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The Salt Composition of Rivers in Wrangel Island

V. Yu. Lavrushin[a] **and A. R. Gruzdev**[b]
[a]*Geological Institute, Russian Academy of Sciences, Pyzhevskii per. 7, Moscow, 119017 Russia*
e-mail: v_lavrushin@ginras.ru
[b]*FGU Wrangel Island State Reserve, Chukotka administrative district, Chaun region,*
Pevek, ul. Obrucheva 38, 689400 Russia
e-mail: islandwrangel@chukotnet.ru

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Abstract—Pioneer information about the chemical composition of river water in Wrangel Island has been obtained. It is shown that the water composition reflects the lithogeochemical specifics of primary rocks and ore mineralization. In contrast to many areas of the Russian Far North, river waters of the island are characterized by an elevated background value of total mineralization (i.e., total dissolved solids, TDS) (0.3–2 g/l) and specific chemical type (SO_4–Ca–Mg). This is related to abundance of Late Carboniferous gypsiferous and dolomitic sequences in the mountainous area of the island. It has also been established that the salt composition of some streams is appreciably governed by supergene alterations of the sulfide mineralization associated with the quartz–carbonate vein systems. They make up natural centers of surface water contamination. Waters in such streams are characterized by low pH values (2.4–5.5), high TDS (up to 6–23 g/l) and the SO_4–Mg composition. These waters are also marked by anomalously high concentrations of heavy and nonferrous metals, as well as REE, U, and Th.

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Study of the chemical composition of water in the Arctic rivers is important for its utilization as a local source of water supply and for the solution of several ecological and scientific issues concerning the specifics of the formation of salt composition of water in areas of the Russian Far North. Groundwater is missing in the water budget of the permafrost regions. Therefore, salt composition of the river water is restricted to the input of salts with atmospheric aerosols (particularly, in maritime regions) and the leaching from rocks in the seasonal thawing zone. Investigation of the salt composition of water in the Arctic rivers also provides insight into the role of natural sources of its contamination. Such sources can be represented by primary rocks containing minerals that are unstable in the retrograde metamorphism zone.

The salt composition of water in Wrangel Island was not studied previously. Therefore, the aim of the present work was to study specific features of the macro- and microcomponent compositions of river water in the Wrangel Island State Reserve. One of the main tasks was to assess the role of various sources of dissolved salts: marine salt composition or products of salt leaching from the water-enclosing rocks. We also attempted to determine the geochemical specifics of various natural sources of river water contamination and their link with some mineral resources or lithogeochemical properties of primary rocks.

MATERIALS AND METHODS

During field investigations in 2006 in the Wrangel Island region, workers of the State Reserve noted that water in some streams has an unusual color: milky white or red. Eleven water samples were taken to examine causes responsible for such anomalies. Sampling was continued in 2007, 2009, and 2010. In total, 32 water samples were taken in the last years. Sampling sites were chosen with the consideration of specific features of streams: the presence of suspended particulates in water, color of bottom sediments, anomalous development of algae, and so on.

The highest anomalies of water color were observed in 2007. The anomalously warm summer of this year provoked an intense thawing of frozen ground, resulting in erosion of the underlying rocks and alteration of the chemical composition of rocks. For example, middle courses of the large Krasnyi Flag and Klark rivers were white and whitish blue. Small rivers flowing from the northern part of the Severnye Mountains were also marked by water color alteration. Water in these rivers was transparent in other years. Therefore, some materials collected in these years characterize the composition of small streams with anomalous properties of water or of streams used for the sampling of potable water. However, almost all these streams make up sources of the major large rivers or their tributaries in the island. Therefore, the data obtained somehow reflect the regional specifics of salt composition in the insular river network. The sampling scheme and

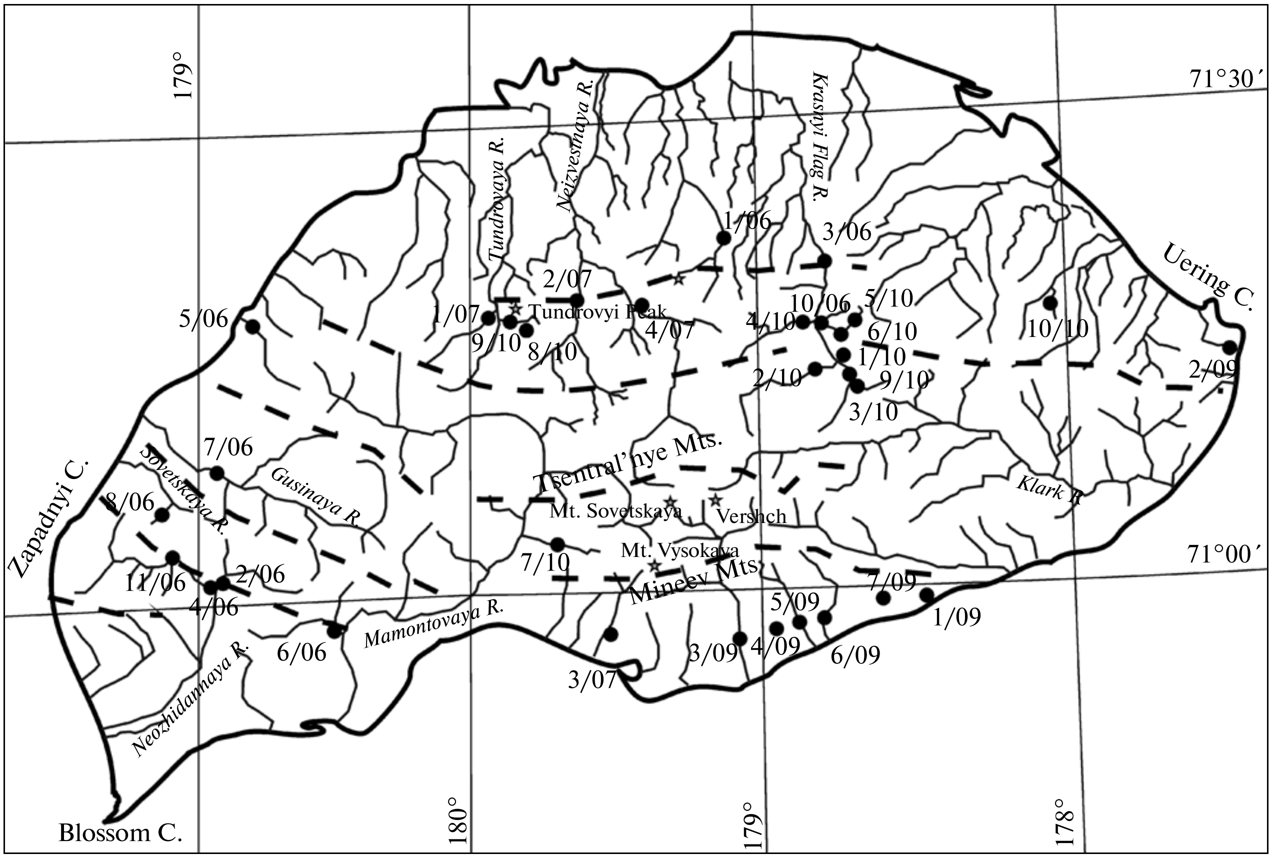

Fig.1. River sampling points in Wrangel Island (dots designate highland systems).

description of sampling sites in 2006–2010 are presented in Fig. 1 and Table 1.

The sampling of water samples and the preliminary description of sampling sites were carried out by workers of the State Reserve. The samples were collected in plastic bottles (1.5–2 l) and then submitted to the Geological Institute, Russian Academy of Sciences, for the subsequent study.

Water samples were taken without any conservation. Therefore, their chemical composition could be distorted and depleted in heavy metals (Zn, Cu, Pb, Sb, Sn, Fe, Mn), Th, U, and REE. All these elements could be absorbed on the wall of bottles or precipitated. Influence of sorption could be maximal in the samples with neutral pH values (6–7.5) and obviously less prominent in waters with pH < 6. Therefore, the microcomponent concentrations determined in waters with the neutral pH values can be considered minimal ones.

The macrocomponent composition (ðÍ, Cl, HCO_3, F) was determined in the Chemical Laboratory of the Geological Institute, Russian Academy of Sciences, Moscow. Samples assigned for the determination of microcomponents were filtered through a 0.45 μ filter. Then, they were analyzed by ICP-AES and ICP-MS methods at the Analytical Center of the Institute of Microelectronics Technology and High Purity Materials, Russian Academy of Sciences (IPTM RAN, Chernogolovka, Moscow region). The determinations were carried out with ICAP-61 (Thermo Jarrel Ash, United States) and X-7 ICP-MS (Thermo Elemental, United States). Analytical uncertainty of this method was 10–15% for some components and could be as high as 50% near the detection limit.

In addition to water sample, an alluvium sample (stones and sandy–gravelly material with iron oxides) was taken at site 10/10. Smear slides of the ferruginated coating prepared in the laboratory were used to obtain the acidic leachate (1Ì HNO_3), which was also analyzed by the ICP-MS and ICP-AES methods at IPTM RAN. The results obtained are presented in Tables 1, 2, and 3.

Interpretation of the REE concentrations is based on their NASC-normalization according to (Gromet et al., 1984).

The Ce anomaly was calculated according to the following formula: $Ce_{an} = Ce/Ce_{NASC}/(0.5 \cdot La/La_{NASC} + 0.5 \cdot Pr/Pr_{NASC})$; the Eu anomaly, according to:

Table 1. Results of the determination of pH, as well as concentrations of HCO_3, C1, and TDS in the river water of Wrangel Island

Sample no. in Fig. 1	Sampling site	pH	HCO_3	Cl	Min
			mg/l	mg/l	g/l
1/06	Pestsovaya R.	7.38	n.d.	49.6	0.34
2/06	Kamnesharka Cr., tributary of the Neozhidannaya R.	7.52	n.d.	28.4	0.17
3/06	tributary of the Krasnyi Flag R. at the exit from the mountains	7.49	n.d.	42.5	0.38
4/06	Neozhidannaya R., near the ravine above the confluence with the Kamnesharka Cr.	7.51	n.d.	28.4	0.14
5/06	Zapad C., creek near lighthouse	7.51	n.d.	45.5	0.20
6/06	Tupee Cr.	7.6	n.d.	56.7	0.30
7/06	Gusinaya R.	7.98	110	28.4	0.46
8/06	tributary of the Sovetskaya R. (red water)	2.43	<10	567	23.01
9/06	right tributary of the Krasnyi Flag R	7.82	61	42.5	0.78
10/06	Krasnyi Flag R.	7.19	17	18.9	0.31
11/06	tributary of the Sovetskaya R. (white water)	4.69	12	28.4	0.57
1/07	Tundrovaya R., mouth of the Syroechkovskii Cr.	n.d.	110	100	1.14
2/07	Lemmingovyi Cr.	n.d.	154	78	1.09
3/07	Somitel'naya R., lower course, 300–350 m from the mouth	n.d.	162	92	1.96
4/07	Tsirkovyi Cr., mouth	n.d.	45	39	1.86
1/09	Bazovyi Cr.	n.d.	48	99	0.53
2/09	Uering C., middle course of the creek flowing from Mt. Zamkovaya and falling into the Draga Bay, depth up to 10 cm, length about 1 km	n.d.	16	28	1.55
3/09	Khishchniki R., 5 m/s	n.d.	73	14	0.90
4/09	Klykovyi Cr., 2 m/s	n.d.	16	14	0.64
5/09	Persykhayushchii Cr., 1 m/s	n.d.	16	14	0.77
6/09	Aterton R., 1 m/s	n.d.	16	14	0.43
7/09	Creek 7 km west of the Ushakovsky Settlement, 1 m/s	n.d.	32	14	0.80
01/10	right tributary of the Krasnyi Flag R. flowing at the middle course (accompanied by the deposition of white sediment in the river)	4.89	6.1	55	1.78
02/10	left tributary of the Krasnyi Flag R., sediment-free transparent water with abundant green algae	4.29	6.1	34	1.09
03/10	above the river influx (sample 01/10), tributary of the Krasnyi Flag R., sediment-free transparent water	7.39	143	55	0.76
04/10	Otrozhnaya R. (left tributary of the Krasnyi Flag R., with red sediment on the bottom)	7.34	131	76	2.15
05/10	right tributary of the Krasnyi Flag R. flowing at the middle course near the ravine (drinking water is taken from this creek). Zones with red and white sediments have been detected above the sampling site	6.85	94	55	1.97
06/10	right tributary of the Krasnyi Flag R. flowing at its middle course (light blue sedimen)	5.35	61	34	0.54
07/10	Sovynyi Cr. (central part of the island), flow rate 0.7 m/s, depth 15 cm	6.87	161	20	1.07
08/10	Tundrovyi peak, Kukhonnyi Cr. (potable water), northern part of the island, flow rate 0.5 m/s, depth up to 70 cm	5.59	6.1	50	2.11
09/10	Tundrovyi peak, Mertvyi Cr., northern part of the island	5.57	6.1	39	6.21
10/10	creek located east of the Shumnaya R. at the exit to Tundra Akademii, with white sediment on the bottom	7.00	12	21	1.32

Note: (n.d.) Not detected; (R.) river; (Cr.) creek; (C.) cape.

$$\mathrm{Eu_{an}} = \mathrm{Eu/Eu_{NASC}}/(0.5 \cdot \mathrm{Sm/Sm_{NASC}} + 0.5 \cdot \mathrm{Gd/Gd_{NASC}}).$$

OVERVIEW OF THE WRANGEL ISLAND ENVIRONMENT

The island is located in the Arctic Ocean at the boundary of the East Siberian and Chukchi seas (70.6N, 178.6W–71.7N, 177.5E). Its maximal length is approximately 140 and 80 km along the nearly latitudinal and meridional strikes, respectively. The island hosts more than 1400 rivers and streams usually marked by small length varying from 5–15 to 35–60 km.

The southern part of the island includes a latitudinal highland system (watershed) extending from Cape Zapadnyi to Cape Uering. Consequently, most rivers flow toward the northern or southern coast of the island. Since the mountainous watershed approaches the southern coast, rivers in the southern sector are 2–4 times shorter relative to the northern sector.

The western and central parts of the watershed are higher. They are often marked by ridges more than 500–800 m high. The highest peaks—Tsentral'nye and Mineev Mountains (Mt. Sovetskaya, 1096 m; Mt. Vysokaya, 1021 m) are situated in the central sector of the mountain chain. The eastern part of the watershed is located at a lower altitude: no more than ~360 m for some highlands.

In the southern sector, the river system was formed in the course of active neotectonic movements. This is evident from the downcutting of nearly latitudinal mountain chains by river valleys, e.g., valleys of the Khishchniki, Mamontovaya, and Neozhidannya rivers. According to (*Ostrov* ..., 2003), amplitude of neotectonic (late Pleistocene?) movements in the southern sector of the island were approximately 50–250 m.

Hydrological activity of the rivers is very short-lived and marked by seasonal character. The snow melting period starts at the beginning of June, whereas the freezing period often begins in the first half of September. Seepage flow of rivers is missing because of the universal development of permafrost. Therefore, the winter period is marked by the termination of river runoff: the rivers dry up or freeze completely. Melt water is intensely discharged during the spring period. Recharge of rivers in the spring-autumn period is related to the thawing of snow patches, atmospheric precipitation, and seasonal thawing of frozen rocks.

The river discharge pattern (recharge type, flow rate, and number of tributaries) is strongly influenced by topographic features of the island: the northern part is boggy lowland, while the southern part is mountainous area. Consequently, rivers in the northern part flowing over the coastal tundra zone are characterized by a calmer flow. Rivers in the southern area are torrentous (flow rate up to 5–7 m/s), and their valleys are filled with coarse-clastic alluvium. It is also evident that the seasonal thawing of frozen rocks plays a greater role in the tundra zone than in the rocky areas, where the recharge of rivers during the summer is mainly related to the thawing of snow patches and atmospheric precipitation.

SPECIFIC FEATURES OF THE GEOLOGICAL SETTING AND MINERAL RESOURCES

The rivers drain various rocks that can contain readily soluble compounds and minerals. They represent different sources of specific macro- and microcomponents in the riverine salt composition. Therefore, we present below an overview of the geological setting and some mineral resources in the island (*Ostrov* ..., 2003).

The Wrangel Island shows exposures varying in age from the Late Proterozoic rocks to Quaternary sediments. The oldest (Late Proterozoic–Early Cambrian) complexes are exposed in cores of anticlinal folds of the Tsentral'nyi anticlinorium (Mamontovaya and Tsentral'nye Mountains). They are represented by crystalline schists formed after basic and intermediate effusives and sills. The upper portion of schist section includes arkosic metasandstones and lenticular marble beds.

The Middle Paleozoic is represented by the Late Silurian–Devonian sequence of mostly terrigenous rocks (sandstones and shales) with an appreciable content of carbonate rocks in the lower part of the complex.

The Late Paleozoic complex is dominated by carbonate rocks (limestones and less common dolomites), local evaporites, and terrigenous rocks (siltstones and shales) with basic and acid rocks in some places.

It is noteworthy that the lagoonal evaporitic complexes include Early Carboniferous rocks. They comprise terrigenous evaporitic (gypsified) rocks with pure gypsum and dolomite beds in some places. The thickest (up to 15 m) gypsum beds are known in the Tsentral'nye Mountains. The gypsified rocks are also exposed in the Mamontovaya Mountains and Gusinaya River basin (*Ostrov* ..., 2003). Thus, the gypsified rocks are exposed on mountains in the western and central parts of the island, which serve as sources for most rivers in the island.

The Mesozoic–Cenozoic rocks are represented by the Late Triassic turbidites, Late Mesozoic–Cenozoic weathering crust, Late Mesozoic–Miocene and Pliocene terrigenous marine rocks (silt and clay), as well as Quaternary polyfacies sediments that are most widespread on lowlands of the island, e.g., Tundra Akademii.

In addition to gypsum deposits, other *mineral resources* of the region are represented by occurrences of nonferrous and noble metals, rock crystal, sedimentary manganese ores, and palygorskite (*Ostrov* ..., 2003).

Table 2. Microcomponent composition in the river water of Wrangel Island

Sample no. in Fig. 1	B	Na	Mg	Al	Si	S	K	Ca	V	Mn	Fe	Co	Ni	Cu	Zn	Se	Br
	μg/l	μg/l	μg/l	μg/l	μg/l	μg/l	μg/l	μg/l	μg/l	μg/l	μg/l	μg/l	μg/l	μg/l	μg/l	μg/l	μg/l
1/06	6.0	4808	22618	<2	795	63195	638	72733	<0.8	0.11	10.3	<0.05	<0.9	1.1	196	<1.5	52.5
2/06	3.7	4584	11828	<2	1154	31254	241	26219	<0.8	3.0	<4	<0.05	2.5	1.0	133	<0.5	54.0
3/06	<2	6510	29674	5.1	795	67967	452	98189	<0.8	60.4	232	0.30	<0.9	1.0	10.5	<0.5	86.6
4/06	<2	3778	8929	3.4	918	24925	227	19920	<0.8	3.5	<4	<0.05	2.1	1.1	97.8	<0.5	29.8
5/06	<2	3988	6073	3.5	958	32457	248	48708	<0.8	0.10	<4	<0.05	<0.9	0.9	81.7	<0.5	33.3
6/06	3.9	7280	24475	<2	878	55332	608	49434	<0.8	0.47	<4	<0.05	1.8	1.9	37.7	<0.5	44.3
7/06	<2	4361	38749	<2	912	91610	376	110339	0.18	0.35	<4	<0.05	<0.9	1.2	15.0	<3	76.0
8/06	<13	24819	2292547	1338944	11698	6674309	404	98737	<4	405712	761490	10987	23879	14107	65187	154	<611
9/06	5.5	6368	43916	11.5	1459	150452	3123	171180	<0.8	2.3	29.5	<0.05	<0.9	<0.5	15.3	12	110
10/06	<2	3986	19053	702	1790	63544	301	62817	<0.8	595	16.3	5.3	32.9	1.7	134	<0.5	57.5
11/06	<2	6049	49428	29914	2318	137714	382	56128	0.30	5861	7192	176	396	148	1399	<2	55.5
1/07	<6	9083	78755	10.3	1377	207208	614	223542	<0.2	1.5	<7	<0.1	<1.2	1.9	8.7	<12	292
2/07	<6	7539	67798	13.6	941	189284	649	216950	<0.2	0.64	<7	<0.1	<1.2	1.2	7.2	<20	262
3/07	<11	30576	169513	<9	1363	394816	958	324692	<0.3	12.5	<7	<0.3	<2	2.3	64.4	<18	293
4/07	<11	8267	161856	28.2	969	452437	1100	246847	<0.3	1.8	<7	<0.3	<2	5.6	12.6	<10	<84
1/09	3.1	24666	37705	5.2	2421	75829	495	87913	0.67	2.3	<9	<0.07	<0.7	1.5	2.0	<0.4	243.9
2/09	9.2	7269	218290	461	1422	386592	423	121775	2.1	5670	<9	167	941	80.9	2604	11.0	62.4
3/09	3.1	4298	85153	2.4	743	198132	301	127669	0.84	1.3	<9	<0.07	<0.7	0.64	3.2	2.9	22.4
4/09	<1	6244	49266	3.4	1009	149068	240	108209	0.87	3.6	<9	<0.07	<0.7	0.81	3.9	2.0	28.9
5/09	2.3	8129	68126	1.3	605	184123	397	113304	1.2	0.70	<9	<0.07	<0.7	0.39	1.4	2.5	28.8
6/09	3.0	5888	34197	1.3	884	96634	333	73623	0.74	0.54	<9	<0.07	<0.7	<0.3	0.77	1.2	19.8
7/09	5.6	18839	68303	2.0	508	186097	396	112277	1.1	1.1	<9	<0.07	<0.7	0.53	1.1	1.9	37.0
1/10	<6	9029	160029	1068	2001	436281	816	299810	<0.3	5399	<9	117	209	20.0	267	14.2	143
2/10	<6	7536	124384	14728	2850	273767	448	136289	<0.3	15972	11.6	322	528	15.9	873	<2.8	104
3/10	<2	8449	64436	82.4	696	169229	645	177773	0.19	143	<9	3.4	19.3	1.0	313	4.5	164
4/10	<12	10130	319387	18	624	569681	632	114693	<1	37.2	<9	18.0	62.3	0.7	53.1	14.3	120
5/10	<12	9203	226440	<10	410	493165	572	257316	<1	14.6	12.2	<0.5	8.9	<1	95.1	9.8	<92
6/10	2.0	6862	59469	255	1373	129880	466	79458	0.11	3621	<9	43.9	89.8	3.1	68.5	<0.8	102
7/10	<2	4552	119920	22.8	1522	251325	801	187365	0.52	21.4	<9	0.40	30.9	2.0	71.6	2.8	34.3
8/10	<12	7201	276263	299	2617	537224	692	209458	<1	8541	18.4	140	290	1.9	104	7.8	<92
9/10	<25	11568	997649	<20	2200	1638393	1287	289290	<1	121	<9	<1	258	5.4	60.0	<7	<184
10/10	<6	4266	149699	11.9	1787	337531	569	152668	<0.3	3652	<9	131	552	0.6	340	2.4	<46

Table 2. (Contd.)

Sample no. in Fig. 1	Sr	Ba	Pb	Li	Be	Rb	Y	Zr	Nb	Mo	Ag	Cd	Sn	Sb	Cs	La	Ce	Pr
	μg/l	μg/l	μg/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l
1/06	197	30.5	0.11	1231	<6	486	<6	14.0	<4	<28	<3	73.8	<37	121	<3	4.7	3.5	0.95
2/06	93	36.9	0.37	657	<6	159	8.0	26.1	17.5	111	<3	85.1	<37	71.9	<3	6.7	4.6	<0.6
3/06	141	43.4	0.31	1989	<6	245	17.6	24.6	10.3	<28	5.4	41.2	<37	25.5	<3	12.7	18.9	2.4
4/06	101	16.1	3.1	322	<6	146	8.4	11.7	10.1	<28	<3	153	<37	81.4	<3	6.7	8.9	1.6
5/06	181	70.6	0.25	178	<6	106	<6	<8	<4	49.6	<3	47.9	<37	78.0	<3	<1	<2	<0.6
6/06	203	21.4	0.25	1210	<6	416	<6	15.8	<4	<28	<3	32.5	<37	466	<3	<1	<2	<0.6
7/06	274	51.9	0.26	1050	<6	73.9	<6	11.1	<4	445	<3	29.5	<37	328	<3	<1	<2	<0.6
8/06	945	35.5	5.7	5248015	19949	1983	1965243	16874	<125	<845	<95	1487926	<1117	<165	143	48641	213606	51744
9/06	339	36.0	0.14	8840	<6	2619	12.2	58.7	<4	46.3	<3	32.4	<37	33.7	7.5	8.8	14.3	1.3
10/06	93.4	29.7	0.33	11313	109	165	2234	221	<4	<28	<3	801	<37	30.1	<3	513	650	128
11/06	185	63.7	1.3	22155	430	330	45148	2343	<4	120	25.0	32703	<37	173	26.7	1295	4913	1026
1/07	593	71.7	0.24	4878	<16	187	31.7	71.7	<6	199	<8	<18	<58	128	15.9	14.0	6.9	1.2
2/07	422	112	5.9	5173	<16	138	<7	<14	<6	117	<8	<18	<58	127	<15	7.0	5.3	1.3
3/07	922	62.3	1.2	1789	<33	132	<14	124	<11	83	<16	<36	<116	123	<30	<6	<6	<2
4/07	791	64.1	0.59	17782	<33	255	<14	<29	<11	<52	<16	<36	<116	153	<30	<6	<6	<2
1/09	269	30.8	0.078	505	17	84	44	85	<0.9	13	<4	21	<6	75	<2	24	27	4.0
2/09	209	43.5	0.13	63180	14	236	15937	17	<0.9	107	<4	38131	<6	57	6.3	1206	1681	301
3/09	331	39.2	0.03	959	6.7	95	54	<4	<0.9	54	<4	<6	<6	135	<2	11	27	3.6
4/09	323	15.6	0.18	252	<4	61	55	16	<0.9	17	<4	22	<6	59	<2	28	14	4.5
5/09	364	13.7	0.04	254	<4	115	45	<4	<0.9	14	<4	15	<6	46	3.3	14	6.3	2.4
6/09	271	7.4	0.048	141	<4	71	25	<4	<0.9	9.6	<4	16.07	<6	33	<2	8.0	7.3	1.5
7/09	436	17.9	0.047	1047	<4	107	42	11	<0.9	16.3	<4	7.38	<6	47	<2	10.9	14.4	2.7
1/10	573	21.4	0.49	109025	183	177	32404	<34	<9	<33	<18	1068	221	52.6	<12	1474	4140	819
2/10	182	16.0	1.5	91448	870	337	86644	443	<9	<33	<18	4119	84.4	53.8	<12	7417	14677	2320
3/10	485	50.3	0.25	7197	<9	841	313	<13	<4	79.7	9.1	360	26.8	113	350	384	318	47.7
4/10	711	30.4	<0.1	14792	<45	123	322	<66	<19	107	<36	607	<107	66.8	<25	<25	<9	<2
5/10	621	36.6	<0.1	4490	<45	633	<45	<66	<19	<66	<36	81.1	<107	141	<25	<25	<9	<2
6/10	84.7	20.3	0.40	24200	117	217	7324	21.9	<2	25.5	15.2	852	42.9	62.5	5.7	611	1219	243
7/10	316	42.8	0.73	2672	<9	293	370	<13	<4	230	36.9	2844	88.6	183	<5	21.9	23.9	6.6
8/10	532	23.4	0.30	24045	165	685	31314	<66	<19	<66	86.7	714	118	<45	<25	4264	8309	889
9/10	782	11.9	<0.3	47012	<90	495	278	<134	<38	236	<72	<109	<214	136	<45	<50	<18	<4
10/10	245	17.8	0.50	5248	<22	292	223	<34	<9	<33	<18	3103	93.4	50.2	<12	33.0	27.8	1.9

Table 2. (Contd.)

Sample no. in Fig. 1	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf	Ta	W
	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l
1/06	<1	<0.9	<0.7	<0.8	<0.3	<0.8	<0.4	<0.6	<0.4	<0.6	<0.3	<0.8	<2	41.7
2/06	3.7	1.6	<0.7	1.5	<0.3	1.7	<0.4	1.8	<0.4	<0.6	<0.3	<0.8	<2	57.1
3/06	11.2	5.9	<0.7	5.6	0.69	5.2	1.0	1.4	0.39	2.5	<0.3	<0.8	<2	<26
4/06	7.7	<0.9	<0.7	2.6	<0.3	<0.8	<0.4	1.1	<0.4	1.0	<0.3	<0.8	<2	<26
5/06	<1	<0.9	<0.7	<0.8	<0.3	<0.8	<0.4	<0.6	<0.4	<0.6	<0.3	<0.8	<2	<26
6/06	<1	<0.9	<0.7	<0.8	<0.3	<0.8	<0.4	<0.6	<0.4	<0.6	<0.3	<0.8	<2	<26
7/06	<1	<0.9	<0.7	<0.8	<0.3	<0.8	<0.4	<0.6	<0.4	<0.6	<0.3	<0.8	<2	<26
8/06	389533	294156	112370	536093	87147	508193	95247	279161	40018	272216	41548	2335	639	<768
9/06	6.7	<0.9	<0.7	3.8	<0.3	3.8	0.78	1.7	<0.4	1.1	<0.3	2.0	<2	<26
10/06	602	200	58.7	383	67.0	342	68.8	174	22.1	138.5	21.6	6.7	<2	<26
11/06	7902	6794	2583	13123	2058	11230	2083	5657	761	5388	805	102	15.9	30.9
1/07	5.0	3.3	<2	5.1	0.88	3.6	0.77	3.4	<0.4	1.9	0.68	<4	<4	16.0
2/07	7.1	3.3	2.2	<1	<0.6	<1	<0.5	<1	<0.4	<2	<0.4	<4	<4	23.3
3/07	<3	<3	<3	<3	<1	<3	<1	<2	<1	<3	<1	<9	<7	<16
4/07	<3	<3	<3	<3	<1	<3	<1	<2	<1	<3	<1	<9	<7	<16
1/09	20	5.3	1.1	7.1	1.2	5.8	1.3	4.4	0.7575	5.4	0.8	<1	<1	<2
2/09	1794	666	251	1875	259	1322	284	734	71.969	340	57.55	9.4	4.3	<2
3/09	13.4	4.9	1.3	6.5	0.70	4.0	1.2	1.9	0.368	2.6	0.49	<1	<1	<2
4/09	16.0	4.2	1.6	7.1	1.2	4.1	1.6	0.8	0.368	2.05	0.19	<1	<1	<2
5/09	11.0	4.2	1.4	3.8	0.54	1.6	0.63	1.5	<0.17	<0.4	0.15	<1	<1	<2
6/09	6.4	0.87	<0.4	1.8	0.37	2.2	0.42	1.2	<0.17	0.8	0.07	<1	<1	<2
7/09	12.5	3.5	<0.4	4.0	0.59	2.2	0.55	2.5	<0.17	0.8	0.19	<1	<1	<2
1/10	5204	2677	829	5899	974	5682	1139	3176	423	2689	404	21.2	<3	593
2/10	11904	4757	1602	12299	2246	13557	2666	7704	1040	6079	961	47.7	<3	410
3/10	142	14.7	4.9	29.1	4.6	28.9	6.1	19.5	2.1	12.6	1.9	<4	<1	<15
4/10	6.6	<6	<4	11.0	3.3	17.3	8.2	<4	2.9	5.4	1.5	<22	<6	101
5/10	<6	<6	<4	<8	<1	<6	<1	<4	<2	<4	<1	<22	<6	199
6/10	1437	602	181	1413	203	1077	209	538	68.6	382	60.8	4.7	<0.6	36.2
7/10	28.6	5.6	2.0	23.1	4.6	27.8	5.8	21.6	1.9	13.9	2.9	<4	<1	<15
8/10	4623	1310	403	3597	497	2933	626	1544	174	772	131	<22	<6	142
9/10	<12	<12	<8	<16	<3	<12	<2	<8	<4	<8	<3	<44	<12	<150
10/10	11.1	<3	<2	11.0	1.4	3.5	1.9	<2	1.7	<2	<1	<11	<3	512

Table 2. (Contd.)

Sample no. in Fig. 1	Re	Os	Ir	Tl	Th	U
	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l
1/06	<1	<1	<0.2	83.6	18.2	37.1
2/06	<1	<1	<0.2	11.4	10.9	1.3
3/06	<1	<1	<0.2	2.0	14.4	70.7
4/06	<1	<1	<0.2	15.7	<4	1.5
5/06	<1	<1	<0.2	3.2	<4	23.8
6/06	<1	<1	<0.2	<0.6	<4	1.1
7/06	4.1	<1	<0.2	0.94	<4	2967
8/06	<35	108	220	152	29227	388098
9/06	4.3	<1	<0.2	12.4	<4	667
10/06	<1	<1	<0.2	1.2	5.1	76.7
11/06	<1	<1	4.3	9.4	503	4790
1/07	8.5	<2	<1	<1	<4	2408
2/07	12.6	<2	<1	<1	<4	3062
3/07	5.4	<4	<2	<3	<7	5351
4/07	<2	<4	<2	<3	<7	175
1/09	0.7	<0.5	<0.1	<2.5	4.3	12.5
2/09	4.9	<0.5	<0.1	8.4	6.7	109
3/09	1.5	<0.5	<0.1	0.6	3.4	1782
4/09	<0.4	<0.5	<0.1	0.6	1.7	1.9
5/09	<0.4	<0.5	<0.1	0.6	1.3	0.9
6/09	<0.4	<0.5	<0.1	<2.5	<1	1.1
7/09	<0.4	<0.5	<0.1	0.4	1.8	30.5
1/10	8	<4	<1	3.6	10.2	1954
2/10	<1	<4	<1	4.7	42.2	761
3/10	7.4	<2	<0.4	6.4	<2	3782
4/10	<2	<9	<2	<5	<9	4274
5/10	<2	<9	<2	<5	<9	1883
6/10	1.5	<0.9	<0.2	1.9	3.1	138
7/10	9.9	<2	<0.4	7.0	<2	4736
8/10	<2	<9	<2	<5	<9	92.7
9/10	<5	<17	<4	<11	<18	14.9
10/10	<1	<4	<1	23.3	<4	55.1

Base metal, copper, and antimony ore occurrences are concentrated in the mountainous part of the island. They are related to the hydrothermal carbonate–quartz veins and stringer zones. These medium-temperature ore-bearing (sometimes with rock crystals) veins usually crosscut the Paleozoic (less commonly, Upper Precambrian) vein systems. Some of them are associated with the Late Carboniferous volcanics. Quartz veins are commonly barren beyond the Paleozoic rock domains.

The ferrous metal mineralization is primarily represented by copper–base metal (Cu, Pb, Sb, and As) occurrences. Purely copper and antimony ores are extremely rare. Most occurrences are confined to a narrow (nearly latitudinal) zone (10–15 km wide) extending in the mountainous part of the island from Cape Uering in the east to Cape Ptichii Bazar in the west. These occurrences are mostly found in the central part of the island at upper reaches of the Perkatkun and Khrustal'nyi creeks, as well as Neizvestnaya and Krasnyi Flag rivers. A copper ore occurrence has been found at upper reaches of the Khischnikov River in Cape Uering (Borodin and Kirpichnikova, 1953).

Sedimentary manganese deposits have been detected in the westernmost part of the island at lower reaches of the Gusinaya River (the Gusinaya and Sovetskaya interfluve area) and in Cape Ptichii Bazar (Ganelin et al., 1989). The Upper Paleozoic section in this area incorporates two manganiferous members (50 and 60 m thick, respectively) confined to the Late Carboniferous and Permian carbonate–clay complexes. The mineralization is represented by abundant concretions and nodules of Mn-bearing carbonates.

RESULTS

Characteristics of the Salt Composition of Water

Organoleptic indicators. Some rivers in Wrangel Island are marked by specific water color. Sometimes, the water is bright red (Sample 8/06, tributary of the Sovetskaya River, Fig. 1) or alluvium on the river bottom is reddish (tributaries of the Krasnyi Flag River at upper reaches: samples 4/10, 5/10, and 10/10). The water is milky white in tributaries at upper reaches of the Sovetskaya and Krasnyi Flag rivers and the Shumnyi Creek (samples 11/06, 1/10, and 10/10). The white precipitation from such water makes up a thin coating on the channel sediments. In this area, the river bottom has a pale blue coating in some places (Sample 6/10, Krasnyi Flag River).

All these features are noted in the mountainous areas in separate tributaries or at the confluence of creeks with the main river channel.

Macrocomponent composition. The water in many tributaries is characterized by neutral to slightly alkaline properties with pH = 7.19–7.98 (Table 1). In contrast, tributaries of the Sovetskaya River are characterized by *red water* (Sample 8/06) and *white water* (Sample 11/06). These samples are marked by low pH values (2.43 and 4.69, respectively). Low pH values (up to 4.29) were also recorded during the sampling in 2010 some tributaries at upper reaches of the Krasnyi Flag and Tundrovaya rivers (Table 1, samples 1/10, 2/10, 6/10, 8/10, and 9/10; Fig. 1).Table 1 also shows that upper reaches of these rivers are marked by very high variations of pH—some tributaries include both slightly acid ($pH < 6$) and neutral waters. With increasing distance from the mountains, the pH value becomes neutral and more homogeneous (Fig. 1; Table 3, samples 3/06, 9/06, and 10/06).

The TDS content in river water in most samples varies from 0.3 to 2 g/l (Fig. 2). This is usually atypical for small rivers of the Arctic region recharged by melt waters with low salt contents. For example, according to our data, TDS in rivers of eastern Chukotka in 2002 and 2004 varied from 50 to 250 mg/l.

The general high mineralization background of island is complicated by separate currents with anomalously high TDS values. For example, the TDS content in water in sample 8/06 (Sovetskaya River), is 23 g/l (!). High TDS value (6.5 g/l) is also marked in sample 9/10 taken from the Mertvyi ("Dead") Creek (upper course of the Tundrovaya River). Probably, such name given to the creek by workers of the State Reserve is not accidental.

Figure 2 also shows that bar chart of the mineralization is asymmetrical. However, the interval of M = 0.2–1.0 g/l shows a nearly normal distribution. Water samples with a relatively low mineralization (<1 g/l) are apparently overlapped with more mineralized water samples. Evidently, the first series characterizes background values of river water mineralization, whereas the second series represents anomalous values.

In terms of the anionic composition, all waters, those with anomalous mineralization and low pH values included, belong to the sulfate type. The share of ion SO_4^{2-} in their composition varies from 57 to 96 mg-equiv % (Fig. 3a). Ions Cl and HCO_3 are subordinate—the share of each of them rarely exceeds 15 mg-equiv %. We can see a clear trend of negative correlation between their relative (in mg-equiv %) concentration and TDS in water (Fig. 4).

Cations are mainly represented by Ca and Mg, and their total share is 87 + 99 mg-equiv % (Fig. 3b). Their ratio (in mg-equiv %) is variable. The share of Mg in the cationic composition shows positive correlation with the TDS (Fig. 5).

The total hardness of river water (Ca + Mg concentration) varies from 1.7 up to 194 mg-equiv/l (average 22.6 mg-equiv/l n = 32). However, the carbonate-related hardness is not high (0.3 + 2.5) mg-equiv/l, and its share rarely accounts for more than 10–15% of the total hardness. Thus, in terms of the total hardness, the major part of water in the island belongs to hard (6–9 mg-equiv/l) and very hard (>9 mg-equiv/l) types (Alekin, 1970).

In general, the least mineralized water (M < 2 g/l) is characterized by the SO_4–Ca–Mg type, sometimes with an increased share of Cl and HCO_3 ions (in water with M < 1 g/l), while the more mineralized water is characterized by the SO_4–Mg–Ca and SO_4–Mg types. The later type includes samples with anomalously low pH values (<4.5).

Thus, waters of Wrangel Island are characterized by elevated mineralization and specific composition of macrocomponents dominated by ions SO_4, Ca, and Mg. These waters are also marked by anomalously high values of total hardness. Ions SO_4 and Mg are the main components in the salt composition of water with TDS no more than 2 g/l (Fig. 5).

Table 3. Chemical composition of Sample 10/10 with a ferruginous coating on stones taken from the mouth of a creek east of the Shumnaya Creek at the exit to Tundra Akademii ((based on the results of the determination of acidic leachate composition)

Element	Content, μg/g	Element	Content, μg/g
Li	1.5	Cd	9.5
Be	1.9	Sn	0.15
B	<5	Sb	1.0
Na	307	Te	0.25
Mg	2036	Cs	0.15
Al	24150	Ba	86.4
Si	14279	La	40.5
P	395	Ce	97.0
S	5322	Pr	12.9
K	668	Nd	70.0
Ca	10029	Sm	20.3
Sc	5.6	Eu	7.1
Ti	30.9	Gd	68.1
V	<6	Tb	11.1
Cr	7.5	Dy	66.8
Mn	432	Ho	15.2
Fe	165945	Er	39.6
Co	29.2	Tm	4.3
Ni	248	Yb	21.1
Cu	158	Lu	3.5
Zn	2174	Hf	0.23
Ga	<0.01	Ta	<0.04
As	1.6	W	<0.08
Se	12.5	Re	<0.02
Rb	2.0	Ir	<0.01
Sr	24.7	Pt	<0.01
Y	680	Au	<0.002
Zr	4.5	Hg	0.18
Nb	0.30	Tl	0.038
Mo	0.70	Pb	8.3
Rh	<0.02	Bi	0.070
Pd	<0.04	Th	0.62
Ag	0.10	U	13.1

Microcomponent composition. The results of chemical analysis (Table 2) showed that the river water is usually characterized by small concentrations of trace elements.

Among the samples analyzed, sample 8/06 (Sovetskaya River) is marked by anomalously high concentrations of most elements: Al (1.3 g/l), heavy metals, such as Pb (5.7 μg/l), Cd (1.5 mg/l), Cu (14 mg/l), Zn (65 mg/l), Fe (760 mg/l), Mn (405 mg/l),

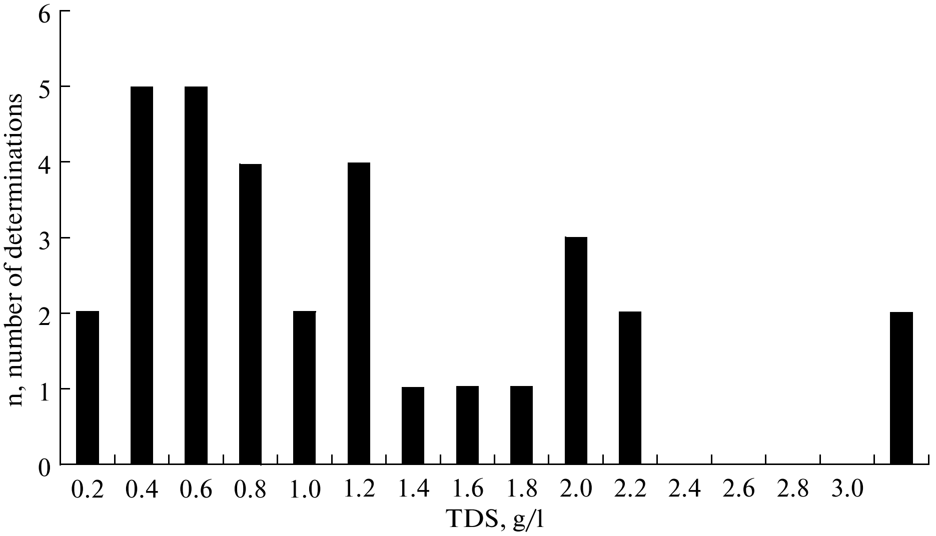

Fig. 2. Bar chart of the TDS distribution in river water in Wrangel Island.

Li (5 mg/l), and all REEs. This water is also distinguished by very high concentrations of U (388 μg/l) and Th (29 μg/l). Actually, water of this river represents a diluted hydrosulfuric acid solution (pH = 2.4) strongly enriched with heavy metals and other toxic elements. Judging from high U and Th concentrations, this water and bottom sediments of the stream can be characterized by elevated radioactivity.

Samples 10/06, 11/06, and 2/09 are also anomalous. Sample 11/06 (“white water”) represents a diluted (approximately 100 times) version of the solution in Sample 8/06. The water contains white finely dispersed particulates. The formation of particulates in this stream is likely related to the precipitation of gypsum ($CaSO_4 \cdot 2H_2O$) and/or aluminum hydroxide due to the mixing of background river waters (characterized by high Ca ion concentration and neutral pH values) with acid sulfate waters.

In the remaining samples of the series (10/06 and 2/09), concentrations of sulfate sulfur and ore elements are appreciably lower. Nevertheless, contents of some elements (particularly, REEs) in them are 10–100 times higher than in the remaining water samples.

The microcomponent composition of most waters is characterized by the presence of Tl (up to 84 ng/l). In Sample 8/06 with an anomalous mineralization of water, concentration of this element reaches 152 ng/l. Twelve water samples also contained Re (0.7–12.6 ng/l). This is a rather specific rare element, which usually occurs as a trace element in the molybdenum and copper ores. The presence of Tl and Re obviously reflects the regional geochemical specifics of rocks washed out by river water.

Some samples taken in 2010 (samples 1/10, 2/10, 6/10, 8/10, and 9/10) are marked by elevated (relative to samples taken in previous years) concentrations of Al (up to 15 mg/l), Mn (up to 8–16 mg/l), Co (up to 300 μg/l), Ni (up to 530 μg/l), Cu (up to 20 μg/l), Zn (up to 870 μg/l), Li (up to 110 μg/l), Be (up to 870 μg/l), Y (up to 87 μg/l), Cd (up to 41 μg/l), and REE. Anomalous concentrations of these elements are accompanied by almost complete absence of Fe (<18 μg/l).

Spectra of chemical elements differ appreciably in the anomalous samples from different areas of the island. For example, samples 1/10 and 2/10 (tributaries of the Krasnyi Flag River) are marked by elevated concentrations of Al, Mn, Co, Ni, Cu, Zn, Pb, Li, Be, Y, Cd, REE, W, and U. Samples from tributaries of the Tundrovaya River (8/10 and 9/10) are marked by a different spectrum of elements: Mg, Ni, Sr, Rb, Ag, and REE.

Concentrations of Cu, Zn, Pb, Cd, Tl, Al, Mn, Mo, and Th are commonly correlated. However, their plots sometimes show clusters deviating from the common trend. For example, the Cu–Zn plot (Fig. 6) shows a cluster located above the correlation trend. This cluster characterizes the Zn-rich waters sampled in the Krasnyi Flag and Neozhidannaya rivers basin. Like differences of some samples in terms of element spectra, such deviation from the general trend can reflect heterogeneity in the composition of natural contamination sources or different rates of the deposition of various chemical elements in bottom sediments.

In the middle course of rivers, concentrations of all elements (particularly, heavy metals), are usually slightly decreased. This is caused by the sorption of metals on the organic and clayey material (e.g., heavy metals) or the dilution of waters flowing from the mountains by ultrafresh waters supplied from the tundra zone.

Concentrations of rare earth elements in river waters show a wide (4–5 orders of magnitude) variation range. Maximal concentrations are recorded in

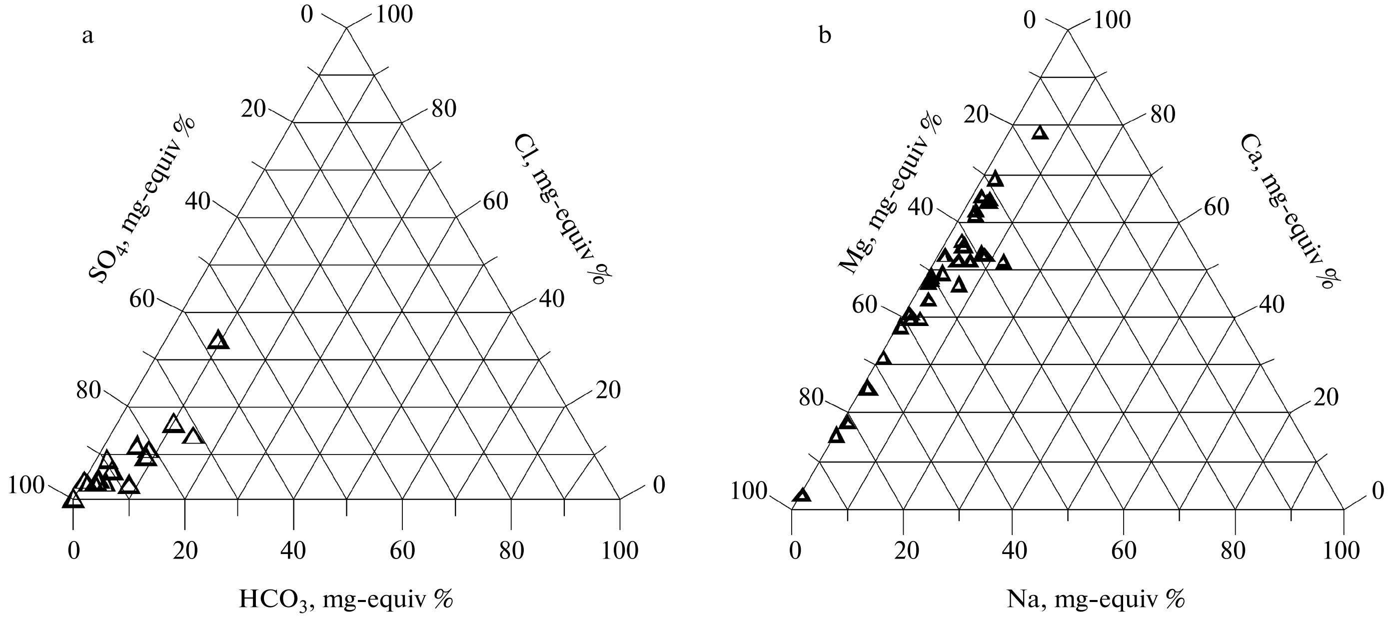

Fig. 3. Anion (a) and cation (b) compositions of river water in Wrangel Island.

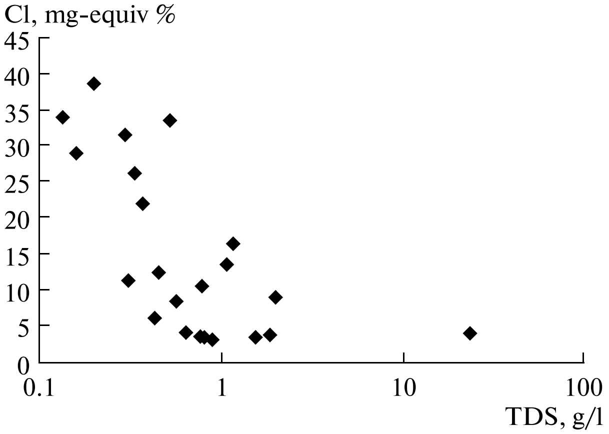

Fig. 4. Relationship between the TDS and relative content of Cl ion in river water in Wrangel Island.

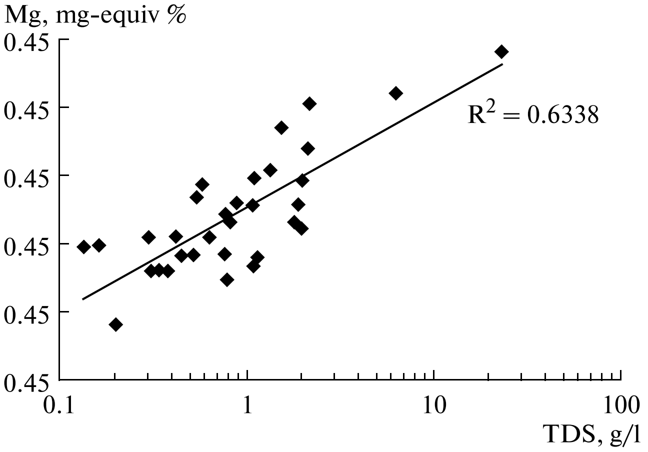

Fig. 5. Relationship between the share of Mg (mg-equiv. %) in the composition of cations (relative to Na and Ca ions) and TDS in river water in Wrangel Island.

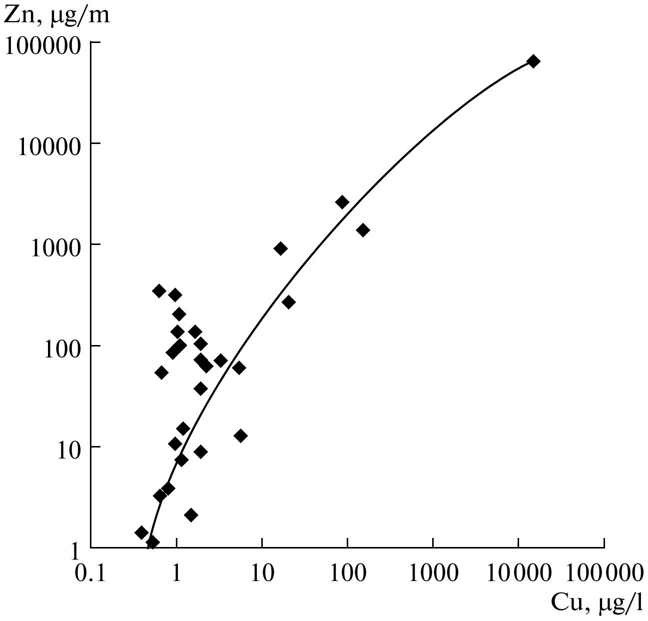

Fig. 6. Relationship between Cu and Zn concentrations in the river water in Wrangel Island.

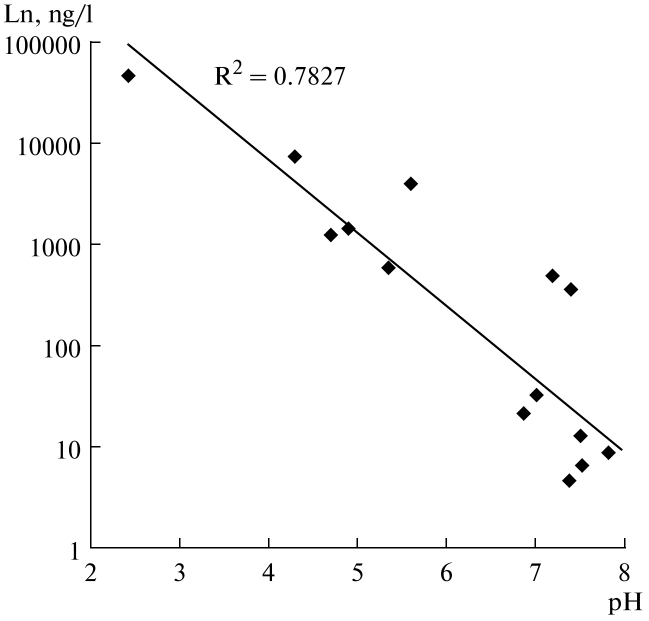

Fig. 7. Relationship between La concentration and pH in river water in Wrangel Island.

Sample 8/06 (anomalous TDS content and acidity). Concentrations of HREE (Gd–Lu) and Y in this water reach ~100 ng/l.

In general, the waters are marked by direct correlation of REE with the TDS and, correspondingly, sulfur content (SO_4) in the solution (Table 2). However, the more significant factor regulating the REE content is water is the pH value (Fig. 7). The reverse relationship of their concentrations with pH is likely governed by the chemical properties of REEs—precipitation of hydroxides of these elements at neutral to slightly alkaline pH values (Balashov, 1976) – and the migration capacity of oxidized forms of Fe and Mn, which serve as excellent sorbents for the dispersed elements (Dubinin, 2006). These elements lose the migration capacity and quit the solution at neutral pH values.

Complete REE spectra were recorded for 12 samples (Fig. 8, Table 2). Almost all spectra are characterized by similar patterns and deficit of LREEs (La–Eu). This group of elements shows a stable positive

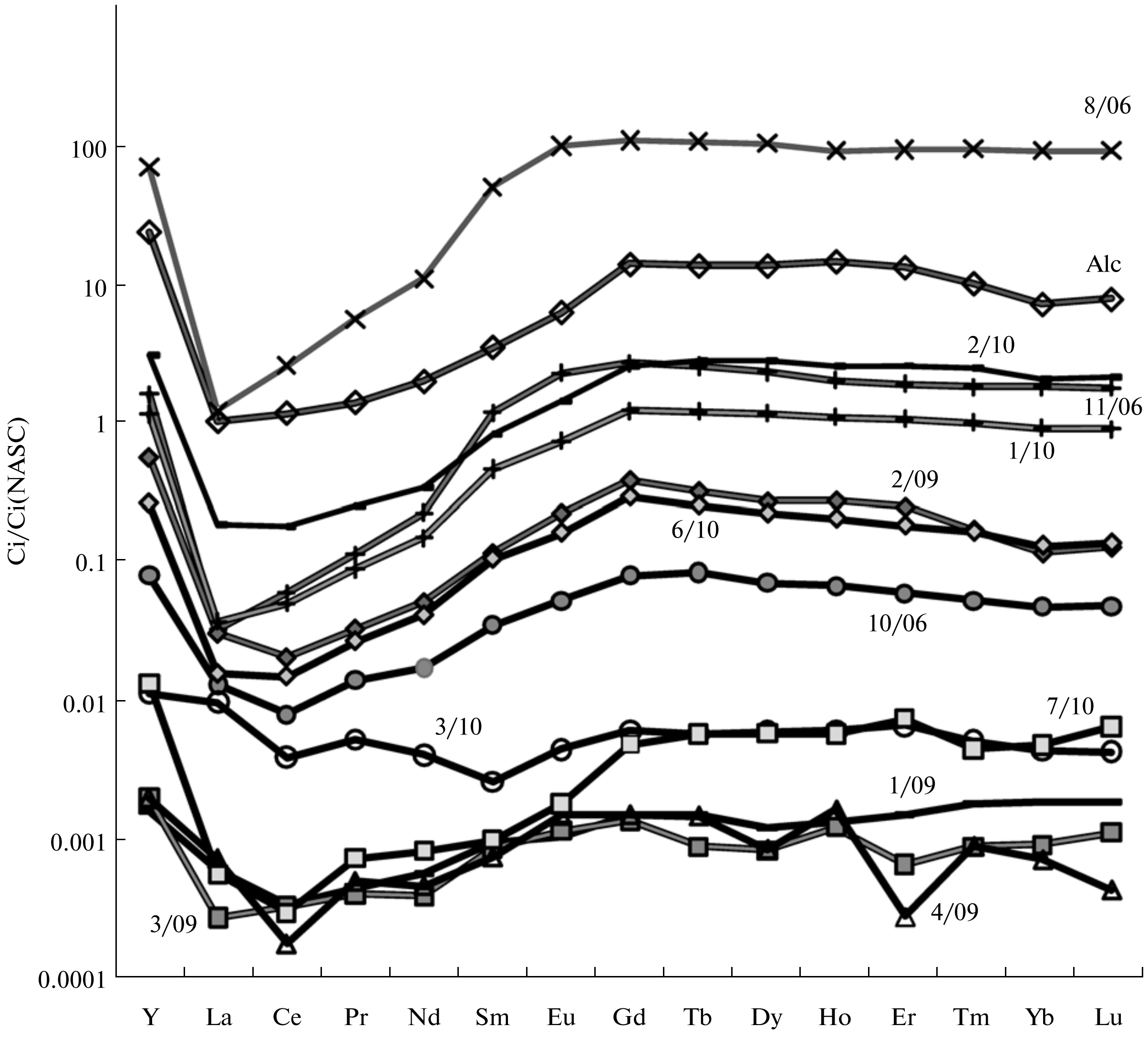

Fig. 8. The REE spectra in river water in Wrangel Island.

correlation of the NASC-normalized concentrations and ordinal number of element. Correspondingly, minimal concentrations are typical of La and Ce.

In contrast to LREEs, the normalized concentrations of HREEs of the Y group (Gd–Lu, Y) are characterized by higher and more homogeneous values (Fig. 8). Maximal discrepancy between the normalized concentrations of LREEs and HREEs is observed in waters with pH < 6.5 and high contents of Cu, Zn, Pb, Si, Al, Mn, Mo, Tl, Zr, Rb, and Li.

The same trends are noted for $\Sigma Ce/\Sigma Y$ coefficients, where $\Sigma Ce = (La... + Eu)$ and $\Sigma Y = (Gd... + Lu + Y)$. They vary from 0.3 to 2.2 (average = 0.7). In the $\Sigma Ce/\Sigma Y$-pH plot (Fig. 9), data points make up two groups. In the first group, maximal values of the coefficient (1.2–2.2) are recorded in waters with neutral pH values (7.4–7.8). In the second group, low $\Sigma Ce/\Sigma Y$ values (0.2–0.6) are observed in waters with both low (2.4–5.6) and neutral pH (6.9–7.2) values.

A common REE distribution is recorded in Sample 3/10 taken at upper reaches of the Krasnyi Flag River (Fig. 8). The spectrum is flattened—discrepancy between the normalized LREE and HREE concentrations is minimal: $\Sigma Ce/\Sigma Y$ is maximal (2.2). Water in Sample 3/10 is characterized by neutral pH values (7.39). It is not ruled out that this spectrum is artifact, because it differs strongly from other water samples taken in the area.

Two water samples (Fig. 8, samples 8/06 and 11/06 taken from tributaries of the Sovetskaya River with red and white waters) are noteworthy: the terminal element in the increasing trend of LREE concentrations is represented by Eu (in other samples, Gd). These samples show a minor positive Eu anomaly ($Eu_{an} = 1.2$ and 1.1, respectively). Higher Eu_{an} values (1.25 and 1.5) are recorded in samples from the Klykovyi and Peresykhayushchii creeks (samples 4/09 and 5/09). In the remaining samples, Eu_{an} varies from 0.59 to 0.98.

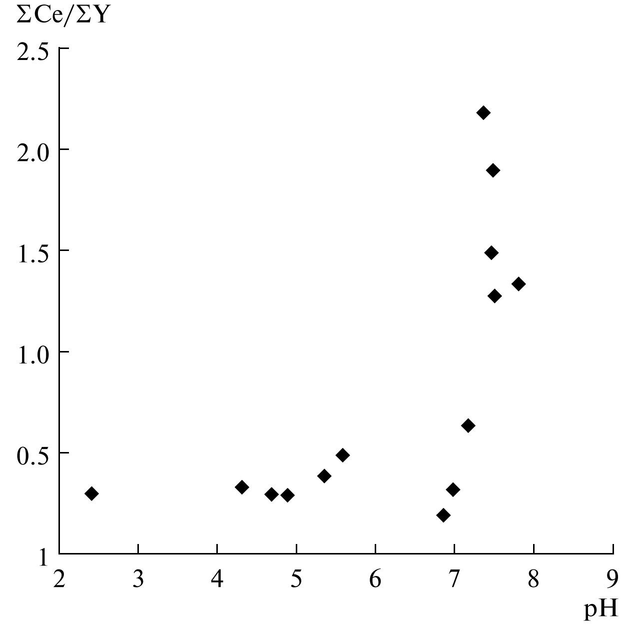

Fig. 9. Relationship between ΣCe/ΣY and pH in river water in Wrangel Island.

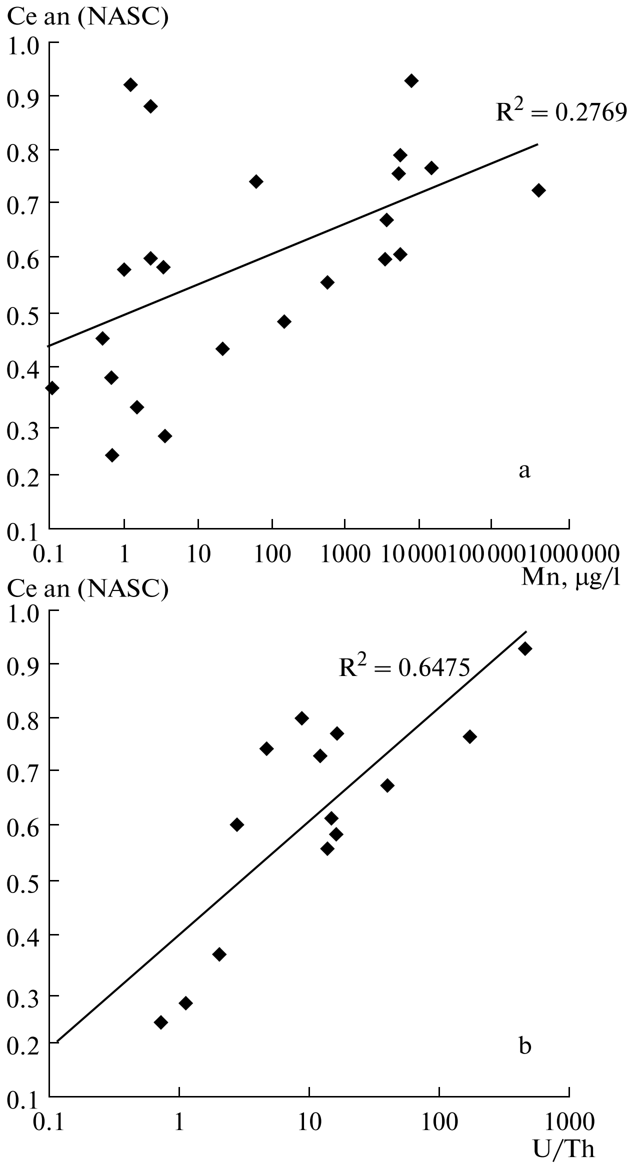

Fig. 10. Relationship between the Ce anomaly and Mn concentration (a) and U/Th (b) in river water in Wrangel Island.

In 23 samples, variation of Ce_{an} (relative to NASC) is 0.23–093 (average 0.59). $Ce_{an} > 0.6$ is observed only in slightly acid waters ($pH < 5.6$). These waters are also enriched in Mn and Th (Figs. 10a, 10b). No correlation is observed between Ce_{an} and sulfate S concentration. In waters with $pH > 6.9$ commonly decreases to 0.36–0.6. However, Ce_{an} in two samples taken from the Krasnyi Flag River and its tributary (3/06 and 9/06) is similar to that in the slightly acid water.

It is known that Ce is the sole REE with an oxidation state of 4^+ under supergene conditions (Balashov, 1976). The oxidized state of Ce is low-soluble. Therefore, Ce^4 is readily evacuated from the solution in the oxygen-saturated waters, resulting in the formation of the negative Ce anomaly in the REE spectrum. Mn and U have similar properties in the retrograde diagenesis zone.

Hence, some rivers in Wrangel Island are recharged with waters draining sediments with reductive Eh values, at which Ce and Mn show minimal oxidation degrees (3^+ and 2^+, respectively). These forms have a higher migration capacity in water. However, upon reaction with the atmospheric oxygen, they are rapidly oxidized and removed from the solution.

Specific compositional features of the acid extract of Sample 10/10. Determination of the leachate composition revealed that the reddish brown coating of stones represents a mixture of iron hydroxides with compounds of Al, Si, Ca, and S (Table 3). Admixtures are represented by Zn, Cu, Cd, and Pb. The Zn concentration in the sediment is an order of magnitude higher than the Cu content. The sample also contains Ag (0.1 μg/g) and U (13 μg/g), which is 21 times higher than Th.

The presence of Hg (0.18 μg/g) suggests that it can be mobilized in the supergene alteration zone of sulfide mineralization. The water is lacking Hg, probably, because of its sorption on walls of the plastic vessel.

The spectrum of REEs in the acid leachate does not differ principally from the typical spectra of water (Fig. 8, spectrum Alc). The former is characterized by enrichment in HREE and the presence of the trend of increase in the normalized concentrations of LREEs (La–Eu). The normalized concentrations of HREE (Gd–Tm) are almost invariable and approximately 13 to 14 times higher than their respective NASC-normalized concentrations. A slight depletion (up to 7.5 times relative to NASC) is recorded only for the end members of the series (Tm, Yb, and Lu). Concentrations of Ln and Ce are similar to the NASC-normalized values.

Relative to NASC, the negative Ce anomaly is almost missing in the ferruginous sediment. However, Ce_{an} (0.92) in the sediment is appreciably higher than that in most water samples (average 0.59). Evidently, the Ce concentration in the sediment is related to oxidation of this element in the oxic medium and the formation of low-soluble compounds of Ce^{4+}. Similarly high Ce_{an} values were recorded only in samples 3/09 and 8/10 (Khishchniki River and Kukhonnyi Creek).

Comparison of components in the sediment and water (Sample 10/10, Tables 2 and 3) shows that the water composition in the creek at the sampling site does not fit the water composition in the oxidation zone of sulfide ores. The water is characterized by neutral pH (7.0) and relatively low TDS (1.3 g/l). The admixture of acidic water, however, suggests a relatively high Mg concentration (Mg > Ca is a typical feature of this water type), high value of total water hardness (20 mg-equiv/l), as well as the presence of appreciable concentrations of Zn (340 μg/l) and Cd (3103 μg/l). The water lacks Fe, but it is enriched in Mn (3.6 mg/l).

Samples of water and sediment were likely taken in a distal zone of ore mineralization characterized by neutralization of pH of water, resulting in extensive precipitation of iron hydroxides that absorb other compounds as well.

DISCUSSION

At present, human economic activity in Wrangel Island is characterized by local scales: seasonal living in reserve camps and visits of rare tourist groups. All residence sites are located on the coast.

Therefore, we can assume that anthropogenic influence on the river system is negligible. Obviously, the formation of the salt composition of river water under such conditions is restricted to natural processes, among which influence of the marine salt complex and leaching of salts from the water-enclosing rocks are the most important ones.

Theoretically, the marine salts can be delivered to river waters from the atmospheric aerosols or the eolian transport of frozen out salts from the coastal zone. Involvement of this factor can be suggested by increase in the concentration of “marine” elements (e.g., Cl, Na, B, and Br) in water near the coastal zone. This relationship, however, is missing in streams of the island. In contrast, some elements (Br, Rb, Li, and U) demonstrate reverse correlation between the concentration of elements and distance from the coast.

Thus, any signs of appreciable participation of the marine salt complex are lacking in the river water composition in Wrangel Island. The materials presented above show that almost all rivers in the island are characterized by the SO_4–Ca–Mg or SO_4–Mg–Ca type of water. The absence of adequate (relative to SO_4 and Mg concentrations) contents of Cl, Na, B, and Br also suggest a nonmarine origin of salts in the river waters.

High concentrations of Ca and SO_4 ions can be related to the leaching of Late Carboniferous gypsiferous rocks that are abundant in the western and central parts of the insular mountain chain. This is the source area of most rivers. Therefore, contamination of waters with calcium sulfate is almost universal in Wrangel Island. The $CaSO_4$ content in river water is ~18 g/l (total mineralization of water is almost completely provided by Ca and SO_4 ions), which corresponds to the solubility of gypsum at low temperatures. For example, at $t = 5°C$, solubility of $CaSO_4$ in the distilled water is 1.855 g/l (Zverev, 1967). The formation of salt composition of the river water due to reaction with evaporates is indirectly suggested by low values of the $\Sigma Ce/\Sigma Y$ coefficient (<2.2), which are generally typical of the arid lithogenesis (Balashov, 1976; Maslov, 2003; Shatrov, 2007). Such values are also recorded in hydrothermal systems of oceanic spreading ridges (Dubinin, 2006).

Obviously, gypsiferous sequences are not the sole source for the salt composition of rocks. For example, leaching of gypsum cannot explain the appearance of waters with TDS = 2.5–23 g/l (dissolution of gypsum cannot provide the TDS of >2.5 g/l), the presence of less mineralized waters of the SO_4–Mg–Ca type, lower pH values (<5.5), and higher concentrations of Al, Fe, Mn, heavy metals, and REE. Such waters often contain fine white particulates (white water) or they are red-colored due to the presence of iron hydroxides.

Sources of such components in the water can be represented by products of the sulfide ore mineralization. The sulfuric acid produced in this process mobilizes compounds of Fe, Mn, heavy metals, and REE. In this process, silicate rocks can also be subjected to acidic leaching, as suggested by high Al and Si concentrations in water with pH < 6.

Participation of oxidation products of hydrothermal sulfides in the formation of the salt composition of some waters in the island is indicated by small positive Eu anomalies (samples 8/06 and 11/06, tributaries of the Sovetskaya River). Prominent Eu anomalies are typical of the high-temperature hydrothermal systems of ocean (Dubinin, 2006). Their formation is attributed to reduction of this element at high temperatures (300–400°C).

The hydrosulfuric solutions with anomalous concentrations of Eu, Fe, Mn, and heavy metals can be provided by weathering products of base metal, copper, and antimony ores confined to the carbonate–quartz vein systems. Such veins are associated with the Late Carboniferous volcanics.

When acid sulfate solutions fall into the river channel, they react with the Carboniferous dolomites and limestones. Like gypsum, these rocks are abundant in the mountainous part of the island. In this process, concentration of Ca ion is limited by the equilibrium with gypsum, while excess of the hydrosulfuric acid is neutralized by Mg ions. Consequently, the salt composition is governed by Mg^{2+} ion, and growth of TDS leads to replacement of the water type by the SO_4–Mg–Ca or SO_4–Mg type (Fig. 5). These processes take place according to the following scheme:

$$FeS + 2O_2 = Fe^{2+} + SO_4^{2-},$$

$$CaMgCO_3 + SO_4^{2-} + 2H_2O$$
$$= CaSO_4 \cdot 2H_2O\downarrow + Mg^{2+} + CO_3^{2-},$$

$$CO_3^{2-} + 2H^+ = H_2O + CO_2\uparrow.$$

Precipitation of gypsum likely explains the milky white color of water in some sectors of the rivers. When acid solutions react with carbonates, the water can be leached to pH ~ 7. This process is also responsible for the precipitation of hydroxides of some elements (Fe, Mn, Cu, and Al), which impart the red or bluish white color to sediments. The formation of suspended particulates can also be provoked by the mixing of genetically different waters (e.g., solutions produced during the leaching of gypsum-concentrate rocks) or the mixing of waters draining the oxidation zone of sulfide mineralization.

In addition to the above-described processes of the supergene destruction of sulfide mineralization and dissolution/precipitation of gypsum, processes of the oxidation of valence-variable elements are also active in the river water. This is suggested by the synchronous decrease of Ce_{an}, Mn, relative concentration of U (U/Th) (Figs. 10a, 10b). These relationships suggest that the supergene leaching of sulfides is accompanied by the input of both oxidized and reduced forms of metals into the river water.

Thus the presence of water coloration or colored coating in the channel alluvium is an indicator of the active influence of processes of sulfide mineralization and gypsum leaching upon the quality of river water.

The materials presented above indicate that mountainous regions of Wrangel Island incorporate numerous sources of the natural contamination of river water. They are mainly related to the supergene destruction of sulfide mineralization. Such contamination of waters is indicated by the anomalous mineralization (>2 g/l), low pH values, water coloration, and hazardous concentrations of various microcomponents. The most contaminated waters are recorded in tributaries of the Sovetskaya and Tundrovaya rivers (Tundrovaya area) (samples 8/06, 11/06, 8/10, 9/10). Study of the ferruginated river alluvium sample (10/10) showed that the water can also contain Hg, in addition to heavy metals.

In terms of microcomponent concentrations, the remaining samples commonly fit the requirements for drinking water (SanPiN, 2001). However, in terms of the content of SO_4 ion, TDS, and total hardness, many samples of the river water do not fit the standard. For example, the TDS value exceeds 1 g/l in all samples taken in 2007 and 2010. The SO_4 content in them also often exceeds the maximum permissible concentration (MPC) = 500 mg/l. High contents of Ca and Mg ions are responsible for the high value of total hardness. Only approximately one-third of the studied 32 water samples fit the accepted MPC requirements.

CONCLUSIONS

Sampling of waters in rivers of Wrangel Island revealed distinct regional specific features mainly related to the leaching of Late Carboniferous gypsiferous rocks. In some cases, the major (sometimes, crucial) source of various chemical components (Mg, sulfate, heavy metals, Al, and others) are represented by oxidation products of sulfide mineralization. Reaction of these products with limestones and dolomites (or even simple mixing with waters of gypsum leaching) leads to enrichment of the salt complex with Mg ion and precipitation of gypsum from water. Consequently, waters in rivers of Wrangel Island are characterized by the SO_4–Ca–Mg or SO_4–Mg–Ca type and rather high TDS content (>1 g/l). This feature is atypical of the Arctic river water.

In some cases, waters of the acidic leaching of sulfide ores make up vigorous sources of natural contamination. In such places, the river water composition resembles the mine water in base metal deposits or infiltrates of tailing dumps. Based on such natural contamination sources, we can study the influence of some mining industries upon the Arctic water and coastal biocenosis. They can also provide insight into specifics of the dissemination/deposition of pollutants in rivers of the Far East.

The quality of river water likely depends on seasonal fluctuations of discharge and varies during the spring–autumn period. From this viewpoint, we should note the representative water sample 10/10, which was characterized by moderate contamination during the sampling. However, the channel sediments were enriched with various microcomponents.

Under conditions of the continuing global warming, thickness of the zone of seasonal ground thawing can increase, resulting in thickening of the supergene zone and acceleration of fluvial erosion of primary rocks. These processes can provoke drastic increase in the contamination degree of some streams and, consequently, influence the insular biota (particularly, flora and phytophagous organisms (lemmings, reindeers, and musk sheep). The island suffered reduction of reindeer population due to the winter ice loads in 2005 and 2006 (Gruzdev and Sipko, 2007). However, despite favorable weather conditions in recent years, growth of reindeer population is not observed here (Gruzdev, 2011). One cannot rule out that variation in the chemical composition of waters in the island can be one of the factors responsible for the inhibition of population growth.

Thus, we can draw the following conclusions.

1. River waters in the island are characterized by specific salt composition (SO_4–Ca–Mg). Contamination with sulfates is marked by regional character and mainly related to the leaching of Late Carboniferous gypsiferous rocks.

2. Influence of marine salts (Cl, Na, Br, and B) is insignificant relative to the regional contamination of waters with sulfates.

3. The virtually universal presence of Tl admixture (0.4–84 ng/l) is a regional feature of these waters.

4. Another local source of salts in the waters is represented by oxidation zone of the vein or disseminated sulfide mineralization. Such waters are characterized by $pH < 6$ and high concentrations of Cu, Zn, Mn, Al, Sb, Cd, Th, and other microelements. Reaction of such waters with dolomites and limestones provokes an intense precipitation of gypsum (“white” water) and metal hydroxides (“red” water). Consequently, the chemical composition of water changes from the SO_4–Ca–Mg type to the SO_4–Mg type and the TDS content increases to 23 g/l.

5. The REE spectra are characterized by prominent deficit of LREEs and the Ce anomaly varies from 0.2 to 0.9. Maximal values of Ce_{an} are typical of the sulfide oxidation zone. They show negative correlation with Mn concentration and U/Th.

6. In areas of the Far East, data on the water composition in small rivers and creeks can be used in geoexploration works to outline areas promising for some mineral resources: base metal and manganese ores, gypsum and salt deposits, and so on.

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