, etc.) despite its low salinity, relatively acidic character, and lack of a direct connection with rocks. Therefore, most of these elements can occur in such waters only as complex compounds or fine mechanical and aerosol admixtures. For example, precipitation contains from 13 to 110 µg/l Al (Table 39), whereas the equilibrium content of this element in weakly acidic and neutral solutions coexisting with Al hydroxide is only 1.0–3.0 µg/l (the sum of all inorganic Al species) (Figs. 30, 31).

Consequently, even during the stage of the atmospheric evolution of natural waters, many metals can be accumulated in them above the solubility levels of the respective hydroxides. In contrast, the silica content of

precipitation is low and very rarely exceeds 0.5 mg/l, which precludes the formation of clay minerals under such conditions.

### 5.5.2. Biogenic stage

In most cases, atmospheric precipitation falling on the surface first encounters plants and soils, which are of utmost importance for the modification of water composition. For instance, rainwater collected under the crowns of coniferous trees in Sweden contained 3 times more calcium and sodium and 17 times more potassium than rainwater collected in open areas [297]. Similar data were reported by other authors (Table 42); in particular, Kiryukhin et al. [212] drew the following conclusions: (1) the total salinity of precipitation usually increases somewhat when it penetrates the forest canopy, especially at the beginning of rain; (2) the salinity increases mainly at the expense of calcium and bicarbonate ions; (3) the appearance of (or enrichment in) ammonium ion (up to 0.1 mg-eq) often occurs owing to the decomposition of organic compounds; (4) vegetation promotes an increase in precipitation acidity to pH 5.5–5.9; (5) the oxygen demand of rainwater increases significantly from 1–4 to 10–20 mg/l O<sub>2</sub>; (6) a silica content of a few milligrams per liter is usually observed; and (7) coniferous trees exert the maximum influence on the chemical composition of rainwater.

Consequently, when precipitation passes through tree crowns, it becomes enriched in biogenic elements concentrated in plants. However, the most significant effect is that of decomposed organic matter concentrated in soil horizons.

Oxygen-rich precipitation first oxidizes organic matter and becomes additionally enriched in carbon dioxide, which leads to a strong increase in its partial pressure. This effect is strengthened by the respiration function of root systems. Simultaneously, organic matter is partly dissolved in groundwater and enriches it in various organic acids (humic, fulvic, formic, acetic, and others) and products of their dissociation.

Organic compounds migrating with groundwater into deeper aquifers are gradually oxidized and serve as an additional source of carbon dioxide, nitrogen oxides, and other oxidation products. In addition, the organic matter supplies biogenic elements (C, N, K, P, Ca, S, and Si, as well as part of Al, Fe, and Mn) to the solution. Silica plays a special role in this process because its content in the solution controls the possibility of formation of biogenic clays. Even within the humic soil horizon, the concentrations of silica become sufficiently high for the thermodynamic stability of particular clay minerals. The evaporative concentration of elements plays an important role in this process in forest steppe, steppe, and desert soils.

The composition of soil water differs among climate zones. For instance, waters with a very high acidity and organic matter content and a relatively low total salinity

**Table 39.** Trace component composition of atmospheric precipitation, µg/l

Component	Mongolia [292]	Crimea [293]	Japan [294]	Italy [290]	Greenland ice [295]
Na	–	–	1100	161	12.3 ± 2.2
Si	1244	–	830	752	6.5 ± 8
Fe	30.3	9.48	230	14.0	6.9 ± 2.6
Al	89.3	13.1	110	13.0	10.7 ± 3.4
Pb	1.83	13.8	–	1.7	0.045 ± 0.02
Sr	91.8	–	11.0	9.9	–
Mn	7.92	7.64	–	4.1	0.139 ± 0.045
Zn	59.0	–	4.2	200	0.077 ± 0.042
Cu	6.45	1.82	0.80	2.0	–
Ni	2.64	0.99	–	2.3	–
V	0.76	0.63	1.40	0.8	0.016 ± 0.006
J	–	–	1.80	–	–
P	–	25.3	14.0	480	–
Mo	1.3	–	0.06	–	–
Hg	–	–	–	–	0.03 ± 0.07
Cd	0.91	–	–	0.11	0.0008 ± 0.003
Ba	66.3	–	–	7.4	–
Co	0.35	–	–	0.1	–

**Table 40.** Partial pressure of gases in the atmosphere, Pa [296]

Gas	Pressure	Gas	Pressure	Gas	Pressure
N <sub>2</sub>	78.1 × 10 <sup>3</sup>	He	5.2 × 10 <sup>-1</sup>	H <sub>2</sub>	5 × 10 <sup>-2</sup>
O <sub>2</sub>	20.9 × 10 <sup>3</sup>	CH <sub>4</sub>	1.5 × 10 <sup>-1</sup>	O <sub>3</sub>	(0.1–1.0) × 10 <sup>-2</sup>
Ar	0.93 × 10 <sup>3</sup>	Kr	1.1 × 10 <sup>-1</sup>	Xe	8.7 × 10 <sup>-3</sup>
H <sub>2</sub> O	(0.1–2.8) × 10 <sup>3</sup>	CO	(0.06–1.0) × 10 <sup>-1</sup>	NO <sub>2</sub>	(0.05–2.0) × 10 <sup>-3</sup>
CO <sub>2</sub>	0.03 × 10 <sup>3</sup>	SO <sub>2</sub>	1 × 10 <sup>-1</sup>	Rn	6 × 10 <sup>-15</sup>
Ne	1.8 × 10 <sup>0</sup>	N <sub>2</sub> O	5 × 10 <sup>-1</sup>		

are formed in podzolic soils. The maximum acidity is observed in forest litter. In such waters, the organogenic component of all elements is much more abundant than the mineral component, which results in the circumstance that acids are not compensated by bases and, correspondingly, an acid medium is formed. Also noteworthy are the high contents of iron, aluminum, and potassium in the waters, which supports the considerable role of decomposing organic matter in the enrichment of water in chemical elements. Such are the formation conditions of the acidic siliceous–organic geochemical type of water (Table 37).

When acidic solutions percolate downward, they interact with the mineral constituents of soils and become gradually more alkaline. For the same reason, the concentration of silica in them increases. In contrast, the contents of some other elements decrease. For instance, according to the summary data of Ponomareva and Sotnikova [298], horizon A of sodded strongly

**Table 41.** Composition of air dissolved in precipitation, % [288]

Gas	Precipitation temperature, °C					Atmosphere composition, %
	0	5	10	15	20	
CO <sub>2</sub>	2.92	2.68	2.46	2.20	2.14	0.03
O <sub>2</sub>	33.88	33.97	34.05	34.12	34.17	21.00
N <sub>2</sub>	63.20	63.35	63.62	63.62	63.62	78.97

podzolic loamy soil retains 50–80% (of the amount migrating from the forest litter) of P, K, Ca, C, N, S, and Mg and 10–30% of Al, Fe, and Na. This is related to the fact that part of elements is absorbed by the roots of living plants and participates in a new biological cycle, whereas another part produces organomineral soil-forming complexes.

**Table 42.** Average composition of precipitation for the Miaochang Range collected at four sites (24 samples), mg/l

Site no.	Site character	pH	<i>M</i> , mg/l	HCO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	NH <sub>4</sub> <sup>-</sup>
1	Open area	6.0	28.3	12.2	7.09	–	1.00	–	8.05	–
2	Under a fir tree	5.7	55.5	30.5	10.6	–	12.0	–	2.30	0.10
3	Under a birch tree	5.9	27.2	12.2	7.09	–	5.61	–	2.30	0.02
4	Under blueberry shrubs	5.9	85.6	18.3	7.09	–	5.61	–	4.60	0.02

Very different conditions are observed in the lysimetric waters of gray forest soils and soils of soda salinization, where alkaline waters with a relatively high salinity are formed. In accordance with the bioclimatic zoning, the waters of gray forest soils are transitional between the low-salinity acidic waters of podzolic soils and the brackish alkaline waters of the soils of soda salinization.

Even more specific conditions are observed in actively washed tropical regions, where laterite soils occur. Their depletion in silica, organic matter, and many other elements, accompanied by high  $P_{CO_2}$ , results in the formation of ultrafresh acidic and weakly acidic geochemical types of waters of peculiar compositions.

The composition of soil waters from various climate zones of the world is controlled not only by the processes of organic matter humification, remineralization, and dissolution, but also by active rock weathering. As a result, the soil waters of each climate zone are enriched in a certain set of chemical elements, including two associations, biogenic and mineral. Since silicon and aluminum play a considerable role in plant ash [64], their amounts in lysimetric waters are also high.

It is important to emphasize that not all of the elements entering the soil solution are removed by the subsurface flow and surface runoff because their major portion participates in a new biological cycle (Table 32). This is especially characteristic of biogenic elements, such as potassium, nitrogen, phosphorus, and others (Section 4.1).

Thus, the role of pedogenic organic matter is the enrichment of groundwaters, primarily in carbon dioxide, various organic acids, and biogenic elements and occasionally in methane. As a result, the gas composition of water changes dramatically in soil horizons ( $O_2$  content decreases, whereas  $CO_2$  and, sometimes,  $CH_4$  increase at an almost constant  $N_2$  concentration), accompanied by a change in the character of the geochemical environment (pH and Eh), some (considerable under the conditions of arid climate) increase in solution salinity, and a change in its composition. The high contents of organic acids (especially humic and fulvic acids) strongly enhance the aggressive properties of solutions with respect to aluminosilicates, which are intensely decomposed under such conditions. This is

additionally assisted by strong microbiological activity, which is characteristic of soil waters.

The differences in the character of geochemical media in soils from various climate zones result in different types of aluminosilicate weathering. The silica content of soil waters from humid temperate zones is sufficiently high even within the humic horizon for the thermodynamic stabilization of clay minerals. Therefore, they are formed rather than dissolved under such conditions (Fig. 24), which, of course, affects the composition of waters. Another situation is characteristic of tropical regions, where laterite soils occur. The percolating waters contain small amounts of silica, and thermodynamic equilibria are shifted toward the stability of iron and aluminum hydroxides, which form there instead of clay minerals.

The diversity of soils throughout the world leads to the diversity of their influence on groundwater composition. In some cases, groundwaters penetrating through the soil horizon almost do not acquire chemical elements, except for  $CO_2$  (humid savanna terrains); in other cases, they are enriched in silicon, aluminum, and organic acids (forest terrains); and in still other cases, they may dissolve considerable amounts of salts (steppe and forest steppe terrains). All these factors result in variable contents of individual compounds in waters and a different character of water interaction with underlying rocks.

Consequently, the evolution of water composition shows fundamentally new changes within the soil horizon, which are not typical of the stage of atmospheric transformations. Concentration limits (geochemical barriers) are established in soil waters not only for hydrolysate elements but also for silicon and, in part, potassium, rubidium, and a number of other elements. Therefore, we proposed the term *biogenic metamorphism* to refer to the soil stage of the evolution of groundwater composition.

Thus, living matter plays an extremely important role: it converts elements to mobile species, concentrates them on the Earth's surface, and thus makes them accessible for precipitation. In this connection, it is appropriate to recall a brilliant study by Polynov, who wrote: "I believe that this [the similarity between the compositions of dry residues of waters and plant ash—*S.Sh.*] provides compelling evidence that the composition of natural river waters is controlled not by simple abiotic reactions of water influence on the minerals of



igneous rocks, i.e., hydrolysis and dissolution, as alleged in textbooks, but by a more complex, although faster, process of element extraction from minerals by organisms and dissolution in water of the ash portion of organisms during their remineralization" [299, p. 61].

### 5.5.3. Lithogenic stage

After passing through the soil horizon, groundwater interacts with the underlying rock. Therefore, the subsequent evolution of its composition is controlled by the type of host rock and the character of water exchange. Since waters are usually already saturated in clay minerals, the latter do not serve as any significant sources of elements.

Carbonate rocks are not in equilibrium with groundwaters under the conditions of humid climate (Fig. 19), and they are dissolved to form calcium and calcium–magnesium bicarbonate waters. The lower the intensity of water exchange and the greater the residence time of water in rocks, the higher its salinity, up to the complete saturation of water in Ca carbonates. The soil waters of forest steppe, steppe, and desert terrains are already saturated in calcite and, therefore, with rare exceptions, cannot dissolve this mineral.

If sulfates and chloride salts occur in the rock, they are rapidly dissolved and form sulfate or chloride waters. However, since the solubility of gypsum is no higher than 2.5–2.8 g/l and that of halite is up to 300 g/l, the maximum salinity of groundwaters is correspondingly limited by these values. If there are other soluble salts, their influence on water composition is also controlled by the degree of their dissolution, intensity of water exchange, and amount of salts in the host rocks.

The chemical evolution of groundwater in aluminosilicate rocks is much more complex because the character of their dissolution depends on the initial composition and pH of solution entering from the soil horizon (Chapter 3). If precipitation passing through the soil horizon remains rather acidic, ultrafresh, and silica-poor (<5 mg/l), the acidic iron–aluminum geochemical type of water is formed (Table 37). In such a case, all mobile cations, almost all silica, and all of the trace elements that are not fixed by the oxides of trivalent elements migrate into the solution; i.e., a major portion of the rock (more than 50%) is transported into the solution. The cation composition of water is strictly controlled by the composition of the initial aluminosilicates.

Owing to intense water exchange, the total dissolved solids of such waters remain rather low (<200 mg/l), and the low contents of cations at high CO<sub>2</sub> partial pressure result in their weakly acidic or acidic character. The extensive extraction of silica from the rocks leads to its high concentrations in the solution. Because of this, these waters are siliceous bicarbonate in composition and enriched in silica relative to other cations. Such waters occur mainly in tropical regions with excessive moisten-

ing and, occasionally, in other climate zones. Their formation requires very high water exchange, short migration paths from the source to discharge regions, and weak development or silica-poor compositions of soils.

When water exchange decreases to such a degree that the groundwater silica content rises to >5 mg/l, kaolinite appears as a stable secondary product instead of aluminum hydroxides. This mineral binds both aluminum and silicon. In such a case, mobile cations continue to accumulate in the solution, and HCO<sub>3</sub><sup>-</sup> content and pH value increase correspondingly (Fig. 26), which leads to the formation of the aluminum–silicon geochemical type of water.

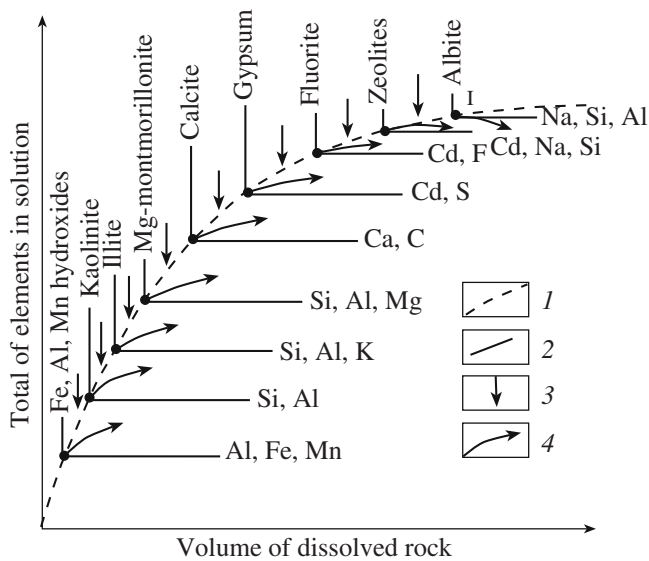
Waters equilibrated with kaolinite are characterized by somewhat higher salinities of 0.1–0.3 g/l, slightly acidic to neutral pH values (6.0–7.0), and bicarbonate compositions. Since there is no barrier for the accumulation of major cations in the solution in this case, the cation composition of waters is completely controlled by the composition of the host rocks. Such waters are widespread under the conditions of both tropical and temperate climate at sites of sufficiently high water exchange within forest terrains.

All other things being equal, tropical environments are more favorable for the formation of this water type because the waters of this zone are more acidic at a certain salinity value (Fig. 26) than waters from the temperate zone. This leads to a higher stability of kaolinite relative to other clay minerals under tropical climate conditions. At higher pH values and the same silica content, illite becomes more stable than kaolinite in the temperate zone. In addition to silicon and aluminum, illite fixes potassium and sorbs elements in different proportions compared with kaolinite. All these features influence the composition of formed water.

If the interaction of water with aluminosilicates continues, the contents of mobile elements and, to some extent, silica and solution pH increase, which results in the saturation of solution in both kaolinite and montmorillonite. In addition to silicon and aluminum, the latter binds part of mobile cations, which leads to the development of the siliceous–sodium or calcium geochemical type of groundwater. The proportion of concentrated and dispersed elements changes dramatically: up to 80% of the total volume of dissolved rock is transformed to the solid phase, and only 20% is retained in the solution.

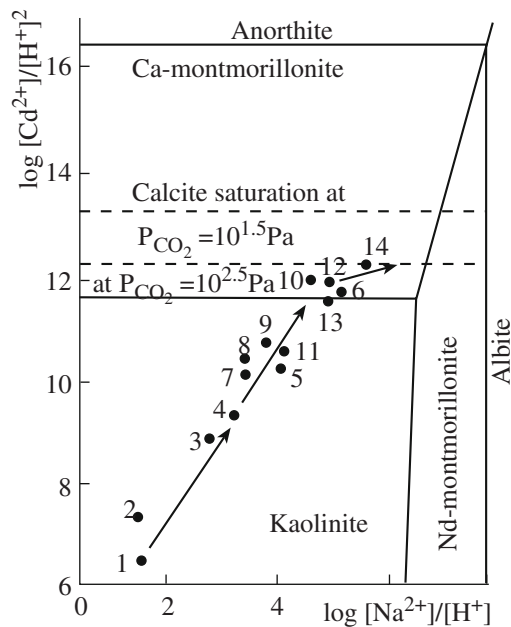
The dissolution of aluminosilicates with the formation of montmorillonite is accompanied by a pH increase, which lowers carbonate solubility. Owing to this, at pH > 7.4 and a total salinity of >0.6 g/l, equilibrium with calcite is reached and the alkaline calcium–carbonate geochemical type of water is formed. Starting from this moment, the composition of solution is controlled by both clays and carbonates.

The above considerations concerning the main steps in the formation of water composition at the lithogenic



**Fig. 35.** Generalized diagram showing the relations of dispersed and accumulated elements during the evolution of the water-rock system. A–I, points corresponding to the beginning of formation of a new secondary phase. (1) Curve of accumulation of dispersed elements, (2) elements concentrated by secondary phases, (3) zones of possible water input to the contact with rock, and (4) sites of possible cessation of water-rock interaction.

stage are summarized in Fig. 35, which illustrates the relations of elements accumulating in the solution in association with the formed secondary minerals. It is important that the formation of secondary phases depends on the intensity of water exchange. If water



**Fig. 36.** System HCl–H<sub>2</sub>O–Al<sub>2</sub>O<sub>3</sub>–Na<sub>2</sub>O–CaO–CO<sub>2</sub>–SiO<sub>2</sub> at 25°C and  $\log[\text{H}_4\text{SiO}_4] = -3.5$  and data on the composition of groundwaters from various landscape zones. The arrow indicates the direction of water composition evolution. Symbols are the same as in Fig. 21.

occurs in the rock for a short time, which is determined by the intensity of water exchange, secondary products of the early stages of system evolution will be formed, i.e., the minerals of phases A, B, and C corresponding to the weathering products of early stages. Later stages do not develop under such conditions because water merely escapes from the rock.

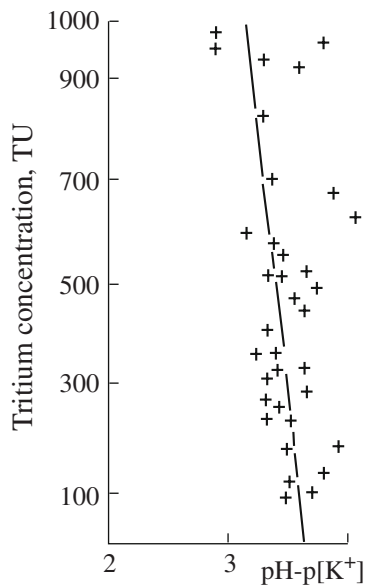
As the time of water–rock interaction increases, i.e., under the conditions of less intense water exchange, there appears a theoretical possibility of the formation of later phases (E–H in Fig. 35). The above considerations lead us to the important conclusion that the limiting possible formation of secondary phases is controlled by the time of water–rock interaction. *An increase in the duration of this interaction provides conditions for the development of later stages of secondary mineral formation.*

It is also important that, under real geologic conditions, rocks do not interact with pure water even at the first stage, but only with aqueous solutions containing varying amounts of chemical elements. Depending on the solution composition, the first produced phase may not necessarily be phase A or B even at the initial stage of interaction. In principle, any secondary phase can be formed. Correspondingly, the development of a particular water–rock system begins in most cases not from the first stage or point A, but from any point on the A–I curve; therefore, the products of the initial stages of water–rock interaction are usually missing.

Hence, under real geologic conditions, there are always hydrogeological and geochemical constraints on the initial and final stages of the evolution of the water–rock system, which results in the formation of secondary products with strictly defined compositions: the products of initial stages do not form because interaction begins not from pure water but from an aqueous solution of a certain composition, and *the products of final stages are missing because water escapes from the rock before their possible formation.* This property of the water–rock system determines its ore-forming activity [300].

The general direction of the evolution of groundwater composition depending on the intensity of water exchange is clearly seen in Figs. 18 and 36. During the initial stages, the calcium content of solution increases faster than that of sodium. Only after the attainment of water–carbonate equilibrium does the character of element accumulation in solution change and the role of sodium increase dramatically. The existence of a carbonate barrier along the path of the direct metamorphism of water is also manifested under the conditions of evaporative concentration. Because of this, there are no calcium varieties among the waters of this type.

The salinity of groundwater increases with increasing time of interaction with rocks both in the latitudinal direction and with depth. In this context, interesting data were obtained in Sweden during the construction of the Kappala Tunnel (Fig. 37). The tritium content of



**Fig. 37.** Correlation between the contents of tritium and potassium and the pH of groundwaters from the Käppala Tunnel.

groundwaters decreases with increasing depth, which indicates an increase in their age and, consequently, the time of water–rock interaction. This is accompanied by an increase in groundwater alkalinity and contents of mobile cations, including potassium [178].

Consequently, the increase in water salinity both in the latitudinal direction and with increasing depth is related to the same factor, the time of water–rock interaction. The produced secondary minerals form peculiar accumulation halos (Table 43).

The widest accumulation halos are characteristic of low-mobility oxides and products of their interaction, i.e., clays. Considering these problems, Kovda noted that “these compounds, forming owing to weathering, soil formation, and metabolic activity of organisms, show relatively low solubility and almost always migrate in natural waters as saturated solutions, hydrosols, or fine suspensions. Therefore, they readily precipitate at or near the sites of their formation. On the other hand, migrating as saturated solutions, they par-

ticipate to a small, but perceptible, extent in accumulation processes in all of the natural zones [italics S.Sh.] where at least partial seasonal evaporation of natural waters occurs” [219, p. 175]. It should be added that the same occurs also owing to water–rock interaction in those areas where evaporation is absent.

*Formation of soda waters.* Owing to their unique composition, soda waters are still a matter of debate. Let us therefore consider this problem in more detail.

The questions of the formation of soda waters are closely related to the general problem of soda formation in nature. The main theoretical aspects of soda formation were considered in [219, 220, 301–306] and many other publications.

With application to groundwaters, the most popular geological hypothesis implies soda formation due to weathering of massive crystalline and sedimentary rocks (F.F. Clark, M.I. Kuchin, I.P. Gerasimov, E.N. Ivanova, Yu.R. Nikol’skaya, N.M. Strakhov, E.V. Posokhov, N.I. Bazilevich, K.F. Filatov, S.L. Shvartsev, etc.). According to this hypothesis, the bases liberated during aluminosilicate weathering are bound by  $\text{CO}_2$ , forming bicarbonates. The appearance of sodium ions together with  $\text{HCO}_3^-$  is related to the weathering of feldspars, polymictic sandstones, arkosic sands, intermediate and silicic igneous rocks, and other similar lithologies. The processes of weathering are accelerated by the presence of  $\text{CO}_2$  and organic matter in water, the influence of vegetation, an increase in water temperature, a decrease in pH, etc.

In addition to  $\text{Na}^+$ , the weathering of aluminosilicates releases  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and in part  $\text{K}^+$  into solution. It is important, therefore, to determine in which cases Na bicarbonate is selectively concentrated in the solution relative to other ions and why soda waters are confined mainly to steppe and forest steppe terrains and are not ubiquitous in the zones of aluminosilicate weathering.

Many researchers have sought to resolve these questions by invoking specific features of climate, which controls the temperature differentiation of salts, different mobility of chemical elements, geochemical work of living matter, sorption capacity of weathering products, etc. For instance, Bazilevich summarized data on the soils of West Siberia affected by soda salinization

**Table 43.** Accumulation halos of the products of weathering and soil formation in continental areas [219]

Halo	Compounds	Accumulation areas
Very wide	$\text{R}_2\text{O}_3$ , $\text{SiO}_2$ , clays	Eluvium, diluvium, proluvium, floodplain and delta alluvium, final basins
Moderately wide	$\text{CaMg}(\text{CO}_3)_2$ , $\text{CaCO}_3$ , $\text{CaSO}_4$	Diluvium, proluvium, floodplain and delta alluvium, lowlands, final basins
Narrow	$\text{MgSO}_4$ , $\text{Na}_2\text{SO}_4$ , $\text{NaCl}$ , $\text{Na}_2\text{CO}_3$	Floodplain and delta alluvium, lowlands, final basins
Very narrow	$\text{NaNO}_3$ , $\text{KNO}_3$ , $\text{CaCl}_2$ , $\text{MgCl}_2$	Central, driest parts of lowlands and deserts



and concluded that “the necessary for the formation of soda accumulations separation of Na bicarbonates from Ca and Mg salts in solutions is ensured by sorption phenomena owing to the higher energy of Ca and Mg adsorption compared with Na, incorporation of Mg and K in the structures of synthetic secondary clay minerals, and more extensive, compared with Na, entrainment of Ca, Mg, and K into biological cycles” [220, p. 36]. Thus, the composition of initial rocks is of little significance for soda formation.

Such an approach to this phenomenon was opposed by Posokhov, who believed that calcium bicarbonate waters are most often formed within igneous rocks and concluded that a favorable environment for the formation of sodium bicarbonate waters is “created only in massifs of peralkaline granite enriched in sodic feldspars” [302, p. 10] and “in sandstones, sands, and conglomerates produced by the decomposition of igneous rocks of the corresponding mineral composition” [302, p. 10]; i.e., he considered the type of rocks as the main factor of soda formation.

Proceeding from the concept developed in this study, it is evident that the type of rock is irrelevant because soda formation is a zonal phenomenon and occurs only under certain water exchange conditions. On the other hand, the reason cannot be the higher sorption of Ca and Mg by clays relative to Na or the more active entrainment of the former into biological cycles. Finally, the main factor is not aluminosilicate weathering, but, as was shown by us previously [6, 29], *the stage of their weathering involving groundwater saturation in calcite, which is accompanied by soda formation*. A spectacular example is provided by the Kuznetsk Basin, where, as was shown above, calcium–sodium bicarbonate waters are replaced at a certain stage by sodium–calcium waters; i.e., initial soda formation is observed and increases with depth.

The above considerations lead us to the important conclusion that soda formation, as a consequence of extensive and prolonged water–rock interaction, cannot occur under the conditions of active water exchange simply because water escapes from the rocks and reaches discharge areas before the onset of the soda accumulation stage. Therefore, soda is actively formed either at the initial stages of continental salinization (forest steppe terrains and adjacent areas), during the prolonged occurrence of waters in rocks below the local basis of erosion (artesian basins and their slopes), or during the descent of infiltration waters along the zones of faults into the deep parts of folded mountain structures.

Thus, the formation of soda waters is a natural consequence of groundwater interaction with aluminosilicate rocks. It is confined to a certain stage of water evolution characterized by the formation of carbonates and montmorillonite clays. In other words, soda formation does not occur during all stages of aluminosilicate weathering but requires favorable conditions, which are

created by water exchange and geochemical environments.

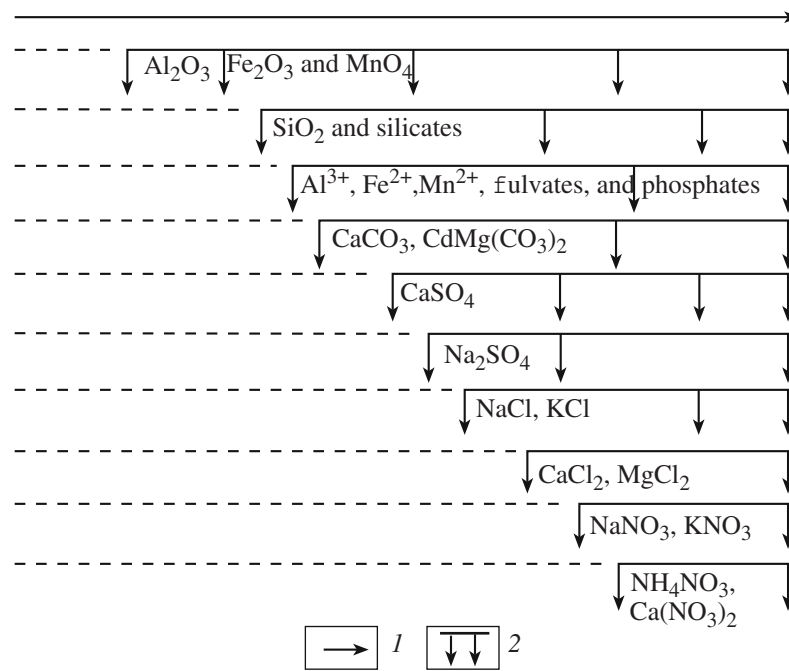
In our firm belief, the geological hypothesis of soda water formation becomes a theory if the following constraint is introduced: *not just any weathering of rocks leads to soda formation, but only weathering that is accompanied by groundwater saturation in calcite*. In this connection, it should be pointed out that, among waters with  $\text{HCO}_3^- > \text{Ca} + \text{Mg}$ , only calcite-saturated waters can be regarded as soda waters. Otherwise, ultrafresh acidic waters from many regions, especially from the tropics, would be classified as soda waters, which is, in principle, incorrect.

Despite the obvious advantages of this geological theory, other approaches are still being developed. For instance, there are many advocates of *the biogenic hypothesis* of soda water formation. According to this hypothesis, *soda is formed either during the remineralization of plant remains* (V.R. Vil'yams, B.L. Isachenko, K. Ya. Kozhevnikov, etc.) or *owing to the activity of microorganisms*, which promote sulfate reduction with the formation of  $\text{H}_2\text{S}$  and occasionally nitrates, as well as organic matter oxidation (I.N. Antipov-Karataev, B.L. Isachenko, V.V. Epshtein, A.N. Buneev, I. Tsabolis, F. Mate, V.A. Kovda, N.I. Bazilevich, E.V. Posokhov, M.S. Gurevich, and many others). It was also hypothesized that soda could be formed *via the Gedroits reaction*, i.e., the replacement in a colloid complex of exchangeable sodium by water-dissolved calcium (K.K. Gedroits, V.A. Kovda, I.P. Gerasimov, M.G. Valyashko, A.F. Gorbov, V.V. Epshtein, V.A. Sulin, G.N. Kamenskii, A.N. Buneev, V.M. Levchenko, I.P. Panteleev, E.V. Pinneker, N.I. Bazilevich, and V.S. Samarina). We demonstrated previously [29] that these hypotheses are not feasible.

#### 5.5.4. Evaporative stage

The problem of groundwater formation during evaporative concentration has been thoroughly investigated by N.S. Kurnakov, G.N. Kamenskii, O.K. Lange, V.A. Kovda, and M.G. Valyashko. These and many other authors have shown that the processes of evaporative concentration are accompanied by the sequential precipitation of Al, Fe, and Mn hydroxides; clay minerals of various compositions; sulfates and phosphates; Ca and Mg carbonates; Ca sulfates; Na sulfates; Na and K chlorides; Ca and Mg chlorides; and, finally, nitrates (Fig. 38). Correspondingly, the total salinity of groundwater increases and its composition changes from siliceous–bicarbonate with various cations, through sodium–calcium and sodium bicarbonate, through sodium sulfate, to sodium and sodium–calcium chloride with all transitional varieties. Two important geochemical types of waters are formed under such conditions: brackish calcium sulfate and saline sodium chloride (Table 37).





**Fig. 38.** Scheme of evaporative differentiation of the products of weathering and soil formation [219]. (1) Direction of runoff and increasing evaporation and (2) saturation of solution and precipitation of components.

Under natural conditions, evaporative concentration occurs during continuous movement of groundwater and its interaction with the country rocks. This results in a rather significant variability of the composition of waters of continental salinization and their equilibrium with secondary products. According to the data of Al-Droubi [307] for the territory of Chad, the first mineral with which groundwaters are equilibrated is Mg-montmorillonite, followed by calcite, amorphous silica, gypsum, jarosite, and mirabilite (Table 44). It is important that waters are equilibrated with calcite and Mg-montmorillonite during the early stages of their evolution, when the concentration factor relative to precipitation is no higher than 2 and the total salinity is 1 g/l. Of course, since the water continues to interact with aluminosilicates during later stages, the processes of clay and carbonate formation play a significant role during all the stages of formation of this water type.

According to our summary data (Section 1.6), the waters of continental salinization are usually weakly alkaline, brackish or saline, and diverse in composition. The contents of some trace components and silica in waters increase with increasing solution salinity and alkalinity, but in most cases, there is no strict proportionality between these parameters, which is related to the coprecipitation of trace elements with salts and clay minerals crystallizing from the solution during its concentration (Fig. 18). Only such mobile elements as bromine, boron, iodine, sulfur, molybdenum, lithium, strontium, and some others can be considerably concentrated together with sodium and chlorine in saline waters. Consequently, as the solution salinity increases,

the number of chemical elements that can be retained and concentrated in the liquid phase decreases monotonously, which results in a decrease in the diversity of water composition and qualitative impoverishment of the spectrum of chemical elements in saline waters and brines, although their absolute contents remain high.

**The problem of salt sources** in the regions of continental salinization remains disputable. There are at least three main hypotheses on the formation of salts in soils and waters of arid regions: (1) marine, (2) continental, and (3) that of atmospheric salt transportation.

The classic concepts on the provenance of salts in arid regions were most comprehensively summarized and formulated by Kovda [219]. Based on the extensive data of generations of researchers, he justifiably concluded that the main source of salts is the rocks of both the closed basins where mobile components are accumulated and the surrounding mountain regions. Chloride-sulfate and chloride salts are accumulated farthest from the mountain systems in the lowest part of continental depressions characterized by arid climate. Although this approach to the problem of salt sources is in general correct, it is not supported by some researchers.

There have been several attempts to demonstrate the inadequacy of the continental hypothesis of salinization. One of the most recent is that of Kazantsev [308], who used the example of the Baraba and Kulunda plains to claim that soils and waters cannot be salinized at the expense of salts introduced from salt-free soil-forming rocks. He concluded that neither marine nor continental rocks of the Baraba and Kulunda could

**Table 44.** Ionic salt composition of groundwaters of different concentration from Chad, ppm

Component	Equilibrium phase					
	Montmorillonite	Calcite	Amorphous silica	Gypsum	Jarosite	Mirabilite
pH	7.20	7.23	7.14	7.11	7.45	7.49
HCO <sub>3</sub> <sup>-</sup>	276	298	252	241	610	672
SO <sub>4</sub> <sup>2-</sup>	306	365	1680	2380	61700	175450
Cl <sup>-</sup>	8.5	10.3	47.6	67.1	2660	7740
Ca <sup>2+</sup>	92.4	110	268	346	220	162
Mg <sup>2+</sup>	26.4	25.4	37.0	47.6	72.6	166
Na <sup>+</sup>	50.6	61.2	282	400	25610	44780
K <sup>+</sup>	31.2	37.0	171	241	9550	26900
SiO <sub>2</sub>	87.1	83.4	120	120	56.4	25.2
Al <sup>X</sup>	5.94	5.67	1.89	1.62	0.81	4.05
Fe <sup>2+</sup>	0.10	0.12	0.51	0.72	28.3	18.6
Fe <sup>3+*</sup>	0.06	0.06	0.06	0.06	0.06	0.06
Total, g/kg	0.88	0.99	2.86	3.84	100.5	255.9
Concentration factor**	1.59	1.90	8.75	12.4	489	1388

Notes: \* ppb.

\*\* Relative to atmospheric precipitation.

serve as the main sources of salts in the modern soils and waters of southwestern Siberia. In his opinion, such sources could be the salt deposits of the neighboring arid regions and marine and oceanic waters, with the salts being transported by an atmospheric mechanism. The important question of the source of salts in the neighboring regions arises. This question has remained unresolved.

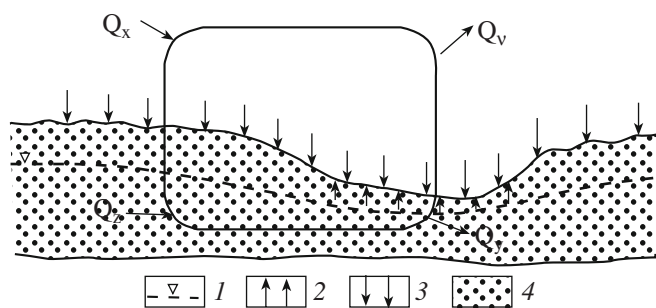
The key point of this problem is again the continuous interaction between water of any salinity and initial rocks (bedrocks), which results in the partial removal of chemical elements from the rocks. Another very important circumstance is the rather weak water exchange

and evaporative concentration of elements in the solution accompanied by the sequential precipitation of various salts (Fig. 38).

As was shown above, similar to other landscape zones, the sources of salts are rocks (Tables 33, 34; Fig. 27), but the salts are to a large degree concentrated in the solution owing to evaporation, which dramatically changes the geochemical environment and the state of equilibrium with gypsum, halite, jarosite, mirabilite, etc.

The formed soluble salts are again dissolved by falling precipitation, which shifts the geochemical environment toward the initial state. Therefore, as already saline water reacts with bedrocks, the equilibrium state that is established in the system promotes the transition of any element from the initial rock into a secondary salt of a certain composition and, of course, clay; i.e., the system always operates in a medium with elevated salinity (points D–G in Fig. 35) and, therefore, forms the same secondary products.

Soluble salts formed on the surface are introduced by wind into the atmosphere, where their dissolution increases the salinity of precipitation, and they return to the initial water–rock system; i.e., like water, salts are entrained into cycling processes, as the general property of mass transfer in the supergene zone. On the other hand, part of salts is removed with subsurface flow into neighboring regions or even into the ocean. Consequently, *the accumulation of salts is possible only if the rate of their input into the system from initial rocks and other sources is higher than the rate of their removal from the system by the subsurface flow* (Fig. 39).



**Fig. 39.** Sources and cycles of salts in the arid region. (1) Groundwater table, (2) areas of intense evaporation, (3) source areas of groundwaters, and (4) aquifer.  $Q_x$  is the input of salts from other regions or the ocean;  $Q_v$  is the removal of salts by wind into other regions;  $Q_y$  is the removal of salts by surface runoff and subsurface flow; and  $Q_z$  is the input of salts from the rocks of the region.

In addition to salts of local origin, the cycle involves salts transported from other regions or the ocean ( $Q_x$ ). Part of salts is removed from the region by wind ( $Q_v$ ) and by surface runoff and subsurface flow ( $Q_y$ ). A certain amount of salts is supplied to water from rocks; the major portion of these salts precipitates under favorable conditions in soils and dissolved rocks ( $Q_z$ ), but a certain fraction always remains in the solution. The sources of salts are the rocks of both the region affected by salinization and surrounding mountain systems, the runoff from which is directed to the continental depression.

As can be seen from Fig. 39, not all salts supplied by precipitation to the region were transported from the ocean because significant fractions of them are secondary or cyclic, i.e., have a local origin and are formed at the expense of rocks. The fraction of cyclic salts is much higher than that of oceanic salts, which was also noted by Kazantsev [308]. Of course, the quantitative proportions of these components are different in different regions and must be accurately determined by future studies. It is important to reemphasize that the high fraction of the atmagenic component of the subsurface chemical efflux characteristic of arid regions is related not to the regional process of salt transportation from the ocean, but to the enrichment of precipitation in locally derived salts. The proportions of oceanic and continental salts must be estimated in each particular case.

Figure 39 also shows that, in principle, three cases with different relations between the salt sources are possible in any region. The first case is

$$Q_x + Q_z > Q_v + Q_y \quad (5.8)$$

It results in the general accumulation of salts in groundwaters, soils, and weathering products, independent of the details of their distribution in the region. In this case, the region is affected by persistent salinization. The zone of salts expands continuously (of course, on the geological time scale), the salinity of water increases, and the amount of salts rises.

The second case is

$$Q_x + Q_z < Q_v + Q_y \quad (5.9)$$

It ensures stable, although slow, desalinization of the region. The third case corresponds to

$$Q_x + Q_z = Q_v + Q_y \quad (5.10)$$

which provides a balance between the input and output of salts. In such a case, the amount of salts remains practically unchanged in the region and processes of salinization–desalinization are not observed. However, this is true only in general because either of these processes may occur in particular parts of the region and the scales of salt redistribution may be significant.

Thus, both soda formation and salt accumulation are consequences of a single stage of water–rock interaction stabilized at a certain period of its evolution, which is attained under conditions of very slow water

exchange, intense evaporation, and geologically prolonged development of the region under the conditions of arid climate. This leads to the accumulation of salts from the rocks of a tremendous watershed in relatively small local areas. The salts are mostly supplied by rocks of nonmarine origin.

#### 5.5.5. Cryogenic metamorphism of groundwater

The evaporative stage of the formation of groundwater composition is mainly confined to middle latitudes. In northern latitudes, its functions are executed to some extent by the freezing out of groundwaters, which also removes free water and thus concentrates elements. The freezing out is part of a more general phenomenon, which was called *cryogenesis* by E.V. Pinneker and is a combination of physicochemical processes occurring in the cryolithosphere and in seasonally frozen rocks. The specific conditions of the development of groundwater composition under the influence of cryogenic processes are related, first, to the occurrence of water in a solid state or at low temperatures (possibly even below zero); second, limited water replenishment; and, third, peculiar processes of rock alteration [10].

Kononova [309] distinguished the following effects of cryogenesis on groundwater composition and salinity.

(1) The freezing out of water results in the formation of a solid phase, ice, whose salinity is lower than that of the initial water, which increases the salinity of the residual solution.

(2) The amount of salts incorporated in ice depends on their concentration in the residual solution, the rock composition, the intensity of water exchange, and the rate of ice formation. Slow and gradual freezing out is favorable for the formation of the least saline ices.

(3) Salts are redistributed between ice and freezing solution. Simultaneously with ice crystallization, those compounds that reach the saturation limit at the given temperature precipitate from the solution. Fresh water produces calcium carbonate and then magnesium carbonate, whereas calcium and sodium sulfates precipitate from saline waters and brines. Freezing out results in the concentration of the most mobile and soluble compounds: sodium bicarbonate, magnesium sulfate, and chlorides of calcium, magnesium, and sodium.

(4) During the subsequent ice thawing, the precipitated salts are incompletely dissolved, and the resulting liquid phase has a lower salinity and a different composition compared with the initial water.

(5) Alternation in time of freezing and thawing of fresh calcium bicarbonate waters eventually results in the formation of less saline sodium bicarbonate waters. The freezing out of saline waters produces brines with high contents of calcium and magnesium chlorides and, at low temperatures, also sodium chloride.

It should also be noted that, according to Pinneker, the processes of freezing and thawing enhance the leaching capacity of water: the amount of salts that can

**Table 45.** Ionic salt composition of groundwaters from the cryolithosphere [44]

Sampling site	Date	Depth, m	Salinity, g/l	Ionic salt composition
<i>Rocks above permafrost</i>				
Second terrace of the Lena R. near Yakutsk	20/XI 1950	1.2	0.31	$\frac{\text{HCO}_3 69 \text{SO}_4 21 \text{Cl} 10}{(\text{Na} + \text{K}) 50 \text{Ca} 32 \text{Mg} 17}$
Khanchala R. valley	24/VII 1964	1.5	1.9	$\frac{\text{SO}_4 63 \text{HCO}_3 32}{\text{Mg} 42 (\text{Na} + \text{K}) 34 \text{Ca} 34}$
Fifth terrace of the Lena R.	12/VII 1960	1.8	1.0	$\frac{\text{HCO}_3 72 \text{Cl} 171}{(\text{Na} + \text{K}) 67 \text{Mg} 22 \text{Ca} 11}$
Lunikha R. valley	12/VII 1960	2.5	1.2	$\frac{\text{Cl} 156 \text{SO}_4 28 \text{HCO}_3 15}{\text{Ca} 52 \text{Mg} 47}$
<i>Waters of unfrozen zones beneath river channels</i>				
Unfrozen zone beneath the Lena R. in the Pokrovsk region	19/III 1958	14.0	0.4	$\frac{\text{HCO}_3 43 \text{Cl} 141 \text{SO}_4 16}{(\text{Na} + \text{K}) 41 \text{Ca} 35 \text{Mg} 24}$
Unfrozen zone beneath the Tamma R.	29/IV 1959	3.0	0.24	$\frac{\text{HCO}_3 98}{\text{Mg} 52 \text{Ca} 44}$
<i>Intrapermafrost lenses with liquid water</i>				
Second terrace of the Lena R.	24/IX 1969	5.1	14.7	$\frac{\text{Cl} 188 \text{SO}_4 12}{(\text{Na} + \text{K}) 49 \text{Mg} 35 \text{Ca} 12}$
First terrace of the Lena R. near Yakutsk	IX 1966	5.0	76.1	$\frac{\text{Cl} 191 \text{SO}_4 8}{\text{Mg} 52 (\text{Na} + \text{K}) 30 \text{Ca} 11}$

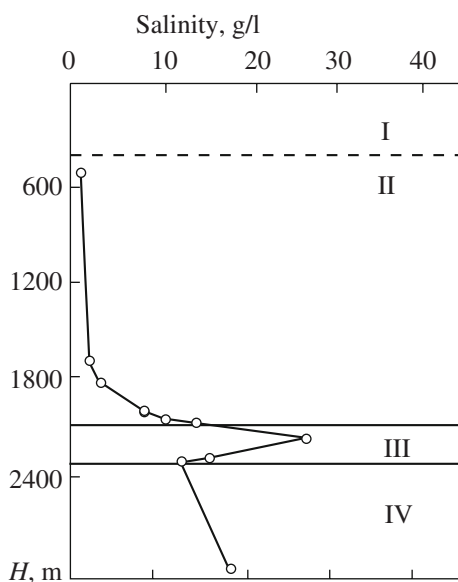
be released from a rock thawed after freezing into a solution is approximately twice that released from a rock unaffected by cryogenesis. Rocks in permafrost

are transformed under the influence of thin water films adsorbed by the surface of particles; this water does not freeze even at negative temperatures [310], dissolves rocks, and forms cryogenic geochemical fields [311].

The cooling of unfrozen rocks results in a significant increase in groundwater salinity. Sodium bicarbonate precipitates at a temperature of  $-1.2^\circ\text{C}$ , and the residual solution is enriched in magnesium chloride. In unfrozen grounds under lakes, the salinity of groundwater may locally reach 3–5 g/l. Even higher values are observed in a liquid phase retained as lenses in the permafrost sequence, where the described process may produce high-salinity magnesium–sodium and magnesium chloride waters. In particular, a lens of brines with salinities of 60–76 g/l was documented in alluvium near Yakutsk (Table 45). The source of salts was both water and the local sulfate and chloride solonchak soil [44].

A peculiar permafrost imprint is observed below the present-day foot of frozen rocks, where a zone of freshened waters is formed and abruptly changes with depth into a zone of high concentrations (Fig. 40). Kononova argued that the latter corresponds to the depth of the maximum freezing during past colder epochs. Groundwaters unaffected by cryogenic processes occur at deeper levels.

According to the data of Pinneker, zones of freshened waters more than 1000 m thick occur under the 500- to 600-m-thick cryolithosphere in the Mesozoic and Permian sandy–clayey and carbonate sequences of



**Fig. 40.** Variations in the salinity of subpermafrost rocks with depth in the Nama Well, Yakutia [309]. Zones: I, waters of diverse salinity; II, freshening; III, concentration; and IV, waters not affected by cryogenic processes. The dashed line is the boundary of frozen rocks.



the Siberian Platform. The groundwaters are sodium bicarbonate or chloride with a salinity of 0.5–6.0 g/l. In the concentration zone, they reach or approach the stage of sodium or calcium chloride brines, transforming with increasing depth into saline waters.

Groundwaters with negative temperatures were called *cryopegs* (cold waters) by N.I. Tolstikhin. They are almost always represented by brines and are widespread in the northern Siberian Platform.

Thin films of bonded nonfreezing water in rocks from permafrost areas show peculiar compositions. According to our data for waters from sulfide deposits, they are highly concentrated sulfate waters with very high contents of heavy metals. Water films may contain liquid carbon dioxide and anomalous contents of other elements. The ascent of such waters and their freezing in the active layer sometimes result in the salinization of suprapermafrost rocks and soil horizons.

#### 5.6. Relation between the Compositions of Groundwaters and Rocks

The problem of the relations between the chemical composition of groundwaters and rocks has a very long history. The ancient Greek philosopher Aristotle (fourth century BC) postulated that “water gets its tastes and colors from the kind of earth it happened to flow through.” A similar statement was made by the Roman scientist Pliny the Elder (first century BC): “As are the rocks, so are the waters” [10]. This postulate is still accepted in one form or another nowadays, which is illustrated by the published concepts of many researchers. For instance, Posokhov argued that the mineral composition and petrochemical characteristics of rocks are the main factors controlling the salinity and chemical composition of groundwaters and pointed out that “... in monomineralic rocks, the chemical composition of waters corresponds to the chemical composition and solubility of the rocks. In polyminerals rocks, the chemical composition of water reflects mainly the compositions of highly soluble minerals” [4, p. 91]. Similar concepts were developed by Pit’eva, who noted that “a general conclusion on the influence of lithological and geochemical characteristics of rocks on hydrogeochemical relationships is the distinct qualitative and quantitative dependence between the compositions of rocks and waters” [7, p. 132]. Similar ideas on the dependence of water chemistry on the composition of rocks can be found in other Russian and foreign publications.

Thus, the geochemical relations between the compositions of waters and rocks have been considered for more than two thousand years as very simple, obvious, and requiring no further substantiation. The observed inconsistencies between the compositions of waters and rocks were regarded as exceptions from the general rule and attributed to the influence of other factors. Even the development of the principle of groundwater

zoning in the early 20th century on the basis of the studies of the great scientist V.V. Dokuchaev and the earlier discovery of fossil sedimentation waters did not change fundamentally the existing concepts. The genius of the founder of modern hydrogeochemistry, Vernadsky, was needed to show that the composition of water is a function of the evolution of the water–rock–gas–organic matter system [1]. Vernadsky argued that gases and organic matter rather than rocks are the main factor in the formation of water composition and drew special attention to the geochemical environment created by these components. In this way, he validated the leading role of the environment and did not consider in detail the relations between water and rock compositions. Subsequently, F.P. Savarenskii, G.N. Kamenskii, A.M. Ovchinnikov, A.I. Perel’man, A.A. Kartsev, E.V. Pinneker, E.V. Posokhov, A.V. Shcherbakov, and others contributed significantly to the development of particular aspects of this problem.

Ovchinnikov summarized the extensive available data and analyzed chemical relations between waters and rocks. He did not find simple dependences between these major components of the Earth’s crust and proposed a new formulation for the ancient postulate: “Water is such as the geologic history of the region where it occurs” [3, p. 3]. However, the new formulation of the postulate, although more advanced, does not reveal the relations between water and rock compositions and between structural (geological) and zonal (climatic) factors of water formation and does not correlate the composition of water with the geochemical character of the environment [312].

Meanwhile, the problem of such relations has acquired increasing theoretical and practical significance. Knowledge of the relations between the compositions of water and rocks is necessary for the development of the hydrochemical method of prospecting; prediction of changes in the quality of water in developed areas; determination of sources of nonmagmatic ores; and solution of the problems of weathering, formation of the chemical composition of groundwater, and diagenetic and catagenetic transformation of rocks. This list is far from exhaustive.

In recent years, new methods were developed for studying water–rock systems, including thermodynamic, kinetic, mass transfer, isotopic exchange, physicochemical, and mathematical simulation techniques and comprehensive combined investigations of the compositions of newly formed mineral products and water as interrelated constituents of a single natural process. This provided insight into fundamentally new aspects of water–rock relations and made it possible to reinterpret the development of this system. It turned out that aluminosilicates play an exceptional role [10], and not only because they are the most common rocks on Earth, but primarily owing to the peculiarity of their interaction with water, which predetermined the geological importance of this system.

**Table 46.** Ratios of the contents of chemical elements in waters relative to those in rocks for various geochemical types of weathering

Geochemical type of weathering	Bedrock	Geochemical type of water	R*			
			Si/Al	Ca/Na	Si/Ca	Fe/Si
Laterite	Dunite	Fe–Al acidic	1.18	0.97	0.34	0.71
	Nepheline syenite		2.27	0.89	0.42	0.23
Monosiallite	Granite	Al–Si	9.61	2.46	0.10	0.29
			8.23	2.52	0.07	0.37
Bisiallite	Basalt	Si–Ca–Na	29.4	1.03	0.04	0.11
	Granite	Si–Na–Ca	38.7	1.22	0.05	0.08
Carbonate	Sandy coaliferous	HCO <sub>3</sub> –Ca alkaline	33.8	0.81	0.06	0.21
	Shale		31.6	0.73	0.07	0.36
Sulfate–chloride	Granite	Chloride–sulfate	27.5	0.39	0.11	0.27
	Sandy–clayey		25.9	0.25	0.13	0.18

\*  $R = \frac{(A/B)_{\text{water}}}{(A/B)_{\text{rock}}}$ , where A and B are chemical elements.

The unique character of the water–aluminosilicate system is related to its continuous physicochemical and geological evolution, including the formation of new secondary minerals and geochemical types of waters, which are involved after their formation in the process of further evolution and influence this evolution. The new geochemical types of waters interact with the initial aluminosilicates from a new starting point, forming new secondary mineral phases and, correspondingly, new geochemical types of water (Fig. 35; Tables 35, 37). This is the essence of one of the most important laws of the physicochemical evolution of the water–rock system, which allows us to approach the problem of the relations between the compositions of water and rocks.

Consequently, the investigation of the relations between water and rock compositions should proceed from the water–endogenous aluminosilicates system because all other rock types are its derivatives. The interaction of water with aluminosilicate rocks has a multistage character (Section 5.4). Each stage of interaction is marked by changes in the proportions of removed and accumulated elements (Tables 33, 34), the compositions of secondary mineral phases, and the geochemical type of waters. It is also important that the evolution of the water–rock system is accompanied by an increase in the total content of chemical elements in the solution, although their fraction in the water decreases relative to that in the secondary mineral phases. As a result, the difference between the compositions of the water and the initial rock increases continuously.

This can be supported by a comparison of element ratios in the initial rocks dissolved in water and groundwaters ( $R$ , Table 46). For instance, the coefficient  $R =$

Si/Al is significantly higher than 1 at all stages of weathering, which indicates that the output of silicon from the rocks is much higher than that of aluminum. This ratio increases during the evolution of the water–rock system, suggesting a higher concentration of aluminum in the secondary mineral phases compared with silicon, although during the latter of the two weathering stages considered, this ratio begins to decrease, which is understandable because silicon is almost completely fixed in clay minerals under such conditions.

In contrast, the ratio  $R = \text{Si/Ca}$  is always lower than 1, which indicates much more extensive removal of Ca compared with Si because the latter is fixed during all weathering stages, except for the first, in secondary mineral phases. This is reflected in a continuous decrease in Si/Ca during the transition of the system to the subsequent types of weathering. The increase in Si/Ca resumes during the carbonate stage of weathering because calcium is also fixed in secondary mineral phases.

The ratio  $R = \text{Ca/Na}$  is close to 1, which indicates practically complete removal of these elements in proportions corresponding to their contents in the rocks. An exception is the last stage of weathering, at which calcium is partly fixed in secondary carbonates and the Ca/Na ratio slightly decreases. More complex relationships are characteristic of  $R = \text{Fe/Si}$ , which is related to the dependence of iron behavior on redox conditions, which are not analyzed in detail here. The Fe/Si values are significantly lower than 1, which indicates incomplete removal of iron and its incorporation in secondary mineral phases.

Thus, even within the supergene zone, where the initial stages of water–rock interaction occur, there is no correspondence between water and rock compositions.

The maximum similarity is typical of the earliest interaction stages (laterite-type weathering), although even this case is far from complete correspondence. The difference increases toward the later stages of weathering.

The discrepancy between the compositions of groundwaters and rocks is evident not only under supergene zone conditions, but also in all other types of deeper waters of different origin. The longer and more advanced the water–rock interaction, the greater the difference between the compositions of the water and the initial rock [312].

All of the above arguments, the analysis of the voluminous data presented in this study, and the identification of the character and fundamental causal relations in water–rock interaction allowed us to reformulate the ancient postulate of Aristotle in the following way: *water is such as the degree of its interaction with rocks controlled by the geologic history of the evolution of this system.*

Thus, in accordance with the concepts developed by us, the composition of water is not controlled by the type of rocks, as is usually assumed, but by the degree of interaction with them, which, in turn, is a function of the geologic history of both the water itself and the whole water–rock system. On the other hand, the new formulation does not negate the old postulate. It only restricts its application to the initial stages of water–rock interaction, when the composition of water resembles that of the rock, which was so perspicaciously recognized by ancient thinkers. Consequently, the ancient postulate reflects a particular case of a more general and complex phenomenon, which has been revealed for us by the achievements of modern science.

### 5.7. Geologic Evolution and Self-Organization of the Water–Rock System

In recent decades, the problem of self-organization of materials in dynamic nonequilibrium systems has been a topic of considerable interest among researchers in various disciplines. Fundamentally new approaches were proposed for the solution of this complex problem. A new science (or more precisely, a new invariant) called synergetics provided fresh insight into the main problems of development, especially in nonliving nature. Considerable contributions to the growth of this research field have been made by I. Prigogine, H. Haken, G. Nicolis, W.R. Ashbey, I. Stengers, P. Glansdorff, W. Ebeling, M. Eigen, and many other authors.

In recent years, the ideas of synergetics have been actively used in geology [e.g., 313–315]. It was shown that most geologic systems can be classed as open, nonlinear, dynamically active, and continually exchanging matter and energy with the environment. All these properties are indicators of self-organizing systems, which can select one of the possible paths of their evolution accompanied by a decrease in entropy production. The process of self-organization necessarily

implies mass and (or) energy exchange between the geologic system and the environment. However, the new structures appearing as a consequence of self-development are not controlled by the character of the external influence but are immanent in the evolving system. According to F.A. Letnikov, examples of self-organization in dissipative geologic systems are the processes of mineral growth and cluster formation; the development of fluid, melt, and fluid–salt systems; metasomatic, metamorphic, and ore-forming processes; etc.

The material presented here suggests that the water–rock system shows all of the main criteria for self-organizing materials considered in the context of modern synergetics: a contradictory nonequilibrium–equilibrium state persistent over the entire geologic history, nonlinearity of main processes, the ability for spatiotemporal development, a mechanism of regulation of relations with the environment, selectivity of the composition of the produced secondary mineral phase capable of reproduction, a mechanism of geologic self-regulation, and, as will be shown below, the existence of structural objects capable of acquiring, accumulating, estimating, and transmitting information [316–318].

According to Prigogine and Stengers [319], the elements (molecules) of a thermodynamically equilibrium system behave independently of one another; i.e., each of them ignores the other elements and behaves passively. They proposed that such elements be referred to as *hypnons*, i.e., in a hypnotically sleeping state. A transition to a nonequilibrium state wakes up hypnons, a coherent connection is established between them, and they lose their mutual independence. In such a case, the system behaves as if it were a container of long-range forces. Although the forces of molecular interaction are short-range ones (operating at distances of about  $10^{-8}$  cm), the system behaves as if each molecule is informed about the state of the system as a whole.

In contrast to cybernetics, synergetics regards nonequilibrium states not as a source of death and destruction, but rather as a basis for the development of ordering and a reason for structure genesis and evolution of the system as a whole [315]. nonequilibrium states are a driving force of evolution, which eventually results in a change in irreversible mass and energy fluxes appearing when a closed megasystem consisting of evolving open systems tends toward equilibrium [320, p. 7].

In the context of the concepts considered here, the nonequilibrium–equilibrium character of the water–rock system is the main factor of evolution of mineral matter in various processes of its self-organization and self-development. The general direction of evolution is defined by the principle of free energy minimization (Dirichlet principle), which specifies the external conditions of the existence of physicochemical systems and probably implies the maximization of the total energy of interatomic bonds [321].



One of the most important indicators of self-organization in a system is the directional appearance, development, and decomposition of new spatiotemporal structures [315]. The interaction of water with rocks, primarily with aluminosilicates, exactly satisfies this condition. As was shown above, the hydrolysis of aluminosilicates results in the decomposition of the initial solid phase, chemical decomposition of water, and simultaneous formation of a new mineral phase of a particular composition.

Consequently, the interaction of two phases (water and rock) leads to the formation of a new (secondary) product, which may appear either at the place of the material destroyed by water, replicating its structure, or at a significant distance from it. In either case, in place of two components of the system (water and rock), three components are formed, which is indicative of the complication and development of the system.

The formation of a secondary mineral phase is, in essence, the birth of a qualitatively new system consisting of new (additional) structural elements, which are more ordered and adapted to environmental conditions; therefore, starting from a local area (generation site), they gradually expand and conquer new geologic space. This can be exemplified by laterites, which occupy tropical areas in the supergene zone; clay products of weathering, which are widespread under temperate climate conditions; ferromagnesian nodules, which occur in the central part of ocean basins; carbonate calcretes of steppe terrains; etc., as well as by various geochemical types of water paragenetically connected with the mentioned secondary products. Among them are the ultrafresh acidic Fe–Al waters of tropical areas associating with laterites, the soda waters of forest steppes associating with secondary carbonates, etc. (Table 37).

Thus, the appearance of a secondary mineral phase stabilizes the system in the sense that it directionally reproduces the newly formed mineral and the certain geochemical type of water, whose number and diversity continue to increase in the system and which gradually increase the area of their occurrence and occupy geologic space. This provides conditions for the peculiar expansion of secondary water and mineral phases of certain compositions on Earth. This property of nonliving matter was later inherited by living matter, which continues to extend the zones of its occurrence.

Information is one of the major factors in the synergetic theory of self-organized materials. “Information, being an intrinsic property of matter, exists as an active factor, as a sort of ‘agent of structuring’ of moving matter” [315, p. 35]. In accordance with the postulates of synergetics, the evolution of both organic and inorganic materials is accompanied by a continuous increase in the value and functional significance of information, which ultimately results in the development and complication of the matter itself. What is the mechanism of the acquisition, evaluation, and use of information?

In this context, it should be remembered that information serves in synergetics as the opposite of entropic uncertainty and appears as a result of resolving an alternative. The evolutionary development of a system and its generation and destruction are an information process, which is imprinted in the structure of appearing objects. Consequently, the structure of the state of the system is the main and, in fact, the only source of information in nonliving nature. In addition to mineral systems, of special importance among appearing secondary phases are developing geochemical types of water, whose structure has long attracted considerable attention owing to its ability to transform in response to minute changes in its composition, thermodynamic conditions of the environment, the state of physical fields, etc. [23].

It is highly important that the directional evolution of the water–rock system, resulting in the selective concentration of chemical elements in aqueous solution, controls changes in structure of water at a fixed temperature. The details and mechanisms of structural transformation of icelike associates or clusters and their relationships with monomer water molecules and dissolved ions are unknown, but it is evident that, at a certain stage of structural transformations, these processes lead to changes in interrelations between dissolved ions, a decrease in distance between them, formation of ion pairs, and, eventually, precipitation in the form of mineral compounds. Consequently, the structural changes in water code information such that it serves as a signal for a change in the behavior of certain ions in solution, their approach to each other, and their precipitation. In turn, a decrease in the part of ions in solution or even a change in their bonds with each other leads to a structural transformation in the solution and, correspondingly, cessation of the precipitation of a certain group of molecules. If other chemical elements are simultaneously concentrated in the solution, they also affect the structure of the solution and thus form a code, which governs their further behavior. Hence, code information is manifested in the interaction of a solution with elements concentrating in it through the creation of special structural cells. This information controls the spatiotemporal coordination of future events and the behavior of the system as a whole.

Since water can concentrate chemical elements only to a certain level, its structure can be imagined as numerous cells resembling a honeycomb in a hive or luggage lockers at a station. Every cell is equipped with a number of “doors” allowing only a specific ion. As the water interacting with a rock accumulates an increasing number of chemical elements, part of the doors in the cells close and some ions are not admitted into part of the cells, although other ions continue to enter the solution. Those ions that received a signal of nonadmittance from the formed structure of the solution (closed doors) are forced to precipitate as secondary solid phases. The higher the number of closed doors, the higher the number of mineral phases with respect to which the water is



saturated and produced secondary phases. Of course, as the doors are closed, the structure of the water changes, which serves as a signal for the behavior of corresponding elements.

The above considerations imply that the structure of the water solution includes mechanisms of information use, evaluation, transformation, and transmission. The diversity of structural elements and their variability under the influence of external factors serve as a source of new information, which is fixed in the newly produced structural forms. This particular case supports the statement of synergetics that “any system unit of inorganic matter involves mechanisms of evaluation and transformation of information owing to its structural character and, under certain conditions, evolves on their basis into a self-organizing and self-regulating object” [315, p. 54]. Water solution species are such a structural unit in geologic systems.

Analyzing the available facts, we concluded that *the main route of information controlling the evolution of the water–rock system is incorporated in the structural characteristics of the water solution* owing to its ability to undergo various structural changes under even a minor influence of chemical ions, temperature and pressure, electric and magnetic fields, etc. [316]. Structural changes in the water solution serve as a basis for information supply, which controls the operation of the mechanism of selection of forms of interaction between dissolved ions with the subsequent formation of species and their apparent expulsion from the generation medium. Similar to crystalline mineral objects, the solution does not contain a structurally localized regulator of information because it is dispersed over the whole structural volume.

Thus, the water–rock system shows all of the main indicators of self-organizing matter described by modern synergetics and, moreover, is characterized by many fundamental properties and mechanisms of interaction that are typical of the whole environment, as well as geologic and biological systems, and that are found in many, if not the overwhelming majority, of physico-chemical processes and phenomena in the upper crust.

The self-organizing properties of the system are determined by two basic premises. (1) In all, without exception, parts of the Earth’s crust, an aqueous solution is not in equilibrium with particular magmatic or metamorphic minerals, which are continuously dissolved in it. Correspondingly, the water–rock system is intrinsically contradictory and capable of spontaneous, continuous, and geologically long development with the formation of fundamentally new mineral phases and geochemical types of water. (2) One of the properties of the structure of the aqueous solution is its ability to change under the influence of internal and external factors, including dissolved chemical elements, gases, organic compounds, physical fields, etc. These structural changes serve as a structurally nonlocalized regu-

lator mechanism that defines the direction of the main evolutionary processes.

Consequently, there is a strong contradiction (antagonism) between water and initial (endogenous) rock, which controls *their continuous interaction* during the whole period of water existence on Earth. In fact, all that we can see in our environment (relief; unconsolidated deposits; salts; geochemical types of water; weathering products; sedimentary rocks; sedimentary, hydrothermal, and metamorphic mineral resources; various minerals; lakes, rivers, and springs) is a result of water–rock interaction. This list should also include everything formed under the influence of organic matter, which is a product of the water–gas–rock system (vegetation, landscape, forest, soil, peat, coal, mud, marsh, etc.). The interaction process is ongoing and continuously produces new compounds, including minerals and rocks, as well as various geologic media, in particular, geochemical types of water. Consequently, the composition of the hydrosphere and products of lithogenesis and biogenesis are the products of this fundamental contradiction between water and initial terrestrial rocks.

At the moment of water’s appearance on Earth, an uninterrupted process of destruction of some rocks and formation of other rocks (sedimentary and metamorphic) was launched. With time, the number of newly formed minerals and geochemical types of water increased. The latter gradually occupied geologic space and new levels of the lithosphere and formed different geochemical environments, which, in turn, enabled the formation of new mineral phases influencing the character of the medium. This process is geologically continuous, infinite, and capable of conquering new areas. Hence, another fundamental property of the water–rock system is its *ability to increase the amounts of secondary products and expand its occurrence area*. In this connection, Vernadsky’s concept of the pressure of life should be mentioned. It is evident that we are dealing with the pressure of secondary products in the mineral world.

The diversity of secondary mineral phases and geologic media resulted in the diversity of biological forms of evolution, which inherited in many respects the type of material interaction and its structure, cycle form, seasonal variability, connection with the environment, ability to occupy space, composition of chemical elements, and many other factors. The most important component that was inherited by biological systems from geologic ones is the information code encrypted in the structure of water. This problem deserves special investigation and discussion. The water–rock system triggered the internal evolution of mineral matter, which subsequently transformed into biomineral and living matter. These processes, in particular, included the sources of formation and development of the environment.

In our opinion, many basic components of the evolution that was revealed by Darwin for the organic world can be seen in the water–rock system. This emphasizes the similarity of geologic and biological systems and supports the suggestion that life originated on Earth in a water–mineral medium rather than being introduced from an external source, as is sometimes supposed.

As a final remark, it should be pointed out that the anthropogenic pollution of the water medium of our planet directly affects the information code incorporated in the structure of water and, consequently, the direction of the basic system of development. The result of this is illustrated by many urgent environmental problems. Their solution on a global scale is impossible without fundamental investigations of self-organization in the water–CO<sub>2</sub>–rock system.

Note finally that the special role of water in the Earth's history was first acknowledged and comprehensively demonstrated by Vernadsky. His major study *History of Natural Waters* remains important today. Previously, some important arguments for the special geological role of water had been advanced by G. Agricola, M.V. Lomonosov, the founders of the Neptunist school (A.G. Werner, J.-B. Lamarck, and others), E. Suess, A. Doubree, I.V. Mushketov, B.L. Lichkov, and others.

In this connection, it is convenient to remember the fundamental conclusion of Vernadsky that “water occupies a special place in the history of our planet. There is no other geologic body that could be compared with it in terms of influence on the course of the main, most grandiose geologic processes” [1, p. 20]. This idea was developed by the great scientist with application to various shells of the Earth: (1) *the most important phenomena* both on the Earth's surface and in the deep parts of the planet are controlled by the presence and properties of water; (2) water generates the main *mechanisms of the Earth's crust*, at least up to the magmatic shell; (3) water imposes and, in part, generates *the electric field of the planet* and its atmosphere; (4) *the properties of water* create the climate and *control the thermodynamics of the atmosphere*; (5) water controls *the chemistry of the Earth's crust and the living environment*; (6) natural water embraces and creates the whole life of humans because there is hardly any other natural body that would influence to such an extent their *social structure, way of life, and existence*; and (7) water controls and generates *the entire biosphere*.

Each of these statements is based on the profound analysis of numerous empirical facts and represents a thought concentrated in a compact phrase defining the paradigm of our knowledge on the role of water in the development of our planet and its special position among natural bodies. It would be appropriate, therefore, to refer to the idea of the scientist that “*water occupies a special place in the history of our planet*” as *the postulate of Vernadsky*.

The significance of this postulate has been supported by a growing body of data, which was considered to some extent in this study. In addition to the special role of water on our planet, this postulate reflects the fundamental character of the properties of the hydrosphere on the whole. Among these properties, Vernadsky emphasized the ubiquity of water, its geologically eternal mobility, the unity of natural waters, the diversity of types and forms of water occurrence, its polyphase character and ability to change its phase state under conditions of the Earth's crust, the dissymmetry in the distribution of the hydrosphere on Earth, the water equilibrium of the Earth's crust, etc.

One can only marvel at this brilliant scientist's profound penetration into the mysteries of nature. We believe that his doctrine on the natural equilibrium and evolution of the water–rock–gas–living matter system is one of the major achievements of 20th-century science. Considering this system, Vernadsky emphasized the role of gases and organic matter in its evolution, whereas the role of rocks received less attention. Therefore, in this study we focused on the evolution of the water–rock system without intending to diminish the role of other systems. The reader will have to judge if we succeeded in this.

#### FINAL REMARKS

The basics of the doctrine of water–rock interaction presented in this study show that we are dealing with a unique system of our planet showing a number of fundamental properties playing a tremendous role in the organization of the environment. This is one of the most important terrestrial systems (if not the only system) capable of continuous internal self-development with the formation of new compounds, structures, geochemical media, and water types and possessing a mechanism of information transfer and, most importantly, a mechanism of internal self-evolution.

Up to now, all evolutionary phenomena in geology have been assigned to changes in some external parameters, primarily in the thermal and geodynamic regimes of the Earth and related energy and mass redistribution in geologic space. The water–rock system is a qualitatively different phenomenon, capable of self-development even without any changes in external conditions. Therefore, we can state that this system shows *an ability for internal self-development or internal self-evolution and self-organization*, which fundamentally changes our concepts on the evolution of inorganic matter. It was found that, owing to the unique structure of water and continuous variability in its composition, the water–rock system can generate new daughter subsystems whose internal properties and energy characteristics are superior to those of the parent system; i.e., *the system shows the property of progressive development*. Consequently, the evolution of geologic pro-

cesses, which the outstanding geologist A.L. Yanshin considered as “a very promising direction of fundamental geological research, in both theoretical and practical aspects” [322, p. 9], includes absolutely new, previously unknown mechanisms and factors, greatly increasing our knowledge.

In accordance with the concepts of modern synergetics, the existence of self-evolution mechanisms in the water–rock system operating independently of changes in external factors (of course, within a certain interval) makes this system one of the most unique among the systems of nonliving matter and reemphasizes that the nonliving matter is capable of profound physicochemical and geologic evolution in a progressive direction. There is compelling evidence that the evolution of the environment, at least on the Earth’s surface, began from the processes of water–rock interaction, and the development of this system can be used as an alternative to the current prevailing geodynamic concepts. It is very important that the evolution of this system is accompanied by the continuous appearance of new subsystems, new structures, and new compounds having greater energy and decreasing the production of entropy, i.e., leading, to cite Prigogine and Stengers, from chaos to order.

The produced new structures, connections, compounds, and interaction mechanisms continuously *diversify the environment*. The ability of the water–rock system to diversify and complicate the environment must be considered as one of its most important fundamental properties. Similar to the structure of aqueous solutions, it is also many-sided and variable and is always manifested when water is available. It is known from the classic studies of Vernadsky that one of the unique properties of water is its ubiquity. The formed new compounds and structures are forced to occupy geologic space because their number and volume increase continuously during the whole period of activity of the initial parental system, which, as was shown above, develops continuously. In this way, a new contradiction appears in the system between the existing materials, each of which tends to occupy more space. It is amazing that mechanisms of a struggle for space exist even at the level of mineral matter under real geologic conditions. They operate through the formation of a corresponding geochemical environment.

Once a daughter subsystem is formed, it continuously produces new subsystems, each requiring its own geologic space. The new subsystems expel earlier ones, which are, in turn, forced to rearrange, change some of their functions, and create mechanisms favorable for the coexistence of different daughter subsystems. In such a way, numerous subsystems represented by different minerals, rocks, facies, associations, ore minerals, petroleum deposits, and geochemical types of water gradually develop in a single geologic space. Some of these subsystems subsequently lose their con-

nection to the parent system and may, therefore, be destroyed.

Thus, as can be seen by the example of the water–rock system, even at the early stages of the evolution of the nonliving water system, *a contradiction appears between the tendency to diversification of the environment and the limitedness of the space necessary for the new systems*. It seems that this contradiction ultimately plays the main role and controls the development of the environment because it is inherited by all daughter subsystems, including biological and social ones.

It is very important that all daughter subsystems are products of particular environments produced by earlier systems. Secondary materials are formed in equilibrium with the environment and inherit many of its compositional features and properties. Therefore, they are adapted to this environment and are not destroyed in it; in contrast, they expand the areas of their residence or distribution. Only changes in environmental characteristics may lead to their destruction. This is also true for biological systems: any living system or individual also formed under the conditions of equilibrium with the particular environment and is closely connected with it. Changes in the environment lead to the death of the formed product if such changes exceed certain limits. This is a manifestation of the genetic unity of an environment and a secondary material, individual, species, etc.

Since all secondary materials are formed in a water medium, they inherit the features of this medium and, correspondingly, the main (initial) mechanisms of interaction. Among the most important are the information code, the continuity of interaction, the mechanisms of development of diversity, the occupation of space, and the ability to change within certain limits in response to variations in environmental characteristics and generate new subsystems and new interaction mechanisms. As a result, biological systems, which are later than geological ones, are much more complicated and seemingly have lost their connections with the initial water–rock system. In fact, these connections always exist in a more obscure and complicated form, and one only needs to know how to detect them. If, for some reason, such connections are lost, the subsystem perishes like Antaeus separated from the Earth.

Despite its extreme diversity in composition, structure, and mobility, our environment, including humans, is united by the existence of several basic or key mechanisms, which are inherited from the water–rock system. Among them is the information code encrypted in the structure of water and controlling the direction of evolution of all the numerous systems, subsystems, and sub-subsystems encircling us. Without this code, progressive self-evolution in the observed form would be impossible.

The second important mechanism, which also stems from the structure of water, is the ability of water–min-



eral systems to diversify the world at any macroscopic level of organization, from a mineral (molecule) to a human being. This tendency is immanent to the structure and independent of the will or wishes of a particular individual. Each product of the water–rock system diversifies the environment merely by the fact of its appearance. A higher stage of evolution produces the ability of secondary structures (for example, plants) to adjust their forms to the character of the environment, which greatly increases the ability of systems to contribute to the diversity of the world. Finally, human beings, endowed with intellectual capacities, tremendously increased these abilities and developed corresponding mechanisms.

The above discussion leads to the intriguing conclusion that the main goal of humans on Earth, as well as other living and nonliving organisms or products of evolution, is the endeavor to diversify the world, which is incorporated in the initial system by nature. Therefore, *the happiness of a particular individual can be formulated as his or her unconscious efforts to diversify the world.* The more successful an individual is in diversifying his or her environment (love, domestic life, science, art, culture, sports, home, children, etc.), the greater his or her happiness. In short, happiness is the ability to diversify all that surrounds us, including thoughts, feelings, the soul, objects, phenomena, beauty, technology, etc.

The third important mechanism incorporated in the water–rock system is its ability to create secondary products, which are forced after their appearance to occupy living space for themselves and gradually expand their residence area. This ability is incorporated in nonliving nature and was inherited by living nature, especially by human beings.

These and other fundamental properties governing the evolution of the environment are rooted in the mechanisms of water–rock interaction and inherited by all daughter subsystems. This reflects a profound genetic relation between biogenic and geologic systems, among which the water–rock system is primordial. This basic system launched the process of the progressive evolution of nonliving matter, which subsequently was inherited by biomineral and living matter and then affected its social forms. In terms of the specific properties of the water–rock system, the evolution of the world can be viewed from the unusual side of nonliving matter, which was previously neglected and not accounted for. The sources of the global self-evolution and self-organization of materials, as well as the sources of organization of the environment and its improvement and progressive evolution, turned out to be concealed in nonliving matter, which serves as the origin and trigger mechanism of the most tremendous phenomenon on Earth, the generation and evolution of the environment and life.

It becomes evident that biogenic systems inherited their basic interaction mechanisms from nonliving matter and the cornerstones of life lie in the structure of water and its ability to continuously increase its complexity and change during the process of prolonged geologic evolution. New data support the idea of Vernadsky that life was created by water. Therefore, the classic statement of R. Dubois that life is animated water is not far from the truth. It is another matter that biogenic systems developed, became more complicated, and created many new mechanisms that are inherent to them only (for instance, cell division), but this became possible only at a certain stage of the progressive evolution of the water–rock system and only on the basis of its fundamental mechanisms and properties of development. Thus, life is not separated from mineral matter, but is its daughter structure and reflects the highest stage of the evolutionary development of the water–rock system, as the most general system incorporated in all systems of the environment.

With the appearance of human beings, the development of matter ascended to a qualitatively higher noospheric level, which shows even a higher ability to diversify the world and influence the course of the most grandiose geologic and biological processes. As the most complicated and youngest daughter subsystem, the sphere of intelligence turned out to be remotest from the parent system, although it inherited its basic mechanisms, including the ability to diversify the world, to occupy space, etc. Since the water–rock system and the sphere of intelligence are separated by numerous intermediate subsystems, very complex connections, structures, forms of existence, and interaction mechanisms, the initial basic connections were hidden, invisible, and hardly discernible. Thus, the mind turned out to be so isolated from the parent system that it does not remember this fundamental genetic relation and, therefore, does not always operate in accordance with the laws of nature.

There appeared a new fundamental contradiction between the relative independence of the sphere of intelligence, its tendency to develop following the laws of this daughter subsystem, and the need to obey the laws of development of the basic system, the genetic relation to which is unguessed at by the mind. In our opinion, this is one of the most fundamental contradictions, hampering in many aspects the progressive development of the whole world and humankind in general at the current stage of evolution. However, this contradiction can be eliminated with the aid of intelligence if the deep roots and connections of the mind with mineral and biomineral matter are acknowledged. The comprehensive investigation of these genetic roots of the mind and its connection with mineral matter will enable humankind to follow the course of development prescribed by nature.



Will the noosphere overcome such a complex and difficult problem? This depends on the tendencies in science and culture, which concentrate the most developed part of the human mind. In addition to elucidating the genetic sources of life; relationships between biogenic and geologic systems; the dynamics and tendencies of evolution in nonliving matter, about which especially little is known; and the structure of water, as the most enigmatic compound on Earth, it is also important to preserve and increase natural tendencies to the continuous development of diversity, including, of course, the diversity of sciences and cultures; the preservation and increase of geologic, biological, and water diversity; etc. The regulation of interrelations between diversity and space is a difficult challenge. This is the main key problem of all of humankind. If it will be solved on the basis of an understanding of the main laws imposed by nature, the environment and the mind will continue to develop. One would like to believe in the supremacy of the mind.

We note finally that the aspects of self-evolution in the environment discussed here raise a number of fundamentally new problems in modern science. The scope of our study is rather narrow, and it is not reasonable to discuss all of these problems here. However, three of them are worth mentioning. The first is self-organization in the water–rock system, whose comprehensive investigation will help in solving many geological and biological problems, including the genetic relations of living and nonliving materials with all the ensuing consequences for the investigation of the global self-evolution of matter. The second is the structure of water, both in its purely physical sense and in its geochemical and biological aspects. In addition to an understanding of the profound role of water in the development of the environment, a fundamentally new level will be achieved in the solution of many geochemical, agricultural (including food processing), medical, biological, and chemical technology problems. We believe that a new breakthrough in the fundamental natural sciences is rooted in the investigation of the structure of water, as the most unusual and most important substance on Earth. The third is the problem of the longevity of humans, which, in our opinion, cannot be solved in purely medical terms. It also requires the development of a comprehensive natural history approach beginning from the water–rock system and the structure of water.

#### REFERENCES

1. V. I. Vernadsky, *History of Natural Waters* (Nauka, Moscow, 2003) [in Russian].
2. H. Schoeller, *Géochimie des eaux souterraines* (Paris, 1965).
3. A. M. Ovchinnikov, *Hydrogeochemistry* (Nedra, Moscow, 1970) [in Russian].
4. E. V. Posokhov, *General Hydrogeochemistry* (Nedra, Leningrad, 1975) [in Russian].
5. V. S. Samarina, *Hydrogeochemistry* (Leningrad. Gos. Univ., Leningrad, 1977) [in Russian].
6. S. L. Shvartsev, *Hydrogeochemistry of the Supergene Zone* (Nedra, Moscow, 1978) [in Russian].
7. K. E. Pit'eva, *Hydrogeochemistry* (Mosk. Gos. Univ., Moscow, 1978) [in Russian].
8. W. Stumm and J. J. Morgan, *Aquatic Chemistry*, 2nd ed. (Wiley, New York, 1981).
9. G. Matthes, *The Properties of Groundwater* (Wiley, New York, 1982).
10. S. L. Shvartsev, E. V. Pinneker, A. I. Perel'man, et al., *Principles of Hydrogeology. Hydrogeochemistry* (Nauka, Novosibirsk, 1982) [in Russian].
11. A. I. Perel'man, *Geochemistry of Natural Waters* (Nauka, Moscow, 1982) [in Russian].
12. T. Pačes, *Zaklady geochemie vod* (Academia, Praha, 1983).
13. J. D. Hem, *Study and Interpretation of the Chemical Characteristics of Natural Water*, U.S. Geol. Surv. Water Supply Pap., No. 2254 (1985).
14. J. W. Lloyd and J. A. Heathcote, *Natural Inorganic Hydrochemistry in Relation to Groundwater* (Clarendon Press, Oxford, 1985).
15. S. R. Krainov and V. M. Shvets, *Geochemistry of Groundwaters of Economic and Potable Use* (Nedra, Moscow, 1987) [in Russian].
16. A. Macioszczyk, *Hydrogeochemia* (Wydawnictwa Geologiczne, Warszawa, 1987).
17. J. I. Drever, *The Geochemistry of Natural Waters*, 2nd ed. (Prentice Hall, Englewood Cliffs, 1988).
18. P. A. Domenico and F. W. Schwartz, *Physical and Chemical Hydrogeology* (Wiley, New York, 1990).
19. S. R. Krainov and V. M. Shvets, *Hydrogeochemistry* (Nedra, Moscow, 1992) [in Russian].
20. G. Matthes, F. H. Frimmel, P. Hursch, et al., *Progress in Hydrogeochemistry* (Springer, Berlin, 1992).
21. V. A. Kiryukhin, A. I. Korotkov, and S. L. Shvartsev, *Hydrogeochemistry* (Nedra, Moscow, 1993) [in Russian].
22. C. A. J. Appelo and D. Postma, *Geochemistry, Groundwater and Pollution* (Balkema, Rotterdam, 1994).
23. S. L. Shvartsev, *General Hydrogeology* (Nedra, Moscow, 1996) [in Russian].
24. W. J. Deutsch, *Groundwater Geochemistry. Fundamentals and Applications to Contamination* (Lewis, Boca Raton, 1997).
25. P. F. Hudak, *Principles of Hydrogeology*, 2nd ed. (Lewis, Boca Raton, 1999).
26. E. V. Pinneker, *Ecological Problems of Hydrogeology* (Nauka, Novosibirsk, 1999) [in Russian].
27. I. S. Zektser and L. G. Everett, *Groundwater and the Environment. Applications for the Global Community* (Lewis, Boca Raton, 2000).
28. J. H. Montgomery, *Ground Water Chemicals. Desk Reference*, 3rd ed. (Lewis, Boca Raton, 2000).
29. S. L. Shvartsev, *Hydrogeochemistry of the Supergene Zone*, 2nd ed. (Nedra, Moscow, 1998) [in Russian].

30. R. F. Black, "Permafrost," *Bull. Geol. Soc. Am.* **85**, 839–855 (1954).
31. E. D. Ershov, *General Geocryology* (Nedra, Moscow, 1990) [in Russian].
32. A. E. Kontorovich, M. A. Sadikov, and S. L. Shvartsev, "Distribution of Some Chemical Elements in the Surface and Ground Waters of the Northwestern Siberian Platform," *Dokl. Akad. Nauk SSSR* **149**, 179–181 (1963).
33. S. L. Shvartsev, "Some Results of Hydrogeochemical Studies under Permafrost Conditions," *Geol. Rudn. Mestorozhd.*, No. 2, 100–110 (1963).
34. S. L. Shvartsev, "On the Hydrogeochemical Prospecting Method in Northern Wetlands," *Geol. Geofiz.*, No. 11, 69–74 (1973).
35. S. L. Shvartsev and N. G. Shubenin, "Character of the Formation of Trace Element Composition in the Groundwaters of the Cryogenic Zone: Evidence from the Western Siberian Platform," *Geol. Geofiz.*, No. 11, 69–74 (1973).
36. M. E. Korolev, *Trace Element Distribution in the Natural Waters of the Yenisei Range* (Kazanskii Univ., Kazan, 1973) [in Russian].
37. P. A. Udodov, I. P. Onufrienok, and Yu. O. Parilov, *Experience of Hydrogeochemical Studies in Siberia* (Vysshaya shkola, Moscow, 1962) [in Russian].
38. Yu. D. Pogrebnyak, *Gold in the Natural Waters of Transbaikalia* (Nauka, Moscow, 1983) [in Russian].
39. Yu. D. Pogrebnyak and V. V. Tolochko, *Hydrogeochemical Prospecting of Ore Deposits in Transbaikalia* (Nauka, Novosibirsk, 1985) [in Russian].
40. L. V. Zamana and N. M. Gladkaya, "Geochemical Features of Natural Waters from the Urov Biogeochemical Region," *Geokhimiya*, No. 2, 269–280 (1993).
41. V. K. Kashin and G. M. Ivanov, "Nickel in Natural Waters of Transbaikalia," *Vodn. Resur.*, No. 3, 311–314 [*Water Resour.* **24**, 285–288 (1997)]
42. M. N. Kosolapova, "Trace Components in the Natural Waters of the Olenek River Basin," in *Geochemical Studies of Gold and Trace Elements in Yakutia* (Akad. Nauk SSSR, 1963), pp. 56–74 [in Russian].
43. V. I. Kuznetsov, "Geochemical Characteristics of the Upper Arman Area on the Basis of Hydrogeochemical Sampling," *Geokhimiya*, No. 9, 1137–1143 (1969).
44. N. P. Anisimova, *Formation of the Chemical Composition of Groundwaters of Taliks Exemplified by Central Yakutia* (Nauka, Moscow, 1971) [in Russian].
45. V. P. Volkova, "Chemical Composition of the Natural Waters of the Mirny Region of the Yakutian ASSR," *Merzlotnye Issled.*, No. 11, 152–160 (1971).
46. N. I. Chizhova, "Geochemistry of the Natural Waters of the Yana–Omoloi Interfluve," *Merzlotnye Issled.*, No. 14, 109–115 (1971).
47. I. B. Nikitina, *Geochemistry of Ultrafresh Waters of Permafrost Terrains* (Nauka, Moscow, 1977) [in Russian].
48. L. G. Filimonova, *Fluorine Geochemistry in the Supergene Zone of Permafrost Areas* (Nauka, Moscow, 1977) [in Russian].
49. V. N. Makarov, V. I. Fedoseeva, and N. F. Fedoseev, *Geochemistry of the Yakutian Snow Cover* (Yakutsk, 1990) [in Russian].
50. E. W. Lohr, "Chemical Character of Public Water Supplies of the Larger Cities of Alaska, Hawaii and Puerto Rico," U.S. Geol. Surv. Water-Supply Pap., No. 1460-A (1957).
51. R. W. Boyle, E. L. Pekar, and P. R. Patterson, "Geochemical Investigation of Heavy Metal Content of Streams and Springs in the Galena Hill-Mount Haldane Area, Yukon Territory," *Geol. Surv. Can. Bull.* **36**, 34 (1956).
52. R. W. Boyle and J. Tupper, *Geochemistry of Pb, Zn, Cu, As, Sb, Mo, Sn, W, Ag, Ni, Co, Cr, Ba and Mn in the Waters and Stream Sediments of the Bathurst Jacquet River District, New Brunswick* (Ottawa, 1966).
53. A. Rozkowski, "Chemistry of Ground Water and Surface Water in the Moose Mountain Area, Southern Saskatchewan," *Geol. Surv. Can. Pap.*, No. 67-9, 37–45 (1969).
54. R. J. Allan and E. H. W. Hornbrook, "Exploration Geochemistry. Evaluation Study in a Region of Continuous Permafrost, Northwest Territories, Canada," *Can. Inst. Min. Metal. Spec. Vol.* **11**, 53–66 (1971).
55. R. J. Allan, E. M. Cameron, and C. C. Durham, "Lake Geochemistry—a Low Sample Density Technique for Reconnaissance Geochemical Exploration and Mapping of the Canada Shield," in *Proceedings of 4th Int. Geochem. Expl. Symp., London, 1972* (London, 1972), pp. 131–160.
56. W. Dyck, A. K. Chatterjee, D. E. Gemmel, and K. Murrice, "Well Water Trace Element Reconnaissance, Eastern Maritime, Canada," *Geochem. Explor.* **6**, 139–162 (1976).
57. J. C. Méranger, K. S. Subramanian, and Ch. Chalifaux, "Survey for Cadmium, Cobalt, Chromium, Copper, Nickel, Lead, Zinc, Calcium and Magnesium in Canadian Drinking Water Supplies," *J. Assoc. Anal. Chem.* **64**, 44–53 (1981).
58. A. A. Antonov, "On the Chemical Composition of Waters from the Khibina Alkaline Massif," *Byull. Mosk. O-va Ispyt. Prir. Otd. Geol.* **39** (2), 104–113 (1964).
59. C. Reimann, D. Banks, I. Bogatyrev, et al., "Lake Water Geochemistry on the Western Kola Peninsula, North-West Russia," *Appl. Geochem.* **14**, 787–805 (1999).
60. T. T. Taisaev, *Geochemistry of Taiga–Permafrost Landscapes and Prospecting of Ore Deposits* (Nauka, Novosibirsk, 1981) [in Russian].
61. N. P. Anisimova, *Cryogeochemical Features of the Frozen Zone* (Nauka, Novosibirsk, 1981) [in Russian].
62. S. V. Alekseev, *Cryogenesis of Groundwaters and Rocks* (Sib. Otd. Ross. Akad. Nauk, Novosibirsk, 2000) [in Russian].
63. A. I. Perel'man and N. S. Kasimov, *Landscape Geochemistry*, 3rd ed. (Astreya, Moscow, 1999) [in Russian].
64. L. E. Rodin and N. I. Bazilevich, *Dynamics of Organic Matter and Biological Cycle in the Main Types of Vegetation* (Nauka, Moscow, 1965) [in Russian].

65. S. L. Shvartsev, "Chemical Composition of the Groundwaters of Tropical Countries as Exemplified by Guinea," *Geokhimiya*, No. 1, 100–109 (1972).
66. G. Roug rie, *Le faonnement actuel des mod les en Cote d'Ivoire forestiere. Memoires d'Afrique noire* (Ifan, Dakar, 1960).
67. D. Orange and J. Y. Gac, "Reconnaissance g ochimique des eaux du Fouta Djallon (Guinee). Flux de mati res dissoutes et en suspension en Haute-Gambia," *Geodyn.* **5**, 35–49 (1990).
68. Y. Tardy, *G ochimie des alt rations.  tudes des ar nes et des eaux de quelques massifs cristallins d'Europe et d'Afrique* (Strasbourg, 1969).
69. I. M. Wackermann, "Corr lations g ochimiques entre eaux phr atiques et niveaux aquif res dans les manteaux d'alt ration du S n gal oriental," *Cah. ORSTROM Ser. Geol.* **4**, 77–89 (1972).
70. I. W. du Preez and W. Barber, *The Distribution and Chemical Quality of Ground-Water in Northern Nigeria* (Lagos, 1965).
71. K. B. Pelig-Ba, "Trace Elements in Groundwater from Some Crystalline Rocks in the Upper Regions of Ghana," *Water, Air, Soil Pollut.* **103**, 71–89 (1998).
72. Yu. Yu. Bugel'skii and F. Formel-Kortina, "Hydrogeochemical Regularities of the Formation of Laterite Weathering Mantles in Cuba," in *Weathering Mantles and Bauxite Deposits* (Moscow, 1973), pp. 199–217 [in Russian].
73. Yu. Yu. Bugel'skii, *Ore-Bearing Weathering Mantles of Humid Tropics* (Nauka, Moscow, 1979) [in Russian].
74. G. Weninger, "Beitr ge zum Chemismus der Gew sser von Neukaledonien (SW-Pazifik)," *Cah. ORSTOM Ser. Hydrobiol.* **2**, 35–55 (1968).
75. I. I. Trescases, "G ochimie des alt rations et des eaux de surface dans le massif ultrabasique du sud de la Nouvelle Cal donie," *Bull. Sew. Carte G ol. Alsace Lorraine* **22** (4), 329–354 (1969).
76. V. M. Fridland, *Soils and Weathering Residues of Humid Tropics: Evidence from North Vietnam* (Nauka, Moscow, 1964) [in Russian].
77. S. H. Patterson and C. E. Robertson, "Weathered Basalt in the Eastern Part of Kauai, Hawaii," *U.S. Geol. Surv. Prof. Pap.*, No. 424-C, 195–198 (1961).
78. S. H. Patterson, "Investigations of Ferruginous Bauxite and Other Mineral Resources on Kauai and a Reconnaissance of Ferruginous Bauxite Deposits on Maui, Hawaii," *U.S. Geol. Surv. Prof. Pap.* **656** (1971).
79. R. L. Hay and B. F. Jones, "Weathering of Basaltic Tephra on the Island of Hawaii," *Geol. Soc. Am. Bull.* **83** (2), 317–332 (1972).
80. J. Boul que, M. F. Benedetti, and P. Bildger, "Geochemistry of Water Associated with Current Karst Bauxite Formation, Southern Peninsula of Haiti," *Appl. Geochem.* **4**, 37–47 (1989).
81. R. Scotte and F. Barker, *Data on Uranium and Radium in Ground Water in the United States, 1954 to 1957* (Washington, 1962).
82. M. W. Skougstad and C. A. Horr, "Occurrence and Distribution of Strontium in Natural Water," *U.S. Geol. Surv. Water-Supply Pap.*, No. 1496-D (1963).
83. D. E. White, I. D. Hem, and G. A. Waring, "Chemical Composition of Subsurface Waters," *U.S. Geol. Surv. Prof. Pap.*, No. 440 (1963).
84. S. N. Davis, "Silica in Streams and Ground Water," *Am. J. Sci.* **262**, 870–881 (1964).
85. J. J. Geraghty, D. W. Miller, F. van der Leeden, and F. L. Troise, *Water Atlas of the United States* (Water Information Center, Washington, 1973).
86. W. D. Silvey, "Occurrence of Selected Minor Elements in the Waters of California," *U.S. Geol. Surv. Water-Supply Pap.*, No. 1535-L (1967).
87. K. S. Johnson, P. M. Stout, W. M. Berelson, et al., "Cobalt and Copper Distributions in the Waters of Santa Monica Basin, California," *Nature*, No. 6164, 527–530 (1988).
88. M. Benedetti, O. Menard, Y. Noack, et al., "Water–Rock Interactions in Tropical Catchments: Field Rates of Weathering and Biomass Impact," *Chem. Geol.* **118**, (1–4), 203–220 (1994).
89. G. I. Bushinskii, *Geology of Bauxites* (Nedra, Moscow, 1971) [in Russian].
90. V. G. Hill and A. C. Ellington, "Chemical Characteristics of the Ground Water Resources of Jamaica," *Econ. Geol.* **56** (3), 533–542 (1961).
91. I. B. Mullor, L. O. de Bielsa, I. B. Vigil, and B. L. de Abramovich, "Estudio yodofluorhidrologicode la provincia de Santa-Fe," *Rev. Fac. Ing. Quim. Univ. Nac. Litorel.* **40–41**, 217–233 (1973).
92. E. A. Lisitsina and M. A. Glagoleva, "On the Geochemistry of Weathering Residues after Mafic Rocks in the Batumi Shore, Caucasus," in *Weathering Residues* (Moscow, 1968) [in Russian].
93. M. Ishikawa and N. Tase, "Geochemistry of Waters in Northeastern Brazil," *Ann. Rept. Inst. Geosci. Univ. Tsukuba*, No. 6, 38–40 (1979).
94. A. Virmond and L. Bittencourt, "Aspecto hidrogeomiquicos da alteracao intemperica de basaltos da basia do Parana: Basia hidrografica do Jacutinda," *Rev. Brasil. Geocienc.* **10** (3), 202–212 (1980).
95. W. O. Andrade, M. L. Machesky, and A. W. Rose, "Gold Distribution and Mobility in the Surficial Environment, Carajas Region, Brazil," *Geochem. Explor.* **40** (1–3), 95–114 (1991).
96. A. M. Korotkii, N. G. Razzhigaeva, L. A. Ganzei, and V. G. Volkov, *Islands of the Vietnam Shelf. Relief, Sediments, and Evolution* (Nauka, Moscow, 1993) [in Russian].
97. V. S. Savenko and E. A. Zakharova, "Phosphorus in the Water of the Primary Hydrographic Network," *Vodn. Resur.*, No. 3, 292–299 (1997) [*Water Resour.* **24**, 266–273 (1997)].
98. J. A. Lenheer, R. L. Malcolm, P. W. Mckinley, and L. A. Eccles, "Occurrence of Dissolved Organic Carbon in Selected Ground Water Samples in the United States," *J. Res. U.S. Geol. Surv.* **2**, 361–369 (1974).
99. N. A. Roslyakov, V. P. Kovalev, F. V. Sukhorukov, et al., *Ecogeochemistry of Western Siberia* (SO RAN, Novosibirsk, 1996) [in Russian].
100. *Scientific Prerequisites for the Development of Swamps in Western Siberia*, Ed. by M. I. Neishtadt (Nauka, Moscow, 1977) [in Russian].



101. P. A. Udodov, P. N. Parshin, B. M. Levashov, et al., *Hydrogeochemical Studies of the Kolyvan–Tom Fold Zone* (Tomsk. Gos. Univ., Tomsk, 1971) [in Russian].
102. G. M. Rogov and V. K. Popov, *Hydrogeology and Catagenesis of the Rocks of the Kuznetsk Basin* (Tomsk. Gos. Univ., Tomsk, 1985) [in Russian].
103. Yu. G. Pokatilov, *Element Biogeochemistry and Noseography of Southern Middle Siberia* (Nauka, Novosibirsk, 1992) [in Russian].
104. Yu. G. Kopylova, E. M. Dutova, and T. I. Romanova, “Ecological–Geochemical State of the Groundwaters of Mountain Taiga Landscapes of the Salair,” *Obskoi Vestn.*, Nos. 3–4, 100–104 (1999).
105. Yu. G. Kopylova, T. I. Romanova, I. V. Smetanina, and A. A. Khvashchevskaya, “Conditions of the Formation of Fluorine-Bearing Waters in the Main Landscape Zones of Southeastern Western Siberia,” *Obskoi Vestn.*, No. 1, 6–12 (2001).
106. N. M. Rasskazov, S. L. Shvartsev, N. A. Trifonova, and N. G. Nalivaiko, “Nonvolatile Organic Matter and Microorganisms in the Groundwaters of the Krapivin Water Reservoir Area of the Tom’ River (Kuznetsk Basin),” *Geol. Geofiz.*, No. 4, 30–36 (1995).
107. S. L. Shvartsev, N. M. Rasskazov, V. S. Kuskovskii, and L. F. Frizen, “Hydrogeochemical Setting of the Krapivin Water Reservoir Area of the Tom River (Kuznetsk Basin),” *Geol. Geofiz.*, No. 8, 89–97 (1993).
108. N. M. Rasskazov and O. G. Savichev, “Hydrogeochemical Conditions of Southeastern Western Siberia Exemplified by the Tom’ River Basin,” *Geoekologiya*, No. 4, 314–320 (1999).
109. L. I. Inisheva and N. G. Inishev, “Elements of Water Balance and Hydrochemical Characteristic of Oligotrophic Bogs in the Southern Taiga Subzone of Western Siberia,” *Vodn. Resur.*, No. 4, 410–417 (2001) [*Water Res.* **28**, 371–377 (2001)].
110. N. A. Ermashova, “Natural Hydrogeochemical Background of the Upper Hydrodynamic Zone of the Middle Ob Region as a Basis for Estimating Its Ecological State,” *Obskoi Vestn.*, Nos. 3–4, 106–112 (1999).
111. V. A. Zuev, O. V. Kartavykh, and S. L. Shvartsev, “Chemical Composition of Groundwaters from the Tomsk Water Supply System,” *Obskoi Vestn.*, Nos. 3–4, 69–77 (1999).
112. E. M. Dutova and D. S. Pokrovskii, “Chemical Composition and Quality of Groundwaters of Economic and Potable Use in Khakassia,” *Obskoi Vestn.*, Nos. 3–4, 103–113 (1999).
113. V. P. Parnachev, I. I. Vishnevetskii, N. A. Makarenko, et al., *Water Resources of the Shirin Area of Khakassia* (Tomsk. Gos. Univ., Tomsk, 1999) [in Russian].
114. V. P. Parnachev, D. Banks, and A. Y. Berezovsky, “Hydrochemical Evolution of Na–SO<sub>4</sub>–Cl Groundwaters in a Cold, Semiarid Region of Southern Siberia,” *Hydrogeol. J.*, No. 6, 546–560 (1999).
115. S. L. Shvartsev, N. M. Rasskazov, T. N. Sidorenko, and M. A. Zdvizhkov, “Geochemistry of Natural Waters of the Bol’shoi Vasyugan Swamp,” in *Bol’shoi Vasyugan Swamp: Modern State and Evolution* (Inst. Optiki Atmosf., Tomsk, 2002), pp. 139–149 [in Russian].
116. P. Lahermo, “Chemical Geology of Ground and Surface Waters in Finish Lapland,” *Bull. Comm. Geol. Finlande* **242** (1970).
117. P. Lahermo, “Hydrogeochemistry and Sensitivity Acidification of Stream Waters in Crystalline Areas of Northern Fennoscandia,” *Environ. Geol. Water Sci.* **18** (1), 57–69 (1991).
118. P. Lahermo, H. Sadstrom, and E. Malisa, “The Occurrence and Geochemistry of Fluorides in Natural Waters in Finland and East Africa with Reference to Their Geo-medical Implications,” *J. Geochem. Explor.* **41**, 65–79 (1991).
119. P. Lahermo, J. Mannio, and T. Tarvainen, “The Hydrogeochemical Comparison of Streams and Lakes in Finland,” *Appl. Geochem.* **10** (1), 45–64 (1995).
120. M. Aström and A. Björklund, “Hydrogeochemistry of a Stream Draining Sulfide-Bearing Postglacial Sediments in Finland,” *Water, Air, Soil Pollut.*, Nos. 3–4, 233–246 (1996).
121. B. Backman and P. Lahermo, “Ground Water Monitoring in the Geological Survey of Finland,” in *Hydrogeology and Land Management* (Bratislava, 1999), pp. 329–333.
122. O. Landström and C. G. Wener, “Neutron Activation Analysis of Water Applied to Hydrogeology,” *Altieb. Atomen* **AE-204** (1965).
123. T. P. Flaten, “Chemical Composition of Norwegian Drinking Water,” in *Proceedings of Int. Symp. Geol. Map. Serv. Environ. Plann., Trondheim, Norway, 1986* (Trondheim, 1986), pp. 86–95.
124. P. Jorgensen, A. O. Stuanes, and S. R. Ostmo, “Aqueous Geochemistry of the Romerike Area, Southern Norway,” *Bull. Norw. Geol. Unders.*, No. 420, 47–71 (1991).
125. M. Aastrup, J. Johnson, E. Bringmark, et al., “Occurrence and Transport of Mercury within a Small Catchment Area,” *Water, Air, Soil Pollut. Spec. Vol.* **56**, 155–167 (1991).
126. A. I. Klimas, “Trace Elements in the Fresh Groundwaters of Lithuania,” *Geokhimiya*, No. 3, 367–375 (1988).
127. B. Adamzyk, K. Oleksynowa, A. Miechwka, and F. Zimny, “Chemizm wod gruntowych w glebach Puszczy Niepolomickiej,” *Stud. Osr. Dok. Fizjogr.* **12**, 197–222 (1984).
128. H. Marszalek, “Groundwater Chemistry of Fractured Crystalline Rocks in Kamienna Watershed (Western Sudetes, SW Poland),” *Acta Univ. Carolinae Geolog.* **40**, 233–246 (1996).
129. T. Scheytt, “Seasonal Variations in Ground-Water Chemistry near Lake Belau, Schleswig-Holstein, Northern Germany,” *Hydrol. J.* **5** (2), 86–95 (1997).
130. A. Fruchart and M. Pinta, “Présence géochimique du lithium dans les eaux souterraines du bassin Parisienne,” *Comp. Rend., Ser. D* **281**, 93–96 (1975).
131. M. Benedetti, “Géochimie de l’or: Mecanismes de transport et de dépôt,” *Sci. Géol. Mét.*, No. 91 (1991).
132. T. Pačes, “Chemical Characteristics and Equilibration in Natural Water–Felsic Rock–CO<sub>2</sub> System,” *Geochim. Cosmochim. Acta* **36** (2), 217–240 (1972).



133. V. Zýka, "Průměrné chemické složení povrchových a spodních (sladkých) vod," Sbor. Ved. TG **10**, 69–90 (1972).
134. V. Zýka, "Stopové prvky (Pb, Cu, Zn, Cd, As) v pitných vodách CSR," Geol. Pruzk., **30** (6), 162–167 (1988).
135. V. Zýka, "Kvalita studničných vod ve východní časti Stredoëského Kraja," Geol. **31** (4), 109–115 (1989).
136. S. Rapant, "Geochemia prirodnych vod kryštalinika Nizkych Tatier," Zap. Karpaty, Ser. Hydrogeol. A Inz. Geol. **12**, 177–219 (1994).
137. S. Barnes and R. H. Wordon, "Understanding Groundwater Sources and Movement Using Water Chemistry and Traces in a Low Matrix Permeability Terrain: The Cretaceous (Chalk) Ulster White Limestone Formation, Northern Ireland," Appl. Geochem. **13**, 143–153 (1998).
138. W. M. Edmunds and R. M. Kay, "Hydrogeochemistry as an Aid to Geological Interpretation: The Glen Roy Area, Scotland," J. Geol. Soc. **153**, 839–852 (1996).
139. D. Banks, C. Reimann, and S. Skarphagen, "The Comparative Hydrogeochemistry of Two Granitic Island Aquifers: The Islands of Scilly, UK and the Hvaler Islands, Norway," Sci. Total Environ. **209**, 169–183 (1998).
140. G. V. Bogomolov, G. N. Plotnikova, and E. A. Titova, *Silica in Thermal and Cold Waters* (Nauka i Tekhnika, Minsk, 1967) [in Russian].
141. L. G. Babii, *Silica in the Waters from the Active Water Exchange Zones of Belorussia* (Nauka i Tekhnika, Minsk, 1985) [in Russian].
142. V. A. Kovalev and A. L. Zhukhovitskaya, *Phosphorous in Wetland Environments* (Nauka i Tekhnika, Minsk, 1976) [in Russian].
143. S. G. Komrakova and K. I. Lukashev, *Iodine in the Natural Waters and Soils of Belorussian Poozerie* (Nauka i Tekhnika, Minsk, 1985) [in Russian].
144. A. V. Kudel'skii, *Hydrogeology and Hydrogeochemistry of Iodine* (Nauka i Tekhnika, Minsk, 1976) [in Russian].
145. U. Zivers, A. V. Kudel'skii, V. K. Lukashev, et al., "Trace Elements in the Surface and Ground Waters of Central and Southeastern Belorussia," Vestsi Akad. Nauk Belarusi, Ser. Khim. Nauk, No. 2, 80–87 (1996).
146. D. L. Parkhurst, S. Christenson, and G. N. Breit, "Groundwater Quality Assessment of the Central Oklahoma Aquifer, Oklahoma. Geochemical and Geohydrologic Investigation," U.S. Geol. Surv. Water-Supply Pap., No. 2357 (1996).
147. J. M. Thomas, A. H. Welch, and M. D. Dettinger, "Geochemistry and Isotope Hydrology of Representative Aquifers in the Great Basin Region of Nevada, Utah, and Adjacent States," U.S. Geol. Surv. Prof. Pap., No. 1409 (1996).
148. S. V. Panno, I. G. Krapac, C. P. Weibel, and J. D. Bade, "Groundwater Contamination in Karst Terrain of Southwestern Illinois," Environ. Geol., No. 151 (1996).
149. G. R. Davidson, R. L. Bassett, E. L. Hardin, and D. L. Thompson, "Geochemical Evidence of Preferential Flow of Water through Fractures in Unsaturated Tuff, Apache Leap, Arizona," Appl. Geochem. **13**, 185–195 (1998).
150. A. E. Fryar, W. F. I. Mullican, and S. A. Macko, "Groundwater Recharge and Chemical Evolution in the Southern High Plains of Texas, USA," Hydrogeol. J., No. 6, 522–542 (2001).
151. K. M. Davletgalieva, *Geochemistry of the Southern Urals, Karatau, and Chu-Ili Ore Belts* (Nauka, Alma-Ata, 1987) [in Russian].
152. M. S. Panin and V. G. Kozintsev, "Lead in the Groundwaters of the Middle Zone of Eastern Kazakhstan," Gidrokhim. Mater. **104**, 180–186 (1988).
153. V. N. Efimov and Z. S. Efimova, "Chemical Composition of Swamp Waters in the North European Part of the Country," Pochvovedenie **11**, 7–36 (1973).
154. P. V. Elpat'evskii, *Geochemistry of Migration Flows in Natural and Natural-Anthropogenic Geosystems* (Nauka, Moscow, 1993) [in Russian].
155. V. P. Zverev, *Hydrogeochemistry of the Sedimentary Process* (Nauka, Moscow, 1993) [in Russian].
156. I. L. Kalyuzhnyi and L. Ya. Levandovskaya, "Hydrochemical Regime and Chemical Composition of Waters from Oligotrophic Swamp Massifs," in *Problems of Wetland Hydrogeology* (Leningrad, 1974), pp. 9–118 [in Russian].
157. A. K. Lisitsyn, *Hydrogeochemistry of Ore Formation* (Nedra, Moscow, 1975) [in Russian].
158. G. A. Maksimovich, *Chemical Geography of Land Waters* (Geografizdat, Moscow, 1955) [in Russian].
159. E. V. Posokhov, *Formation of the Chemical Composition of Groundwaters* (Gidrometeoizdat, Leningrad, 1969) [in Russian].
160. A. M. Chernyaev, L. E. Chernyaeva, and V. N. Babchenko, *Hydrochemistry of Minor, Trace, and Scattered Elements (Southern Urals, Transurals, and Northern Kazakhstan)* (Gidrometeoizdat, Leningrad, 1970) [in Russian].
161. V. A. Chudaeva, *Migration of Chemical Elements in Waters of the Far East* (Dal'nauka, Vladivostok, 2002) [in Russian].
162. V. I. Baranov, N. G. Morozova, T. G. Akimova, and A. V. Orlova, "Natural Radioelements in Surface and Soil-Ground Waters," Geokhimiya, No. 3, 334–341 (1968).
163. A. I. Germanov, "Uranium in Natural Waters," in *Main Features of Uranium Geochemistry* (Moscow, 1963), pp. 290–336 [in Russian].
164. I. I. Ginzburg and E. S. Kabanova, "Silica Content and Speciation in Natural Waters," in *Weathering Residues* (Moscow, 1960), No. 3, pp. 313–342 [in Russian].
165. V. V. Dobrovol'skii, *Trace Element Geography. Global Dispersion* (Mysl', Moscow, 1983) [in Russian].
166. V. P. Zakutin and V. A. Shcheka, "Selenium in Low-Salinity Groundwaters," Dokl. Akad. Nauk SSSR **289** (2), 489–493 (1986).
167. I. S. Lomonosov, A. E. Gapon, S. N. Dmitriev, et al., "Efficiency of the Hydrogeochemical Method of Gold Prospecting," Sov. Geol., No. 8, 86–93 (1986).
168. B. F. Mitskevich, Yu. Ya. Sushchik, and A. I. Samchuk, *Physicochemical Conditions of Exogenic Haloes and Beryllium Dispersion Fluxes* (Naukova dumka, Kiev, 1984) [in Russian].
169. P. V. Ostapenya, Ts. A. Kagan, and E. A. Gel'fer, "On the Problem of the Contents of Fluorine, Bromine,

- Iodine, and Copper in the Natural Waters of the Polesie Lowland," *Gidrokhim. Mater.* **28**, 76–82 (1959).
170. G. D. Supatashvili, T. A. Kikabidze, and G. A. Makhharadze, "Study of Aluminum Distribution and Speciation in Natural Waters," *Tr. Tbil. Univ.* **287**, 71–79 (1989).
171. N. M. Shvartseva, "Antimony in the Groundwaters of the Kadamzhan Deposit," *Dokl. Akad. Nauk SSSR* **207**, 1220–1222 (1972).
172. V. M. Shvets, *Organic Matter of Groundwaters* (Nedra, Moscow, 1973) [in Russian].
173. S. Bloch, Ch. D. Gay, and D. E. Dunbar, "Uranium, Chromium, and Selenium Concentrations in Water from Garberwellington Aquifer (Permian), Central Oklahoma," *Oklah. Geol. Notes* **41** (3), 72–80 (1981).
174. J. E. Brasaembl and R. G. Corbett, "Fluoride in Ground Water," *Soc. Sci. Med.* **D14** (1), 55–61 (1980).
175. L. Capitani and F. Rodeghiero, "Fluoride Distribution in Spring Waters and Soils from Southalpine Crystalline Basement (Valpompia, Northern Italy)," *Mem. Sci. Geol.* **42**, 212–228 (1990).
176. M. Dall'Aglio, E. Ghiara, and W. Proetti, "New Data on the Hydrogeochemistry of Selenium," *Rend. Soc. Ital. Miner. Petrol.*, No. 2, 591–604 (1978).
177. E. Driesher and J. Gelbrecht, "Phosphat im unterirdischen Wasser. 1. Mitteilung zum vorkommen von Phosphat im Grundwasser—eine Literatubersicht," *Acta Hydrophys.* **32** (4), 213–235 (1988).
178. E. Erriksson and V. Khunakasem, "The Chemistry of Ground Water," in *Ground Water Problems* (Pergamon, Oxford, 1968), pp. 110–146.
179. M. J. Fishman and J. D. Hem, "Lead Content of Water," *Geol. Surv. Prof. Pap.*, No. 957, 35–41 (1976).
180. M. Fleischer, "Fluoride Content of Ground Water in the Conterminous United States," *Geol. Soc. Am. Spec. Pap.* **65** (1968).
181. S. R. Gislason and S. Arnorsson, "Saturation State of Natural Waters in Iceland Relative to Primary and Secondary Minerals in Basalts," *Fluid Miner. Intarct. Spec. Publ.* **2**, 373–393 (1990).
182. R. Herrman and K. Pecher, "Behaviour of Aluminium Species within the Hydrological Cycle," *Aqua* **41**, 169–180 (1992).
183. Y. Kitano, R. Yoshioka, S. Okuda, and K. Okunishi, "Geochemical Study of Ground Waters in the Matsushiro Area, Pt I," *Bull. Disaster Prev. Res. Inst.*, No. 2, 47–71 (1967).
184. D. P. H. Laxen, W. Davidson, and C. Woof, "Manganese Chemistry in Rivers and Streams," *Geochim. Cosmochim. Acta* **48**, 2107–2111 (1984).
185. *Trace Elements in Natural Waters*, Ed. by B. Salbu and E. Steinnes (CRS Press, Boca Raton, 1995).
186. R. F. Spalding, A. D. Druliner, L. S. Whiteside, and W. Struemler, "Uranium Geochemistry in Groundwater from Tertiary Sediments," *Geochim. Cosmochim. Acta* **48** (12), 2679–2692 (1984).
187. G. Stamatis, "Chemismus der Quellwasser der Halbinsel Athos (Aghion Oros, Nord-Griechenland)," *Z. Deutsch. Geol. Ges.* **142** (2), 283–299 (1996).
188. C. Reimann and P. de Caritat, *Chemical Elements in the Environment* (Springer, Berlin, 1998).
189. S. L. Shvartsev, "Chemical Element Clarkes of Hypergenic Zone" in *Development of Deep Aquifers and Problems of Drinking Water Treatment* (Vilnius, 1998), pp. 73–74.
190. J. Diliunas and A. Jurevicius, *Iron in Fresh Groundwater of Lithuania* (Vilnius, 1998).
191. N. P. Akhmet'eva and E. E. Lapina, "Variations in the Chemical Composition of Groundwater of the Ivan'kovskoe Reservoir Protection Zone," *Vodn. Resur.* No. 2, 169–173 [*Water Resour.* **24**, 148–152 (1997)].
192. J. Rozkowski, "The Reasons of the Upper Jurassic Aquifer Potable Water Quality Worsening in the Cracow-Czestochowa Upland (Poland)," in *Development of Deep Aquifers and Problems of Drinking Water Treatment* (Vilnius, 1998), pp. 66–69.
193. R. S. Harmon, W. B. White, J. J. Drake, and J. W. Hess, "Regional Hydrochemistry of North American Carbonate Terrains," *Water Resour. Res.* **11** (6), 963–967 (1975).
194. B. A. Vorotnikov, *Dispersion Water Flows of Sulfide Mineralization of the Altai and Their Prospecting Significance* (Nedra, Moscow, 1974) [in Russian].
195. N. A. Roslyakov, V. S. Kuskovskii, G. V. Nesterenko, et al., *Katun': Mercury Ecogeochemistry* (Novosibirsk, 1992) [in Russian].
196. S. L. Shvartsev, A. A. Lukin, V. S. Kuskovskii, et al., "Geochemical Conditions of Mercury Migration in the Groundwaters of the Project Area of the Katun' Hydroelectric Station," *Vodn. Resur.* **22**, 50–59 (1995).
197. Yu. G. Kopylova, E. I. Bol'shakov, A. I. Nevol'ko, et al., "Experience in the Application of the Hydrogeochemical Method during Mineral Prospecting in the Northwestern Salair," in *Hydrogeochemical Prospecting of Mineral Deposits* (Nauka, Novosibirsk, 1990) [in Russian], pp. 55–77.
198. S. L. Shvartsev and O. G. Savichev, "Basic Sites of Hydrogeochemical Observations—A New Methodological Basis for the Solution of Aqueous Ecological Problems: Evidence from the Upper and Middle Ob Basin," *Obskoi Vestn.*, Nos. 3–4, 27–32 (1999).
199. Yu. G. Kopylova, I. V. Smetanina, and V. M. Maruleva, "Ecological State of the Natural Waters of the Kommunar-Balakhchin Ore Zone," *Obskoi Vestn.*, Nos. 3–4, 42–47 (1999).
200. S. L. Shvartsev, Yu. S. Kolmakov, and O. G. Savichev, "Basic Sites of Hydrogeochemical Observations in the Upper Ob Basin in 1998," *Obskoi Vestn.*, No. 1, 2–5 (2001).
201. S. L. Shvartsev and E. M. Dutova, "Hydrochemistry and Mobilization of Gold in the Hypergenesis Zone (Kuznetsk Alatau, Russia)," *Geol. Rudn. Mestorozhd.*, No. 3, 252–261 (2001) [*Geol. Ore Dep.* **43**, 224–233 (2001)].
202. I. H. Feth, C. E. Roberson, and W. L. Plozer, "Sources of Mineral Constituents in Water from Granitic Rocks, Sierra Nevada," *U.S. Geol. Surv. Water-Supply Pap.*, No. 1534 (1964).
203. I. P. Miller, "Solutes in Small Streams Draining Single Rock Types, Sangre de Cristo Range, New Mexico," *U.S. Geol. Water-Supply Pap.*, No. 1535 (1961).
204. H. E. Legrand, "Chemical Character of Water in the Igneous and Metamorphic Rocks of North Carolina," *Econ. Geol.* **53**, 178–189 (1958).

205. D. Banks, B. Frengstad, A. K. Midtgard, et al., "The Chemistry of Norwegian Groundwaters: I. The Distribution of Radon, Major and Minor Elements in 1604 Crystalline Bedrock Groundwaters," *Sci. Total Environ.* **222**, 71–91 (1998).
206. D. Banks, G. Hall, C. Reimann, and U. Siewers, "Distribution of Rare Elements in Crystalline Bedrock Groundwaters: Oslo and Bergen Regions, Norway" *Appl. Geochem.* **14**, 27–39 (1999).
207. B. Frendstad, A. K. M. Skrede, D. Banks, et al., "The Chemistry of Norwegian Groundwaters: III. The Distribution of Trace Elements in 476 Crystalline Bedrock Groundwaters, as Analysed by ICP-MS Technique," *Sci. Total Environ.* **246**, 21–40 (2000).
208. G. A. Vostroknutov, "On the Geochemistry of Natural Waters from the Greenstone Zones of the Middle Urals," *Razved. Okhr. Nedr.*, No. 10, 41–48 (1962).
209. Yu. Ya. Sushchik and V. I. Marus, "Geochemical Features of Natural Waters from the Ukrainian Carpathians," in *Geological Problems of Sedimentary Sequences of Ukraine* (Naukova Dumka, Kiev, 1972), pp. 180–189 [in Russian].
210. G. A. Goleva, *Hydrogeochemical Prospecting of Hidden Mineralization* (Nedra, Moscow, 1968) [in Russian].
211. S. R. Krainov, *Geochemistry of Trace Elements in Groundwaters* (Nedra, Moscow, 1973) [in Russian].
212. V. A. Kiryukhin, N. B. Nikitina, and S. N. Sudarikov, *Hydrogeochemistry of Fold Areas* (Nedra, Leningrad, 1989) [in Russian].
213. B. A. Kolotov, *Hydrogeochemistry of Ore Deposits* (Nedra, Moscow, 1992) [in Russian].
214. A. W. Gosling, E. A. Jenne, and T. T. Chao, "Gold Content of Natural Waters in Colorado," *Econ. Geol.* **66**, 309–313 (1971).
215. B. G. Katz, O. P. Bricker, and M. M. Kennady, "Geochemical Mass-Balance Relationships for Selected Ions in Precipitation and Stream Water, Catocin Mountains," *Am. J. Sci.* **285**, 931–962 (1985).
216. J. M. Reid, D. A. Macleod, and M. S. Cresser, "The Assessment of Chemical Weathering Rates within an Upland Catchment in North-East Scotland," *Earth Surf. Process. Landforms*, No. 5, 447–457 (1981).
217. Ch. Walter, "Chemismus von Bodensickerwassern," *Hydroch. Hydrogeol.*, No. 5, 118–138 (1983).
218. V. M. Stepanov, "On the Problem of the Formation of the Chemical Composition of Groundwaters in Transbaikalia," in *Problems of the Hydrogeology and Engineering Geology of Eastern Siberia* (Irkutsk, 1974), pp. 37–42 [in Russian].
219. V. A. Kovda, *Principles of Soil Sciences* (Nauka, Moscow, 1973), Vols. 1, 2 [in Russian].
220. N. I. Bazilevich, *Geochemistry of Soils of Soda Salinization* (Nauka, Moscow, 1965) [in Russian].
221. R. J. Ebens and H. T. Shacklette, "Geochemistry of Some Rocks, Mine Spoils, Stream Sediments, Soils, Plants, and Waters in the Western Energy Region of the Conterminous United States," *Geol. Surv. Prof. Pap.*, No. 1237 (1982).
222. R. S. Fisher and W. F. Mullican, "Hydrochemical Evolution of Sodium–Sulfate and Sodium–Chloride Groundwater beneath the Northern Chihuahuan Desert, Trans-Pecos, Texas, USA," *Hydrogeol. J.* **5** (2), 4–16 (1997).
223. M. G. Atwia, A. A. Hassan, and Sh. A. Ibrahim, "Hydrogeology, Log Analysis and Hydrogeochemistry of Unconsolidated Aquifers South of El-Sadat City, Egypt," *Hydrogeology*, No. 12, 27–38 (1997).
224. G. Calderoni, U. Masi, and V. Petrone, "Chemical Features of Spring Waters of the East Africa Rift: A Reconnaissance Study," *Geol. Romana*, **291**, 163–169 (1993).
225. J. M. M. Arthur, J. V. Turner, W. B. Lyons, et al., "Hydrogeochemistry on the Yilgarn Block, Western Australia: Ferrollysis and Mineralisation in Acidic Brines," *Geochim. Cosmochim. Acta* **55** (5), 1273–1288 (1991).
226. P. Briot, "L'environnement hydrogéochimique du calcaire uranifère de Yeelirie (Australie occidentale)," *Miner. Deposita* **18**, 191–206 (1983).
227. S. C. Gupta, M. P. Sangneria, and P. Rai, "Contents and Distribution Patterns of Trace Elements in Groundwater of Jodhpur District in Western Rajasthan," *Ann. Arid Zone*, **29** (4), 265–269 (1990).
228. N. J. Pawar, "Geochemistry of Carbonate Precipitation from the Ground Waters in Basaltic Aquifers: An Equilibrium Thermodynamic Approach," *J. Geol. Soc. India* **41** (2), 119–131 (1993).
229. E. Salameh, M. Alawi, M. Batarseh, and A. Juries, "Determination of Trihalomethanes and the Ionic Composition of Groundwater at Amman City, Jordan," *Hydrogeol. J.* **10** (2), 332–339 (2002).
230. O. F. Vasil'ev, S. A. Sukhenko, A. A. Atavin, et al., "Ecological Aspects of the Project of the Katun' Hydroelectric Station Related to the Presence of Hg in the Gornyi Altai Environment," *Vodn. Resur.*, No. 6, 107–123 (1992).
231. *Iodine and the Health of the Siberian Population*, Ed. by V. A. Trufakin, (Nauka, Novosibirsk, 2002) [in Russian].
232. G. I. Gavich, I. S. Zektser, V. S. Kovalevskii, et al., *Principles of Hydrogeology. Hydrodynamics* (Nauka, Novosibirsk, 1983) [in Russian].
233. D. A. Livingstone, "Chemical Composition of Rivers and Lakes," *Geol. Surv. Prof. Pap.*, No. 440-G (1963).
234. K. K. Turekian, "The Oceans, Streams and Atmosphere," in *Handbook of Geochemistry*, ed. by K. H. Wedepohl (Springer, Berlin and New York, 1969), Vol. 1, pp. 297–323.
235. J. M. Martin and M. Meybeck, "Elemental Mass-Balance of Material Carried by World Rivers," *Marin. Chem.* **7**, 173–206 (1979).
236. M. Meybeck, "Concentrations des eaux fluviales en éléments majeurs et apportés en solution aux océans," *Rev. Geol. Dyn. Géogr. Phys.* **21** (3), 215–246 (1979).
237. M. Meybeck, "Carbon, Nitrogen and Phosphorus Transported by World Rivers," *Am. J. Sci.* **282**, 401–450 (1982).
238. E. E. Belyakova, A. A. Reznikov, L. E. Kramarenko, et al., *Hydrochemical Method of Prospecting of Ore Deposits* (Gosgeoltekhizdat, Moscow, 1962) [in Russian].



239. A. I. Perel'man, *Geochemistry of the Biosphere* (Nauka, Moscow, 1973) [in Russian].
240. A. P. Vinogradov, "Average Content of Chemical Elements in the Major Types of Igneous Rocks of the Earth's Crust," *Geokhimiya*, No. 7, 555–571 (1962).
241. R. M. Garrels and C. L. Christ, *Solutions, Minerals, and Equilibria* (Harper and Row, New York, 1965).
242. A. S. Reeve and E. S. Perry, "Carbonate Geochemistry and the Concentrations of Aqueous  $Mg^{2+}$ ,  $Sr^{2+}$  and  $Ca^{2+}$ : Western North Coast of the Yucatan, Mexico," *Chem. Geol.* **112** (1–2), 105–117 (1994).
243. W. D. Keller, *The Principles of Chemical Weathering* (Lucas Broth., Missouri, 1957).
244. S. L. Shvartsev, "Interaction of Water with Aluminosilicate Rocks: A Review," *Geol. Geofiz.*, No. 12, 16–50 (1991).
245. S. R. Gislason and H. R. Eugster, "Meteoric Water-Basalt Interaction. II. A Field Study in NE Iceland," *Geochim. Cosmochim. Acta* **51** (10), 2841–2855 (1987).
246. N. A. Ogil'vi, *Physical and Geological Fields in Hydrogeology* (Nauka, Moscow, 1974) [in Russian].
247. R. M. Garrels and F. T. Mackenzie, *Evolution of Sedimentary Rocks* (Norton, New York, 1971).
248. A. I. Perel'man, *Geochemistry of Epigenetic Processes* (Nedra, Moscow, 1968) [in Russian].
249. J. J. Drake and T. M. L. Wigley, "The Effect of Climate on the Chemistry of Carbonate Ground Water," *Water Resour. Res.* **11** (6), 958–962 (1975).
250. I. N. Skrynnikova, "Soil Solutions of the Southern Part of the Forest Zone and Their Role in the Recent Processes of Soil Formation," in *Modern Processes in the Forest Zone of the European USSR* (Akad. Nauk SSSR, Moscow, 1959), pp. 50–169 [in Russian].
251. *Rates of Chemical Weathering of Rocks and Minerals*, Ed. by S. M. Colman and D. P. Dethier (Academic Press, Orlando, 1986).
252. *Chemical Weathering Rates of Silicate Minerals*, Ed. by A. F. White and S. L. Brantley, *Rev. Mineral.* **31** (Book Crafters, Michigan, 1995).
253. M. A. Glazovskaya, *World Soils. Main Families and Types of Soils* (Mosk. Gos. Univ., Moscow, 1972) [in Russian].
254. R. Maignien, *Le cuirassement des sols en Guinée* (Strasbourg, 1958).
255. N. P. Remezov, "On the Relationships between Biological Accumulation and Eluvial Processes beneath a Forest Canopy," *Pochvovedenie*, No. 6, 1–12 (1958).
256. F. A. Makarenko and V. V. Zverev, "Underground Chemical Flow in the USSR Territory," *Litol. Polezn. Iskop.*, No. 6, 30–37 (1970).
257. V. P. Zverev, V. I. Kononov, V. A. Il'in, et al., *Migration of Chemical Elements in the Groundwaters of the USSR* (Nauka, Moscow, 1974) [in Russian].
258. E. G. Kukovskii, *Transformations of Phyllosilicates* (Naukova Dumka, Kiev, 1973) [in Russian].
259. C. D. Ollier, *Weathering* (Oliver and Boyd, Edinburgh, 1969).
260. G. Millot, *Geologie des argiles* (Masson, Paris, 1964; Nedra, Leningrad, 1968).
261. C. W. Correns, "The Experimental Chemical Weathering of Silicates," *Clay Min. Bull.*, No. 4, 249–265 (1971).
262. V. I. Fin'ko, S. S. Chekin, and N. D. Samotoin, "Kaolinization of Rock-Forming Silicates in Weathering Residues," in *Problems of the Theory of the Formation of Weathering Residues and Exogenic Deposits* (Nauka, Moscow, 1980), pp. 196–201 [in Russian].
263. V. A. Alekseev, *Kinetics and Mechanisms of Feldspar Interaction with Aqueous Solutions* (GEOS, Moscow, 2002) [in Russian].
264. O. A. Alekin and L. V. Brazhnikova, *Runoff of Dissolved Matters from the USSR Territory* (Nauka, Moscow, 1964) [in Russian].
265. N. M. Strakhov, *Principles of the Theory of Lithogenesis* (Akad. Nauk SSSR, Moscow, 1960), Vol. 1 [in Russian].
266. K. I. Lukashev, *Zoned Geochemical Types of Weathering Residues in the USSR Territory* (Belorus. Gos. Univ., Minsk, 1956) [in Russian].
267. B. B. Polynov, *Selected Works* (Akad. Nauk SSSR, Moscow, 1956) [in Russian].
268. G. Pedro, "Contribution à l'étude expérimentale de l'altération géochimique des roches cristallines," *Ann. Agron.* **15** (12), 85–191 (1964).
269. A. S. Kashik and I. K. Karpov, *Physicochemical Theory of the Formation of Zoning in Weathering Residues* (Nauka, Novosibirsk, 1978) [in Russian].
270. A. S. Kashik, *Formation of Mineral Zoning in Weathering Residues* (Nauka, Novosibirsk, 1989) [in Russian].
271. I. I. Ginzburg, "Main Problems in the Formation of Weathering Residues and Their Significance for the Prospecting of Mineral Deposits," *Geol. Rudn. Mestorozhd.*, No. 5, 21–36 (1963).
272. M. L. Jackson, S. A. Tyler, A. L. Willis, et al., "Weathering Sequence of Clay Size Minerals in Soils and Sediments. Fundamental Generalization," *J. Phys. Colloid Chem.*, **52** (8), 1237–1260 (1948).
273. A. P. Nikitina, I. V. Vitovskaya, and K. K. Nikitin, *Mineralogical and Geochemical Tendencies in the Formation of Profiles and Mineral Resources of Weathering Residues* (Nauka, Moscow, 1971) [in Russian].
274. I. D. Sedletskii, "Genesis of Montmorillonite-Group Minerals in Soil Colloids," *Dokl. Akad. Nauk SSSR* **17** (7), 371–373 (1937).
275. H. Paquet, *Evolution géochimique des minéraux argileux dans les altérations et les sols des climats méditerranéens tropicaux saisons contrastées* (Strasbourg, 1970).
276. J. Déjou, J. Gyuot, and M. Robert, *Evolution superficielles des roches cristallines et cristallophilliennes dans les régions tempérées* (INRA, Paris, 1977).
277. Y. Tardy, *Pétrologie des latérites et des sols tropicaux* (Masson, Paris, 1993).
278. B. Fritz, *Étude thermodynamique et simulation des réactions entre minéraux et solutions. application à la géochimie des altérations et des eaux continentales* (Strasbourg, 1975).
279. S. L. Shvartsev, "Laterites of Guinea and Geochemical Conditions of Their Formation," *Kora Vyvetrivaniya*, No. 15, 51–70 (1976).



280. A. A. Afifi, O. P. Bricker, and J. C. Chemerys, "Experimental Chemical Weathering of Various Bedrock Types at Different pH-Values. 1. Sandstone and Granite," *Chem. Geol.* **49** (1–3), 87–113 (1985).
281. H. May, "The Hydrolysis of Aluminum: Conflicting Models and the Interpretation of Aluminum Geochemistry," in *Proceedings of 7th Symposium on Water–Rock Interaction, Rotterdam* (Brookfield, Rotterdam, 1992), Vol. 1, pp. 13–21.
282. H. W. Nesbitt and R. E. Wilson, "Recent Chemical Weathering of Basalts," *Am. J. Sci.* **292** (10), 740–777 (1992).
283. B. A. Bogatyrev, L. A. Matveeva, V. V. Zhukov, and L. O. Magazina, "Kaolinite and Halloysite Synthesis in the Gibbsite–Silica Solution System under Normal Conditions," *Geokhimiya*, No. 8, 851–862 (1997) [*Geochem. Int.* **35**, 747–757 (1997)].
284. M. I. L'vovich, *World's Water Resources and Their Future* (Mysl', Moscow, 1974) [in Russian].
285. L. Barshad, "The Effect of a Variation in Precipitation on the Nature of Clay Mineral Formation in Soils from Acid and Basic Igneous Rocks," in *Proceeding of International Clay Conference, Jerusalem, Israel* (Jerusalem, 1996), Vol. 1, 167–173.
286. P. Warneck, *Chemistry of the Natural Atmosphere* (Academic, New York, 1988).
287. R. A. Duce, I. W. Winchester, and I. van Nah, "Iodine, Bromine and Chlorine in the Hawaiian Marine Atmosphere," *J. Geophys. Res.* **70**, 1775–1799 (1965).
288. A. A. Kolodyazhnaya, *Regime of the Chemical Composition of Atmospheric Precipitation and Its Metamorphism in the Aeration Zone* (Akad. Nauk SSSR, Moscow, 1963) [in Russian].
289. V. M. Drozdova, O. P. Petrenchuk, E. S. Selezneva, and F. P. Svistov, *Chemical Composition of Precipitation in the European Part of the USSR* (Gidrometeoizdat, Leningrad, 1964) [in Russian].
290. R. Caboi, A. Cristini, and F. Frau, "Metal Concentrations in Rainwater (Sardinia, Western Mediterranean Sea)" in *Water–Rock Interaction* (Balkema, Rotterdam, 1995), pp. 337–340.
291. D. Carroll, "Rainwater as a Chemical Agent of Geologic Processes," *Rev. Water-Supply Pap.*, No. 1535-G (1962).
292. G. Tuvaanzhav and N. A. Marinov, "Chemical Composition of the Atmospheric Precipitation of Ulan Bator," *Vodn. Resur.*, No. 6, 667–673 (1994).
293. L. I. Belyaev and E. I. Ovsyanyi, "Study of Trace Elements in the Atmospheric Precipitation of a Coastal Region with Application to Some Problems of Chemical Oceanography," *Gidrokh. Mater.* **51**, 3–12 (1969).
294. K. Sugawara, "Chemical Composition of Rain in Japan," *J. Earth Sci. Nagoya Univ.*, Nos. 1–2 (1967).
295. M. Herron, Ch. C. Langway, H. V. Weiss, and J. H. Gradin, "Atmospheric Trace Metals and Sulfate in the Greenland Ice Sheet," *Geochim. Cosmochim. Acta* **41** (7), 915–920 (1977).
296. B. A. Mirtov, *Gas Composition of the Earth's Atmosphere and Methods of Its Analysis* (Akad. Nauk SSSR, Moscow, 1961) [in Russian].
297. E. Gorham, "On the Acidity and Salinity of Rain," *Geochim. Cosmochim. Acta* **7**, 231–239 (1955).
298. V. V. Ponomareva and N. S. Sotnikova, "Systematics of Element Migration and Accumulation in Podzolic Soils," in *Biochemical Processes in the Podzolic Soils* (Nauka, Leningrad, 1972), pp. 6–55 [in Russian].
299. B. B. Polynov, "On the Geological Role of Organisms," *Vopr. Geogr.* **33**, 45–64 (1953).
300. S. L. Shvartsev, "Ore-Generating Processes in the Evolution of the Water–Rock System," *Geol. Rudn. Mestorozhd.* **36** (3), 261–270 (1994).
301. I. N. Antipov-Karataev, "Problems of the Origin of Geographical Distribution of Solonetz in the USSR," in *Solonetz Melioration in the USSR* (Akad. Nauk SSSR, Moscow, 1953) [in Russian].
302. E. V. Posokhov, *Origin of Soda Waters in Nature* (Gidrometeoizdat, Leningrad, 1969) [in Russian].
303. Yu. V. Batalin, B. S. Kasimov, and E. F. Stankevich, *Natural Soda Deposits and Conditions of Their Formation* (Nedra, Moscow, 1973) [in Russian].
304. V. G. Popov, R. F. Abdrakhmanov, and I. N. Tugushi, *Exchange–Absorption Processes in the Underground Atmosphere* (Ufa, 1992) [in Russian].
305. R. Blake, "The Origin of High Sodium Bicarbonate Waters in the Otway Basin Victoria, Australia," in *Proceedings of 6th Symposium on Water–Rock Interaction, Rotterdam, 1989* (Brookfield, Rotterdam, 1989), pp. 83–85.
306. W. P. Kelley, *Alkali Soils, Their Formation, Properties and Reclamation* (Reinhold, New York, 1951).
307. A. Al-Droubi, *Géochimie des sels et des solutions concentrées par évaporations. Modèle thermodynamique de simulation. Applications aux sols salés du Tchad* (Strasbourg, 1976).
308. V. A. Kazantsev, *Problems of Pedohalogenesis* (Nauka, Novosibirsk, 1998) [in Russian].
309. R. S. Kononova, "Cryogenic Metamorphism of Subpermafrost Waters from the Eastern Siberian Artesian Area," *Sov. Geol.*, No. 3, 106–115 (1974).
310. I. A. Tyutyunov, *Processes of Alteration and Transformation of Soils and Rocks at Negative Temperatures* (Akad. Nauk SSSR, Moscow, 1960) [in Russian].
311. S. L. Shvartsev, "Geochemical Activity of Permafrost," *Priroda*, No. 7, 66–73 (1975).
312. S. L. Shvartsev, "On the Relationships between the Compositions of Groundwaters and Rocks," *Geol. Geofiz.*, No. 8, 46–54 (1993).
313. F. A. Letnikov, *Synergetics of Geological Systems* (Nauka, Novosibirsk, 1992) [in Russian].
314. A. E. Kontorovich, "General Theory of Naphthidogenesis. Main Concepts and Ways of Their Construction," in *Theoretical and Regional Problems of Oil and Gas Geology* (Nauka, Novosibirsk, 1991), pp. 29–44 [in Russian].
315. A. S. Shcherbakov, *Self-Organization of Matter in Inorganic Nature: Philosophical Aspects of Synergetics* (Mosk. Gos. Univ., Moscow, 1990) [in Russian].
316. S. L. Shvartsev, "On the Problem of Self-Organization in the Water–Rock Geological System," *Geol. Geofiz.*, No. 4, 22–29 (1995).

317. S. L. Shvartsev, "Water–Rock Geological System," Vest. Ross. Akad. Nauk, No. 6, 518–524 (1997).
318. S. L. Shvartsev, "The Water–Rock System Synergy," Earth Sci. Front., No. 1, 36–46 (2001).
319. I. Prigogine and I. Stengers, *Order Out of Chaos. Man's New Dialogue with Nature* (Heineman, London, 1984).
320. V. S. Golubev, "Coupled Processes and Evolution," in *Idea of Evolution in Geology: Compositional and Structural Aspects* (Nauka, Novosibirsk, 1990), pp. 5–13 [in Russian].
321. O. V. Esterle, "Evolution of Inorganic and Living Matter of the Earth from the Viewpoint of Statistical Chemistry," in *Idea of Evolution in Geology: Compositional and Structural Aspects* (Nauka, Novosibirsk, 1990), pp. 5–13 [in Russian].
322. A. L. Yanshin, "Origin of the Problem of the Evolution of Geological Processes," in *Evolution of Geological Processes in the Earth's History* (Nauka, Moscow, 1993), pp. 9–20 [in Russian].