Geochemistry of brines in Vendian deposits of the Siberian platform

D A Novikov[1,2], A V Chernykh[1,2] and F F Dultsev[1]

[1] Trofimuk Institute of Petroleum Geology and Geophysics SB RAS, Novosibirsk, Russia,
[2] Novosibirsk State University, Novosibirsk, Russia

E-mail: NovikovDA@ipgg.sbras.ru

Abstract. Results of the geochemical studies on natural brines from regional Vendian reservoirs (Lower-Danilov, Tira, Nepa and Vilyuchan) of the Siberian platform are presented. TDS values of the studied groundwaters and brines range from 17.3 to 583.1 g/dm^3, where brines with salinity 280 – 400 g/dm^3 are predominant. Brines identified within the Ayan, Bratsk, Balaganka, Upper Chona, Shamanka and other areas, have the highest TDS values.The most widely spread brines belong to five chemical types of Cl Na to Cl Ca composition. TDS concentrations vary widely from 197 to 580 g/dm^3 in the Lower Danilov and Tira horizons, and from 170 to 470 g/dm^3 in the lower-sitting Nepa and Vilyuchan horizons. Na Cl brines whose TDS concentration reaches the halite precipitation phase should be assigned to infiltration-formed brines on account of salt rock leaching, while strongly metamorphosed brines (S > 300) mostly of Cl and Ca Cl Ca-Mg composition – to sedimentogenic type accounting for those descended from Cambrian salt-bearing deposits, thereby largely explaining the phenomenon of inverse hydrogeochemical zonality in subsalt horizons. The third genetic type, of Cl Ca-Na composition, is rooted in the processes of mixing sodium and calcium types of brines.

1. Introduction

Arctic sedimentary basins are of great interest as a region with high hydrocarbon potential. At the present, commercial petroleum pools have been found in many basins worldwide: Siberian platform, Athabasca, Beaufort-Mackenzie, West Siberian, Sverdrup and others [1-5]. The Siberian platform is unique in terms of its hydrogeological structure and geothermal, hydrodynamic and hydrogeochemical conditions, which have been amply discussed in the works of A. S. Antsiferov, E. A. Baskov, M. B. Bukaty, M. G. Valyashko, V. I. Vozhov, G. D. Ginsburg, V. V. Pavlenko, E. V. Pinneker, E. V. Stadnik, N. I. Tolstikhin, and many others [5-17].

Subsurface brines of the Siberian platform are characterized by high levels of salinity (up to 650 g/dm^3) and metamorphization, as well as by unique concentrations of numerous micro-constituents (Li, Rb, Sr, Br, B, I etc.). In recent years, the interest to the study area has been fueled by Gazprom company's works seeking for justification of the discoveries of giant gas fields in the Republic of

Sakha (Yakutia) area, and by the construction of the largest "Power of Siberia" (Sila Sibiri) and "ESPO - Pacific" gas- and oil-pipeline systems, and ongoing prospecting works in order to keep these facilities in operation ensured by sufficient hydrocarbon resource base.

Notably, the extent of hydrogeological study of the sedimentary cover of the Siberian platform is extremely varied, with terrigenous Vendian deposits being no exception, although they account for more than 50% of the total in-place gas resources and about 18% of total reserves and resources of crude oil [18]. The existing literature overviews fail to provide a comprehensive analysis of the currently available drilling data and results of geochemical testing of the regional horizons (top – down): Lower- Danilov, Tira, Nepa, and Vilyuchan.

2. Materials and Methods

The hydrogeochemical materials, which served as the basis for this work are the results of numerous dedicated research conducted over a long period of time. The electronic database includes results of a comprehensive chemical analysis (including micro constituents) of 809 conditioned samples, results of testing more than 1,237 objects within 101 prospecting areas. Based on the methodological approaches and chemical classifications after V.A. Sulin, A.A. Kartsev, S.L. Shvartsev, V.E. Pinneker, A.S. Antsiferov, E.A. Baskov, M.B. Bukaty, M.G., Valyashko, V.I. Vozhov and other researchers, geochemical signatures of subsurface brines have been thoroughly investigated.

The chemical types of brines were determined according to the S. A. Shchukarev’s classification proposed in 1934 using the Kurlov formula. Unlike the latter, the component which is present in the amount of at least 25 equiv.% is considered to be predominant. Of the six main ions, by grouping them by two, three, four, five and six, S. A. Shchukarev identified as many as 49 classes of natural waters. These classes are represented in the form of a square whose sides are divided into seven equal parts. Of them, Shchukarev interprets Ca HCO_3, Na Cl и Ca SO_4 as staple, since their waters formed as a result of direct leaching of rocks. All other classes are a product of water mixing, metamorphization of their salt composition and cationic exchange [19]. Using the rNa/rCl, Cl/Br, Ca/Cl, $r(HCO_3+CO_3)/r(Ca+Mg)$, B/Br, $Br/Cl \cdot 10^{-3}$, $Sr/Cl \cdot 10^{-3}$ relationships, other indications of the origin of subsurface brines have been inferred. The degree of their metamorphization was determined from the integrated index of brine metamorphization (S) after S. L. Shvartsev [9] and the Ca/Cl, $Br/Cl \cdot 10^{-3}$, $Sr/Cl \cdot 10^{-3}$ relationships.

3. Results and Discussion

Subsurface waters and brines with TDS from 17.3 to 583.1 g/dm^3 are established in the Vendian reservoirs (table 1). In terms of the cationic composition, the investigated brines vary widely from sodium chloride to chloride with a predominance of calcium and magnesium cations (figure 1).

Despite the hydrogeochemical field varying significantly locally within Vendian deposits, the lateral zoning of the brine composition is clearly observed, particularly, in the zone of the Siberian platform joint with adjacent folded structures, where distribution of sodium brines is assumed to have resulted from leaching of rock salt. As the distance from the platform boundary increases, this zone is replaced by a strip of brines of mixed cationic, sodium-dominated composition, which are subsequently replaced by calcium-dominated brines. The calcium-magnesium brines are distributed locally, in the Nepa and Vilyuchan horizons within the Kupskaya area in the north of the Angara-Lena structural step, southern part of the Siberian platform. Brines from the Tira and Lower Danilov horizons tend to be of chloride type with their composition predominated by magnesium and calcium cations, revealed in brines within the Kupskaya Gruznovka, Bolshaya Tira and Ozernaya areas. The Nepa and Vilyuchan horizons are characterized by brines with the TDS concentrations from 170 g/dm^3 to 470 g/dm^3 (Figure 2). The Preobrazhenskaya, Ozernaya, Dulisma, Balagankino and Verkhne-Chona areas the TDS values reaches its maximum 430-470 g/dm^3. Brines with salinity up to 200 g/dm^3 are established on Omorinsk and South Solnechnaya areas. The overlying Tira and Lower-Danilov horizons are featured by distribution of brines with mineralization from 197 to 583 g/dm^3. The ultrahigh salinity brines are assigned to Ayan, Bratsk, Upper-Chona, Lower Uda, Ognevka, Ozerny, Preobrazhenka, Soba, Talakan and Shamanovka areas (table 1).

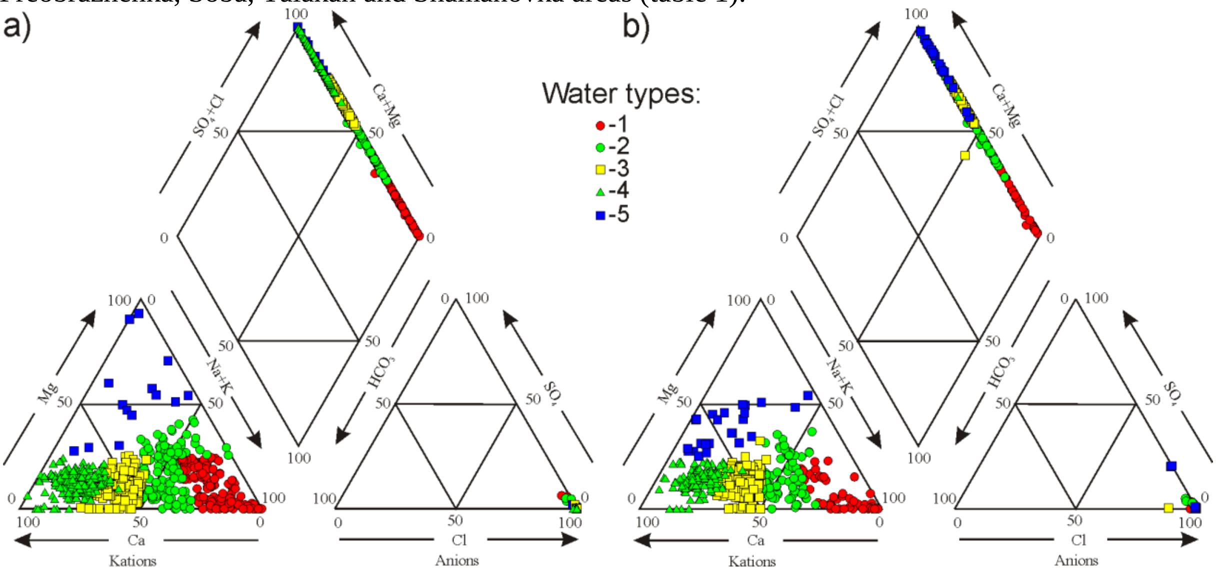

Figure 1. Piper diagram of groundwater composition of the regional Vendian reservoirs: a) Nepa and Vilyuchan and b) Lower-Danilov and Tira.

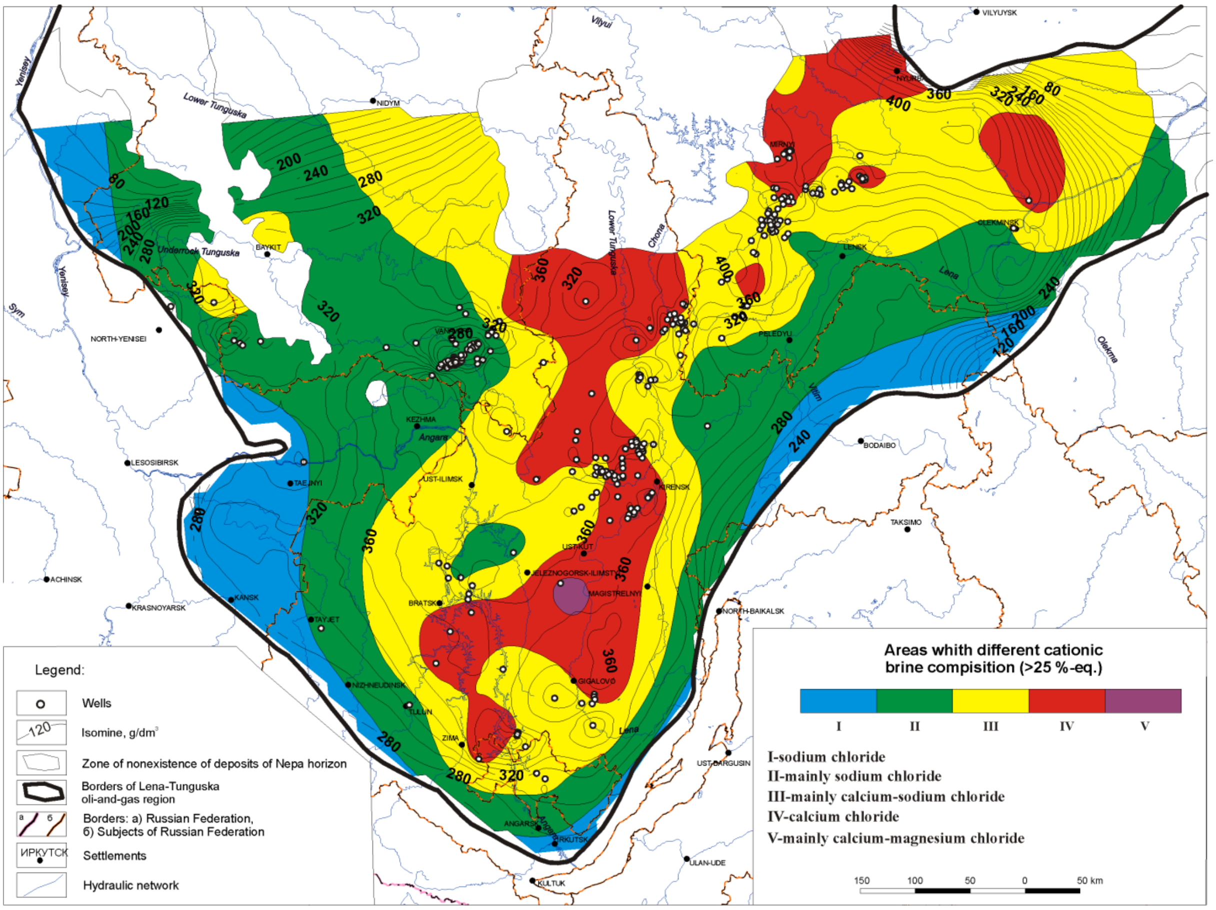

Figure 2. Map of TDS and chemical composition of brines of the Nepa and Vilyuchan regional Vendian reservoirs.

Table 1. Hydrogeological characteristics of regional reservoirs of Vendian deposits.

Index	Unit	Regional reservoirs			
		Lower Danilov	Tira	Nepa	Vilyuchan
Constitution of underground water[a]					
HCO_3^-	mg/dm^3	4-1819 (351,2)	2-1830 (229,3)	6-2440 (262,3)	12-290 (101,5)
SO_4^{2-}	- ” -	87-3827 (964,8)	0,1-8723 (572,8)	5-16000 (648,5)	0,4-415 (141,8)
Cl^-	g/dm^3	14-267 (194,8)	10,2-410,6 (203,3)	5,9-291,2 (199,1)	173,7-257,7 (220,
Br^-	- ” -	0,09-10,73 (2,7)	0,004-11,1 (3,6)	0,003-10,7 (3,6)	0,2-6,2 (3,1)
I^-	mg/dm^3	0,2-63 (12,3)	0,1-316 (29)	0,1-2200 (40,8)	2,5-105,5 (29,8)
F^-	- ” -	1,9-11 (6,4)	0,4-19 (9,1)	0,3-125 (18,2)	-
Na^+	g/dm^3	8,3-125,4 (60,7)	2-125,4 (47,8)	1-146,4 (45,7)	12,2-85,6 (36,9)
Ca^{2+}	- ” -	0,7-120,2 (45,9)	0,7-120,2 (55,7)	0,6-130,4 (56,4)	22-104 (82,9)
Mg^{2+}	- ” -	0,1-41,5 (6,5)	0,1-66,2 (10,5)	0,1-42,3 (9,9)	0,6-15,8 (6,4)
K^+	- ” -	0,1-21,3 (7,2)	0,1-45,4 (6,7)	0,1-25 (5,9)	0,2-42 (4,6)
Sr^{2+}	- ” -	0,2-3,8 (1,2)	0,01-6,8 (2,1)	0,01-7,2 (1,7)	0,5-4 (2,2)
Li^+	mg/dm^3	1,4-72 (28,6)	0,5-439 (57,2)	1-168 (42,1)	0,9-38 (19,4)
Rb^+	- ” -	0,4-59 (7,1)	0,1-98 (1,3)	0,05-130 (7,8)	1,6-10 (2,9)
Cs^+	- ” -	0,3-0,6 (0,4)	0,3-2 (0,7)	0,01-3 (0,2)	-
Cu^{2+}	- ” -	0,2-2 (0,8)	0,08-12,9 (1,4)	0,03-42 (1,1)	1-2 (1,7)
Zn^{2+}	- ” -	0,87-5,8 (1,3)	0,2-1100 (55,1)	0,002-400 (29,3)	2,7-98 (30)
Pb^{2+}	- ” -	16	0,5-16 (1,1)	0,06-11,5 (1,5)	2
Mn^{2+}	- ” -	6-286 (72,3)	2-994 (127,2)	0,01-1000 (100)	72-210 (130,3)
NH_4^+	- ” -	0,04-1025 (255,4)	0,03-1183 (249,8)	0,03-7500 (231,7)	24-313 (118,2)
SiO_2	- ” -	2,6-20 (14,7)	0,2-66 (25,1)	0,3-102 (23,2)	95
Al^+	- ” -	0,8-10 (3,3)	0,02-120 (7,9)	0,02-23 (4,3)	640
B^+	- ” -	6-160 (41,1)	0,03-200 (41,9)	0,01-583 (39)	4,9-36 (12,5)
Fe общ.	- ” -	0,9-450 (60,1)	0,1-1746 (198,8)	0,1-3000 (155,4)	0,3-380 (131,5)
TDS	g/dm^3	196-424,5 (316,5)	24,0-583,1 (325,4)	17,3-470,1 (318,6)	278,9-398,8 (350,8)
rNa/rCl	decimal quantity	0,07-1,07 (0,52)	0,01-1,01 (0,39)	0,01-1,55 (0,39)	0,08-0,72 (0,27)
Cl/Br	- ” -	30-1176 (194)	23-910 (202)	18-939 (659)	39-755 (114)
Ca/Cl	- ” -	0,01-0,53 (0,22)	0,01-0,74 (0,26)	0,01-0,74 (0,26)	0,12-0,44 (0,37)
$Sr/Cl \cdot 10^3$	- ” -	1,1-15,7 (5,7)	0,01-137,4 (11,1)	0,01-137,2 (8,8)	2,9-17,6 (10,3)
$Br/Cl \cdot 10^3$	- ” -	0,02-32,5 (12,7)	0,01-43,1 (16,5)	0,01-993,3 (18,9)	0,9-25,2 (13,9)
S	- ” -	6-527 (189)	6-842 (249)	7-842 (236)	117-501 (270)
Composition of waters (S.A. Shchukarev)		Na Cl, Na-Ca Cl, Ca Cl, Ca-Na Cl, Mg-Ca Cl	Na Cl, Na-Ca Cl, Na-Ca-Mg Cl, Na-Mg Cl, Na-Mg-Ca Cl, Ca Cl, Ca-Na Cl, Ca-Na-Mg Cl, Ca-Mg Cl, Mg Cl, Mg-Ca Cl, Mg-Na Cl		Ca Cl, Ca-Na Cl

[a] min-max (avarage).

Statistical analysis of hydrogeochemical data allowed to reveal specific characteristics of both hydrogeochemical background and anomalies. The background brines of the Vendian horizons are predominantly of chloride calcium-sodium composition with the TDS concentration averaging 323 g/dm^3. The amount of HCO_3^- does not exceed 0.25 g/dm^3, SO_4^{2-} is 0.6 g/dm^3, Na^+ – 45.1 g/dm^3, Ca^{2+} - 58.3 g/dm^3, Mg^{2+} – 10.1 g/dm^3, K^+ – 6.1 g/dm^3; Sr^{2+} is not more than 1.84 g/dm^3, Br^- is not more than 3.65 g/dm^3, NH_4^+ is not more than 0.23 g/dm^3, etc.

Thirteen types of hydrogeochemical anomalies in the amounts of I, Br, B, SiO_2, Rb, Sr, Zn, Cu, Mn, Li, NH_4, Al, Cs were identified and delineated within the Vendian reservoirs. Thus, among the "traditional" micro-components, the highest concentrations of iodine > 0.03 g/dm^3 are established at Elokhta, Payga, Soba, Middle Botuoba, Taas-Yurakh, Byuk-Tanar and other areas; bromine (Br) in amounts > 3,6 g/dm^3 within the Ayan, Bratsk, Upper Dzhalinda, Upper Chona, Dulisma, Krivaya Luka, Markovo and other areas; boron (B) in amounts > 0,04 g/dm^3 was encountered in brines within the Ayan, Bratsk, Vakunayka, Upper Lena, Imbinsky, Payga, Sedanka, Middle-Botuoba, Yurubchen and other areas.

With respect to the alkaline constituents, the concentrations of rubidium in excess of 8.7 mg/dm^3 were established within the Bratsk, Vanavar, Imbinsky, Peleduy, Sedanka, Shamanovka and other areas; and that of lithium >46,1 mg/dm^3 - within the Ayan, Balagankino, Upper Lena, Engida, Kovykta, Sedanka, Shamanovka and other areas. Among alkaline earth elements, anomalously high are found to be Sr concentrations (> 1.84 g/dm^3) observed in the brines within the Ayan, Bolsheokinskoye, Bratsk, Upper-Vilyuchan, Kasatkino, Krivaya Luka, Markovo, Shamanovka, Yarakta and other areas. The zinc-dominated zones (>43.0 mg/dm^3) subsume brines from the Bratsk, Elochta, Soba, Chamba and other areas. Manganese concentrations are found to be remarkable >112.1 mg/dm^3 in brines from the Balagankino, Bratsk, Buyk-Tanar, Upper Tira, Dulisma, Kiya, Krivaya Luka, Middle Botuoba, Yarakta and other areas. Anomalous values of ammonium cation (in excess of 232.0 mg/dm^3) were revealed at Ayan, Bratsk, Upper Katanga, Dulisma, Katanga, Krivaya Luka, Soba, Tutura, Yarskaya and other areas. The hydrogeological retrospective of the study area and comprehensive analysis of the hydrogeochemical data suggest the presence of three major genetic types of brines within the Vendian reservoirs: 1) predominantly infiltration-driven sodium brines, 2) sedimentogenic-ancient infiltration-formed calcium-sodium and, less commonly, magnesium-sodium brines, 3) predominantly sedimentogenic chloride sodium-calcium and calcium brines (figure 3, table 1).

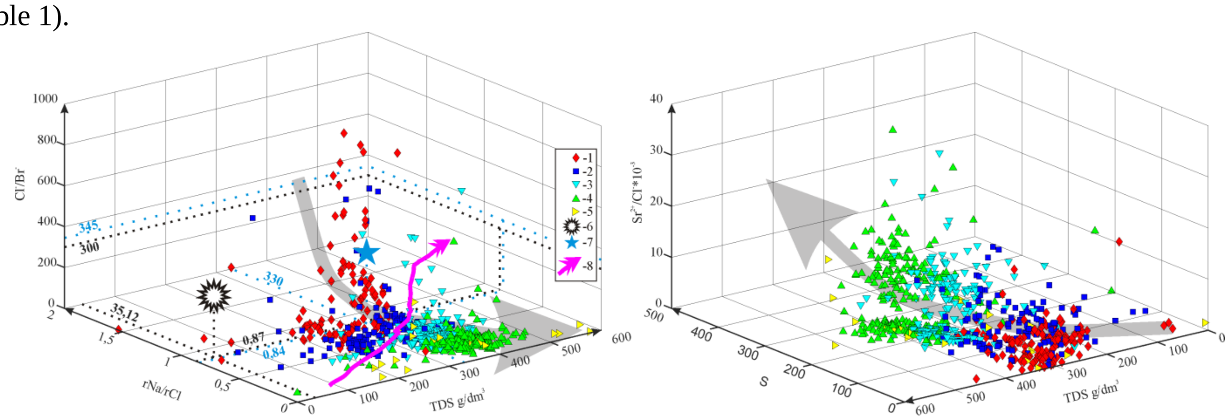

Figure 3. Variation of the metamorphization degree in subsurface brines of Vendian deposits within the Siberian platform, depending on the TDS concentrations.
The cationic composition of chloride brines: 1 – sodium, 2-with a predominance of sodium cations, 3-with a predominance of calcium and sodium cations, 4-calcium, 5-with predominance of calcium and magnesium cations; coefficient values for: 6-sea water, 7 – brines of the halite precipitation phase (after M. G. Valyashko); 8-McCaffrey curve [20].

The most metamorphosed, primarily, sedimentogenic chloride sodium-potassium and calcium brines were revealed near the southern boundary of the basin in the junction zone of the Pre-Sayany-Yenisei syneclise and the Angara-Lena structural step. They are represented by members of a uniformly continuous series featured by the increasing concentration of calcium and depletion of sodium. The TDS values of these brines vary from 344 to 583.1 g/dm^3.

The sodium-calcium to calcium brines ratio (both along the lateral and throughout the section) is governed by an increase in relative content of calcium and in mineralization of the enclosing rocks. Calcium brines with salinity in the range from 350 to 410 g/dm^3 appear to be dominating in the lower part of the sedimentary cover within the south-eastern margin of the Tunguska basin, delimited by the north-western slope of the Nepa-Botuoba anteclise. Brines of only sodium-calcium chloride composition are most common in the western part of the study region.

The distribution pattern of the second type of sodium chloride brines has a form of a narrow strip extending along the southwestern margin of the platform. Its composition and main genetic coefficients values show affinity to the modern evaporate-formed brines, however, at depths greater than a kilometer they bear evidence of the chemical composition metamorphization, specifically, a decrease in sulfate constituent, while relative concentrations of alkaline earth metals, bromine and other halogenic and halophilic micro constituents tends to increase. The studied sodium brines of Vendian deposits are therefore interpreted as transitional from leaching to metamorphosed brines whose TDS concentration does not exceed 440 g/dm^3, varying from 24 g/dm^3 within the Upper Chona area to 439.1 g/dm^3 within the Delikuton area. The salinity levels of the mixed sedimentogenic and ancient infiltration-formed calcium and sodium and, less commonly, magnesium-sodium brines, studied within the Kuyumba, Yurubchen, Taiga, Soba and other areas in the sediments of the Nepa horizon (southern part of the Siberian platform) do not exceed 455,8 g/dm^3. The formation of their chemical composition is associated with the processes occurring in the flushed paleo-karst reservoir within Riphean sandstones and the Vendian horizons of terrigenous complex characterized by largely hindered relationship between the overlying sulfate-terrigenous and sulfate-carbonate rocks of the Oskoba, Katanga, and Soba Formations.

At this, calcium-sodium type of brines is associated with a substantially desalinated, predominantly carbonate composition of brine-bearing rocks. This makes them significantly distinguished from the brines of sodium-calcium and calcium composition formed in the rocks of sulfate-bearing carbonate-terrigenous and sulfate-carbonate composition of the Ushakovka and Nepa Formations in the southeastern regions of the Yenisei syneclise and northwestern parts of the Angara-Lena step. Calcium and sodium brines occupying intermediate position between sodium- calcium and calcium levels by the metamorphization ratios and the presence of micro-constituents in their composition. As a distance from the boundaries of the platform increases, their salinity becomes lower and the macro-constituent composition is subject to alteration, which makes them in many aspects almost identical to the calcium type, allowing to separate them into a special genetic type; while the origin of brines from the marginal areas (the Taiga area) are most likely to result from the processes of mixing sodium and calcium types.

4. Conclusion

Summarizing the discussion above, the following inferences can be made. The brines of the Vendian horizons is mainly of sodium-calcium chloride and calcium chloride composition. Their salinity varies from 17.3 to 583.1 g/dm^3. Vendian deposits tend show a gradually decreasing trend in mineralization and concentrations of most macro-components from top downward, with the increasing distance from the salt beds of the Usol'ye Formation. Despite the local variability of the hydrogeochemical field of the Vendian horizons, there is a distinct regional zonality of brines of the Siberian platform, especially in the junction zone with adjacent folded structures, suggesting distribution of sodium- dominated leaching brines. With the increasing distance from the platform boundary, this zone is replaced by brines of mixed cationic composition with predominance of sodium, which become subsequently replaced by brines of mixed composition dominated by calcium (and sometimes magnesium), being dominant in the interior parts of the Nepa-Botuoba anteclise and other major structures in the southern part of the Siberian platform. As such, the hydrogeochemical zoning is influenced by many factors, among them is that the major salt-bearing strata is dated Lower Cambrian, allowing the Tira regional horizon to receive physically associated intercrystalline brines squeezed from the salt beds, and largely explaining the existence of the inverse hydrogeochemical zonality in the subsalt horizons.

Acknowledgments

The research was supported by the Russian Foundation for Basic Research within the scope of scientific project № 18-05-70074 «The Arctic Resources».

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