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Geochemistry and stable isotopic signatures, including chlorine and bromine isotopes, of the deep groundwaters of the Siberian Platform, Russia

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Abstract

The chemical composition and the isotopic characteristics of formation waters from the Siberian Platform are presented. The study involved samples of formation brines from depths ranging from 100 to ~4000 m at five different sites covering a large area of the Siberian Platform. Four water types were identified. The two main water types that were found are: (1) Ca–Cl brines that are believed to be the residual of an evaporated paleoseawater; and (2) Na–Cl brines that are derived mainly from halite dissolution. The origin of a third group of highly saline samples was not determined. However, the chemical and isotopic characteristics of this group of samples suggest that they were produced by various complex scenarios such as metamorphism, water–rock interaction, permafrost freezing and mixing. The last group of samples represents fresh and brackish waters across the area.

A wide range for the natural variation of Br stable isotopes (between −0.80‰ and +3.35‰) was found. The $\delta^{81}Br$ results obtained during this study indicate that Br stable isotopes can have large natural variations and that different evolutionary processes affecting water chemistry may cause significant fractionation.
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1. Introduction

The origin of concentrated brines in the sedimentary rocks of the Siberian Platform is of great interest. This knowledge can be very crucial in understanding the hydraulic connection between different geological sections and accordingly its application in various fields such as waste disposal and oil exploration. As a result several studies were carried out over the years to investigate and determine the history of these brines (Borisov, 1976; Lepin and Borisov, 1979; Pinneker et al., 1987; Kraynov and Ryzhenko, 1997; Shvartsev, 1998, 2000; Alexeev and Alexeeva, 2003). These authors concluded that Siberian Platform brines have different origins and result from complex geochemical evolutionary processes. In this study, chemical analyses and several stable isotopes were employed to better examine and understand the origins of the Siberian Platform brines. The data obtained were

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evaluated based on the classical approach in investigating formation waters in sedimentary basins using chemical compositions and traditional stable isotopes (H, O). However, data will also be presented for Cl and Br stable isotope in order to confirm or refute the conclusions developed from the classical approach.

Attempts to measure Br stable isotopes were made as early as 1920. However, the complexity in analyzing Br stable isotopes and the poor precision that was associated with the different techniques used postponed its use and application until 2000. Eggenkamp and Coleman (2000) were the first to report δ^{81}Br signatures of natural samples. In their study, they reported the δ^{81}Br of 11 oil field brines and established the first natural range of variation for Br stable isotopes. In 2005, a new methodology for analyzing Br stable isotopes by Continuous Flow Isotope Ratio Mass Spectrometry (CF-IRMS) was developed (Shouakar-Stash et al., 2005). Through examining 26 sedimentary and crystalline shield formation waters, a new range for the natural variation of Br stable isotopes was reported (0.00‰ to +1.80‰ relative to Standard Mean Ocean Bromide (SMOB)). The range obtained by Eggenkamp and Coleman (2000) and Shouakar-Stash et al. (2005) showed the potential of using Br stable isotope ratios to determine the solute sources of natural waters and evaluating geochemical and hydrogeological processes. In this study Cl and Br stable isotopes are used together to evaluate and study formation waters.

The objectives of the present study were: (1) the characterization of the geochemistry and isotopic signatures of Siberian Platform waters; (2) the determination of Br and Cl stable isotope ratios in the different water types found in the Siberian Platform; and (3) the assessment of the usefulness of Cl and Br stable isotopes as tools in differentiating water types and evaluating evolutionary processes.

2. Study area

The Siberian Platform located in the central part of the Russian Federation extends from approximately 85°E to 135°E longitude and 50°N to 75°N latitude (Fig. 1). It is bordered by the Laptev Sea in the North and Lake Baikal in the South. Although samples were not taken from the entire Siberian Platform, those that were collected for this study are from five different sites that cover a large geographic area. Fig. 1 illustrates the location of these sites: (1) the Daldyn–Alakit area (Site I) which is situated in the central part of the Yakutain diamond-bearing province; (2) the Malo–Botuobinskiy region (Site II) which occupies the southern part of the Yakutain diamond-bearing province; (3) the Nepskiy artesian basin (Site III) which is situated north of the Angara–Lena Terrace; (4) the Tungusskiy artesian basin (Site IV) located in the western part of the Siberian platform; and (5) the Irkutskiy artesian basin (Site V) which is part of the Angara–Lena Province and is located in the southern part of the Siberian Platform.

3. Geology

The Siberian Platform consists of thick sedimentary rocks underlain by an Archaean–Proterozoic crystalline basement. The thickness of the sedimentary cover reaches almost 12 km, but its general range is between 2 and 3.5 km. Although the sedimentary rocks in the Siberian Platform range in age from Jurassic to Cambrian, they are dominated by Cambrian sediments that are mostly terrigenous-carbonate and evaporites of gypsum, anhydrite and halite rocks. The sedimentary cover increases in depth towards the west and the north with the deepest part in the Tungusskiy basin (Site IV) to the west.

The geology of the Daldyn–Alakit area (Site I) consists of Archaean basement covered by more than 2.5 km of sedimentary strata ranging from Proterozoic (Vendian) to Paleozoic (Cambrian). The basement consists of gneisses and quartzite–gneisses. The Vendian is mainly dolomites inter-layered with marls and sandstones. The Cambrian sediments consist of dolomite and limestones inter-layered by argillites, clayey limestones and gritstones. There are numerous Late Devonian to Early Carboniferous intruded Kimberlite pipes that are confined to tectonic faults in the area. The stratigraphy of the Malo–Botuobinskiy region (Site II) is illustrated in Fig. 2 to show an example of the general stratigraphy of the Siberian Platform. Generally, the basement crystalline rocks are 3 km deep, Proterozoic in age and consist of granite–gneisses, amphibolites and granites. The basement is covered immediately by Vendian–Cambrian sediments that are made up primarily of dolomites inter-layered with argillites, anhydrites, limestones and gritstones. Above the Vendian–Cambrian sediments are Cambrian sediments that consist of dolomite and limestone inter-layered with marls, argillites, anhydrites and rock

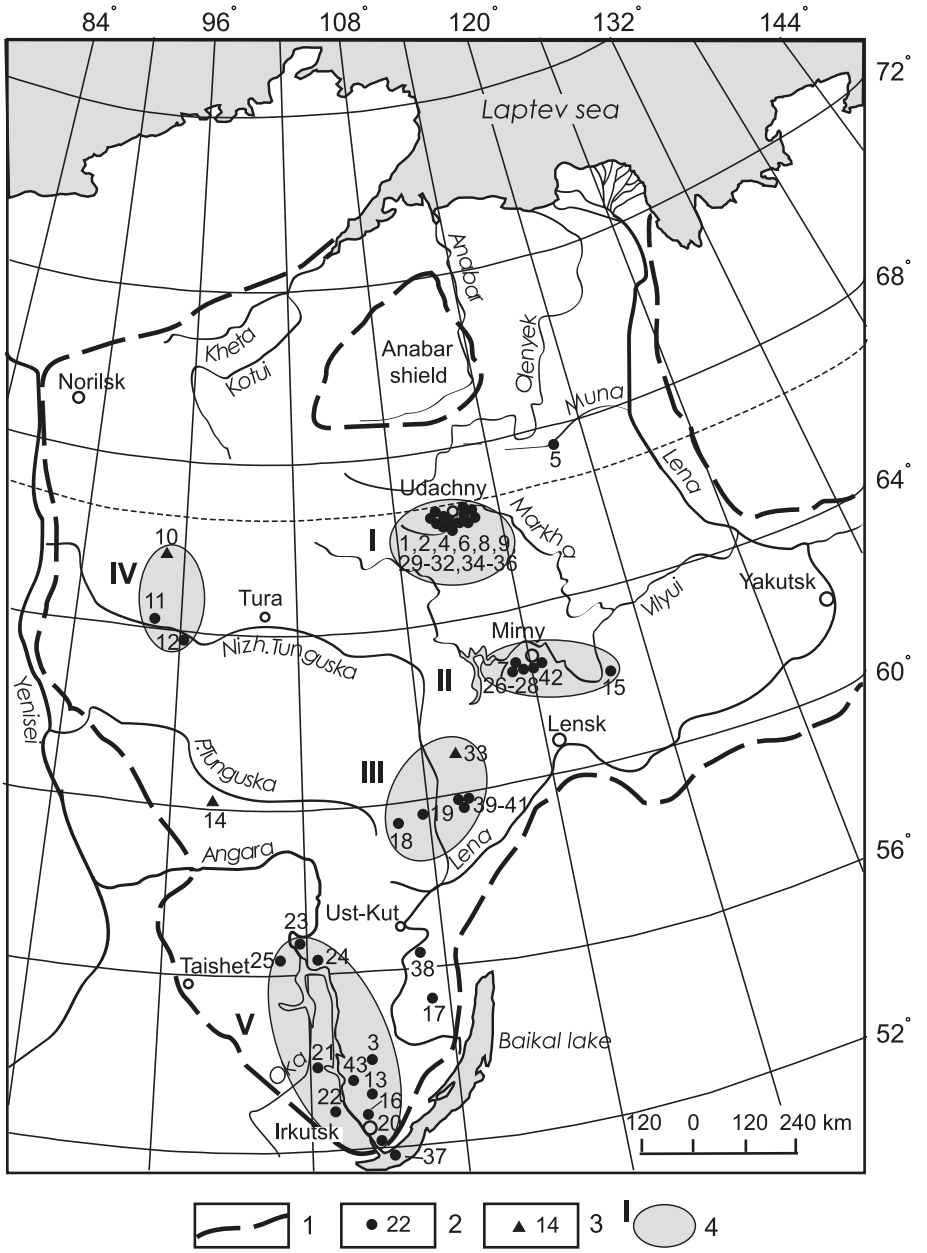

Fig. 1. Map of the Siberian Platform showing the five sampling sites.

salts. Immediately above and exposed at the surface are thin layers of sandstones and clays of Jurassic age. Middle Paleozoic Kimberlite pipes are also present in this region. The stratigraphy of the Nepskiy artesian basin (Site III) is underlain by Archaean–Proterozoic basement at around 2.2 km depth overlain by Cambrian sediments. The Cambrian sediments are mainly dolomites interlayered largely with rock salts at different depths and some beds of limestone and sandstone. The rock salt stratum is the thickest and most persistent strata in the entire area. The stratigraphy of the Tungusskiy artesian basin (Site IV) is the most complex in comparison to the other sites due to the presence of sediments of various ages. The crystalline rock Archaean–Proterozoic basement exists at 3.4 km depth and is covered immediately by approximately 1 km of Proterozoic sediments made up mainly of carbonaceous–terrigenous rocks. This is overlain by 1.4 km of Cambrian to Early Carboniferous sediments consisting of

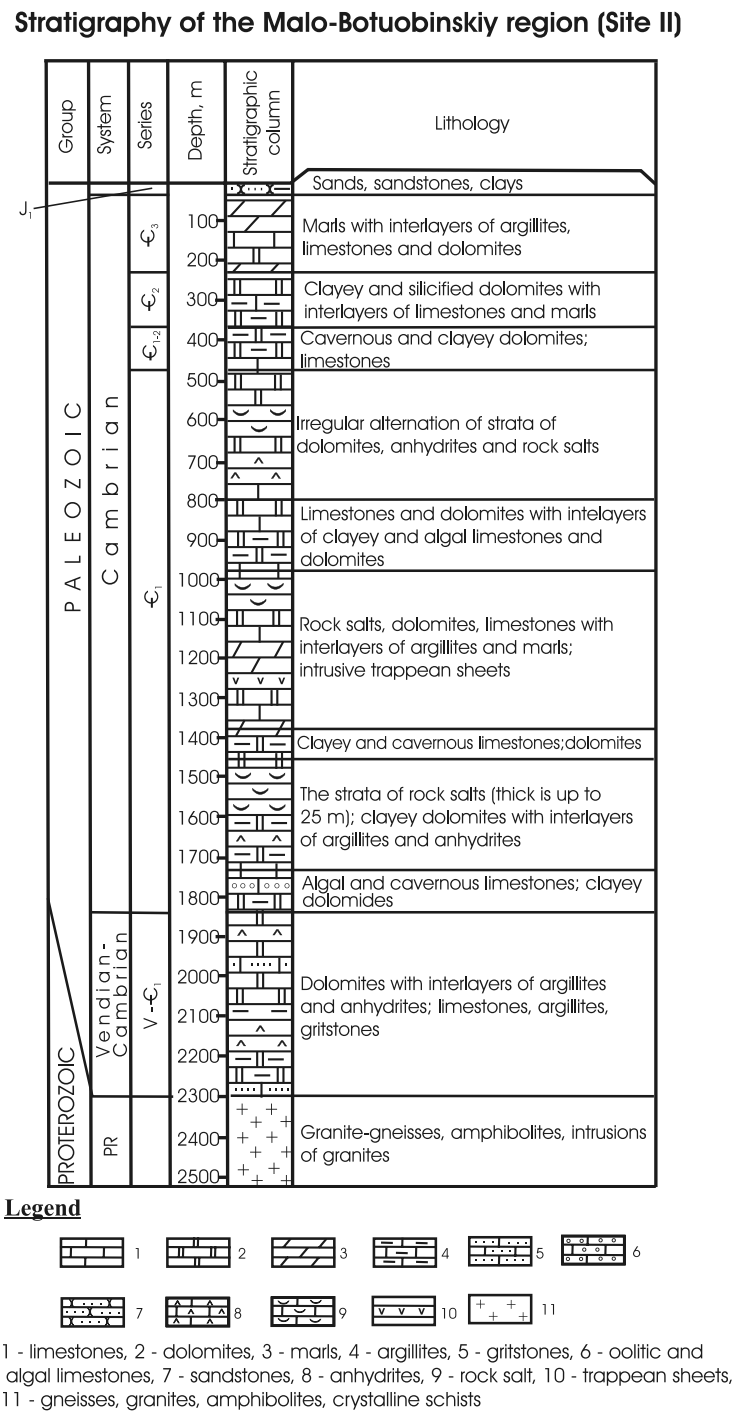

Fig. 2. Stratigraphic column of the Malo–Botuobinskiy region (Site II) located in the southern part of the Yakutain diamond-bearing province.

limestone inter-layered with anhydrite and rock salts, and dolomites inter-layered with argillite and gritstones. Above this is a Permo-Triassic cover of sediments made up of limestones, argillites, carbonaceous shales, sandstones, clays and coal strata. In addition, numerous volcanogenic tuffs of Triassic age are also present. In the Irkutskiy artesian basin (Site V), the crystalline basement rocks are of

Archaean–Proterozoic age consisting of granites, metamorphic schists and porphyritic volcanics at 2.3 km depth. Covering the basement are Cambrian sediments that consist mainly of dolomites with layers of limestones, rock salts (up to 100 m thick), anhydrites, clays, sandstones, argillites, gritstones, marls and gypsum. The Cambrian sediments are covered by 100 m of Jurassic sediments made up of sandstones, siltstones and coal beds.

4. Hydrogeology

The Siberian Platform is generally characterized by continuous permafrost in the northern and western areas while frozen ground tends to be discontinuous in the southern areas. 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 base of the permafrost layer fluctuates annually between −2.90 °C and −8.75 °C in the northern areas of the Siberian Platform and between 0 °C and −3 °C in southern parts. Recent work by Alexeev and Alexeeva (2002, 2003) has indicated that the total thickness of the cryogenic ground (cryolithozone) that consists of ice-rich permafrost, dry permafrost and frozen sedimentary rocks, including cryopeges (negative temperature waters), ranges from 25 to 1450 m in depth. In their study, they also identified two hydrodynamic zones in the cryogenic ground of the Siberian Platform: (1) the active water-exchange zone (assumed to have strong elements of advective flow), and (2) the passive water-exchange zone (dominated by diffusive processes). The active and passive water-exchange zones differ from one another by the relative rates of water movement: from hundreds to thousands of years in the active zone to million of years in the passive zone (Alexeev and Alexeeva, 2003). The minor accumulations of fresh groundwater are confined to the seasonally thawed layer at near surface and to active zones of flow under and in unfrozen taliks associated with lakes (Alexeev and Alexeeva, 2003). The active water-exchange zone is present in ice-rich ground and is completely frozen. A dry permafrost layer present below the active water-exchange zone separates this zone from the passive water-exchange zone located in the frozen sedimentary rocks below. Layers of dry permafrost are also present within the passive water-exchange zone in frozen sedimentary rocks. The thickness of these three zones varies dramatically from one part to another in the Siberian Platform, where they are generally thicker in the north and thinner in the south. The thicknesses of these zones vary locally as well as within one area. The active water-exchange zone varies in thickness from 60 to 700 m in the northern areas and from 10 to 50 m in southern areas. The thickness of the dry permafrost ranges between 30 and 50 m. The thickness of the passive water-exchange zone ranges between 700 and 800 m. The water types in the active water-exchange zone are HCO_3–Ca–Mg–Cl and Ca–Mg–Cl. The passive water-exchange zone is characterized by few different types of waters. The northern part of the Siberian Platform (Site I) is characterized by two water types; Ca–Mg–Cl and Mg–Ca–Cl, while the southern parts (Site II–V) are characterized by Na–Cl and Ca–Cl type waters (Alexeev and Alexeeva, 2003).

5. Sampling and analyses

Sample locations and numbers are shown on Fig. 1. Samples in this study were collected mainly from deep exploration boreholes and from some springs and lakes. Samples collected from boreholes are usually bailer samples taken periodically during drilling and may in many cases represent fluids from a wide interval in the borehole (Table 1). Samples were analyzed for chemical composition and stable isotopes (^{18}O, ^{2}H, ^{37}Cl and ^{81}Br). The chemical compositions were determined by ICP-MS/ICP-AES and Ion Chromatography (IC) for cations and anions, respectively. High concentration samples were diluted 20 times before they were analyzed. The detection limits for Ca, Na, K, Mg, Li and Sr of the ICP-MS/ICP-AES method are 100, 200, 10, 100, 0.1 and 0.1 μg/L, respectively. The detection limits for Br, Cl and SO_4 of the IC method are 100, 200 and 100 μg/L, respectively. The ^{18}O, ^{2}H, ^{37}Cl and ^{81}Br stable isotopes were analyzed by Isotope Ratio Mass Spectrometry (IRMS).

Oxygen stable isotope measurements were performed on CO_2 by the CO_2–H_2O equilibration method following the procedure of Epstein and Mayeda (1953) and modified by Moser (1977). Hydrogen stable isotope measurements were performed on H_2 gas using the Mn reduction method of Shouakar-Stash et al. (2000). Chlorine stable isotope analyses were performed on methyl chloride (CH_3Cl) gas following the procedure described in Eggenkamp (1994). Bromine stable isotope analyses were carried out on methyl bromide (CH_3Br) gas

Table 1
Location, depth, major ions, charge balance and stable isotopes of the Siberian platform samples

Sample ID	Sample name	Site	Depth (m)	TDS (g/L)	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	Cl (mg/L)	SO_4 (mg/L)	Br (mg/L)	Sr (mg/L)	Li (mg/L)	Charge balance (%)	δ^2H (‰)	$\delta^{18}O$ (‰)	$\delta^{37}Cl$ (‰)	$\delta^{81}Br$ (‰)
	Group A																	
1	Udachnaya open pit Borehole N 9-G	I	550	323 000	48 518	13 113	16 451	9930	160 931	122	3648	869	126 361	0.3	−66.4	−3.94	−0.40	0.07
3	Znamenka groundwater deposit Borehole N 3A	V	1818–1826	589 690	95 351	28 190	1988	3183	220 840	61	8587	349	366 334	2.4	−47.3	−9.91	−0.53	−0.09
4	Udachnaya area sedimentary rocks Borehole N 308	I	805–1150	353 220	37 157	7540	10 171	8313	155 949	135	3621	548	123 946	−15.3	−61.7	−2.43	−0.35	0.07
6	Udachnaya area deep oil Borehole N 703	I	1390–1567	395 800	61 202	10 983	12 098	15 656	179 098	44	4910	1198	162 493	−0.4	−45.3	1.80	−0.34	0.14
7	Mir kimberlite pipe Borehole N 82 [S37]	II	600	434 850	46 417	9853	4025	4432	173 338	38	4712	888	25 012	−17.7	−39.3	−2.01	−0.32	0.24
17	Kazatchinnsk Boehole 89	V	2756–2782	366 170	75 330	5743	22 266	5951	179 793	10	4828	3080	43 075	2.1	−35.9	−2.47	−0.16	−0.07
23	Kuturminsk Borehole 156	V	3067	446 865	96 021	9303	8764	19 843	161 699	43	4252	4052	166 291	5.6	−49.4	−0.20	−0.32	0.00
24	Bratsk Borehole 8	V	3382–3395	358 900	42 733	13 311	37 177	9871	169 649	282	4188	1897	50 852	3.2	−38.4	−0.60	−0.41	−0.05
27	Mir Pipe, Borhole 82	II	884–1024	362 910	86 041	13 870	11 294	7574	158 918	100	3816	1791	19 459	1.7	−51.8	−5.23	−0.15	0.18
28	Mir Pie, Borehole 83	II	600	387 950	73 761	12 499	19 191	6308	163 375	86	3421	1584	20 693	1.6	−50.5	−4.94	0.04	0.27
29	Udachnaya Pipe, Borehole 314	I	449–800	316 990	74 691	12 976	15 872	13 395	192 444	131	4440	1164	125 946	3.8	−67.3	−5.52	−0.22	0.18
31	Udachnaya Borehole 1-OP	I	400–650	315 200	63 465	12 359	21 600	10 934	151 202	88	3229	1040	88 628	3.4	−69.9	−4.37	−0.23	−0.04
32	Udachnaya Borehole 330	I	504–750	316 080	70 923	11 693	19 870	12 095	139 435	10	3094	1127	89 407	3.5	−70.5	−4.96	−0.20	0.24
35	Udachnaya Borehole 310	I	834–1470	381 360	94 723	15 306	5066	17 678	212 280	38	5637	1600	177 138	4.5	−73.3	−8.20	−0.27	−0.07
36	Udachnaya Borehole 312	I	583–952	344 610	69 117	10 953	19 720	12 515	199 151	87	4354	1138	165 178	0.4	–	−2.00	−0.24	−0.13
38	Omoloyskaya borehole 13	V	1830–1888	443 274	110 952	23 790	1151	2199	231 899	23	6317	464	215 906	1.3	−69.6	−10.93	−0.08	0.19
39	Verhnechonskaya Borehole 31	III	1674–1667	384 000	100 808	10 744	8228	7819	184 261	86	5206	2515	25 933	1.7	−44.9	−1.37	−0.21	0.06
40	Verhnechonskaya Borehole 53	III	1623–1633	358 000	76 395	10 134	18 559	6383	171 839	314	3928	1764	22 585	1.6	−78.3	−7.21	−0.24	0.13
41	Verhnechonskaya Borehole 77	III	1380–1408	399 000	77 988	16 659	9229	5979	164 859	200	2026	1131	51 776	1.8	−194.6	−12.30	−0.39	−0.01
42	Irelyahskaya Borehole 746	II	2777–2784	396 000	108 747	4005	10 406	1195	187 668	183	4725	2279	5245	0.3	−30.6	−6.15	−0.67	−0.31
43	Balagankinskaya Borehole 2	V	2258–2296	511 000	119 885	9024	2775	15 141	205 786	27	5135	3851	119 318	3.7	−50.7	−4.24	−0.14	−0.11
	Group B																	
14	Spring, near salt factory (OSKOBA)	IV	0	87 080	1475	375	27 191	118	44 236	3571	49	33	827	−1.2	−136.7	−17.51	0.01	0.73
15	Lake Mohsogoloh, near Kempendrai River	II	0	64 189	369	39	22 771	11	34 686	945	4	7	24	0.0	−93.8	−0.45	0.17	0.65
18	Gazhenka Borehole 6	III	120	77 000	792	302	27 076	562	38 423	2656	36	13	207	0.6	−152.1	−20.01	−0.25	0.71
19	Nepa Borehole 5-6	III	419–481	44 000	1094	484	13 427	166	21 857	3946	17	19	436	−1.1	−147.5	−18.47	−0.13	–
21	Novonukutsk Borehole 3-6M	V	455–500	64 000	1275	460	14 758	85	22 088	4845	20	29	534	0.2	−134.0	−16.72	0.08	–

22	Usolie Borehole 3	V	700–1000	242020	1114	80	98388	795	132866	3111	92	15	328	3.9	–	−15.20	−0.06	0.20			
26	Mir Pipe, Borehole 28	II	500	87400	1028	739	27996	161	42159	4134	51	32	1401	0.2	−113.2	−9.57	1.54	–			
	Group C																				
2	Zarnitsa kimberlite pipe Borehole N 14	I	260–270	111330	12737	5285	4843	2060	59535	688	1167	392	27694	−11.0	−123.0	−13.10	0.01	0.38			
5	Muna area Hydromineral object Borehole N 20Y	II	600	85650	3707	2232	9569	<0.7	49895	18	749	571	3194	−27.8	−108.8	−14.06	1.30	2.31			
8	Udachnaya area Borehole N 35	I	210	39920	6225	3002	4352	660	26305	1176	412	186	5922	0.2	−139.6	−16.45	0.52	0.73			
9	Udachnaya area polygon Borehole N 6	I	110–120	98340	15479	10247	8545	2418	76242	925	1458	308	32492	−2.3	−109.4	−10.22	0.21	0.18			
10	Spring, near Tutonchany River, near Salt factory	IV	0	87550	11270	25	19548	220	56021	542	289	198	571	−5.6	−124.9	−17.07	−0.17	0.03			
12	Nizn. Tunguska Borehole N TP-1	IV	2100	286300	26899	1420	70728	657	165215	246	1243	449	17887	−1.1	−88.5	−12.31	−0.11	0.70			
13	Osinskaya Borehole N 1	V	1630–1660	46525	986	–	9921	3937	165345	178	258	13	81411	16.7	−90.7	−9.25	−0.29	−0.07			
25	Bratsk Borehole 2-S	V	733–760	32000	2656	955	7667	103	17538	2162	219	58	3483	0.5	−96.4	−12.20	0.56	3.35			
30	Daldyn Borehole 24	I	313	91300	14461	4419	19172	2355	62810	1349	849	285	11521	1.8	−95.9	−10.22	−0.40	−0.80			
	Group D																				
11	Nizn. Tunguska Borehole N 44P	IV	300	318	16	3	4	1	1	63	<0.1	0.1	7	−1.2	−121.1	−15.22	0.58	–			
16	Mineral water Borehole North Irkutsk	V	3–400	1729	222	82	208	2	303	684	0.3	2	67	0.3	−131.9	−16.76	−0.13	–			
20	Zeleny Mys Borehole 3	V	600	7000	283	127	2218	18	3500	894	4	9	903	0.6	−113.2	−15.71	0.10	–			
33	Spring, near the Chona River	III	0	11200	270	200	3685	34	639	707	2	8	45	0.3	−124.0	−17.65	0.35	–			
37	Lake Baikal	V	0	8659	27	4	20	2	36	22	0.2	0.2	37	3.6	−103.0	−14.37	–	–			

Samples are presented according to the group they belong to. The majority of the samples have a charge balance of <5%. Few samples show charge balance that are >10%.

using a CF-IRMS following (Shouakar-Stash et al., 2005). The analytical precisions for the ^{18}O, ^{2}H, ^{37}Cl and ^{81}Br isotopes are 0.2‰, 1.0‰, 0.1‰ and 0.1‰, respectively.

6. Results

The chemical compositions and isotopic signatures of the Siberian Platform samples are presented in Table 1. Samples were collected at various depths ranging from near surface to almost 4 km. The results show large variations in TDS ranging from less than 1 g/L to almost 600 g/L. The samples are also characterized by different chemical compositions; the two main chemical compositions of waters found in the Siberian Platform are Ca–Cl and Na–Cl waters. The Cl content of the samples shows large variations (~1 to >300 000 mg/L). Generally, the Br content of the samples varies over a large range (<1 to >8500 mg/L). The Br to Cl weight ratio (Br/Cl) of these samples range between 0.0001 and 0.0389. The low end is typical for fresh waters and the high end exceeds most concentrated brines of marine origin reported in the literature (Frape et al., 2004). The Br/Cl for seawater is typically around 0.0034.

The δ^2H and $\delta^{18}O$ results range between −195‰ and −31‰; and −20‰ and +2‰, respectively. The pattern obtained from the δ^2H and $\delta^{18}O$ values is similar to that previously reported by Pinneker et al. (1987). The $\delta^{37}Cl$ values range between −0.67‰ and +1.54‰. This range is within the known variation for Cl stable isotopes of formation waters (Kaufmann et al., 1984, 1988, 1993; Desaulniers et al., 1986; Eggenkamp, 1994; Eastoe and Guilbert, 1992; Eastoe et al., 1999, 2001; Ziegler et al., 2001; Frape et al., 2004; Stewart and Spivack, 2004). The $\delta^{81}Br$ values have a wide variation and range between −0.80‰ and +3.35‰. This variation is larger than the previously reported range (0.00‰ to +1.80 ‰) for Br stable isotopes for natural samples (Eggenkamp and Coleman, 2000; Shouakar-Stash et al., 2005).

7. Discussion

7.1. Classical interpretation based on geochemical parameters

The samples collected for this study were divided and classified according to their Cl and Br content as well as their location on the log(TDS) versus

log(Br) plot relative to the seawater evaporation line (Fig. 3). Based on this classification, samples were divided into 4 groups; A, B, C and D.

Samples in group A are at an advanced stage of seawater evaporation and they plot in the upper right corner of Fig. 3. All samples of this group are characterized by high TDS (>300 000 mg/L) and their Br content ranges between 2000 and 8500 mg/L (Fig. 3). Br–Cl or TDS evolutionary schemes would interpret the group A samples to be the result of extreme evaporation followed by a long interval of water rock interaction in the subsurface (Valyaskho, 1956; Rittenhouse, 1967; Carpenter, 1978; Kharaka and Hanor, 2004). These types of fluids have often been associated with evolution beyond or in conjunction with the precipitation of the bitter salts of K, Mg, Ca. The age of the strata, extensive rock salt and anhydrite beds, and the Ca, Mg, K-rich chemistry, would tend to support this evolutionary model.

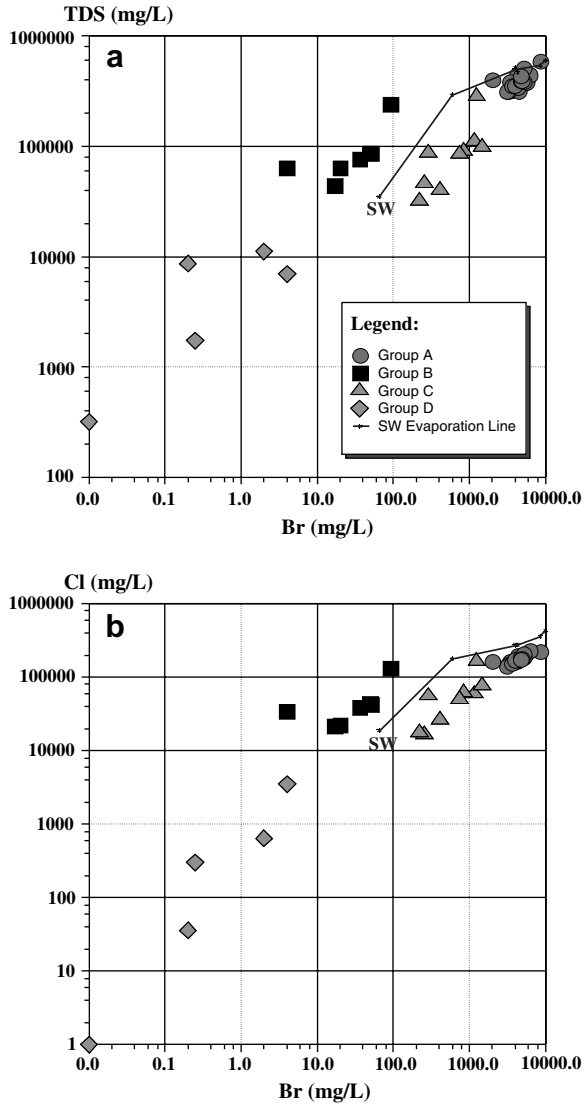

Fig. 3. (a) Logarithmic plot of TDS (mg/L) versus Br (mg/L) for the Siberian Platform samples. (b) Logarithmic plot of Cl (mg/L) versus Br (mg/L) for the Siberian Platform samples. The plot includes the seawater curve and illustrates the position of the four Siberian Platform groups relative to the seawater curve. The seawater curve data are taken from Collins (1975).

Group B samples have TDS values higher than seawater. Most of the TDS values of these samples range between 44 000 mg/L and 87 000 mg/L, however, one of the samples (#22) has a higher TDS value that extends the range to 242 000 mg/L (Fig. 3). The Br content of these samples is less than that expected from simple seawater concentration and they range between 4 and 92 mg/L. The position of these samples in Fig. 3 would normally be interpreted as a result of halite dissolution. The presence of rock salts in the stratigraphic columns, the very low Br content, and the dominant Na–Cl chemistry would tend to support this assumption of salt dissolution for the chemical source of group B samples.

Group C samples are characterized by high TDS values. Eight of nine samples have TDS values that range between 32 000 mg/L and 111 000 mg/L. One sample (#12) of this group has a much higher TDS value (286 000 mg/L) than the rest of the samples (Fig. 3). Samples from this group plot to the right and below the seawater evaporation line. The Br contents of these samples are higher than that expected from simple seawater evaporation. The simplistic interpretation of this set of samples would be a mixture of a typical group A brine chemistry with a dilute fresh water or seawater. In some cases it appears that the halite associated group B fluids may be involved in this dilution or mixing scenario.

The fourth type of waters found in the Siberian Platform presented as group D are characterized by low TDS values that range between 318 mg/L and 11 200 mg/L. Their Br content ranges between <0.1 and 4 mg/L. These samples plot in the lower left corner of the diagram and below group B samples. The TDS values of these samples are less than that of seawater and their Br/Cl ratios are less than that expected from seawater dilution by fresh waters. Their origin is associated with various mixtures of fresh and brackish near-surface waters.

The depths at which the four groups of samples were collected are illustrated in Fig. 4. The majority of group A samples were collected from wells that

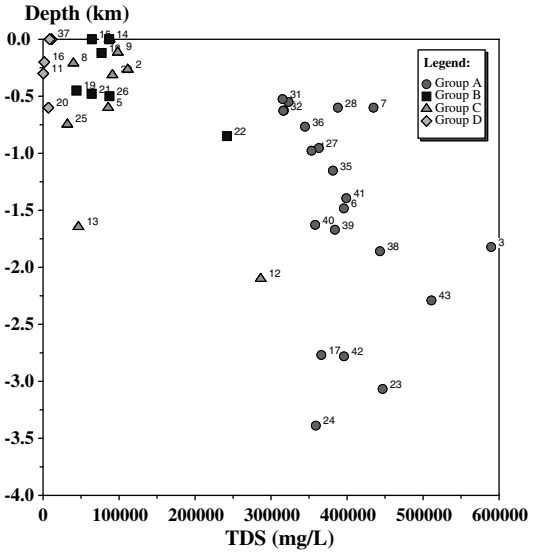

Fig. 4. Depth (km) versus Total Dissolved Solids (TDS) (mg/L) of the Siberian Platform samples. Group A samples were collected from deeper parts of the basin. They are characterized by higher TDS values relative to the other three groups.

are below 1000 m. Group B samples were collected from shallower depths that range between 0 and 1000 m. Although most of the samples from group C are from depths between 100 and 1000 m, a couple of samples are from deeper rock units (1650 and 2100 m). Samples in the D group were collected from surface waters and depths down to 600 m. The previous interpretation for Br versus Cl or TDS is supported by the depth intervals at which the various chemical end members occur.

Further support for the interpretation of origin and evolution of the different groups can be found in Fig. 5. The piper diagram in Fig. 5 demonstrates the chemical compositions of the Siberian Platform samples from the various groups A, B, C and D. The two main distinctive water groups illustrated in Fig 5 are groups A and B. The majority of group A samples are Ca–Cl type brines while group B samples are characterized as Na–Cl type brines. Group C samples, however, show more complex and diverse chemical compositions; the majority of these samples are either Na–Ca–Cl or Na–Cl water types. Nonetheless, Ca–Mg–Cl and Mg–Ca–Cl type waters do also exist. Group C samples appear to have components of A and B but in some cases a third end member or process seems to be influencing the chemical composition. The samples of group D have no characteristic water type and are rather different from one another (Fig. 5).

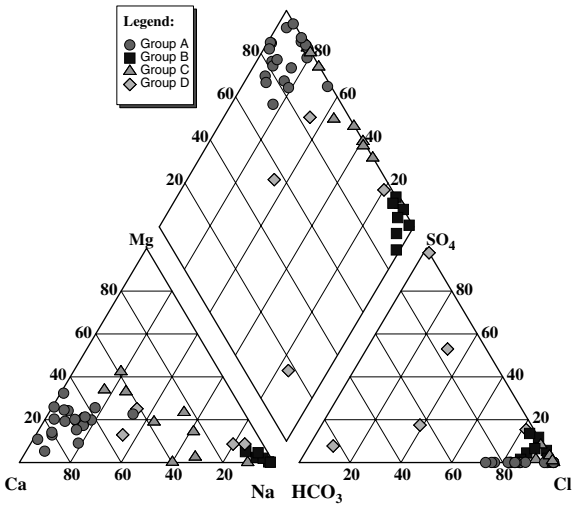

Fig. 5. Piper diagram of the Siberian Platform samples major ion results. The diagram illustrates the different chemical compositions of the four groups. The two major groups are Group A (Ca–Cl) and Group B (Na–Cl).

Fig. 6 demonstrates Cl (mg/L) versus Br to Cl (Br/Cl) weight ratios of the Siberian Platform samples and how they compare to the Br/Cl ratio of seawater (0.0034). The Br/Cl ratios of both groups A and C are far greater than the Br/Cl ratio for seawater. The Br/Cl ratios of group A samples are greater than 0.02 and the Br/Cl ratios of group C samples are between 0.0052 and 0.0196. Group B

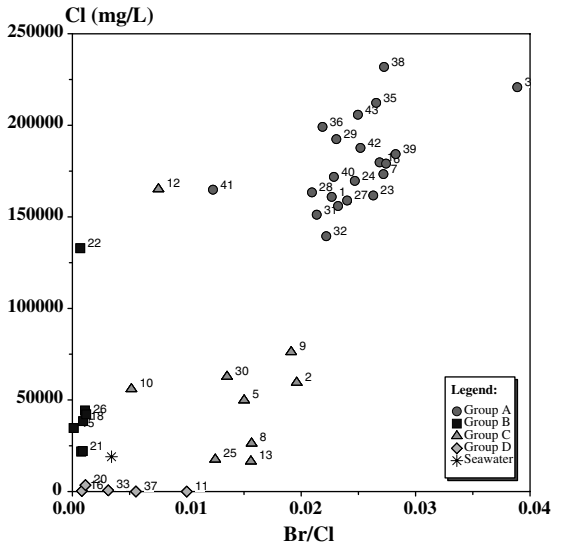

Fig. 6. Plot of the Cl concentrations (mg/L) versus Br to Cl weight ratios of the Siberian Platform Samples. Group A (Ca–Cl) samples are characterized by high Br/Cl ratios while Group B (Na–Cl) samples are characterized by low Br/Cl ratios.

samples, however, are characterized by Br/Cl ratios less than 0.0012, which are much lower than that of seawater. The Br/Cl ratios of group D samples are between 0.0008 and 0.0100. Theses values range from less than the seawater Br/Cl ratio to greater than that of the seawater ratio. However, their Cl contents are far less than that of seawater. The most interesting aspect of this diagram is the extreme Br/Cl ratio of many of the group A samples. Very few analyses in the literature for sedimentary or crystalline brines have Br values as concentrated as the Siberian Platform fluids (Frape et al., 2004). This again would support extreme evaporation, long subsurface residence times and/or strong water–rock interaction. Group A and C brines with their high Br/Cl ratios could have interacted with rock salt (halite) and, by selective diffusive processes and/or consecutive dissolution/precipitation reactions, acquired additional Br from the salt (Land and Prezbindowski, 1981). The presence of interbedded salt in the strata and the low Br group B fluids may lend support to this assumption.

The Cl versus the Na contents (on milli-equivalent bases) of the Siberian Platform samples are shown in Fig. 7. Group B and D samples fall on the 1:1 (Na:Cl) line. Group A and C samples fall above the 1:1 (Na:Cl) line. This diagram helps to confirm that group B samples are heavily impacted by a Na–Cl source that is most likely halite rock salt.

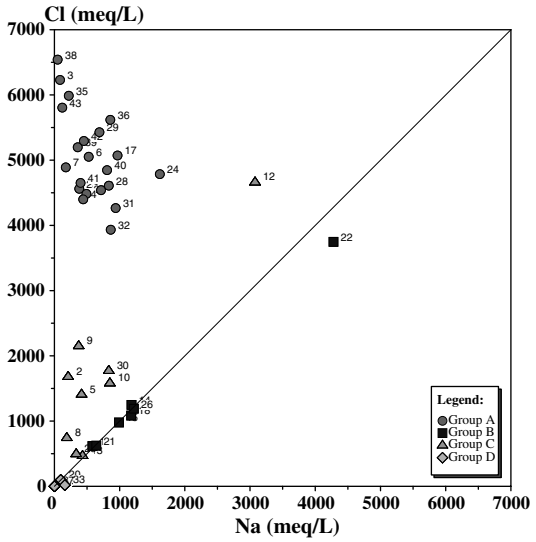

Fig. 7. Chloride concentrations (meq/L) versus Na concentrations (meq/L) for the Siberian Platform samples. Group B (Na–Cl) samples fall on the 1:1 (Na:Cl) line, while Group A samples are located above the 1:1 (Na:Cl) line.

Major ions, minor ions and isotopes can be used to indicate an evaporated seawater signature. The TDS, Cl and Br content of group A samples and where they plot relative to the seawater evaporation line implies that these brines are the residual of evaporated paleoseawater. If the samples of group A are a residual of evaporated paleoseawater, then according to their Br content, they should have undergone extensive evaporation with an approximate evaporation ratio of 30–128 times. Some of the supporting observations of this scenario are the increasing concentrations of Mg, K, Cl and Br and the decreasing concentration of Ca, Na with progressive evaporation (Carpenter, 1978). All of these trends agree well with what is expected during the evaporation of seawater except for the Ca content of these samples which increases instead of decreases (Table 1). This implies that, if evaporated seawater was the precursor, intensive water–rock interactions have replaced Na, Mg and K by Ca. This mechanism can be supported by the fact the Na, Mg and K concentrations of these samples are much lower than what is expected as a result of seawater evaporation for samples with such high TDS. Furthermore these waters are characterized by lower concentrations of SO_4, which is again the opposite of what is expected in the case of a seawater evaporation scenario. One mechanism that could remove SO_4 is forming gypsum, which is common in the geological strata.

Another theory that may explain the observed high Ca concentrations and low SO_4 concentrations, of these samples would be by starting with a $CaCl_2$ type water that is rich in Ca and poor in SO_4. The presence of $CaCl_2$ paleoseawaters that are rich in Ca and poor in SO_4 has already been put forward by [Lowenstein et al., 2003]. They concluded that the paleoseawaters of the Cambrian to Mid-Devonian period were Ca-rich and SO_4-poor. This finding can explain the Ca-rich and SO_4-poor brines found in the Siberian Platform.

Theoretically, brines can occur in sedimentary basins as a result of other mechanisms such as halite dissolution. However, this scenario was not considered for group A samples due to a number of issues that contradict this possibility. The first is that chemical compositions of these brines are Ca–Cl type waters and not Na–Cl type waters, which would be typical for halite dissolution. The brines from this group, as mentioned earlier, are not close to the 1:1 (Na:Cl) line (Fig. 7) expected for brines originating from halite dissolution. Furthermore,

the high concentrations of Br of these samples are not consistent with brines formed by halite dissolution.

The concentrations of minor ions such as Li and Sr are also elevated in group A fluids (Table 1 and Fig. 8). The majority of group A brines have Li concentrations between 40 and 240 mg/L, and Sr concentrations between 1000 and 4000 mg/L. These elevated concentrations are thought to be consistent with evaporated seawater (Davisson and Criss, 1996).

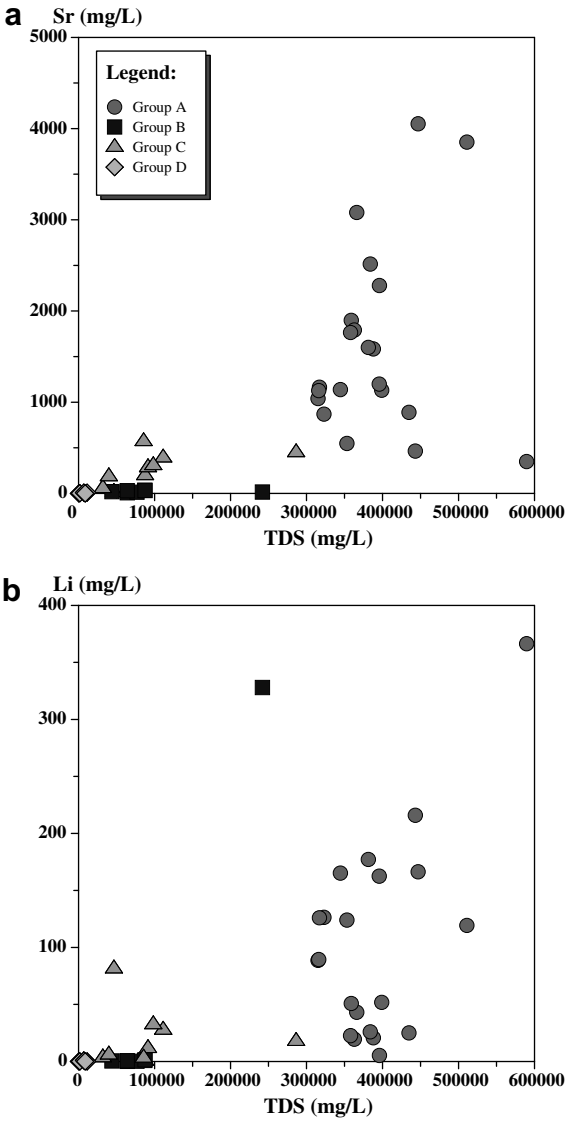

Fig. 8. (a) Strontium (mg/L) versus TDS (mg/L) and (b) Lithium (mg/L) versus TDS (mg/L) of the Siberian Platform samples. Group A (Ca–Cl) samples show elevated Sr and Li contents in comparison with the other 3 groups.

The concentration of the major ions such as Na, Ca, Mg and Cl of group B samples suggest the involvement of dissolution of chemical precipitates, particularly halite (NaCl). The position of the group B samples (Fig. 3) agrees with Rittenhouse's (1967) classical log TDS versus log Br for brines impacted by halite dissolution. During the dissolution of halite, waters progressively increase in Cl and Na while gaining relatively little Ca, HCO_3 and SO_4. In the group B brines, Na concentrations range between 2200 mg/L and 98 000 mg/L, while the Cl concentrations range between 3500 mg/L and 133 000 mg/L, and they comprise between 80% and 97% of the major ion composition on a meq basis. The concentrations of Na and Cl fall on the 1:1 line (Fig. 7) suggesting that they were derived, or at least heavily affected, by halite dissolution. The low concentrations of Ca, Mg, K and Br and low Br/Cl ratios (<0.0012) are consistent with waters derived from halite dissolution.

The elevated Cl concentrations in comparison to Na of group C samples and their location on Fig. 7 relative to the 1:1 (Na:Cl) line suggest that these samples are not derived from halite dissolution or, at least, halite dissolution is not the major cause in forming these saline waters. The high concentrations of Ca, Mg, K, Br and high Br/Cl ratios also lend support to the conclusion that these samples are not primarily derived from halite dissolution. Instead, the ion concentrations and Br/Cl ratio point toward seawater evaporation as the process responsible for the composition of these saline waters. However, the overall chemistry of these samples does not support such a conclusion. In fact, the chemical composition of these samples, especially the major ions (Fig. 5), indicates that these samples are intermediates between group A and group B and that group C samples are a product of mixing between the two other end members with possible modification by water–rock interaction.

Samples from group D represent a few examples of fresh to brackish waters. The samples are from three shallow bore holes and two surface waters (a spring near the Chona River (#33) and from Lake Baikal (#37)).

7.2. Classical interpretation based on traditional isotopes (^{18}O and ^{2}H)

Fig. 9 shows the δ^2H versus $\delta^{18}O$ values of the four groups of samples. The different water groups are not distinguished from each other based solely

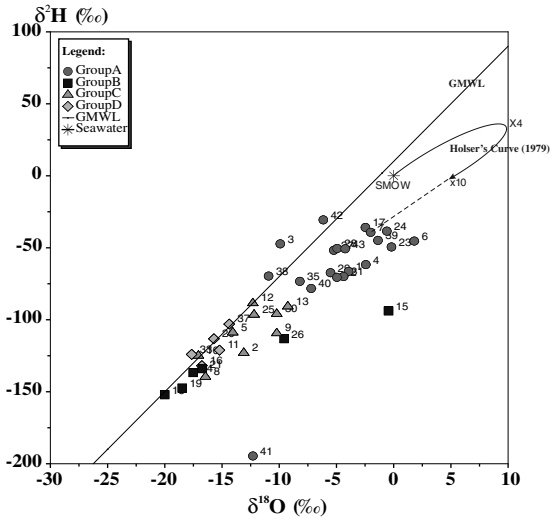

Fig. 9. Stable isotopic composition (δ^2H and $\delta^{18}O$) of water samples from the Siberian Platform samples compared to the Global Meteoric Water Line (GMWL). Group A (Ca–Cl) samples are characterized by enriched δ^2H and $\delta^{18}O$ values relative to results from the other groups.

on their chemical composition; they are also distinguishable based on isotopic characteristics. The O and H stable isotope signatures of group A samples are the most enriched in comparison to the other groups and they fall to the right of the GMWL and along a possible evaporation line. Holser (1979) estimated the behavior of δ^2H and $\delta^{18}O$ of seawater during evaporation. According to his estimates, both δ^2H and $\delta^{18}O$ values are enriched progressively during the first stage of evaporation. Once seawater is concentrated four times both δ^2H and $\delta^{18}O$ values of the saline solutions start a reversal trend toward depleted values. The samples from group A plot further down the estimated curve of Holser (1979) (Fig. 9) for concentrating seawater 10 times by evaporation. This indicates that these brines underwent extensive evaporation that exceeds a 10-fold increase in seawater concentration. This lends support to evaporation as the major evolutionary process that affected the original water. It is also in agreement with the assumption made earlier based on the TDS and Br concentrations that these samples experienced evaporation of 30–128 times. Although these samples cluster together, they also show some variation in their isotopic characteristics, which is consistent with what is observed through their chemical composition. This is probably due to the large geographic distances that these samples cover resulting in various degrees of evaporation at the time of formation.

Five of the seven group B samples fall on the GMWL indicating that these samples did not experience significant evaporation and suggesting that the origin of these samples is probably fresh meteoric waters that were impacted by the salt deposits. This is consistent with the sample depth (Fig. 4) where infiltration of fresh water is feasible. The δ^2H versus $\delta^{18}O$ values of group B samples are the most depleted of all samples and their signatures are very different from group A signatures. They are typical of recharge under colder climate conditions and differ from the isotopic signatures of present day shallower samples found in group D samples. The isotopic differences, along with the chemical differences discussed previously, indicate that groups A and B are representative of two different types of brines from two different processes and sources. One of the two samples deviating from the GWL and showing enriched values for δ^2H and $\delta^{18}O$ ($-113‰$ and $-9.6‰$, respectively) is from Lake Mohsogoloh (sample #15). The enrichment in both stable isotopes is explained by the evaporation effect on lake water. The other sample that showed some deviation from the GMWL is sample #26, which was sampled from a 500 m borehole in a dolomite aquifer. This specific sample, besides being enriched in δ^2H and $\delta^{18}O$ ($-94‰$ and $-0.5‰$, respectively), has the highest pH value of all samples (8.4). It has the lowest water temperature (-1 °C) of this group and the most enriched $\delta^{37}Cl$ ($+1.54$ ‰) value of all samples. The enrichment in δ^2H and $\delta^{18}O$ can be explained by evaporation. The enriched $\delta^{37}Cl$ value is greater that any reported $\delta^{37}Cl$ values for evaporites ($-0.5‰$ to $+1‰$) in the literature (Kaufmann et al., 1984; Eggenkamp and Schuiling, 1995; Eggenkamp et al., 1995; Eastoe et al., 1999, 2001; Eastoe and Peryt, 1999; Stewart and Spivack, 2004). Although the presence of evaporites outside this range is possible, this enriched $\delta^{37}Cl$ value is not easily explained simply by halite dissolution. It is probably more reasonable to assume that this specific sample underwent other processes in combination with halite dissolution, such as water–rock interaction with some minerals that were enriched in $\delta^{37}Cl$.

Group C samples either fall on the GMWL or to right of the GMWL on possible evaporation lines. The location of these samples on the δ^2H versus $\delta^{18}O$ plot is intermediate between group A and group B samples, with a tendency to be closer to

group B samples. This observation is consistent with the discussion on the chemical data and further supports the assumption that these samples are the probable result of mixing between group A and B brines.

The δ^2H and $\delta^{18}O$ of group D samples are within the local precipitation range. All samples in group D fall on or just below the GMWL, suggesting that these samples do represent the local meteoric waters in each of the areas.

7.3. Additional information to be learned from ^{37}Cl and ^{81}Br isotopes

The Cl and Br stable isotope results of Group A samples show narrow variations (Fig. 10). The $\delta^{37}Cl$ values fall between $-0.67‰$ and $+0.04‰$ (range of $0.71‰$) and the $\delta^{81}Br$ values are between $-0.31‰$ and $+0.27‰$ (range of $0.58‰$). The relatively narrow variation of these two isotopes might suggest that the $\delta^{37}Cl$ and $\delta^{81}Br$ signatures of the original source waters are within the isotopic ranges obtained. The small variations would be due to the large geographical area over which the samples occur or to post depositional evolution(s) that affected the composition of the waters. Although the variations for both isotopes are not wide, they are significant enough to state that they are the result of various degrees of evolution or mixing, which is consistent with the assumptions made earlier based on chemical composition and traditional isotopes (δ^2H and $\delta^{18}O$).

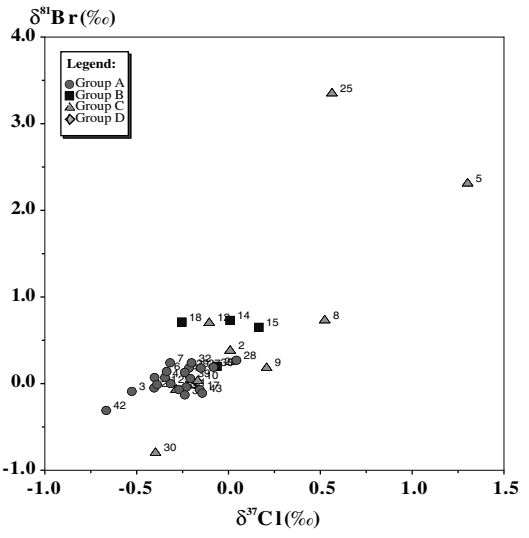

Fig. 10. The $\delta^{37}Cl(‰)$–$\delta^{81}Br(‰)$ relationship for the Siberian Platform samples. Group C samples show the widest spread of both $\delta^{37}Cl$ and $\delta^{81}Br$ values. These $\delta^{81}Br$ values demonstrated an increased range ($-0.80‰$ to $+3.35‰$) for $\delta^{81}Br$ in natural samples.

Four samples (#17, #23, #24 and #42) of group A were obtained from the crystalline basement (AR-PR) from two different sites (II and V) (Fig. 1). These samples have isotopic signatures (δ^2H, $\delta^{18}O$, $\delta^{37}Cl$ and $\delta^{81}Br$) that are characteristic of crystalline type brines (Frape et al., 2004). A careful examination of the isotopic values of the 4 brines shows some small discrepancies. Sample #42 has δ^2H and $\delta^{18}O$ values that plot above (to the left of) the GMWL while the other three samples plot below (to the right of) the GMWL unlike crystalline shield brines. Values above the GMWL are not uncommon in crystalline type brines (Fritz and Frape, 1982; Frape et al., 2004). This is most likely due to hydration processes and the formation of clay minerals that affected the isotopic signature and enriched both δ^2H and $\delta^{18}O$ values (Fritz and Frape, 1982). The isotopic signatures of these group A basement brines, unlike typical crystalline brine signatures, may be more representative of Cambrian sedimentary formation fluids that have penetrated the underlying rocks. Examining the $\delta^{37}Cl$ and $\delta^{81}Br$ values of these four brines shows that their values are very close to those reported for Canadian Shield brines (Shouakar-Stash et al., 2005). It is worth noting here that sample #42 shows the most depletion of $\delta^{37}Cl$ and $\delta^{81}Br$ compared to all other samples (Fig. 10), as well as a significant isotopic shift for ^{18}O (Fig. 9). It is hypothesized that hydration and other forms of long term water–rock interactions between brines and crystalline rocks have modified the Cl and Br stable isotope signatures in these samples. This coincidence between δ^2H and $\delta^{18}O$ values plotting above the GMWL and the $\delta^{37}Cl$ and $\delta^{81}Br$ values that are more depleted is also observed in sample #3. This might suggest some common element altering δ^2H and $\delta^{18}O$ and a similar alteration of $\delta^{37}Cl$ and $\delta^{81}Br$ as a result of some specific geochemical process(es).

The $\delta^{37}Cl$ values of group B samples range between $-0.25‰$ and $+1.54‰$; however, four of the samples fall within a narrow range, $-0.25‰$ and $+0.17‰$ (Fig. 10). These values are consistent with and within the reported range for halite ($-0.5‰$ and $+1.0‰$) (Kaufmann et al., 1984; Eggenkamp and Schuiling, 1995; Eggenkamp et al., 1995; Eastoe et al., 1999, 2001; Eastoe and

Peryt, 1999; Stewart and Spivack, 2004). The $\delta^{81}Br$ values range between +0.20‰ and +0.73‰. The $\delta^{81}Br$ values of this group are generally more enriched than group A samples. The relatively small variation of these two isotopes suggests that the processes that affected these samples were limited to halite dissolution and evaporation. From the chemical composition and the isotopic characteristics of the samples of this group, it is concluded that halite dissolution as a result of recharge of a ^{2}H and ^{18}O depleted colder climate water is the major process in creating these saline waters. It is speculated that isotopic alteration of Br stable isotopes during halite dissolution is not a major fractionation process. Therefore, the $\delta^{81}Br$ signature of halite deposits in the study area are probably similar to those of $\delta^{81}Br$ values obtained from group B brine samples (+0.20‰ and +0.73‰).

The $\delta^{37}Cl$ values of group C samples range between −0.40‰ and +1.30‰, with 6 of 9 samples between only −0.40‰ and +0.56‰ (Fig. 10). The $\delta^{81}Br$ values of this group have the greatest range of all samples collected, between −0.80‰ and +3.35‰ (Fig. 10). The combination of these results with the $\delta^{37}Cl$ results (Fig. 10) strongly dismisses the simple mixing scenario discussed above between group A and group B (e.g., Figs. 5,7,9). Although the major ion composition and the $\delta^{2}H$ and $\delta^{18}O$ results suggest a mixing scenario between group A and B samples to produce group C samples, this argument is not convincing when considering the $\delta^{37}Cl$ and $\delta^{81}Br$ results. A more complex scenario for brine evolution such as water–rock interaction and/or permafrost freezing needs to be considered. Although a definite answer is not attainable with data available, it is clear that it is not a simple mixing scenario. The large spread observed for the $\delta^{81}Br$ implies that these samples evolved as a result of several potential natural processes that resulted in the large fractionation of Br stable isotopes.

Fig. 11 illustrates sample depth versus $\delta^{37}Cl$ and $\delta^{81}Br$ signatures. A positive correlation between depth and both $\delta^{37}Cl$ and $\delta^{81}Br$ is apparent for most of the shallower samples of group C. Both isotopes tend to be more enriched with depth. The relationship with depth is more obvious for ^{81}Br and the fractionation is larger. This is probably due to the lower concentration of Br within the saline fluids. It is speculated that the fractionation mechanisms are most likely caused by extreme evolutionary processes near surface such as permafrost freezing, diffusion and/or water–rock interaction.

The $\delta^{37}Cl$ values of group D samples range between −0.13‰ and +0.58‰ (Table 1). They tend to be more positive than the deeper samples and are typical of most shallow groundwaters reported in the literature (Frape et al., 2004; Stewart and Spivack, 2004). These samples were not analyzed for $\delta^{81}Br$ due to the very low Br content and small sample volumes.

Fig. 12 shows the $\delta^{37}Cl$ and $\delta^{81}Br$ values obtained from group A samples based on the

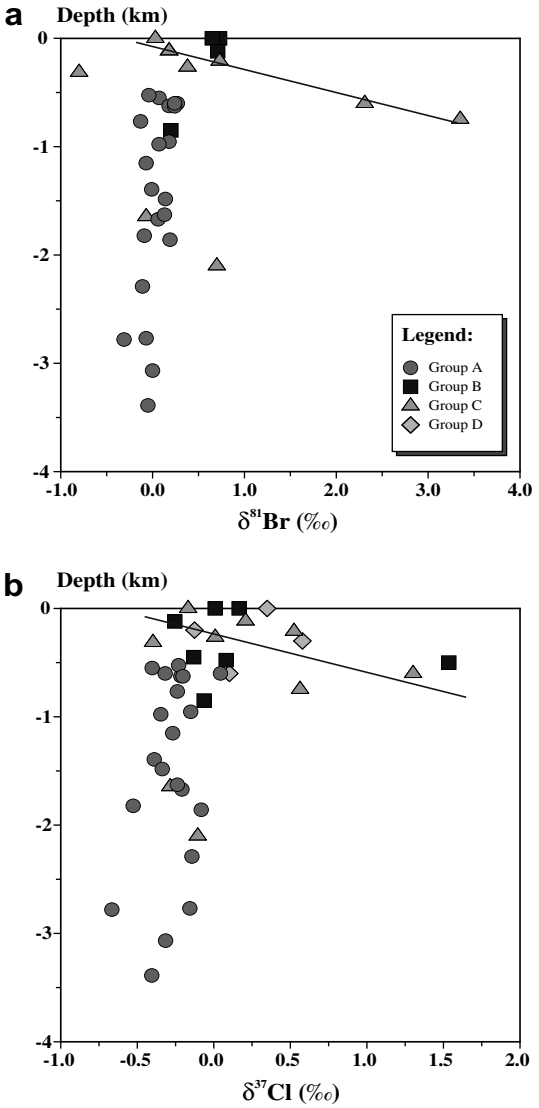

Fig. 11. (a) Depth (km) versus $\delta^{81}Br$(‰) and (b) depth (km) versus $\delta^{37}Cl$(‰) of the Siberian Platform samples. Group C samples show the most diverse range for both isotopes. An enrichment of both isotopes with depth in the shallower samples of group C is indicated.

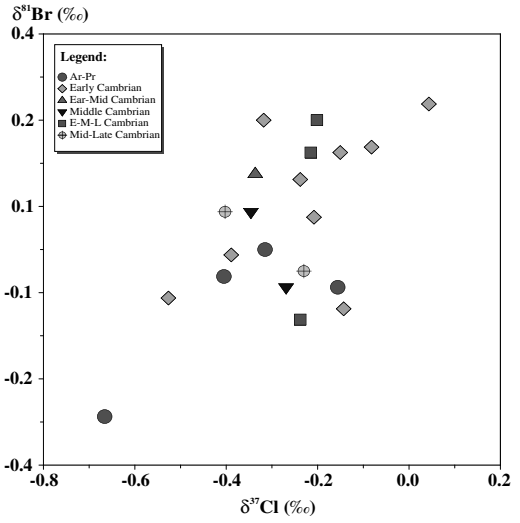

Fig. 12. $\delta^{37}Cl(‰)$–$\delta^{81}Br(‰)$ relationship of group A samples of the Siberian Platform according to the geological section from which they were sampled.

geological section from which they were sampled. This plot is presented to determine if there is any relationship between the isotopic signatures of the two isotopes and the stratigraphy in group A, as these samples represent paleoseawater. The majority of group A samples are either Archaean–Proterozoic crystalline brines or Early Cambrian sedimentary brines. However, there are some samples that are associated with Early to Middle, Middle, and Middle to Late Cambrian formations. All of the Archaean–Proterozoic crystalline brines belong to group A. Their $\delta^{37}Cl$ values range between $-0.67‰$ and $-0.16‰$ and their $\delta^{81}Br$ values range between $-0.31‰$ and $0‰$. This group is characterized by having the most depleted range in both isotopes. The Early Cambrian sedimentary brines $\delta^{37}Cl$ values range between $-0.53‰$ and $+0.04‰$ and their $\delta^{81}Br$ values range between $-0.11‰$ and $+0.27‰$. The $\delta^{37}Cl$ and $\delta^{81}Br$ values of the Early to Middle, Middle, and Middle to Late Cambrian formation waters fall within the range for the Early Cambrian brines. This suggests that the Cambrian sedimentary brines and the Crystalline brines in this area have a common origin. However, interactions of the brines with crystalline rock have modified their isotopic signature towards more depleted values. This, in turn, implies that the $\delta^{37}Cl$ and $\delta^{81}Br$ signatures of the crystalline rocks in that area are depleted and characterized by negative values with respect to both SMOC and SMOB.

The fractionation of Cl stable isotopes during precipitation of halite is reported to be very small (Eggenkamp et al., 1995). Fractionation of Br stable isotopes during the same process is not known. However, the authors think that changes of Br stable isotope signatures of the brines during evaporation and subsequently halite precipitation are negligible. The amount of Br that is incorporated in halite during precipitation is very small in comparison to the residual Br in solution. Therefore, a measurable fractionation can only occur in the Br co-precipitated with halite, and not in the residual brines. Thus, the obtained $\delta^{37}Cl$ and $\delta^{81}Br$ ranges of the Early Cambrian formation waters could represent the range of $\delta^{37}Cl$ and $\delta^{81}Br$ of the original paleoseawaters that formed these brines.

8. Conclusions

The water samples collected from the Siberian Platform were examined and classified into four different groups based on their chemical composition. The four groups were addressed in this paper as A, B, C and D. The samples of these groups are distributed throughout different geographical locations across the Siberian Platform.

Group A samples are Ca–Cl type waters. They are from depths below 1000 m and are characterized by high TDS (>300 000 mg/L). The $\delta^{2}H$ versus $\delta^{18}O$ values of this group of samples range between $-78‰$ and $-31‰$; and between $-10.9‰$ and $+1.8‰$, respectively The $\delta^{37}Cl$ and $\delta^{81}Br$ values of this group of samples range between $-0.67‰$ and $+0.04‰$; and between $-0.31‰$ and $+0.27‰$, respectively. Based on their chemical composition and isotopic signatures, it is postulated that they are residual brines of evaporated paleoseawaters.

Group B samples are Na–Cl type waters. They occur at shallower depths (0–1000 m) and their TDS values range between 44 000 mg/L and 242 000 mg/L. The $\delta^{2}H$ versus $\delta^{18}O$ values of group B samples range between $-152‰$ and $-94‰$; and between $-20‰$ and $-0.5‰$, respectively. The $\delta^{37}Cl$ and $\delta^{81}Br$ values of this group of samples range between $-0.25‰$ and $+1.54‰$; and between $-0.25‰$ and $+0.17‰$, respectively. The chemical and isotopic data obtained for group B samples indicate that these samples are derived from halite dissolution, most likely as a result of recharge in a colder climate, possibly Pleistocene derived water.

Group C samples are not characterized as one primary water type. However the majority of these

samples are either Na–Ca–Cl or Na–Cl type waters. Samples are from various depths ranging from 100 to 2100 m and are characterized by high TDS values between 32 000 mg/L and 286 000 mg/L. The δ^2H and $\delta^{18}O$ of group C samples range between −140‰ and −89‰; and between −17.1‰ and −9.3‰, respectively. The $\delta^{37}Cl$ and $\delta^{81}Br$ values of these samples range between −0.40‰ and +1.30‰; and between −0.40‰ and +0.56‰, respectively. The chemical compositions and isotopic signatures of this group of samples showed differences so that data interpretation could not lead to a definite brine source. However, the available data suggest that these samples were modified greatly via a number of scenarios; geochemical evolutionary processes such as permafrost freezing, mixing, leaching of salt and water–rock interaction could have all affected their chemistries and isotopes.

Group D samples represent fresh and brackish waters in the area and are not characterized by one specific water type. They are either surface waters or from shallow wells. They are characterized by low TDS values that range between 318 mg/L and 11 200 mg/L. The δ^2H and $\delta^{18}O$ of group D samples range between −132‰ and −103‰; and between −17.7‰ and −14.4‰, respectively, and are local meteoric in origin. The $\delta^{37}Cl$ values of these samples range between −0.13‰ and +0.58‰.

The Br stable isotope results obtained from this study are very similar for most samples (−0.30 to +0.75‰), but a few samples from group C extend the known isotopic range between −0.80‰ and +3.35‰. This variation is wider than previously reported results (0.00‰ to +1.80 ‰) for Br stable isotopes of natural samples (Eggenkamp and Coleman, 2000; Shouakar-Stash et al., 2005). The Archaean–Proterozoic crystalline brines were found to have $\delta^{37}Cl$ values that range between −0.67‰ and −0.16‰ and $\delta^{81}Br$ values that range between −0.31‰ and 0‰, while the Early Cambrian sedimentary brines have $\delta^{37}Cl$ values that range between −0.53‰ and +0.04‰ and $\delta^{81}Br$ values range between −0.11‰ and +0.27‰. There is a slight enrichment in values with decreasing age and/or depth of sample which may be due to seawater variation with time or long term water–rock interaction.

The variation of Br stable isotopes observed in this study can imply two things: (1) different water types may have different Br stable isotope signatures, i.e., they are originally different, and (2) various geochemical processes may affect the Br stable isotopes of the waters differently and cause significant fractionations. These differences could be a valuable tool to investigate the origins of formation waters or to explore the geochemical evolution processes that influence formation water chemistry and, consequently, to improve understanding of the hydrogeological behavior of sedimentary basins and crystalline shield areas. This knowledge can be very crucial in understanding the hydraulic connection between different geological sections and, accordingly, its application in various fields such as waste disposal and oil exploration. Therefore, it is important to further investigate and examine the behavior of Br stable isotopes in nature and during geochemical and physical processes such as water–rock interaction, halite impact, permafrost effects, diffusion and ion filtration.

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