

Hydrogeochemistry of the permafrost zone in the central part of the Yakutian diamond-bearing province, Russia

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Abstract The hydrogeochemical characteristics and zonation of the permafrost zone in the central part of the Yakutian diamond-bearing province formed mainly under the influence of cryogenic processes that occurred in the late Cenozoic. On the basis of field and experimental studies, conclusions were formulated that the perennial cryogenesis of the sedimentary cover in this region resulted in increasing the concentration of carbonate and sulfate compounds in groundwaters as well as increasing the concentration of easily soluble compounds (sodium, magnesium, and calcium chlorides).

Résumé Les caractéristiques hydrogéochimiques et la zonation de la région de permafrost dans la partie centrale de la province diamantifère de Yakoutie ont été acquises principalement sous l'influence des processus cryogéniques qui existent depuis la fin du Tertiaire. Sur la base d'études expérimentales et de terrain, on conclut que la cryogénèse permanente de la couverture sédimentaire de cette région a provoqué un accroissement de la concentration des composés carbonatés et sulfatés dans les eaux souterraines, en même temps que celui de composés facilement solubles, comme les chlorures de sodium, de magnésium et de calcium.

Resumen Las características hidrogeoquímicas y la zonación del permafrost existente en el centro de la provincia de Yakutia, rica en diamantes, se formaron fundamentalmente bajo la influencia de procesos criogénicos durante el tramo final del Cenozoico. Con base en estudios de campo y experimentales, se ha concluido que la criogénesis perenne de la cubierta sedimentaria de la región ha provocado un aumento de la concentración de

compuestos de carbonato y sulfato en las aguas subterráneas, además de incrementar la concentración de compuestos solubles, como el sodio, magnesio y cloruros de calcio.

Keywords Hydrogeochemistry · Permafrost zone · Russia · Siberian platform · Yakutian

Introduction

The Yakutian diamond-bearing province is unique to the Siberian platform based on a study of the extent of cryolithozone (syn.: cryolithosphere). The active industrial Daldyn–Alakit region, shown in Fig. 1, is located within this province. This region, with a total area of not more than 10,000 km², is unique in view of the extreme cooling of the geological section. The area is also host to

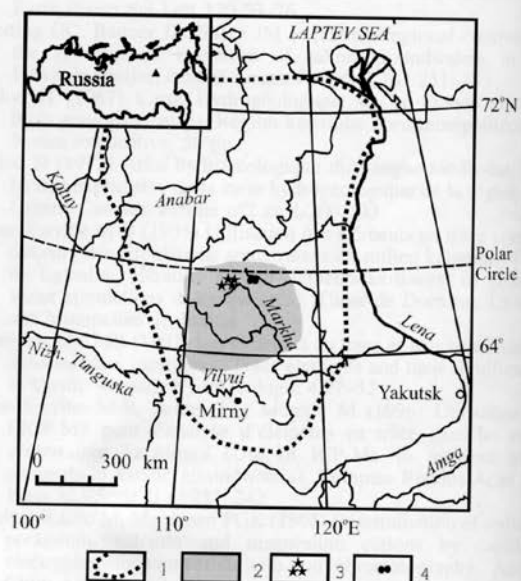


Fig. 1 Location of the Daldyn–Alakit region within the Yakutian diamond-bearing province; 1 Location of the Daldyn–Alakit region; 2 Kimberlite pipes: Udachnaya, Zarnitsa, Yakutskaya, Popugayevoy; 4 Wells Nos. 1 and 2

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a high concentration of diamonds. Extensive mining of this area has resulted in a complex array of geocryological and hydrogeological research opportunities (Fig. 1).

For the last 30 years, the Joint-Stock Company ALROSA has done a considerable amount of the prospecting in this region. More than 100 hydrogeological wells and some deep exploration wells have been drilled in a small part of the region. A vast amount of data regarding the main characteristics of the cryolithozone has been gathered by a combined effort of both the industry personnel and scientific researchers. At the Institute of the Earth's Crust (SB RAS) there is a unique hydrochemical data bank concerned with the structure of forming ice in sedimentary rocks and kimberlite pipes (more than 200 samples), and the associated saline groundwaters and brines (more than 1,100 samples) from the central part of the Yakutian diamond-bearing province. The statistical processing of these data and the analysis of the available published and unpublished information have allowed the authors to describe hydrogeochemical features of the cryolithozone of the Daldyn-Alakit region as well as to update its zonation to a new degree.

Geocryological Section

The Daldyn-Alakit region is situated in an area of continuous permafrost and is characterized by the presence of thick zones of negative temperatures. According to updated data concerning the geocryological section of the region (Alexeev and Pinneker 1997), the cryolithozone represents the interlayering of ice-rich permafrost, dry permafrost, and cooled sedimentary rocks of the Lower Paleozoic. The cooled rocks are saturated with the negative-temperature waters called "cryopegs".

Formation and evolution of the cryolithozone in the region are controlled by global variations of heat exchange in the atmosphere—lithosphere system with a global cooling of the climate beginning at the end of Neogene epoch (Kondratieva et al. 1989). The deep freezing of the geological section and annual heat cycling of the section began as a result of the formation of negative mean-annual temperatures in the rocks. At constant or nearly constant conditions within the frozen rocks, the thickness of the cryolithozone was determined by three parameters: the temperature of the surface layer, the ability of the rocks to conduct heat, and the Earth's heat flow (Balobaev 1991). At present, the regional features of the cryolithozone are also determined by the spatial distribution of these parameters within the geological section.

The Daldyn-Alakit region is characterized by low mean annual air temperatures (up to -11°C), by the rocks' high thermal conductivity [$2.2\text{--}4.1\text{ W}/(\text{m}^{\circ}\text{C})$], and by the lowest intensity of heat flow ($0.021\text{--}0.027\text{ W}/\text{m}^2$) in this part of Russia. These characteristics have caused the formation of the unique thermal field with low rock temperatures and the low thermal gradients. Moreover,

major mechanisms for the deep cooling of the geological section have also resulted from the interaction between permafrost and cryopegs or negative-temperature groundwaters, the ability of the cryopegs to move through permafrost over considerable distances, the diluting effect of ice inclusions in rocks (Pinneker et al. 1989), and the considerable decrease of temperature during the process of cryopeg migration (Melnikov 1967).

Primary information on the geothermal parameters of the cryolithozone in the region was obtained in the 1960s. According to the results of the observations in wells Nos. 1 and 2, situated on the Markha River near the Polar Circle, it was determined that the zone of negative temperatures within the rocks reached a depth below 1,450 m. New data obtained by the researchers of the Permafrost Institute SB RAS (Balobaev et al. 1983; Klimovsky and Gotovcev 1994) indicated that the temperature of the rocks at the base of the layer had annual temperature fluctuations ranging from -2.9 to -8.75°C (at the different sites), and the thickness of cryolithozone varies from 720–1,100 m.

Using vertical electric sounding, it was determined that the permafrost thickness along regional profiles had intense and chaotic variations extending to depths of up to several hundreds of meters (Yakupov et al. 1984; Kalinin and Yakupov 1989). In the opinion of these authors, these variations were controlled by different salinities of the sub-permafrost salt waters and brines, and by the level of heat conduction of the rocks. The estimates of the thickness of the modern cryolithozone, the geothermal gradient, and the mean annual frozen-rock temperatures of the region are 1,580 m, $0.0054^{\circ}\text{C}/\text{m}$, and -8.5°C , respectively. The temperature of the rocks does not exceed $5\text{--}16^{\circ}\text{C}$ at a depth of 2.5 km, and the temperature gradient in the depth interval 0.9–1.4 km is $0.9\text{--}1.1^{\circ}\text{C}/100\text{ m}$.

Hydrogeochemical Conditions

A complex set of factors influences the formation and evolution of the hydrogeochemical section of the cryolithozone of the region. The main factors are (1) predominance of sedimentary carbonaceous rocks in the geological section; (2) multiphase kimberlite and flood-basalt magmatism; (3) repeated tectonic events; (4) a great number of the faults which have considerably increased the permeability of the sedimentary rock cover; (5) evolution of the erosional base level of the rivers; and (6) cryogenesis of the groundwater and rock system (Kovalskiy and Bilanenko 1986; Alexeev and Pinneker 1997; Pinneker et al. 1998). Structurally, before the beginning of perennial freezing, there were two hydrodynamic zones clearly distinguishable in the region: (1) the active water-exchange zone that is now completely frozen; and (2) the passive water-exchange zone (Fig. 2). These zones differ from one another by the relative rates of water movement; from hundreds to thousands of years in the active zone to a million years in the passive zone.

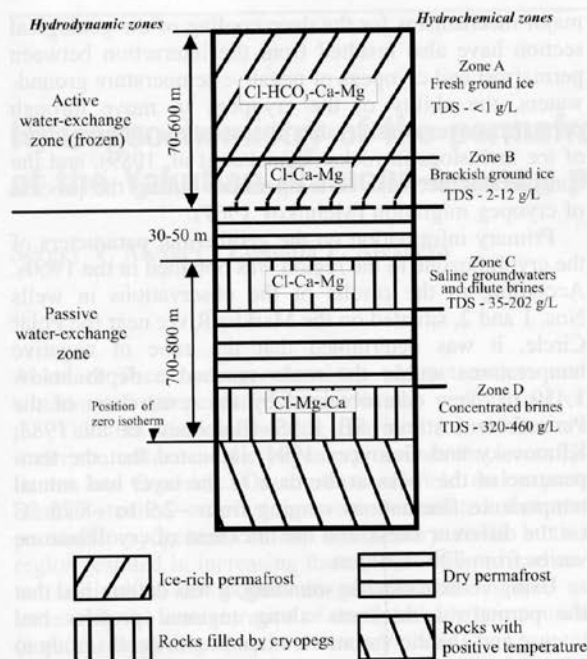


Fig. 2 Hydrogeological and geocryological section of Daldyn-Alakit region

The minor accumulations of fresh groundwaters are confined to the seasonally thawed layer, also to active underflow in taliks and under lakes.

Geochemical Features of Ground Ice

The ground ice (groundwaters in the solid phase) has been studied within the limits of the Zarnitsa, Popugaevoy, and Yakutskaya kimberlite pipes and in the containing terrigenous-carbonate rocks of the Upper Cambrian. Core samples of the structure-forming ice were taken at interval from wells drilled without water circulation after purging of the well face with compressed air.

The core samples obtained by the authors provided a description of the hydrogeochemical characteristics of the frozen active water-exchange zone. In its vertical section two hydrochemical zones were identified: (1) the fresh ground ice zone (A) with TDS of less than 1,000 mg/l; and (2) the brackish ground ice zone (B) with TDS of 2,000–12,000 mg/l.

The thickness of zone A varies from 30 m in the valley bottoms to 180 m on higher ground. At a depth between 30–150 m, the ice composition is bicarbonate or chloride-bicarbonate Ca–Mg (or Mg–Ca). Both hydrochemical types are within the limits of the Udachnaya and Zarnitsa diamond pipes as well as in the sedimentary rocks (Ustinova 1964; Alexeev and Borisov 1985). Ice with concentration of TDS at this depth does not exceed 100–400 mg/l. Between the depths of 160–180 m, the chemical composition changes to bicarbonate-chloride, and the

TDS increases to level of 1,000 mg/l. The concentration of the sulfate ion is 15–25 mg/l, and bromine is present at a concentration of approximately 1–2 mg/l. Within the area of the Popugaevoy kimberlite pipe to a depth of 120 m, the ground ice composition is sulfate-bicarbonate Ca–Mg, and the TDS varies from 160 to 390 mg/l.

The thickness of zone B is between 30–40 m. The composition of the ground ice samples is exclusively chloride (Ca–Mg and Mg–Ca), except in the Udachnaya kimberlite pipe where calcium sulfate predominates in the ground ice composition. For the other kimberlite pipes, the typical concentration of the sulfate ion ranged from 30–1,135 mg/l, and bromine between 5–56 mg/l.

The distribution of major and minor elements in the ground ice of hydrochemical zones A and B is listed in Table 1. The analysis of the correlation matrix shows the close correlation between ions of potassium, sodium, magnesium, calcium, and chloride. Coefficients of the correlation are presented in Table 2 and range from 0.88–0.99. Bromine has a significant but lesser correlation with the other elements. Sulfate weakly correlates with the other chemical components, and the bicarbonate does not correlate very well.

Geochemical Features of Saline Waters and Brines

Two hydrochemical zones also can be distinguished in the vertical section of the hydrodynamic passive water exchange zone. The groundwaters of the Upper Cambrian aquifer complex are contained in zone C, which has saline waters and dilute brines. Zone D, which has concentrated brines, integrates groundwaters of the Middle and Lower Cambrian, and Upper Proterozoic aquifer complexes.

The thickness of zone C is limited, varying between 10–20 m and corresponds to the Upper Cambrian sub-permafrost aquifer complex. The concentration of TDS in this zone varies from 35–202 g/l. The chemical composition of saline waters and dilute brines are only chloride, and predominantly magnesium. It is confirmed by the value $Ca/Mg = 0.7-2.1$ instead of 2.3–4.5, which is typical for concentrated brines (Grudin and Kiselev 1987). The average concentration of sulfate is 0.98 g/l, and the average content of bicarbonate is 0.13 g/l.

The distribution of major and minor components of this zone of saline waters and dilute brines is shown in Table 3. A strong correlation between sodium, magnesium, calcium, and chloride ions and TDS is evident in Table 4 with coefficients of correlation ranging from 0.77–0.96. Among the trace-element components such as bromine, there is a positive correlation with other elements (lithium and strontium). The relationship of $Cl/Br = 40-80$ and $Na/Cl = 0.1-0.4$ are relatively constant for all values of TDS.

The thickness of zone D is on the order of 2,000 m. It contains brines of the Cambrian and Upper Proterozoic aquifer complexes. TDS values range from 223–404 g/l (average value of 323 g/l) and increase depending on the depth of the groundwater occurrence. The brines in this zone are geochemically more uniform in correlation and

Table 1 Range of concentration of constituents in the groundwaters of zones A and B. Zone A is shown in *bold*; zone B is not in bold; TDS total dissolved solids

Concentration, mg/l	Constituent											
	TDS	K ⁺	Na ⁺	Mg ²⁺	Ca ²⁺	Cl ⁻	Br ⁻	SO ₄ ²⁻	HCO ₃ ⁻	Li ⁺	Rb ⁺	Sr ²⁺
Max.	860.3 12,414	100 437	185.7 893	84.2 1,325	133.7 1,443	471.6 8,013	6.45 55.9	147.9 1,135	366.1 732.2	0.13 2.29	0.008 0.17	4.58 12.6
Min.	69.6 1,025.8	0.72 3.56	1.57 4.5	1.2 46.8	9 50.1	0.71 30.1	0 0	0 4	42.7 32.95	0 0.15	0 0.05	0 0.2
Average	315.46 2,614.5	7.81 72.31	16.22 185.42	21.42 243.22	37.74 331.42	66.07 1,414.78	0.86 17.78	13.84 213.06	152.60 146.00	0.04 0.73	0.003 0.07	0.49 5.52
Standard deviation	169.91 2,230.5	12.17 78.24	28.70 167.8	15.82 238.2	22.04 293.3	91.60 1,475.3	1.35 14.13	26.88 262.65	68.07 130.29	0.04 0.75	0.003 0.07	1.06 4.40

Table 2 Correlation matrix of constituents in groundwaters of zones A and B. TDS Total dissolved solids

Constituent	Coefficient of correlation							
	K ⁺	Na ⁺	Mg ²⁺	Ca ²⁺	Cl ⁻	Br ⁻	SO ₄ ²⁻	HCO ₃ ⁻
TDS	0.915	0.940	0.983	0.975	0.988	0.694	0.486	-0.070
K ⁺	1.000	0.909	0.909	0.841	0.924	0.516	0.358	-0.153
Na ⁺		1.000	0.906	0.878	0.946	0.687	0.355	-0.119
Mg ²⁺			1.000	0.936	0.986	0.678	0.400	-0.069
Ca ²⁺				1.000	0.950	0.680	0.566	-0.081
Cl ⁻					1.000	0.681	0.367	-0.131
Br ⁻						1.000	0.364	-0.068
SO ₄ ²⁻							1.000	-0.151
HCO ₃ ⁻								1.000

Table 3 Distribution of constituents in the groundwaters of zones C and D. Zone C is shown in *bold*, zone D is not in bold. TDS Total dissolved solids

Concentration	Constituent										
	(g/l)							(mg/l)			
	TDS	K ⁺	Na ⁺	Mg ²⁺	Ca ²⁺	Cl ⁻	Br ⁻	Li ⁺	Rb ⁺	Cs ⁺	Sr ²⁺
Max.	203.3 404.30	4.62 23.05	29.15 48.24	21.8 28.00	34.56 97.50	135.4 253.70	2.57 6.47	120.8 568.20	7.72 106.10	0.66 1.04	710 2138.20
Min.	31.1 223.56	0.03 2.39	3.07 8.42	2.06 1.82	2.06 34.28	18.62 137.83	0.32 2.33	3.05 34.13	0.2 3.04	0 0.01	58 375.00
Average	89.6 323.68	1.68 11.96	7.71 24.42	7.51 13.51	13.49 65.93	57.25 204.01	1.05 4.13	35.13 165.24	1.20 11.26	0.03 0.17	301.18 1109.43
Standard deviation	41.53 46.28	1.07 3.84	4.44 7.16	4.32 3.13	6.84 12.98	27.52 29.04	0.55 0.92	28.03 90.21	1.42 10.73	0.12 0.20	174.78 333.00

composition (see Table 3). Ninety-eight percent of the anion balance is represented by chloride and the average concentrations of sulfate and bicarbonate ions make up 0.34 and 0.33 g/l respectively; bromine concentrations vary from 2.3–6.5 g/l. The cation balance is represented by four elements (K⁺, Na⁺, Mg²⁺, and Ca²⁺). Their mean concentrations (%) are Ca²⁺: 50–70, Na⁺: 15–30, Mg²⁺: 15–25, K⁺: 3–5. The positive correlation between the major and minor components is generally consistent (see Table 4). The chlorine–bromine relationship has a range of 34–66 units and the value of the sodium–chloride relationship fluctuates between 0.1–0.5.

The composition of saline waters and brines of the kimberlite pipes are identical to the waters within the surrounding sedimentary strata. Concentrated brines are

metamorphosed by complex hydrogeochemical processes and similar fluids exist across the whole Siberian platform.

The isotope studies have helped determine the conditions of brine formation in the sections not containing halide depositions. For the Daldyn–Alakit region it is established that at depths lower than the frozen active water exchange zone, the only concentrated Na–Mg–Ca chloride brines are widespread (Kovalskiy and Bilanenko 1986; Pinneker et al. 1987). The sub-permafrost waters of other geochemical types are absent in this area and there are no rock salt layers among the depositional units (for example, in the south of the Yakutian province).

The general change of isotopes of hydrogen and oxygen in the brines is expressed in Fig. 3. The values for

Table 4 Correlation matrix of constituents in the groundwater of zones C and D. Zone C in bold, zone D is not in bold; TDS Total dissolved solids

Constituent	Coefficient of correlation								
	K ⁺	Na ⁺	Mg ²⁺	Ca ²⁺	Cl ⁻	Br ⁻	Li ⁺	Rb ⁺	Sr ²⁺
TDS	0.542	0.797	0.760	0.922	0.966	0.922	0.622	0.193	0.742
K ⁺	0.115	0.662	0.827	0.970	0.996	0.962	0.686	0.448	0.830
Na ⁺	1.000	0.412	0.418	0.612	0.586	0.613	0.529	0.346	0.596
Mg ²⁺	1.000	0.789	0.859	0.883	0.887	0.871	0.688	0.520	0.783
Ca ²⁺		1.000	0.462	0.763	0.772	0.686	0.324	0.077	0.654
Cl ⁻		1.000	0.881	0.872	0.930	0.521	0.202	0.068	0.340
Br ⁻			1.000	0.640	0.810	0.816	0.754	0.213	0.716
Li ⁺			1.000	0.926	0.953	0.820	0.520	0.360	0.620
Rb ⁺				1.000	0.960	0.926	0.608	0.228	0.860
				1.000	0.965	0.965	0.024	0.102	0.179
					1.000	0.961	0.651	0.205	0.846
					1.000	0.959	0.685	0.439	0.826
						1.000	0.726	0.295	0.828
						1.000	0.746	0.457	0.843
							1.000	0.490	0.595
							1.000	0.563	0.699
								1.000	0.226
								1.000	0.378

meteoric waters are slightly displaced from the line of Craig–Epstein ($\delta D = 8\delta^{18}O + 5$) showing increasing enrichment of $\delta^{18}O$ values with depth and concentration.

The isotopic composition of calcium-chloride brines (both weakly and strongly mineralized) depends on two parameters: the TDS value and the depth of the stratigraphic unit. With an increase of TDS at depth, there is an enrichment of the hydrogen and oxygen isotopes. The range of change of the values δD and $\delta^{18}O$ is large and is in the range from -6 – 103‰ (for $\delta^{18}O$) and from -0.1 – 11.1‰ (for δD) at TDS values of 260–500 g/l and depths of 0.5–3.5 km. Considerable variations of the isotope contents of strongly mineralized calcium-chloride waters demonstrate more complex processes of brine formation than the simple altering of parent brines by syngenetic precipitations and their metamorphism. The weak calcium-chloride brines (with TDS less than 200 g/l) occur under the permafrost rocks and show isotopic ratios identical to surface waters and meteoric precipitation values, indicating that their origin and evolution are most likely related to meteoric fluids.

Formation of Hydrogeochemical Section of the Cryolithozone During the Late Cenozoic

The events of the Late Pleistocene cryochron, one of the coldest periods in the history of the Earth, have played a major role in the formation of hydrogeochemical features of the modern cryolithozone in the central part of the Yakutian diamond-bearing province.

The depth of cooling of the sedimentary section has controlled the modification of hydrogeochemical zones; primarily the groundwaters of the active water-exchange zone have been exposed to the primary cryogenic metamorphism.

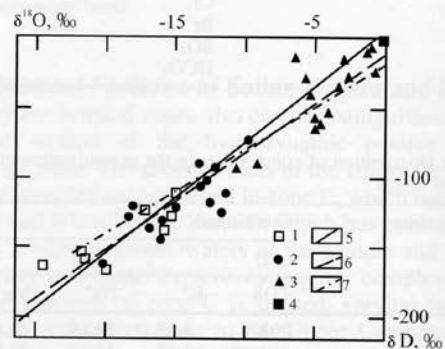
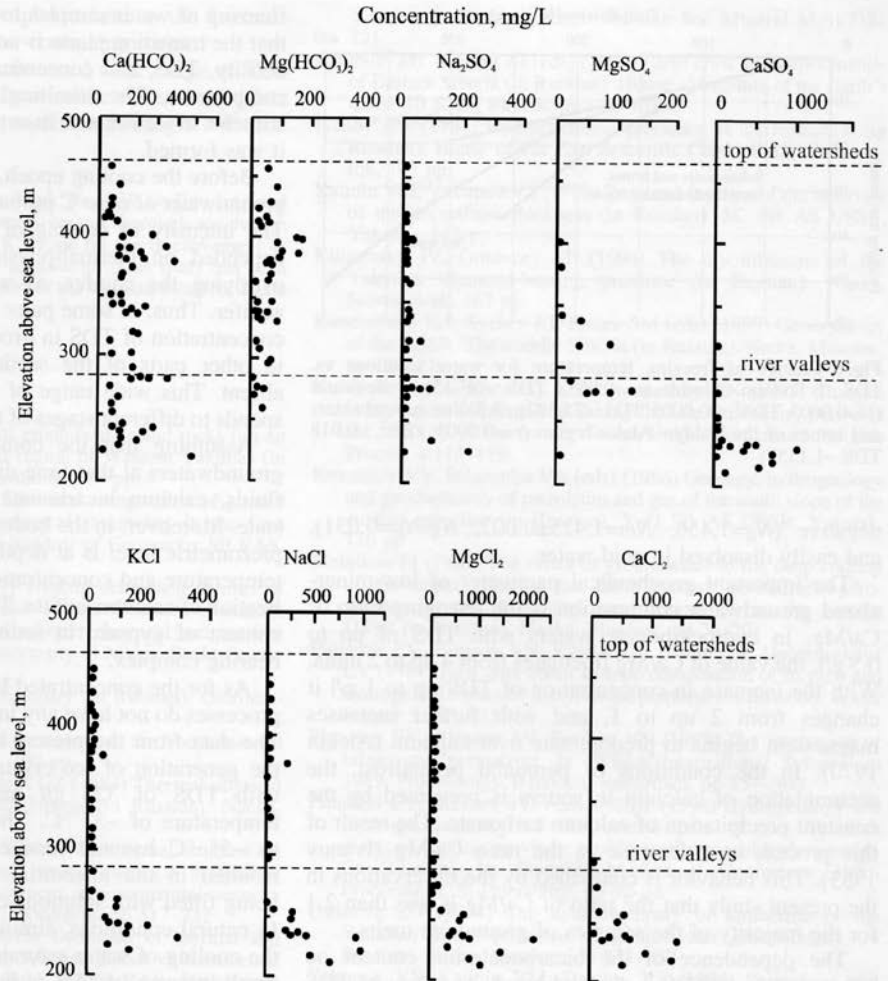


Fig. 3 Isotopic plot of $\delta^{18}O$ vs. δD in different types of waters found in the Siberian platform. 1 Rivers, lakes, precipitation; 2 Sub-permafrost mainly calcium-chloride dilute brines (35–189 g/l); 3 Concentrated calcium-chloride brines (300–500 g/l) of western Yakutia; 4 Standard mean ocean water (SMOW); 5 Meteoric waters of the Earth ($\delta D = 8\delta^{18}O + 5$); 6 All types of waters studied on the Siberian platform ($\delta D = 7\delta^{18}O - 12$); 7 Calcium chloride brines ($\delta D = 6.1\delta^{18}O - 1$)

For the paleohydrogeological reconstructions, recalculation of ionic composition of ground ice melts was undertaken. This method has allowed the evaluation of the degree of cryogenic transformation of waters in the active water-exchange zone. Figure 4 shows that, with depth, the sedimentary strata show an insignificant decrease of calcium, magnesium, and bicarbonate, an accumulation of sodium, magnesium, and calcium sulfates, as well as chloride salts. Data from the kimberlite pipes show a similar trend where cryogenic groundwater concentration is controlled by freezing.

The maximum paleogeocryological conditions of central Yakutia in the Sartan cooling epoch (18,000–20,000 years ago) have been reconstructed. In that period,

Fig. 4 Change in concentration of selected constituents of ground ice melts at depth in Cambrian sedimentary deposits



the temperature of frozen rocks was 10–13 °C lower than modern day temperatures (Balobaev 1991; Kondratieva et al. 1993; Duchkov and Balobaev 2001a, 2001b). Moreover, in western Yakutia, it has been established that the degree of the Earth's interior heat flux was even lower. Therefore, some salts were able to reach eutectic conditions (–21 °C) aiding groundwater freezing. The deposition of calcium and magnesium carbonates was connected to this change and resulted in the carbonaceous system shifting equilibrium in the direction of monocarbonates. The crystallization of hexahydrate ($\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$), and mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) could have occurred as a result and the decrease of their solubility at such negative temperatures seems to be confirmed by the increases in these mineral compositions, as shown on the Fig. 4.

The eutectic temperature of sodium sulfate is –3.5 to –8.2 °C, magnesium sulfate is –4.8 °C, and calcium sulfate is known to precipitate within the temperature interval of –15 to –17 °C. Cooling of water-saturated rocks was sufficient to cause the increase in concentration

of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ and for their full transition into the solid phase. The accumulation of calcium sulfate could result from squeezing and expulsion of more concentrated solution as the moving freezing front progressed down the stratigraphic section. Similarly, the concentration of sodium, magnesium, and calcium chlorides also increased in the groundwaters with increasing freezing at depth.

The traces of cryogenic metamorphism in groundwater composition within the active water-exchange zone were displayed as secondary salts in rocks. In the fractures and caverns of the Zarnitsa kimberlite pipe, encrustations of calcite on the rocks were collected by the authors as well as in fragments in the ice mass. The horizons of calcite precipitation are traced throughout the depth interval of 60–200 m. For the first time, in the Osennaya kimberlite pipe at a depth of 60 m, hexahydrate magnesium sulfate (hexahydrate— $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$) was found (Egorov et al. 1987). The hexahydrate is represented by thin, lengthy (5–25 mm) prismatic crystals, which are optically biaxial-

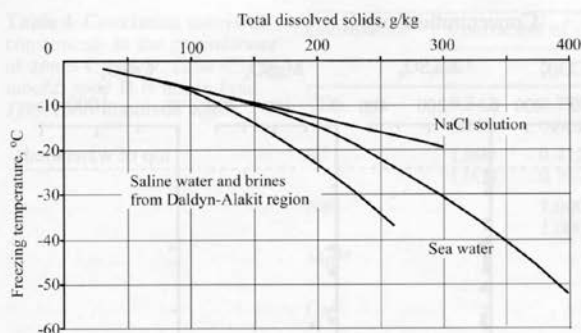


Fig. 5 Change of freezing temperature for water solutions vs. TDS. 1 Sodium chloride ($t=-0.0633 \text{ TDS} - 6E-15$); 2 Seawater ($t=-0.0003 \text{ TDS}^2 - 0.0005 \text{ TDS} - 2.8587$); 3 Saline groundwaters and brines of the Daldyn-Alakit region ($t=-0.0005 \text{ TDS}^2 - 0.018 \text{ TDS} - 1.1558$)

negative ($N_g=1.456$, $N_m=1.425 \pm 0.002$, $N_g - N_p=0.031$), and easily dissolved in cold water.

The important geochemical parameter of low-mineralized groundwater composition is the changing ratio of Ca/Mg. In hydrocarbonate waters with TDS of up to 0.5 g/l, the value of Ca/Mg fluctuates from 4 up to 2 units. With the increase in concentration of TDS up to 1 g/l it changes from 2 up to 1, and with further increases magnesium begins to predominate over calcium (Alekin 1970). In the conditions of perennial permafrost, the accumulation of calcium in waters is prevented by the constant precipitation of calcium carbonate. The result of this process is a decrease in the ratio Ca/Mg (Ivanov 1983). This behavior is confirmed by the observations in the present study that the ratio of Ca/Mg is less than 2:1 for the majority of the samples of ground-ice melts.

The dependence of the bicarbonate-ion content on concentration of TDS is also indicated. At values of TDS up to 600 mg/l, the HCO_3^- concentration increases quickly with the increase in relative concentration of magnesium and sodium. Then, HCO_3^- concentration decreases with a simultaneous increase in sulfate ions and chloride in the solution.

Some geochemical features of groundwaters in the solid phase are inherited from the conditions that existed at the beginning of the cooling epoch, as is demonstrated by the high enrichment of chloride salts in the meltwater. The most probable source of chloride is the water-containing rocks. The presence of the readily soluble compounds in the rocks is connected with the conditions of formation of sedimentary rocks and the kimberlite pipes. The formation of the initial chemical composition of groundwaters was mainly a result of dissolution and leaching of salts from the rocks by infiltrating groundwaters before the cooling epoch.

Groundwaters of the passive water-exchange zone were exposed to the cryogenic transformation as well. It is experimentally established (Alexeev 2000) that the crystallization temperature of saline waters and dilute brines (zone C) changes from -1.9 up to -18.7 °C (Fig. 5). The

freezing of water samples to TDS 30–75 g/kg has shown that the transition phase is accompanied by an increase in density, TDS, and concentration of the residual solution components. The resulting concentrations of the constituents in ice is lower than those in the water from which it was formed.

Before the cooling epoch, the concentration of TDS in groundwater of zone C probably did not exceed 30–40 g/l. The intensity of cooling of water-bearing rocks mainly depended on thermal-physical properties of the rocks overlying the aquifer, as well as on the depth of the aquifer. Thus, in some parts of the geological section, the concentration of TDS in groundwaters was increased and in other parts of the section the increase was almost absent. This wide range of TDS in groundwaters corresponds to different stages of their cryogenic concentration.

Assuming that the composition of the mineralized groundwaters at that time differed little from the present fluids, calcium bicarbonate could achieve the eutectic state. Moreover, in the bottoms of river valleys where the piezometric level is at depths of 100–130 m, there were temperature and concentration conditions for the crystallization of calcium sulfate. This is evident from the higher content of gypsum in sedimentary rocks of the water-bearing complex.

As for the concentrated brines of zone D, the freezing processes do not have any influence on their composition. The data from the present experiments have shown that the generation of ice crystals in calcium-chloride brine with TDS of 323 g/l has taken place only at the temperature of -37 °C. The cooling of these brines up to -55 °C has not resulted in complete freezing and resulted in the interstitial spaces between ice crystals being filled with solutions containing TDS up to 360 g/l. In natural conditions, similar temperatures did not exist; the cooling of water-saturated rocks could lead only to a small increase of TDS in brine.

Conclusions

The hydrogeochemical zonality of the central part of the Yakutian diamond-bearing province is essentially transformed under the effect of the perennial cryogenesis of the sedimentary rock cover. The events of the Late Pleistocene cryochron have played a significant role in the formation of geochemical parameters of the modern cryolithozone of the region. Cryometamorphosed water has kept a record of the physical-chemical processes and paleotemperatures of the geological section. The deep freezing of the western part of the Yakutian artesian basin was accompanied by the formation of the solid phase (ice), the evolution of groundwaters with different TDS concentrations and compositions, precipitation of carbonaceous and sulfate salts, and density growth of readily soluble compounds (chlorides of sodium, magnesium, calcium). The intensity of the cryogenesis processes essentially depended on the initial concentration of TDS in groundwater, on the occurrence and

depth of the water-bearing complexes, and on the thermal-physical properties of the water-containing rocks.

As a result, the currently observed wide range of TDS concentrations of sub-permafrost saline waters and dilute brines directly corresponds to different stages of their cryogenic concentration.

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References

- Alexeev SV (2000) Cryogenesis of groundwaters and rocks (on an example of the Daldyn-Alakit region of Western Yakutia) (in Russian). SPC UIGGM. Novosibirsk, 119 pp
- Alexeev SV, Borisov VN (1985) Chemical composition of ground ice of Severnaya pipe: glaciological researches in the East Siberia (in Russian). House of Institute of Geography SB RAS, Irkutsk, pp 129–137
- Alexeev SV, Pinneker EV (1997) Hydrogeochemical futures of cryolithozone of Daldyn-Alakit region (Western Yakutia): problems of researches of groundwater chemical composition (in Russian). St.-Petersburg University of Mines, Sankt-Petersburg, pp 27–30
- Alekin OA (1970) Bases of geochemistry (in Russian). Gidrometeoizdat, Leningrad, 440 pp
- Balobaev VT (1991) Geothermy of permafrost of the North Asia (in Russian). Nauka, Novosibirsk, 192 pp
- Balobaev VT, Pavlov A.V, Perlshtein GZ (1983) Thermal-physical researches of cryolithozone of Siberia (in Russian). Nauka, Novosibirsk, pp 22–34
- Duchkov AD, Balobaev VT (2001a) Geothermal studies of permafrost response to global natural changes: permafrost response on economic development, environmental security and natural resources. Kluwer, Dordrecht, pp 317–332
- Duchkov AD, Balobaev VT (2001b) Evolution of thermal and phase permafrost condition in Siberia: global environmental changes: 2001 (in Russian). Publ. of SB RAS, Department GEO, Novosibirsk, pp 79–104
- Egorov KN, Ushchapovskaya ZF, Shvyrev GG, Sizykh UI, Kadurin VA, Nartova NV (1987) Hexahydrite in the kimberlites of Yakutia (in Russian). Trans Russian Soc Mineral M(6):718–721
- Grudinin MI, Kiselev AI (eds) (1987) Earth crust and upper mantle of Eastern Siberia (in Russian). House of Institute of the Earth's Crust SB RAS, Irkutsk, pp 146–153
- Ivanov AV (1983) Hydrochemical processes at ice formation (in Russian). House of Far East Scientific Center RAS, Vladivostok, 107 pp
- Kalinin VM, Yakupov VS (1989) Regional features of the behavior of the permafrost thickness (in Russian). SC SB AS USSR, Yakutsk, 142 pp
- Klimovsky IV, Gotovcev SP (1994) The cryolithozone of the Yakutian diamond-bearing province (in Russian). Nauka, Novosibirsk, 167 pp
- Kondratieva KA, Sychev KI, Fotiev SM (eds) (1989) Geocryology of the USSR. The middle Siberia (in Russian). Nedra, Moscow, pp 183–214
- Kondratieva KA, Khruzky SF, Romanovsky NN (1993) Changes in the extent of permafrost during the late Quaternary period in the territory of the former Soviet Union. Permafrost Periglac Process 4:113–119
- Kovalskiy VV, Bilanenko VA (eds) (1986) Geology, hydrogeology and geochemistry of petroleum and gas of the south slope of the Anabar anticline (in Russian). YaD SB AS USSR, Yakutsk, 176 pp
- Melnikov PI (1967) The effect of groundwater to the deep cooling of the upper zone of the Earth's crust: permafrost-hydrogeothermal and hydrogeological researches in the eastern USSR (in Russian). Nauka, Moscow, pp 24–29
- Pinneker EV, Borisov VN, Kustov UI, Brandt SB, Dneprovskaya LV (1987) New data about isotope composition of oxygen and hydrogen of brines of the Siberian platform (in Russian). Water Resour 3:105–115
- Pinneker EV, Alexeev SV, Borisov VN (1989) The interaction of brines and permafrost. In: WRI-6 International Symposium 1989, Proceedings. Balkema, Rotterdam, pp 557–560
- Pinneker EV, Alexeev SV, Alexeeva LP (1998) Hydrogeology and Hydrogeochemistry of the central part of the Yakutian diamond-bearing province: problems of regional hydrogeology (in Russian). In: Scientific-Methodical Conference 1997, Proceedings, St.-Petersburg, pp 32–36
- Ustinova ZG (1964) The hydrochemistry of kimberlite of the Yakutian pipes: problems of groundwater geochemistry (in Russian). Nedra, Moscow, pp 237–252
- Yakupov VS, Kalinin VM, Danilov VS (1984) Permafrost and cryopegs in Western Yakutia according geophysics data. In: XXVII International Geological Congress, Proceedings, vol 8, pp 185–186