

# The Hydrochemical Evolution of Water in Lake Karymskii during 1996–2015 after an Underwater Eruption in Kamchatka

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**Abstract**—This study considers variations in the physical and chemical characteristics of water in Lake Karymskii for the period from January 1996, when a phreatomagmatic eruption occurred in the lake, until 2015. Our monitoring revealed two characteristic sets of components whose behavior characterizes the hydrochemical evolution of lake water: a comparatively rapid exponential decay of the concentrations of SO<sub>4</sub>, Ca, and Mg and a slow decrease in the concentrations of Cl, Na, and K. We arrived at the conclusion that two components of the fluid flow (a fumarolic and a hydrothermal component proper) simultaneously occurred during the eruption and thus had an effect on the lake water. We adduce evidence to show that the water balance and the chemical composition of Lake Karymskii stabilized toward 2015.

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## INTRODUCTION

Hydrogeochemical studies on the impact of a simultaneous underwater eruption in the calderic Lake Karymskii and the 1996 eruption of Karymskii Volcano have both theoretical and practical (ecologic) value. This recent eruption in a fresh-water lake provided a theoretical contribution to the science of volcanology, showing that this calderic feature could experience a resumption of magmatic activity, although it was thought to have been inactive during several thousand years. The present study is a follow-up on (Nikolaeva et al., 2005; Karpov et al., 2008) where extensive data were used to show that it is possible to calculate the impact of sudden volcanic occurrences on the environment.

The practical importance of such studies consists in the attempt at prediction of underwater eruptions in caldera lakes, which may be surrounded by human settlement centers, as well as concerning fish breeding in such lakes during inter-disaster periods.

Since the data are very extensive, we merely formulate some of the processes under study here without attempting a theoretical interpretation. We plan to take up these issues again later.

The goal of the present study is to examine the hydrogeochemical evolution of Lake Karymskii water after the underwater eruption upon the background changes in the chemical composition of thermal occurrences, both those which had existed previously

and those which came into being following the 1996 eruption.

## THE METHOD OF STUDY

Multidisciplinary hydrogeochemical monitoring of the Lake Karymskii basin has been conducted each season since 1996, with the focus being on the hydrochemical characteristics of the lake water.

It seemed an important task to monitor the variation in the salinity and gas compositions of the water in order to find the time required for the recovery of hydrogeochemical characteristics of the water that existed before the catastrophe of 1996.

The lake has been sampled during 20 years of observation to varying degrees of detail (during the 1999–2005 period this was done using a catamaran equipped with a hoist for lifting a bathymeter) at two stations:  $S_1$  at the center of the Tokarev underwater crater that was formed in 1996 and  $S_2$  at the center of the lake.

Twice each year (in winters this was April, with sampling being conducted from the ice, and in summers, July and August, using the catamaran) we took representative samples of water at intervals through the following depth intervals: 0–10–20–30–40–50–60 m (and in the intervals 2, 5, and 7 m in the shallow water layer) for complete hydrochemical analyses and for the concentration of dissolved O<sub>2</sub>, with occasional analy-

sis for microelements. Simultaneously, we also measured the water temperature and pH of the horizons we sampled.

Diving operations were conducted in the lake in order to detect underwater hydrothermal discharges. The bottom discharges of gas and hydrothermal fluids that were discovered in 1999–2005 were visited afterwards (down to 20 m depth) by aqualung divers using photography and visual observations, and via sampling.

During the summer of 2001 we carried out a hydrochemical sampling at ten stations along an S–N line, from the coastal zone of the Akademii Nauk hot hydrothermal discharges (into the lake) through the Tokarev crater toward the area of thermal occurrences in the beach zone of the northern part of the structure (the line A–B). A GPS navigator was used to record areas of thermal discharges around the lake and to investigate all larger thermal occurrences by measuring temperatures and sampling water and gas.

The hydrochemical sampling of Lake Karymskii water was carried out using tip-over bathymeters manufactured by HYDRO-BIOS KIEL, Sweden equipped with deep-water thermometers. Temperature measurements of deeper regions in the lake during winter time (April) was conducted from the ice using a “trail” with GTH-1160 thermistors manufactured by Greisinger (and equipped with Ni/Cr thermocouples) spaced at intervals of 10 m.

Water samples for determining the concentration of  $O_{2\text{dissolv}}$  were captured in sealed glasses with ground-in corks and were analyzed by the standard technique (Reznikov et al., 1970). Complete hydrochemical analyses of the water samples were carried out at the Analytical Center of the Institute of Volcanology and Seismology, Far East Branch (FEB) of the Russian Academy of Sciences (RAS) by analysts S.V. Sergeeva, O.V. Shul’ga, V.V. Dunin-Barkovskaya, and A.A. Smyshlyaeva. The concentrations of microelements in water and sediment were determined at the attested laboratory of the Department of Geology, Moscow State University using an Element-2 ICP–MS, Germany; a Plasma Quard-2 VG ICP–MS, England; and an ICAP-6, Thermo Jarrell ICP–OES, United States.

## A GENERAL DESCRIPTION OF THE LAKE AND HYDROTHERMAL OCCURRENCES IN THE AKADEMII NAUK CALDERA

### *The Morphology and Main Characteristics of Lake Karymskii*

Lake Karymskii fills a deep depression in the Akademii Nauk caldera, which is situated in the southern part of the Karymskii Volcanic Center (KVC). The lake is being drained. A single river (Karymskii River) flows from its northern sector (Fig. 1) and empties its waters into the Kronotskii Bay of the Pacific Ocean.

Prior to the 1996 eruptions, a hydrothermal system had been acting there for a long period of time (and is active at present); the system has surface manifestations in the form of discharges of thermal water in two adjacent calderas, viz., the Akademii Nauk (the Akademii Nauk nitrogen–carbonic-acid chloride–sodium thermal waters) and the Karymskii caldera proper (the Karymskii carbonic-acid springs of the narzan type) (Troitskii, 1947; Ivanov and Shuvalov, 1971; Ivanov, 1974; Pilipenko, 1989). The discharge of hot thermal water in these calderas, as well as periodic eruptions of Karymskii Volcano, provided evidence of an ongoing activity in the volcanic center.

Lake Karymskii has a regular complete freezing period beginning in October and ending in May. The Lake Karymskii basin includes surface drainage from the edifices in the Akademii Nauk and Odnobokaya calderas. The drainage area is 32 km<sup>2</sup> as reported in (*Gidrologicheskaya ...*, 1966) and 30.8 km<sup>2</sup> as we determined. Prior to the 1996 eruption, Lake Karymskii was nearly round in shape. For comparison this figure shows the lake outline (Karpov and Dvigalo, 2009) before and after the eruption (see Fig. 1).

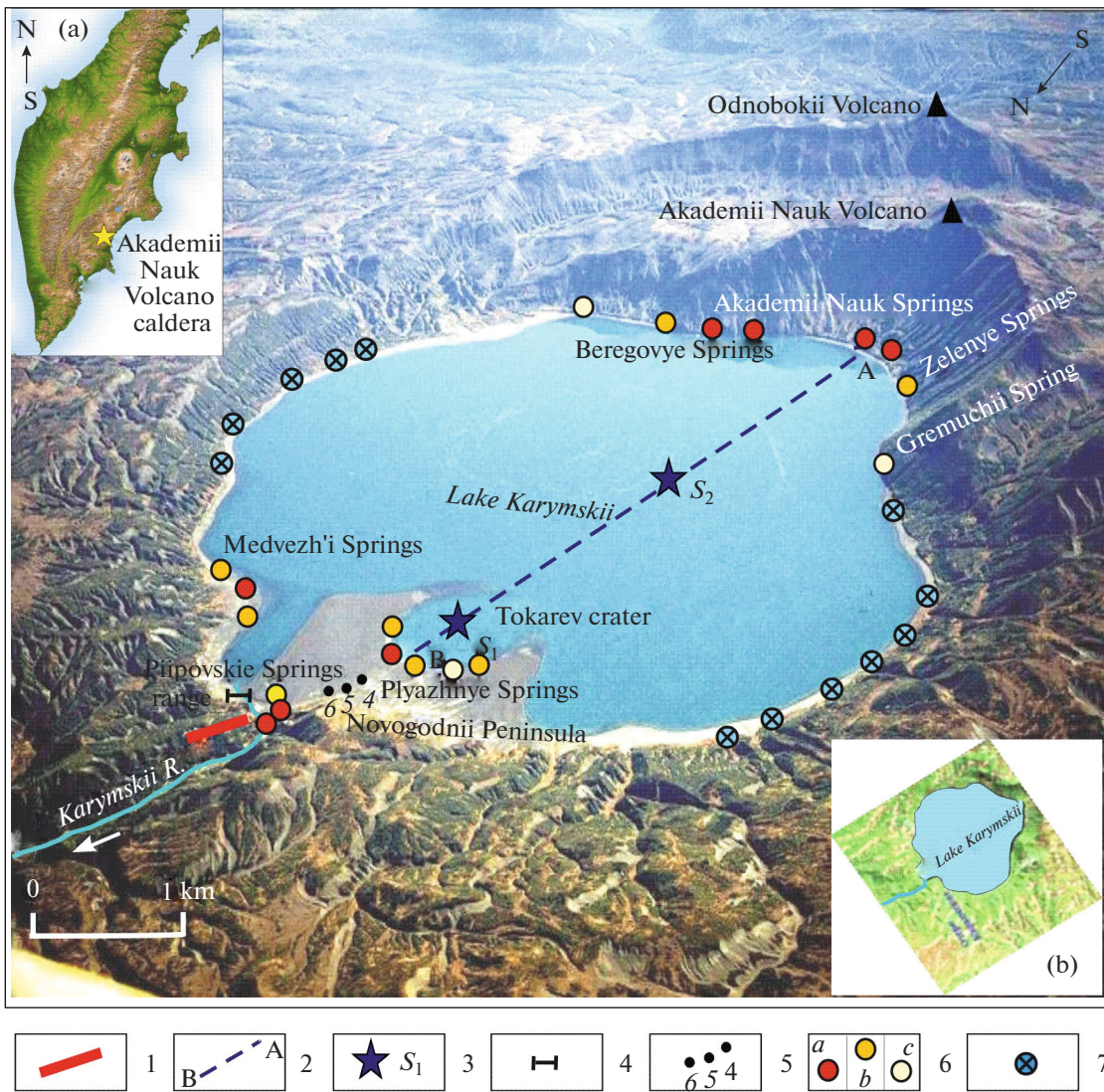
The water area of lake Karymskii was previously 10.7 km<sup>2</sup> (*Gidrologicheskaya ...*, 1966), but shrank to 9.8 km<sup>2</sup> after the eruption. The water line stood at +623.91 m and the volume of the water was  $544 \times 10^6$  m<sup>3</sup> (Karpov, 2004). According to Ivanov (1970), the lake was 65–70 m deep in places during the 1960s. Multiple changes in water level occurred during the active phase of the eruption and after it (Murav’ev et al., 1997).

At present, the lake basin has the shape of a cup with maximum depths of 64 m near the southern sector of the lake. The depth rapidly increases to reach 50 m along the entire perimeter of the lake at distances of 250–300 m off the shore.

The Tokarev crater, which was formed in the northern sector of the lake in 1996, had the shape of an inverted cone at first. As time went on, the bottom of the cone assumed an oval shape that was elongate NW–SE. The upper part of the crater was ~650 m in diameter, while the bottom part was nearly 100 m across. The crater is 58–60 m deep. Its northern sector had a gentle slope until depths of 30 m were reached. The crater walls are gradually slumping down owing to a high water saturation of the constituent rocks; this reduces the depth.

### *The 1996 Volcanic Eruptions in the Karymskii Volcanic Center*

Signs of an imminent eruption. According to geodetic measurements (Magus’kin and Sharoglazova, 1992), a general relative subsidence of the ground surface had occurred during more than 20 years of observations in the Karymskii Volcanic Center (KVC). The base of Karymskii Volcano was observed to rise in 1995 due to an isometric pressure source beneath the



**Fig. 1.** A view of Lake Karymskii in the caldera from NW (photograph with our data added). (1) 1996 fissure; (2) line of hydrochemical observation (A–B) 2001; (3) permanent hydrologic stations on Lake Karymskii ( $S_1$  is the center of Tokarev underwater crater,  $S_2$  is lake center); (4) range at head of Karymskii R.; (5) explosion–collapse funnels of 1996; (6) discharges of thermal water at temperatures of 80–100°C (a), 40–60°C (b), and 10–20°C (c); (7) discharges of cold water at temperatures of 2–4°C. Inset shows: (a) a map of Kamchatka with indication of the Akademii Nauk caldera; (b) a view of Lake Karymskii before the 1996 eruption in it (topographic map of scale 1 : 200000).

volcano, with the top of the source being ~1.5 km from the ground surface (Magus'kin et al., 1997, 2008). Beginning in March 1995, the KVC was showing increased seismicity, probably resulting in resumed activity of the fault zones on the bottom of Lake Karymskii; these zones might conduct volatile compounds from depths into the lake. This can be seen from chemical analyses of water sampled from the lake in 1984, 1989, and 1993, showing increased concentrations of characteristic elements in lake water such as  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{Ca}^{2+}$ , and B (Table 1). These observations might provide precursory signs of an imminent eruption, but they were disregarded at the time. On the eve of the KVC eruptions, in the evening of December 31,

1995, a large tectonic earthquake ( $M = 5.6$ – $5.8$ ) occurred in the southern part of the Kronotskii Bay. In an hour another earthquake ( $M = 6.9$ ) occurred 25 km south of Karymskii Volcano (Fedotov, 1997). Seismic activity increased in the area of Karymskii Volcano in the later half of January 1, 1996; this culminated in a large crustal earthquake of magnitude 6.9 at a depth of approximately 18 km (Fedotov, 1997).

The explosive eruption of Karymskii began on January 2, 1996 to be followed after the lapse of a short time ( $\approx 15$  hours) by an underwater phreatomagmatic eruption in Lake Karymskii (Fedotov, 1997; Murav'ev et al., 1997).

**Table 1.** The chemical composition of waters in Lake Karymskii before the eruption and immediately after it (1984–1996)

#	Sampling date	T, °C	pH	Chemical composition, mg/L																	Salinity			
				H <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>-</sup>	HCO <sub>3</sub> <sup>-</sup>	F <sup>-</sup>	H <sub>4</sub> SO <sub>4</sub>	H <sub>3</sub> BO <sub>3</sub>	Zn <sup>2+</sup>	Ni <sup>2+</sup>	Mn <sup>2+</sup>	Fe <sub>tot</sub>	Cu <sup>2+</sup>		Sr <sup>2+</sup>	Al <sup>3+</sup>	
1	19 Jun 1984*	1.0	7.05	–	–	10.4	1.6	1.6	0.5	8.5	3.8	35.1	0	48.0	0	–	–	–	–	–	–	–	–	109.6
2	25 Apr 1989**	1.5	6.70	–	0.1	11.5	1.3	2.8	0.3	11.0	6.2	25.0	0	49.5	0	–	–	–	–	–	–	–	–	107.7
3	30 Jul 1993***	12.0	7.45	–	0.9	14.0	1.4	6.0	0.6	21.3	5.0	22.0	0.1	52.0	0.1	0.0090	0.0002	0.0060	0.0020	0.0004	–	0.0002	–	123.4
4	22 Jan 1996****	22.0	3.22	0.6	–	57.0	8.5	66.0	19.5	49.0	405.9	0.0	6.3	192.0	0.9	0.0420	0.0190	1.9000	8.6300	0.0520	0.1900	5.8900	–	882.4

The data are from \* (Pilipenko, 1989), \*\* (Vakin and Pilipenko, 1998), \*\*\* (Fazlullin et al., 2000), \*\*\*\* (Karpov, 2004); a dash means no data.

We thus see that the eruption in Lake Karymskii was preceded by significant seismic and geochemical events.

The phreatomagmatic eruption in Lake Karymskii in 1996. The magmatic event of 1996 in the Akademii Nauk caldera was unexpected. It was actually the third subaqueous event in the lake during Holocene time. Two older eruptions (Braitseva, 1997; Belousov et al., 1997) also occurred in the northern part of the lake. The repose period between the two older eruptions was approximately 100 years.

The 1996 eruption in the lake covered by 1 m of ice lasted less than 24 hours, but was very strong. As mentioned above, it occurred simultaneously with a terminal eruption on Karymskii Volcano.

This underwater eruption produced a geologic feature of the “Karymskii” type: (Fedotov, 1997) in the place of the eruptive center in the northern sector of the lake, namely, the Tokarev underwater crater, while the Novogodnii bulk-earth peninsula was formed in the coastal part of the lake; this feature has an area of 0.47 km<sup>2</sup>, and stands 17–18 m above lake level (Murav’ev et al., 1997).

## THE RESULTS

### *The Composition of the Volcanogenic Material that was brought into Lake Karymskii in Connection with the Eruptions*

The underwater eruption in Lake Karymskii was a short-lived event (16–20 hours), but it led to catastrophic consequences. Considerable changes have been wrought in the composition of the entire lake water mass, which acquired extra acidity (pH 3.2) and a Cl-SO<sub>4</sub>/Na-Ca salinity reaching 1 g/L.

When the eruption was over, the entire surface of the lake was steaming. The steam cloud rose to heights of 3 km. The surface water in the lake had a temperature of 22–25°C. This heating of the vast reservoir and of its ice blanket required (Karpov, 2004) a heat of 5.30 × 10<sup>16</sup> J, which is equivalent to the annual heat discharge of 27 present-day hydrothermal systems such as the Geyser Valley in Kamchatka, according to Belousov and Sugrobov (1976).

The volcanic volatiles had essentially halogen sulfurous compositions during the eruption, judging from the water salinity. High concentrations of H<sub>2</sub> and the presence of CO, HCl, HF, and SO<sub>2</sub> were recorded in the free gas of the steam jet (funnel no. 6) that occurred at once after the eruption on the Novogodnii Peninsula in January 1996 and was functioning during almost 1 year (Rozhkov et al., 2001).

The dissolved gases in the near-bottom water of the new Tokarev crater were found to be CO, H<sub>2</sub>, and CO<sub>2</sub> (Rozhkov et al., 2001) and their concentrations rapidly decreased farther away from the crater. A similar phenomenon was observed immediately after the eruption for the distribution of dissolved CO<sub>2</sub> as well, while no dissolved O<sub>2</sub> was detected in the lake water. According to the calculations of Karpov (2004), 18 × 10<sup>6</sup> t of deep water (which was in the magmatic material before the eruption) entered the lake during the eruption along with approximately 27200 t of Cl<sup>-</sup> ion and 203456 t of SO<sub>4</sub> ion. The endogenous components that came together with magmatic material could be inferred from salinity in the lake and in the thermal springs that were formed in the northern circumference of the eruption area and on the southern shore of the lake. Judging from analyses of a water sample taken immediately after the eruption, the lake water showed a sharp increase in the concentrations of Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Cl<sup>-</sup>, S, B, and S (see Table 1), and of heavy metals Zn, Ni, Mn, Fe, and Cu (Karpov et al., 1996; Karpov, 2004). The hot springs that came into existence under a terrace on the left bank at the source of the Karymskii River were found to have water compositions that were dominantly Cl–Na, which is close to the composition of water in the geysers that were functioning on the southern shore of the lake.

A considerable inflow of sulfurous compounds is also corroborated by hydrogen sulfide detected (up to 20 mg/L) in the water of explosion–collapse funnel no. 6 on the Novogodnii Peninsula, as well as by deposits of native sulfur in the steam-and-gas discharges around the funnel (Vergasova et al., 1998).

The lake bottom received deposits of andesite ash brought by air currents from the erupting Karymskii Volcano. Samoilenko and Karpov (2007) used experimental



data acquired using ash samplers for 2006 to derive the amount of ash that entered the lake during a 24-hour period; it was estimated as  $4.3 \times 10^{-3} \text{ kg/m}^2$ ; accordingly, the value for the entire 2006 was  $(6 \pm 3) \times 10^4 \text{ t}$ .

Karpov (2004) derived an approximate estimate for the amount of magmatic material that rose from the magma chamber and is now under the lake bottom:  $3.6 \times 10^9 \text{ t}$ . Using  $3.0 \text{ g/cm}^3$  as an approximate mean density of gabbro (the petrochemical equivalent of basalt), we obtained the result that the magmatic "body" under the bottom must have an approximate volume of  $1.2 \text{ km}^3$ .

The material that was ejected from the Tokarev crater itself was diverse, including basalts, andesites, dacites, rhyolites, and inclusions of sedimentary and hydrothermally altered rocks. Juvenile basalts were also encountered among this material (Grib, 1997). The basalts discharged by the 1996 eruption in the Akademii Nauk caldera are of the calc-alkaline high-alumina type of moderate overall acidity and potassium content. They have a comparatively constant chemical composition. Similar poorly differentiated basalts were already discharged in the northern KVC area during Early Pleistocene time (*Vulkanicheskii tsentr ...*, 1980; Ivanov, 1970; Selyangin, 1987].

One distinguishing feature of this underwater eruption consisted in the presence of bombs that were occasionally as large as 1 m across; in the center of a bomb pumice-like rhyodacites were found with as much as 75%  $\text{SiO}_2$  and a material of basaltic composition in the outer shell. They were ejected during the terminal phase of the eruption. The rhyodacites made up approximately 2–3% of the basaltic material. E.N. Grib believed that this material was produced when hot basalts acted on the granite material of the upper crustal magma chamber (Grib, 1997).

#### *The Hydrogeochemical Evolution of the Lake Karymskii Water*

The evolution of physical and chemical parameters of lake water (pH,  $T^\circ\text{C}$ ,  $\text{O}_2$  dissolv). Prior to the 1966 eruption, the water in Lake Karymskii and in the Karymskii River that starts from it had low salinity (130 mg/L), a  $\text{Cl-HCO}_3\text{-Na}$  composition, and pH 7.1 (Pilipenko, 1989). This caldera lake was successfully used as an experimental base by the KamchatNIRO (the Kamchatka Research Institute of Fisheries and Oceanography) for dissemination of lacustrine salmon fish, or kokanee (*Oncorhynchus nerka kennerlyi* Suckley) (Kurenkov, 1985). Unfortunately, we could not find any information on the chemical composition of water during this breeding effort, either in reports or in publications of researchers at the KamchatNIRO.

After the eruption, the lake water was well mixed up over the entire depth and had approximately homogeneous characteristics for  $T^\circ\text{C}$ , pH,  $\text{O}_2$  dissolv and for

chemical composition over the entire depth range both in the crater and in the lake itself (Fazlullin et al., 2000). However, a stratification of the lake water according to several parameters became apparent as early as in 1998. A north–south hydrochemical line of measurement was visited in the lake to update the state of stratification in 2001.

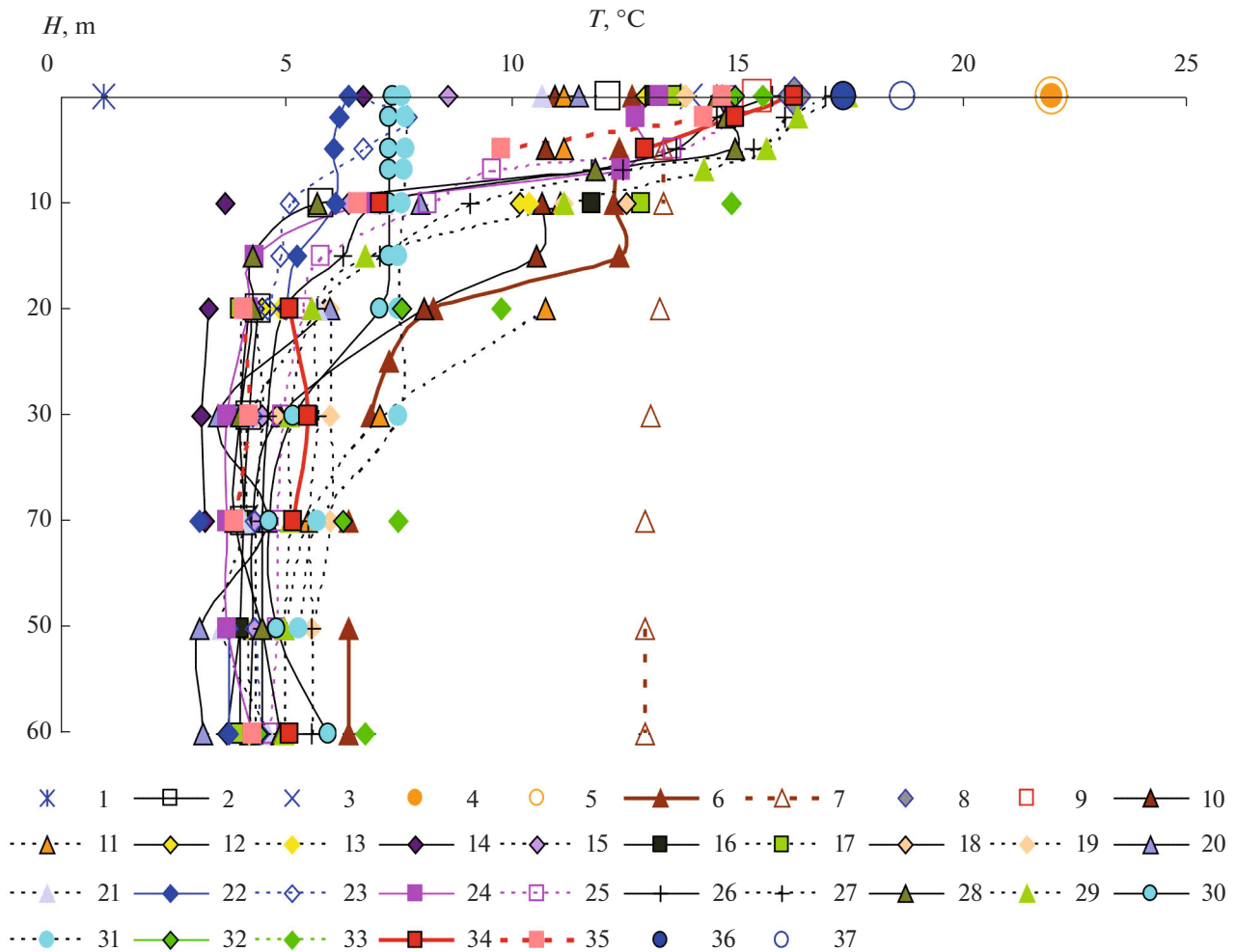
**Temperature ( $T^\circ\text{C}$ ).** The distribution of temperature in the lake water was not yet stable during the summers of 1998–2001 (Fig. 2). The temperature at the lake surface ( $7\text{--}9^\circ\text{C}$ ) at that time was below the seasonal values ( $12\text{--}14^\circ\text{C}$ ). The layer of maximum temperature gradient (thermocline) over the entire water reservoir began at different depths (10–15 m, occasionally at 20 m). As an example, it began at 15 m in the lake water area, afterwards at 30 m, to be followed by a gradual decrease in temperature. Downwards, as far as the bottom, the temperature was  $4^\circ\text{C}$  (Karpov et al., 2008). One exception consisted in some areas in the near-bottom part of the lake reservoir where the temperature was recorded to rise by a few tenths of a degree, which must in all probability be due to local discharges of bottom hydrothermal springs (Nikolaeva et al., 2005).

The temperature distribution in the Tokarev underwater crater was somewhat different. The layer of increased temperature gradient (thermocline) began at a depth of 20 m, with the water temperature gradually decreasing to depths of approximately 30–35 m ( $4.32^\circ\text{C}$ ) where a temperature increase was again recorded by nearly  $0.2^\circ\text{C}$  ( $4.48^\circ\text{C}$ ), which can also be thought to result from the discharge of thermal waters from the side walls of the underwater crater edifice. Below that layer the water temperature gradually decreased to reach  $4.3^\circ\text{C}$ . Overall, the Tokarev crater showed a persistently higher water temperature throughout the entire depth range (by  $1^\circ\text{C}$  on the average).

The thermocline in the southern sector of the lake, near the Akademii Nauk springs, was recorded to be as shallow as 10 m (in contrast to stations  $S_1$  and  $S_2$ ). Below this depth there was a layer of mixed water (thermal and cold waters) at temperatures above  $5^\circ\text{C}$ ; then, downwards as low as the bottom (25 m) the water temperature decreased to  $3.5\text{--}4.0^\circ\text{C}$ .

By the summer of 2004 the temperature in the surface water layer was  $11\text{--}12^\circ\text{C}$  nearly over the entire lake area, reaching  $14\text{--}16(17)^\circ\text{C}$  after 2005. Below the thermocline the temperature gradually decreased down to the bottom. This distribution of the temperature was also characteristic for the lake at later times (Nikolaeva et al., 2005, 2013, 2016).

**The hydrogen parameter (pH).** Following the 1996 underwater eruption, the lake water gradually began to become more alkaline and fresher because of mixing with atmospheric waters, while overall, the surface water in the lake, as far down as the thermocline (approximately to depths of 10–15 m, occasionally deeper, 20 m) was diluted more intensively than was its



**Fig. 2.** The distribution of  $T^{\circ}C$  in a vertical profile across Lake Karymskii based on the 1984–2015 observations at stations  $S_1$  and  $S_2$ . (1) 1984; (2) 1985; (3) 1993; (4–7) 1996; (8) 1997; (9) 1998; (10, 11) 1999; (12, 13) 2000; (14, 15) 2001; (16, 17) 2002; (18, 19) 2003; (20, 21) 2004; (22, 23) 2006; (24, 25) 2007; (26, 27) 2008; (28, 29) 2009; (30, 31) 2010; (32, 33) 2012; (34, 35) 2013; (36, 37) 2015. The dashed lines indicate that the data are based on sampling over depth at the center of the Tokarev underwater crater ( $S_1$ ), while the continuous lines indicate sampling in the middle of Lake Karymskii (station  $S_2$ ).

deeper part. The dilution process can be characterized fairly well by pH. Areas with lower or higher pH were occasionally recorded in the lake (Fig. 3). A rather rapid alkalization and desalinification was observed after 2005. In August 2004 the hydrogen parameter pH reached 5.4, with the respective values being 5.6–5.8 for 2005 and 6.0–6.4 for 2007. Later, the values began to increase still more rapidly.

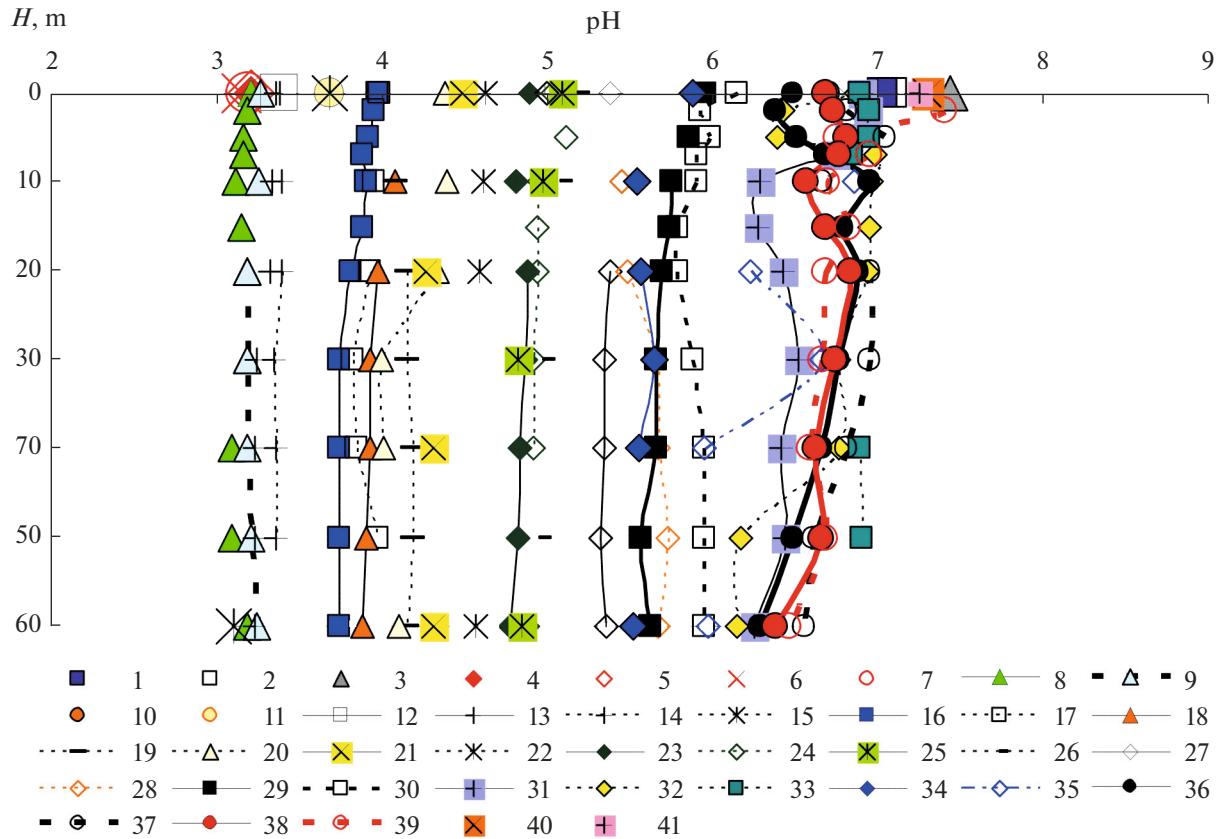
An especially noticeable increase in pH was observed in the Tokarev crater and at the head of the Karymskii River. By 2015 the pH and bulk salinity in the river approached its pre-catastrophic level.

**Dissolved oxygen ( $O_{2dissolv}$ ).** There was no dissolved  $O_2$  in the lake immediately after the 1996 eruption, not only in the near-bottom layer, but also in the shallow layer down to depths of 10–15 m where gas exchange between water and air usually occurs. Naturally, all life became extinct in the lake. A few months after the

1996 catastrophic events, the lake water began to show the presence of  $O_{2dissolv}$ . Its distribution over the vertical was not uniform. Its values reached 9 mg/L in 2 years after the eruption (Fig. 4). The saturation of lake water with  $O_2$  was accelerated later. Clearly expressed horizons at depths of 10–15 m (where the thermocline layer was observed) were found with maximum values of  $O_{2dissolv}$  reaching 14–15 mg/L and at a depth of 40 m where the concentration was  $O_{2dissolv} = 12.5–13.5$  mg/L.

The recorded variations in the concentration of  $O_{2dissolv}$  in lake water seem to have been caused both by oxygen entering ground water whose discharges were in the northwestern and eastern sectors of the lake and by the activity of biota, which occurred again (Lupikina, 2005).

**The evolution of the gas composition in lake water.** High concentrations of  $H_2$ ,  $CO_2$ , and  $CO$  were



**Fig. 3.** The distribution of pH values in a vertical profile of Lake Karymskii based on the 1984–2015 observations at stations  $S_1$  and  $S_2$ . (1) 1984; (2) 1985; (3) 1993; (4–11) 1996; (12–14) 1997; (15) 1998; (16, 17) 1999; (18–20) 2000; (21, 22) 2001; (23, 24) 2002; (25, 26) 2003; (27, 28) 2004; (29, 30) 2005; (31) 2007; (32) 2009; (33) 2010; (34, 35) 2012; (36, 37) 2013; (38, 39) 2014; (40, 41) 2015. The dashed lines indicate water sampling over depth at the center of the Tokarev underwater crater ( $S_1$ ), while the continuous lines indicate sampling in the middle of Lake Karymskii (station  $S_2$ ).

recorded in the Tokarev underwater crater during some time after the eruption. In addition, helium was detected in some sporadic samples, which might provide evidence of volcanic gases coming from the mantle, in the opinion of A.M. Rozhkov (2001). The concentrations of these gaseous components rapidly decreased farther away from the crater.

Numerous gas discharges were observed in a shallow zone near the northern rim of the Tokarev crater during 1996–1999, with the concentrations of Rn being on the order of  $n \times 10^3$  Bq/m<sup>3</sup>. The source of Rn was probably the decay of radioactive elements deeper beneath the caldera (Andreev and Nikolaeva, 2012).

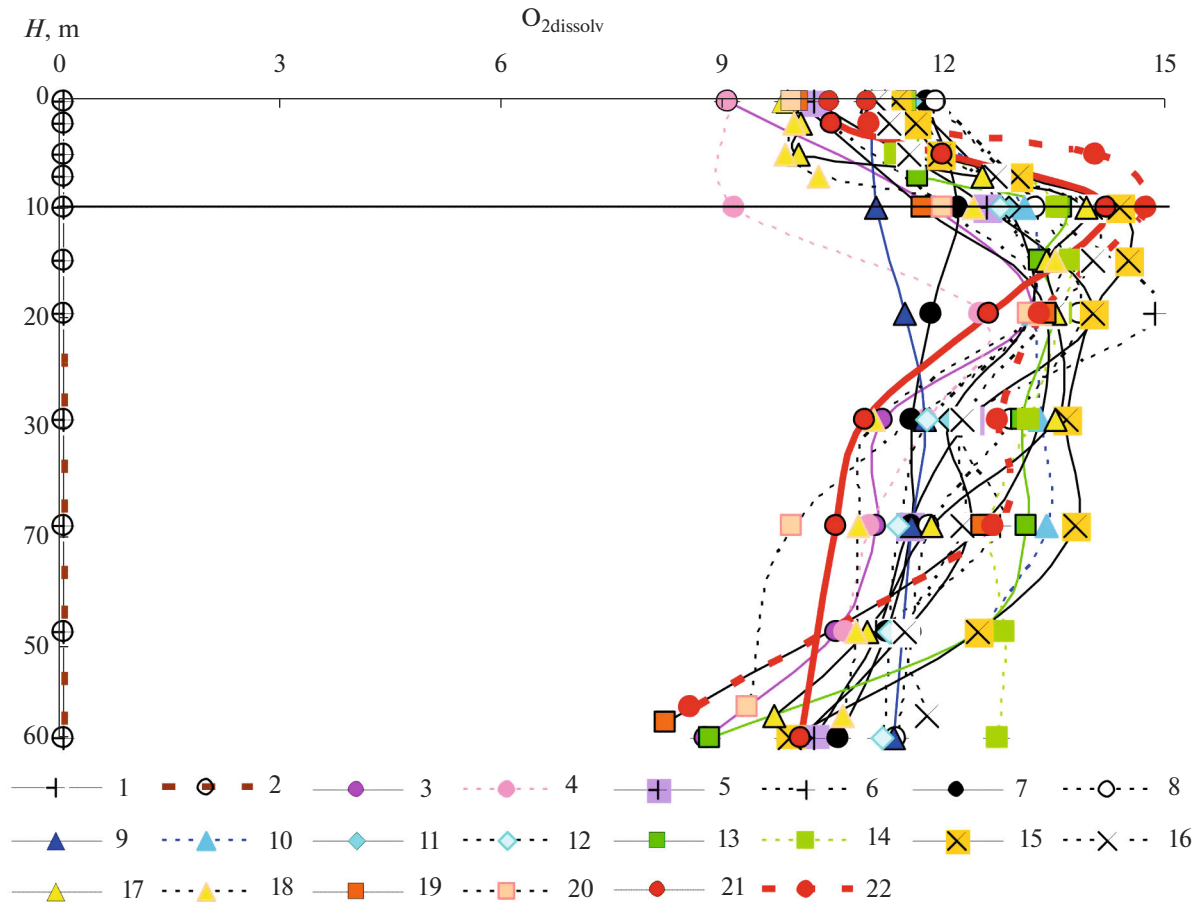
As time passed, changes in the composition of spontaneous gases occurred in the Tokarev crater, with N<sub>2</sub> becoming the dominant component by the late 1990s. However, it was noted that the abundance of Ar was still almost two times higher than the concentration in air (Kuz'min et al., 2007). No gas discharges were observed by 2015, either along the beach edge of the northern part of the crater or in its shallow zone. The gases that were sampled during more recent years of observation were dominated by nitrogen, both in

new and in older locations of thermal discharges. Nevertheless, some rare discharges of CO<sub>2</sub> were observed in the area of the Medvezh'i springs and the Zhelanaya Bay.

The evolution of the chemical composition of lake water. The lake water showed rapidly increasing concentrations of the following chemical components at once after the eruption: Na, K, Mg, Cl, F, B, Si, and SO<sub>4</sub>; the consequence was to increase the bulk salinity (up to 1 g/L). In addition, rather high concentrations of Fe, Zn, Ni, Mn, Cu, Al, and Sr were also recorded (Karpov et al., 1996; Karpov, 2004).

According to the accepted hydrochemical classification, the water of Lake Karymskii was of the sulfate class (with an appreciable admixture of the chloride component) and of the Cl-SO<sub>4</sub>-Na-Ca type. This type of water persisted for a long period in the lake. It was only after the lapse of nearly 2 decades after the eruption that the concentrations of nearly all components in the lake water reverted to their original values (Fig. 5).

As stated above, Mg occurred in the lake water at once after the 1996 eruption, which is explainable by



**Fig. 4.** The distribution of  $O_{2dissolv}$  (in mg/L) in a vertical profile of Lake Karymskii based on the 1984–2015 observations at stations  $S_1$  and  $S_2$ . (1, 2) 1996; (3, 4) 1998; (5, 6) 2000; (7, 8) 2001; (9, 10) 2003; (11, 12) 2004; (13, 14) 2007; (15, 16) 2008; (17, 18) 2009; (19, 20) 2012; (21, 22) 2013. The dashed lines indicate water sampling over depth at the center of the Tokarev underwater crater ( $S_1$ ), while the continuous lines indicate sampling in the middle of Lake Karymskii (station  $S_2$ ).

the fact that it was brought along with the ash component of the eruption and with the flow of magmatic fluids that were discharged on the lake bottom. High concentrations of  $Fe_{dissolv}$  (7–12 mg/L) were also observed, which had subsided to 1–2 mg/L by the summer of 1997 in the near-bottom water and to 0.1–0.5 mg/L in surface water, but the abundance of  $Fe_{susp.}$  was simultaneously increased by nearly an order of magnitude (Karpov, 2004).

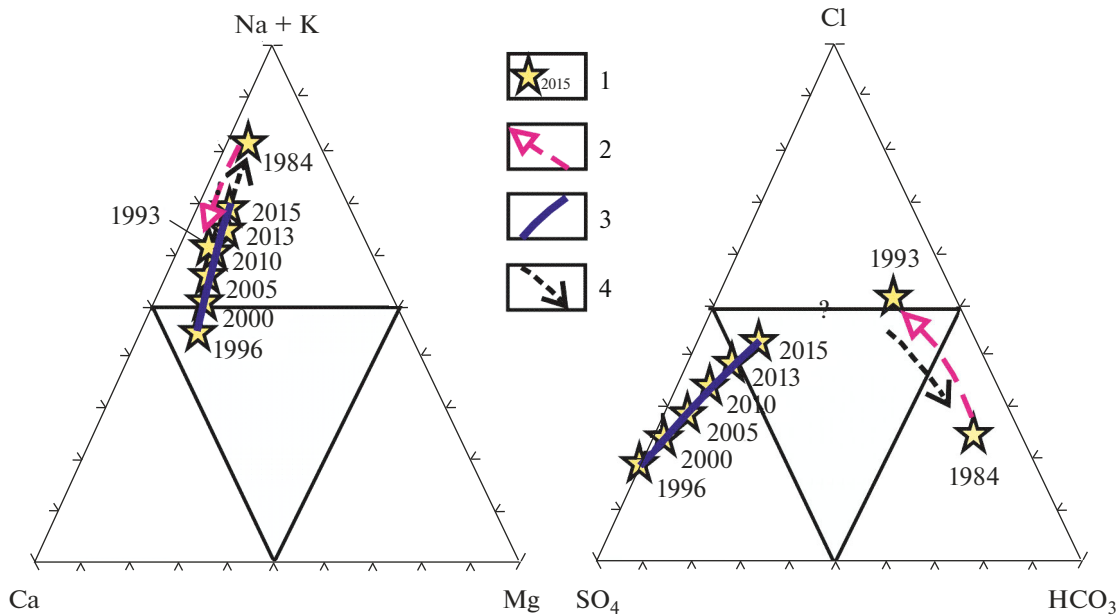
As early as 2001 an appreciable stratification of the water in bulk salinity was recorded along the A–B line. By that time the concentrations of Mg, Ca,  $SO_4$ ,  $H_4SiO_4$  and the bulk salinity in lake water had appreciably diminished. However, the near-bottom water layer showed higher concentrations of components such as  $Na^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Cl^-$ ,  $SO_4^{2-}$ , and B, which might result, in our opinion, from both insufficient mixing of water masses and from the discharge of thermal water along the north–south line of measurement in the lake bottom.

The Tokarev crater had steadily increasing concentrations of nearly all components during the few first years after the eruption between the 20-m-depth horizon and the bottom. Intensive arrival of thermal waters was occurring there; we detected discharges of those waters in the northeastern and western sides of the subaqueous edifice. Over time, however, the discharge began to decrease; this also affected the concentrations of several chemical components.

The cycle of the complete change of the water in Lake Karymskii takes nearly 10 years, according to our calculation. The lake water should have reverted to its original characteristics during that time, but this did not occur, although obvious changes were nevertheless recorded.

As an example, the color of Karymskii water changed in 2012 from the former blue-turquoise (since the eruption of 1996) to become greenish-grey. This was interpreted to have been due to a significant diminution of the concentration of  $SO_4$  ion in the water (Nikolaeva et al., 2013).





**Fig. 5.** A diagram that shows the evolutionary trends of salinity in Lake Karymskii (1984–2015). (1) data points with indication of the sampling year; (2) the trend of salinity variation in lake water until the disaster (1984–1996); (3) the trend of salinity variation in lake water for 1996–2015; (4) the hypothetical trend of salinity recovery to reach the former condition.

The bulk salinity of the lake water decreased by a factor of nearly 2 over 20 years, as inferred from observations at stations  $S_1$  and  $S_2$  (Table 2, Fig. 6). One clearly distinguishes two sets of components whose behavior characterizes the chemical evolution of the lake water: (1)  $\text{SO}_4$ , Ca, and Mg; (2) Na, K, and Cl. The former of the two sets exhibits a simple exponential decay of the concentrations over time, while the behavior of the latter set has been more complex. We believe that the components of the former set, when entering the lake water in increased amounts owing to the 1996 underwater eruption, as well as due to the leaching of the ashes discharged by Karymskii, were not replenished as actively later; their concentrations in the water gradually diminished due to natural dilution in the lake–river system. This is apparent in the plot showing a time-dependent logarithmic relationship for the concentrations of  $\text{SO}_4$ , Ca, and Mg (Fig. 7a). The latter set of components exhibited a different behavior. Their concentrations were decreasing more slowly (see Fig. 7b), because there was an additional source of supply with emanations from hydrothermal discharges underwater. This source of replenishment for the Cl–Na component could result from the local cracking processes that took place before and during the eruption (Magus’kin et al., 1997; Leonov, 1997); the result was to disturb the permeability of the top of the hydrothermal system beneath the Akademii Nauk caldera.

The former set of components ( $\text{SO}_4$ , Ca, and Mg) is characteristic for acid “fumarolic” thermal discharges, while the latter was a “thermal” set and was characteristic for thermal Cl–Na waters in the areas of

volcanogenic hydrothermal systems such as the Uzon–Geyser, the Bol’she-Semyachik, the Pauzhetka, the Yellowstone, and other systems.

**The hydrochemical zonality of lake water.** The processing of continuously recorded data on the composition of water in Lake Karymskii prompted the observation that the near-bottom water in the Tokarev crater and in the main water mass of the lake had a higher bulk salinity compared with the water above. This applied to depths of 15–20 m and deeper. At that time the lake showed a complicated distribution of water salinity in the vertical section.

The concentrations of nearly all chemical components were observed to increase throughout the entire lake water mass. Components such as Ca,  $\text{SO}_4$  and, more locally, Cl were recorded to have their highest concentrations in the near-bottom layer for a long time. Greater contrast in this pattern was observed in the near-bottom waters of the Tokarev underwater crater where the concentrations of Cl ion were over 50 mg/L and those of  $\text{SO}_4^{2-}$  ion over 220 mg/L. The preferred enrichment of the bottom water layer with Ca and Mg ions could be caused by leaching of these ions from ash sediments.

The concentrations of alkaline elements (Na and K) had a slightly different pattern in their distributions. The highest concentrations of  $\text{Na}^+$  ions (up to 70–72 mg/L in 2000 and over 80 mg/L in 1996) occurred in the water lens in the center of the lake in depth ranges of 20–40 m. Since 2000 some slight increases in the concentration of Na were observed at a depth of 30 m in

**Table 2.** Observations of changes in the concentrations of components for the saline composition of water in Lake Karymskii over depth during the summers of 1984–2015 (mg/L)

Station of continuous observation $S_2$ (center of Lake Karymskii)																		
Na <sup>+</sup>																		
H, m	1984*	1993**	1996***	1996**	1997	2000	2001	2002	2003	2004	2005	2006	2008	2009	2012	2013	2015	
0	10.4	14	75	78.1	69.2	66.7	48.6	58.1	49.5	47	45.6	46.3	44.1	42.8	38	35.1	29.1	
10	–	–	–	73.2	–	65.6	50	57.8	49.5	48	47.3	49.6	43.9	41.4	38	37.5	–	
20	–	–	–	82.1	–	68.4	60.12	60.15	8									
5	48.9	48.6	44.5	44.1	41.4	38	37.5	–										
30	–	–	–	74.2	–	69.3	60.8	61.8	58.4	48.9	51.2	44.5	44.1	41.4	–	37.5	–	
40	–	–	–	70.1	–	70.9	61.28	61.5	57.8	49.1	54.2	45.2	44.1	42.3	38.6	37.8	–	
50	–	–	–	82.2	–	75	61.2	61.5	58	51	54.2	45.2	46	45.5	–	–	–	
60	–	–	–	79.4	–	71.8	60.98	62.7	58.3	56.2	55.1	45.4	48.6	46	40.5	41.4	–	
K <sup>+</sup>																		
H, m	1984*	1993**	1996***	1996**	1997	2000	2001	2002	2003	2004	2005	2006	2008	2009	2012	2013	2015	
0	1.6	0.8	7.3	20	6.3	8	6	6.5	6.4	6.5	5.6	5.2	4.6	4.5	3.9	3.1	3.2	
10	–	–	–	17.5	–	7.6	6.5	6.5	6.4	6.5	5.5	4.9	4.6	4.4	3.9	3.5	–	
20	–	–	–	19.8	–	8.5	7.6	6.8	7	6.6	5.7	4.6	4.6	4.4	4	3.5	–	
30	–	–	–	15	–	8.6	7.5	7	7.1	6.6	6.1	4.6	4.6	4.4	–	3.5	–	
40	–	–	–	16.8	–	8.6	7.6	7.2	7.1	6.7	6.3	4.6	4.6	4.7	4	3.5	–	
50	–	–	–	15	–	9.1	7.7	7.2	7.2	6.9	6.6	4.6	5.3	4.7	–	–	–	
60	–	–	–	18	–	9	7.7	7.5	7.3	7.1	6.5	4.7	5.3	5.1	4.1	3.9	–	
Ca <sup>2+</sup>																		
H, m	1984*	1993**	1996***	1996**	1997	2000	2001	2002	2003	2004	2005	2006	2008	2009	2012	2013	2015	
0	1.6	6	65	60	40	35.3	28.1	29.7	28.1	25.6	22.4	20.1	18.4	–	16.8	11.2	10	
10	–	–	–	64.2	–	38	30	28.9	28.1	26.4	23.2	20.4	20.4	16.4	16.8	12	–	
20	–	–	–	65	–	38	37.7	31.3	32	26.4	24	24.1	19.6	17.2	17.2	12	–	
30	–	–	–	64.1	–	40	38	33.7	32.1	26.4	24.8	24.1	19.6	32.9	–	12.4	–	
40	–	–	–	64	–	42	37.7	33.7	32.3	26.4	25.6	23.2	20	17.2	17.6	12.4	–	
50	–	–	–	64.1	–	42	37.6	34.5	32.7	27.2	25.6	22.8	19.6	18.4	–	–	–	
60	–	–	–	65	–	42	37.7	35.3	32.9	27.2	25.6	20.8	19.2	18.4	18.4	12.8	–	
Mg <sup>2+</sup>																		
H, m	1984*	1993**	1996***	1996**	1997	2000	2001	2002	2003	2004	2005	2006	2008	2009	2012	2013	2015	
0	0.5	0.8	14.4	18.4	9.7	8.5	7.3	8.8	7.8	6.8	5.8	5.3	3.4	–	4.1	2.2	1.7	
10	–	–	–	17.2	–	13.3	8	9.7	7.8	6.3	6.3	6.1	3.7	3.9	4.4	2.2	–	
20	–	–	–	18.8	–	13.3	9.7	9.7	8.4	6.3	6.8	5.4	2.9	4.4	4.4	2.4	–	
30	–	–	–	18.9	–	13.3	9.5	9.7	8.3	6.3	7.3	5.4	3.9	4.4	–	2.4	–	
40	–	–	–	20.2	–	12.1	9.7	9.7	8.3	6.3	7.3	5.4	3.7	4.6	3.9	2.4	–	
50	–	–	–	18.3	–	12.1	12	9.2	8.3	6.3	7.8	6.8	3.9	3.9	–	–	–	
60	–	–	–	18.2	–	12.1	22.9	9.2	8.3	6.3	7.8	6.9	4.6	3.9	3.9	2.7	–	
Cl <sup>–</sup>																		
H, m	1984*	1993**	1996***	1996**	1997	2000	2001	2002	2003	2004	2005	2006	2008	2009	2012	2013	2015	
0	8.5	21.3	53.7	45	39	43.1	37.6	41.8	41.1	42.2	35.2	35	36.2	–	32.6	32.6	31.2	
10	–	–	–	44.7	–	45.1	–	41.8	41.1	42.2	38.3	39.1	37.6	36.9	34.7	33.3	–	
20	–	–	–	52	–	47.2	46.1	44	44	42.2	37.6	35.5	36.9	36.9	34.7	34	–	
30	–	–	–	41.8	–	49.4	–	45.4	45.4	42.5	41.4	35.5	36.9	37.6	–	34	–	
40	–	–	–	52.1	–	47.2	–	45.4	46	42.5	41.8	35.5	36.9	39	34.7	34	–	
50	–	–	–	40.2	–	51.8	46.8	45.4	47.1	44	43.3	35.5	36.9	39.7	–	–	–	
60	–	–	–	50	–	49.4	46.8	47.7	48.2	47.2	43.3	38	39.1	40.4	36.9	39	–	

Table 2. (Contd.)

Station of continuous observation $S_2$ (center of Lake Karymskii)																		
SO <sub>4</sub> <sup>2-</sup>																		
H, m	1984*	1993**	1996***	1996**	1997	2000	2001	2002	2003	2004	2005	2006	2008	2009	2012	2013	2015	
0	3.8	4.8	379	351	207	201.7	153.7	172.9	148.9	153.7	134.5	120	101.8	—	67.2	55.2	48	
10	—	—	—	400	—	211.3	137	163.3	148.9	153.7	134.5	129.6	103.7	86.5	76.8	58.6	—	
20	—	—	—	358	—	220.9	182.5	182.5	175	153.7	144.1	127.7	103.7	96.1	76.8	60	—	
30	—	—	—	350	—	230.5	202	201.7	177.7	153.7	158.5	127.7	103.7	96.1	—	60	—	
40	—	—	—	517	—	240.1	211.3	211.3	172	153.7	163.3	127.7	105.6	100.9	86.5	60.5	—	
50	—	—	—	390	—	240.1	214	211.3	176	158.5	163.3	128.6	107.5	105.7	—	—	—	
60	—	—	—	391	—	240.1	220.9	211.3	187.3	163.3	163.3	130	107.5	105.7	86.5	63.4	—	
HCO <sub>3</sub> <sup>-</sup>																		
H, m	1984*	1993**	1996***	1996**	1997	2000	2001	2002	2003	2004	2005	2006	2008	2009	2012	2013	2015	
0	35.1	22	0	0	0	0	1.2	2.4	0.6	0	2.6	3.6	6.1	—	15.9	13.4	15.4	
10	—	—	—	0	—	0	1.1	2.4	0.6	0	2.6	2.4	7.3	11	15.9	13.4	—	
20	—	—	—	0	—	0	1	2.4	0.6	0.2	2.6	6.1	8.5	9.8	14.6	12.8	—	
30	—	—	—	0	—	0	0.6	2.4	0.6	0	2.6	6.1	6.1	9.8	—	12.8	—	
40	—	—	—	0	—	0	0.6	2.4	0.6	0.2	3.8	3.7	6.1	11	14	12.8	—	
50	—	—	—	0	—	0	0.6	2.4	0.6	0.2	3.8	4	11	11	—	—	—	
60	—	—	—	0	—	0	0.6	2.4	0.6	0.2	3.8	4	11	11	14	10.4	—	
Salinity, in mg/L																		
H, m	1984*	1993**	1996***	1996**	1997	2000	2001	2002	2003	2004	2005	2006	2008	2009	2012	2013	2015	
0	109.6	125.7	921.7	985	524	501	424	463.3	519	481.3	370.1	—	315	—	294.1	300	250.5	
10	—	—	—	—	—	510	471	443.5	520	481.5	379.5	363.6	322.9	349.1	305.2	312.7	—	
20	—	—	—	—	—	560	512	473.1	524.5	482.3	392.1	369.4	325.7	347.5	297.9	320.1	—	
30	—	—	—	—	—	564	539	500.8	535	503.9	423.4	360.1	325.1	351.1	—	320.2	—	
40	—	—	—	—	—	556	529	512.3	530	495.5	446.8	353.7	326.6	354.4	303.1	322.9	—	
50	—	—	—	—	—	570	547	515.6	541	486.1	448.1	342.8	335.8	356.6	—	—	—	
60	—	—	—	—	—	578	592	513	594	528.3	477.2	—	340.2	349	311.2	340.6	—	
Station of continuous observation $S_1$ (center of Tokarev underwater crater)																		
Na <sup>+</sup>																		
H, m	1996***	1996**	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2012	2013	2015
0	78	78.6	63.5	65	64	66.1	59.8	51.6	52.8	55.7	45.1	55.5	40.9	43.4	37.2	30.8	35	31.1
10	—	77.1	—	—	67	68.1	63.8	52.5	52.8	56.3	47.3	57.3	42.9	43.6	41.6	30.8	36.8	—
20	—	77.6	—	—	67	68.5	67.8	52.5	56.8	56.9	50.3	56.8	43.9	46.8	45.1	31.5	40.1	—
30	—	81.2	—	—	67	74.6	67	54	60.4	62.3	55.9	58.4	49.6	49.2	45.3	—	42.1	—
40	—	77.1	—	—	68.2	72	67.6	57.8	60	63.6	57.2	61.8	51.2	49.2	46	33.8	43.4	—
50	—	82.4	—	—	64.8	72.4	67	58.1	60.5	64.2	56.8	62	50.4	49.2	46.7	—	—	—
60	—	76.1	—	67.1	—	71	65.4	60	62.1	64.8	56.4	62.3	51.2	49.2	46.7	42.3	43.7	—
K <sup>+</sup>																		
H, m	1996***	1996**	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2012	2013	2015
0	7.3	10.5	6.8	8.5	7.7	7.1	4.6	8.8	6.4	6.5	5.4	5.9	4.6	4.5	4	3.9	2.8	4
10	—	6.6	—	—	7.7	7.8	5.1	7.6	6.4	6.5	5.4	4.9	4.6	4.6	4.3	4	3.6	—
20	—	17	—	—	7	7.3	5.4	7.9	6.9	6.5	6.3	5.1	4.6	4.6	4.7	4	3.7	—
30	—	10.2	—	—	7.7	7.8	6	8	7.7	6.5	6.4	5.1	4.9	5.3	4.9	—	4	—
40	—	10.3	—	—	7.7	7.8	6.8	8.5	7.5	6.8	6.6	5.5	5.4	5.3	5	4.3	4	—
50	—	10	—	—	7.1	7.9	7.3	—	7.7	7.1	7	5.4	5.1	5.3	5	—	—	—
60	—	9.8	—	9.1	—	7.7	8	8.8	7.8	7.1	6.7	5.2	5.3	5.3	5	4.4	4	—

Table 2. (Contd.)

Ca <sup>2+</sup>																		
H, m	1996***	1996**	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2012	2013	2015
0	67	66	50.1	42	40.1	36	30.5	30.5	28.9	26.4	21.6	21.6	19.6	18.4	12.8	16.4	10.8	3.6
10	—	66.2	—	—	40.1	36.4	33.7	30.5	28.9	28.1	23.2	21.6	20.4	18.4	15.2	16.4	12.4	—
20	—	67	—	—	40.1	40.4	36.9	30.5	31	28.1	24.8	21.6	20.4	19.6	16.8	17.2	12.8	—
30	—	64.6	—	—	40.1	40.1	37	32.9	32.1	29.7	27.2	22.9	23.7	20.4	32.9	—	13.2	—
40	—	65	—	—	40.1	39.2	37.5	34.5	32.5	29.7	28.1	24.1	22.8	20	18.4	18.4	13.6	—
50	—	65	—	—	40.1	39.7	37.9	34.5	32.1	29.7	28.1	23.9	23.6	20.4	18.8	—	—	—
60	—	64	—	48	—	40.1	38.5	35.3	33	29.7	28.1	23.3	23.6	20.4	18.4	18.4	13.6	—

Mg <sup>2+</sup>																		
H, m	1996***	1996**	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2012	2013	2015
0	13.2	20.2	9.7	9.7	10.9	10.2	8.8	8.3	7.3	7.3	6.3	4.9	3.9	3.4	3.4	5.8	2.2	1
10	—	20.1	—	—	8.5	7.7	8.8	8.3	7.3	6.8	6.3	5.4	3.7	4.6	3.9	5.8	2.2	—
20	—	20.1	—	—	8.5	7.7	9.7	7.3	7.8	9.7	8.3	5.4	3.7	4.6	4.9	5.8	2.2	—
30	—	20.3	—	—	9.7	10.2	9.9	8.3	8.3	8.8	7.3	5.4	3.4	4.8	4.4	—	2.4	—
40	—	19	—	—	9.7	9.7	10.2	9.2	8.8	8.8	7.3	4.9	5.1	4.8	4.1	6.1	2.4	—
50	—	18.3	—	—	9.7	10	11.3	9.7	9.2	8.8	6.8	5.6	5.1	4.1	4.4	—	—	—
60	—	18.2	—	13.4	—	10.2	12.2	10.2	9	8.3	6.8	5.8	5.1	3.9	4.9	3.9	2.4	—

Cl <sup>-</sup>																		
H, m	1996***	1996**	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2012	2013	2015
0	39	40	41.2	46.7	46.2	44.6	40.4	44.7	41.8	39.7	35.3	39	41.2	36.9	32.6	34.7	30.5	34
10	—	39.1	—	—	45.4	43.9	43.3	42.6	41.8	41.1	37.6	40.4	43.3	36.9	36.2	34.8	32.6	—
20	—	39.9	—	—	45.4	48.2	45.4	43.3	45	41.8	40.4	41.1	43.3	37.6	39.7	35.5	35.5	—
30	—	39.3	—	—	45.4	46.1	44.1	46.1	48.2	44.7	45.4	44	49.7	37.6	40.4	—	36.9	—
40	—	39.4	—	—	47.6	48.2	46.2	49.7	48.7	46.1	45.4	44	49.7	39.1	41.4	37.6	38.3	—
50	—	35.5	—	—	44	48.9	48.6	—	49.3	46.1	44.7	—	44.7	39.1	41.8	—	—	—
60	—	35.7	—	44.7	—	51.1	49.6	49.7	50	47.5	44.7	44.7	48.9	39.1	41.8	37.6	39	—

Station of continuous observation  $S_1$  (center of Tokarev underwater crater)

SO <sub>4</sub> <sup>2-</sup>																		
H, m	1996***	1996**	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2012	2013	2015
0	380.1	378	255	249.6	220.9	201.7	172.9	182.5	—	163.3	134.5	115.3	103.7	101.8	76.8	63.9	54.8	48
10	—	359	—	—	220.9	201.7	192.1	172.9	158.5	163.3	134.5	123	108.5	105.6	96.1	66.3	61.5	—
20	—	343	—	—	220.9	211.3	211.3	182.5	163.2	168.1	144.1	123	113.4	108.5	105.7	67.2	61.5	—
30	—	340	—	—	230.5	230.5	215	192.1	187.3	168.1	163.3	123	116.2	113.3	105.7	—	63.8	—
40	—	400	—	—	240.2	230.5	220.1	192.1	185	168.1	163.3	130.6	119	115.2	105.7	72.5	66.8	—
50	—	350	—	—	220.9	220.0	225.4	197.5	187.3	168.1	163.3	145.3	115.2	115.2	110.5	—	—	—
60	—	351	—	268.8	—	211.3	230.5	201.7	190	168.1	163.3	153.7	127.6	114.2	110.5	76.8	67.2	—

HCO <sub>3</sub> <sup>-</sup>																		
H, m	1996***	1996**	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2012	2013	2015
0	0	0	0	0	1.1	4.3	3	2.4	1.2	1	3.8	1.2	—	6.1	11	17.1	14.6	17.1
10	—	0	—	—	0	2.4	2.4	2.4	1.2	1	2.6	4.9	—	7.3	12.2	14.6	13.4	—
20	—	0	—	—	0	2.4	1.8	2.4	1	1.2	3.8	—	—	7.3	11	14.6	14.6	—
30	—	0	—	—	0	2.4	1.6	2.4	0.6	2.4	3.8	—	—	8.5	11	—	15.3	—
40	—	0	—	—	0	3.7	1.5	2.4	0.7	2.4	3.8	—	—	7.3	12.2	14.6	15.9	—
50	—	0	—	—	0	2.6	1	2.4	0.6	2.4	3.8	—	7.3	7.3	12.2	—	—	—
60	—	0	—	0	0	2.4	0.6	2.4	0.6	1.2	3.8	—	—	8.5	13.4	13.4	15.9	—



Table 2. (Contd.)

H, m	Salinity, in mg/L																	
	1996***	1996**	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2012	2013	2015
0	920.1	692	579.4	575.5	552.3	517.1	319.3	465.3	470.0	520.7	370.3	454.2	311.5	316.2	301.7	335.6	280.1	255.7
10	—	—	—	—	548.8	520.0	349.2	460.9	471.8	527.7	371.3	425.5	318.2	322.8	348.8	346.0	307.4	—
20	—	—	—	—	549.1	547.8	378.4	455.5	578.0	548.5	397.8	587.3	324.9	331.0	384.5	362.7	311.2	—
30	—	—	—	—	566.7	575.0	—	499.9	603.2	553.9	439.8	603.2	348.1	344.1	404.0	—	349.9	—
40	—	—	—	—	581.8	565.1	—	486.4	603.8	561.0	445.8	622.9	352.3	346.2	389.1	357.4	331.5	—
50	—	—	—	—	552.1	542.3	—	492.8	604.7	561.8	464.0	—	350.9	346.9	395.2	—	—	—
60	—	—	—	459.4	—	529.2	630.8	511.6	607.0	580.2	451.4	627.4	360.4	351.0	412.5	332.1	337.1	—

The analyses were performed by the Hydrochemical Team of the Central Chemical Laboratory, Institute of Volcanology and Seismology, Russian Academy of Sciences by Analysts S.V. Sergeeva, A.A. Smyshlyaeva, O.V. Shul'ga. *H*, m denotes the depth of the water layer. The data are from \* (Pilipenko, 1989), \*\* (Fazlullin et al., 2000), \*\*\* (Karpov, 2004). The data for 2002 and 2004 were kindly provided by S.V. Ushakov. A missing year means that no water was sampled at either station during that year. A dash indicates no data.

the bottom waters of the crater and the lake. As an example, the concentration of  $\text{Na}^+$  in the bottom water of the Tokarev crater was 5–12 mg/L above that at the surface. A slight increase in the concentration of  $\text{Na}^+$  was recorded near the northern and southern sectors of the lake where thermal springs were discharged. The same was also observed for  $\text{K}^+$ .

The lake water was found to have an anomalous distribution of  $\text{H}_3\text{BO}_3$ . We note that the concentrations of  $\text{H}_3\text{BO}_3$  in the water of the Tokarev crater were higher than those in the other parts of the Lake Karymskii water mass. The concentration of  $\text{H}_3\text{BO}_3$  in deeper water was 3 times that in surface waters in 2000. Later, in 2002–2003, the concentrations of  $\text{H}_3\text{BO}_3$  began to become more uniform over the entire water mass. However, the Tokarev crater again showed increased concentrations of  $\text{H}_3\text{BO}_3$  in bottom water since 2004, which probably resulted from changes in the activity of Karymskii Volcano (Senyukov et al., 2006).

**The zones of underwater hydrothermal discharges.** Immediately after the underwater eruption, observations detected seeping hydrothermal discharges along the northern periphery of the Tokarev crater. They were especially well pronounced (they were intensively steaming) in an area 1–1.5 m wide that extended for approximately 300 m (up to 500 m later) in the ring sector of the crater beach zone and in the newly generated Goryachii Brook at the head of the Karymskii River (see Fig. 1).

Observations in pits up to 20–30 cm deep in the crater beach zone detected water with pH 7.2–7.5 and temperatures reaching 80°C, while the water in the shallow part of the lake adjacent to the beach was heated to attain 50°C (Vakin and Pilipenko, 1998). In some places in shallow water, approximately down to depths of 2.5–3 m, thin films of algae communities were formed with a chain of intensively discharged gases being observed deeper in the water.

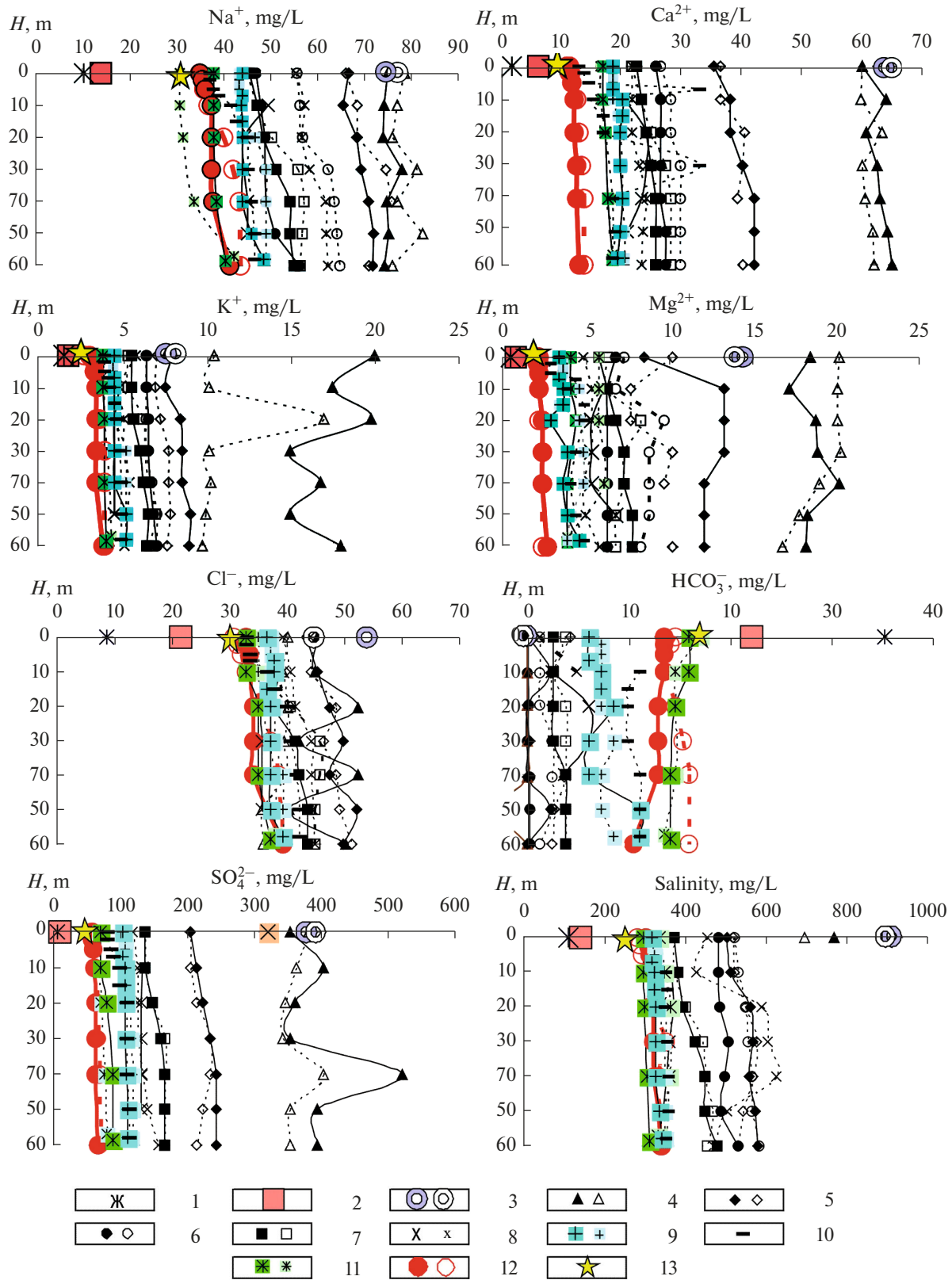
The value of pH in the lake water was 4.0–4.2 by the summer of 1999. The bulk salinity was on the order of 1 mg/L. Subsequently, the salinity was diluted very slowly. This slow increase in the characteristics provided evidence of a substantial underwater hydrothermal discharge in the lake. Divers found areas of bottom hydrothermal discharges ( $T = 32\text{--}64^\circ\text{C}$ , pH 6.2–6.6) with accumulations of algae around them at depths of 6–10 m in the northern, western, and southern sectors of the Tokarev crater. These discharges were detected within narrow trough-like depressions striking nearly north–south, in agreement with the orientations of surface breakage in the wall of the Karymskii River (Leonov, 1997).

A so-called false bottom was discovered in the Tokarev crater, where bottom sediments that were a mixture of volcanic ash and mud did not adhere firmly to the bottom, but were suspended as if being supported by gases. Gas was sampled in that location with dominant  $\text{N}_2$  (as high as 97 vol %). We succeeded in measuring the temperature of the underwater discharges, ranging between 21 and 40°C at various locations (the ordinary temperature of bottom water was 4–4.5°C), and sampled water for chemical analysis (Table 3).

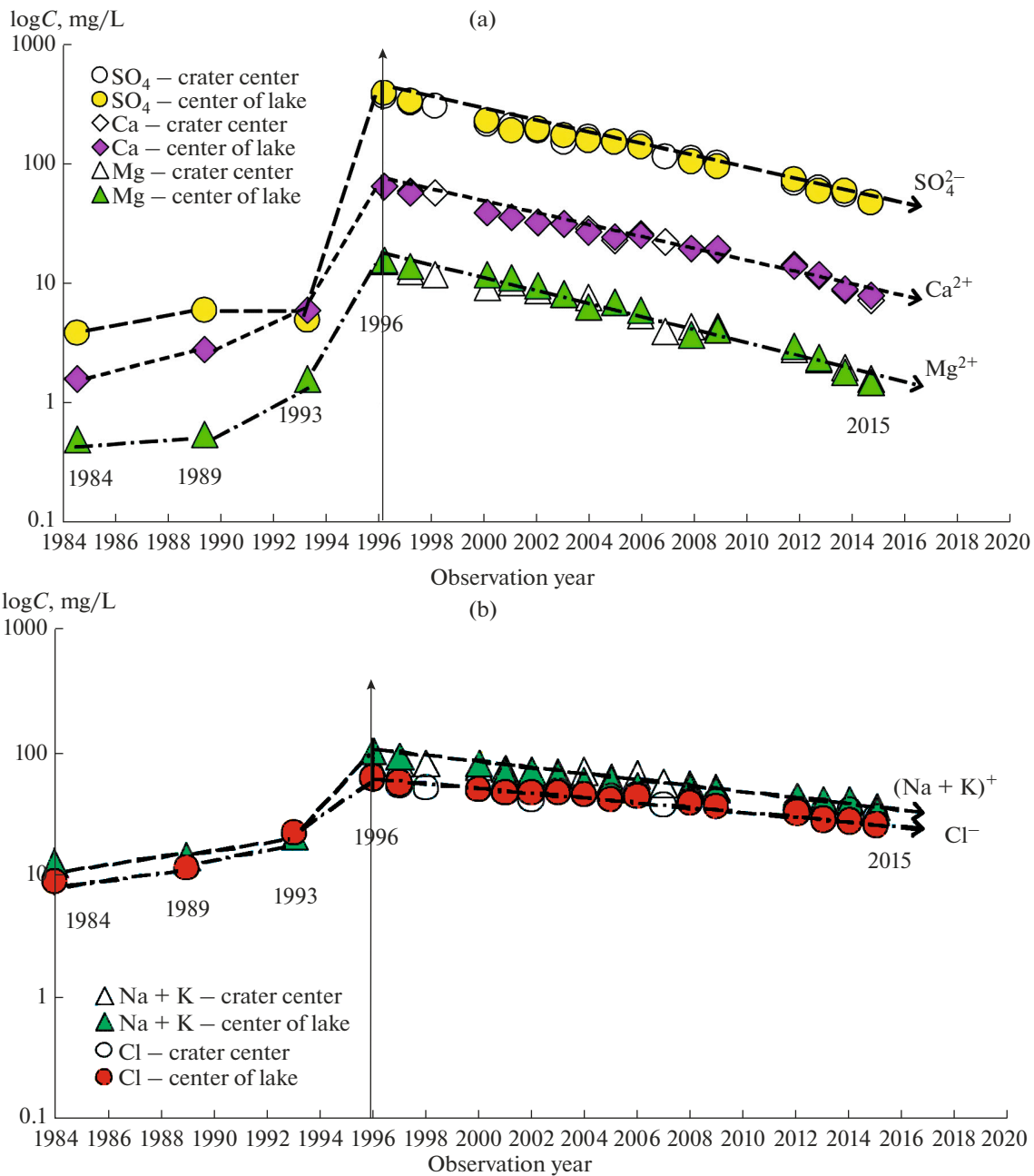
A diving survey of the Tokarev crater bottom in July 2004 showed that the bottom was covered with a viscid black mud in the locations of the underwater hydrothermal discharges involving orange spots (ferrous oxides). The funnels were surrounded by very thin films of algae, which were whitish and pale green in color.

*The Factors that Impeded the Recovery of Water Composition in Lake Karymskii to the Level before the 1996 Underwater Eruption.*

Our surveys have followed the characteristic features in the evolution of hydrogeochemical characteristics in lacustrine and thermal waters in the Akademii Nauk caldera for a period of 20 years. Two lahars descended from the lake along the Karymskii River in



**Fig. 6.** The depth-dependent variations in the concentrations of chemical components ( $\text{SO}_4^{2-}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $(\text{Na} + \text{K})^+$ , and  $\text{Cl}^-$ ) in the water of Lake Karymskii based on continuous observations at stations  $S_1$  (dashed line) and at  $S_2$  (continuous line) for 1984–2013. (1) 1984 data; (2) 1993; (3) (winter) 1996; (4) (spring) 1996; (5) 2000; (6) 2004; (7) 2005; (8) 2006; (9) 2008; (10) 2009; (11) 2012; (12) 2013 (heavy line); (13) 2015.



**Fig. 7.** The trends of the variation for averaged concentrations of  $\text{SO}_4^{2-}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  (a) and  $(\text{Na} + \text{K})^+$ ,  $\text{Cl}^-$  (b) in water as measured at station  $S_1$  and  $S_2$  for the 1984–2015 period (on a logarithmic scale).

1996; this was followed by a rapid lowering of the lake water level to reach the normal value, 623.4 m (Andreev and Nikolaeva, 2012). However, ice was formed on the lake in 1997. The reservoir began to recover its pre-catastrophic condition.

The chemical composition of lake water was recovered under the influence of several factors, with the leading factor being the lake–river water exchange. Water is supplied to the lake by atmospheric precipita-

tion in the drainage area of the two calderas, that is, the Akademii Nauk and that of Odnobokii Volcano. The stratification of lake water that we detected showed that the upper layer (0–15 m, up to 20 m in places) was involved in the replenishment of the water mass by dilution by fresh water. The water from that layer was mostly discharged by runoff into the Karymskii River. The bulk of the lake water below the thermocline was hardly involved in the process. It was

**Table 3.** The chemical composition of bottom discharges in Tokarev crater, Lake Karymskii

Name of source	Sample no.	Sampling date	T, °C	pH	Chemical composition, mg/L												Salinity
					NH <sub>4</sub> <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup>	F <sup>-</sup>	H <sub>3</sub> BO <sub>3</sub>	H <sub>4</sub> SiO <sub>4</sub> dissolv	H <sub>4</sub> SiO <sub>4</sub> coll	
Bottom discharges	002s	4 Aug 02	64.0	7.74	0.2	98.3	7.6	37.7	8.3	74.8	230.5	50.0	—	6.8	118.0	9.0	641.2
	003p	4 Aug 02	64.0	7.44	0.1	153.5	17.1	29.7	4.4	95.0	288.2	70.8	—	8.0	175.0	9.0	850.8
	66s/13	4 Aug 02	42.7	5.12	0.0	52.5	7.7	31.3	8.3	45.4	172.9	1.2	—	4.3	103.0	74.0	500.6
	4598	12 Aug 03	45.0	5.23	0.1	62.0	11.4	27.2	7.8	45.4	153.7	8.5	—	4.3	123.0	8.0	451.4
	4777-2	11 Jul 06	38.0	6.78	0.0	96.5	6.7	28.9	5.8	83.7	144.1	29.3	0.5	7.1	137.9	66.3	1411.7

The chemical analysis was performed at the Central Chemical Laboratory of the Institute of Volcanology and Seismology, Far East Branch, Russian Academy of Sciences by Analyst S.V. Sergeeva. A dash stands for *no data*; *dissolv* stands for *dissolved* and *coll* for *colloidal (form)*.

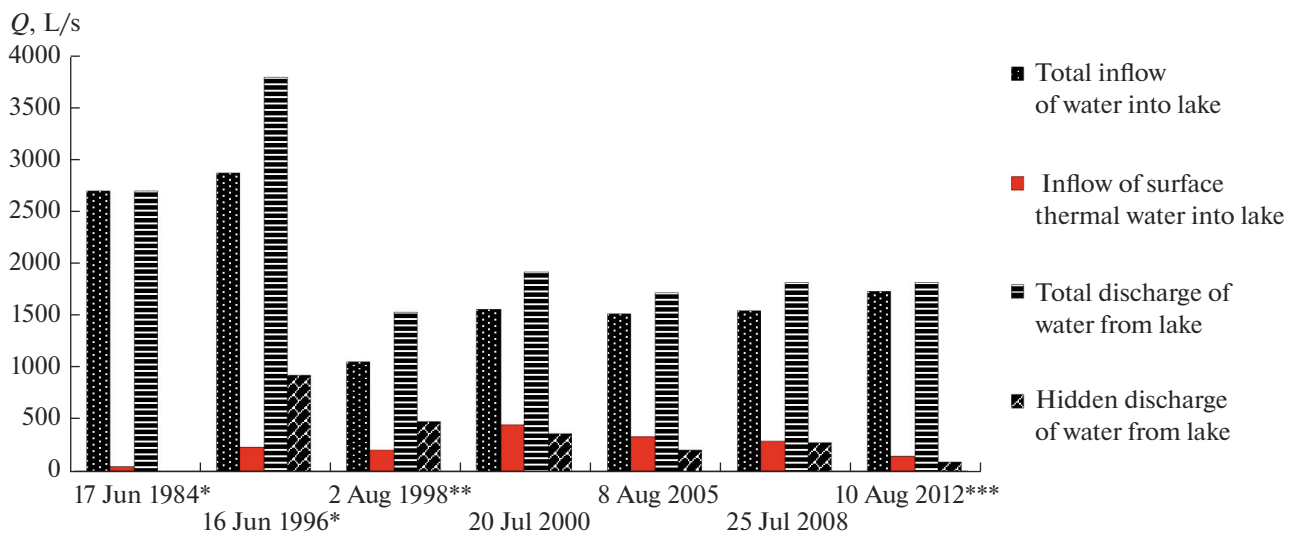
only during seasonal mixing or during strong storms that these waters experienced more intensive dilution and mixing with the epilimnion zone.

Hydrothermal discharge was an important factor that slowed the recovery of the pre-eruption characteristics of lake water. It can be supposed that the low-alkaline and alkaline thermal waters from the springs surrounding Lake Karymskii could quickly neutralize the acid and low-acid lake waters; however, their total discharge rate was insufficient for the task, in spite of their high salinity. It was only by 2013 that the physical and chemical parameters of lake waters approached the pre-eruption values. The lake water had long been without any dissolved oxygen. It was only in 1998 that it occurred in some places and its concentration began to increase. Thermophilic biota appeared in the lake at the same time (Lupikina, 2005).

One certainly important factor that impeded the recovery of the lake water during several years after the underwater eruption was the activity of Karymskii

Volcano, whose eruption actually continued as long as until May 2015. This was accompanied by ashfall on the lake surface and on the drainage area. The action of ash on the chemical composition of lacustrine water is still not known in sufficient detail. On the one hand, desorption of acid gases from ash surfaces might make the water more acid, while on the other hand, the high chemical activity of ash and its solubility might make the water more alkaline due to bases being washed away. Immediately after the eruption, when the lake water had a low pH of 3.2–3.5, the alkalifying effect was dominant owing to active dissolution of the ashes in an acid solution. Later, however, as pH increased, the ashes discharged by Karymskii Volcano may have impeded neutralization, because they brought in occluded acidic components.

The multi-year continuous measurements of the water discharged by the Karymskii River detected substantial changes in its water balance after the eruption. As an example, the discharge of water at the head of



**Fig. 8.** Components of the water balance for the Lake Karymskii basin based on the 1984–2012 continuous observations. Stars denote the same data as in Table 4.



**Table 4.** Measurements of water regime in the Akademii Nauk caldera for 1984–2012 (L/s)

Date of observation	Elements of water balance							Hidden output ( $Q_{hr} = Q_{out} - Q_{inpt}$ )
	inflow			total input ( $Q_{inpt} = Q_{cold} + Q_{therm} + Q_{a.p.}$ )	output		total output ( $Q_{out} = Q_{ev} + Q_{riv}$ )	
	total inflow into the lake from cold brooks ( $Q_{cold}$ )	total inflow into the lake from surface thermal waters ( $Q_{therm}$ )	atmospheric precipitation ( $Q_{a.p.}$ )		evaporation from lake surface ( $Q_{ev}$ )	water outflow at head of Karymskii R. ( $Q_{riv}$ )		
17 Jun 1984*	2650	50	–	2700	–	2700	2700	0
16 Jun 1996*	2650	230	–	2880	–	3800	3800	920
2 Aug 1998**	600	202	250	1052	124	1400	1524	472
20 Jul to 10 Aug 2000	862	445	250	1557	124	1800	1924	367
3–8 Aug 2005	938	330	250	1518	124	1600	1724	206
25 Jul–2 Aug 2008	1012	283	250	1545	124	1700	1824	279
10 Aug 2012***	1350	140	250	1740	124	1700	1824	84

The data are from \* (Pilipenko, 1984), \*\* (Vakin and Pilipenko, 1998), and \*\*\* (Taran et al., 2013); the rest are our data.

the Karymskii River was considerably in excess of the total discharge of all brooks, both cold and thermal, that emptied their waters into the lake. It proved to be a useful tool for investigating the relationships between the components in cold and hot waters to use concentrations of  $H_3BO_3$ , which show high contrasts for the waters in the area. The concentration of  $H_3BO_3$  in ground water is ordinarily below 0.02 mg/L, while rising to reach 38–40 mg/L in thermal waters. The concentrations in the water of Lake Karymskii were 0.5–1.5 mg/L, depending on season and depth.

The behavior of boron ( $H_3BO_3$ ) is generally conservative, with no processes that could bring it out of the system. Its concentration in cold water varies widely from season to season; this variation could be used to find the total amount of the hydrothermal component in the recharge of the lake. As an example, based on the concentration of  $H_3BO_3$  in the water of Lake Karymskii, we obtained the result that the total discharge of thermal waters, assuming their composition to be similar to that of the Akademii Nauk springs, must have been on the order of 400–500 L/s in 2000, with 200–250 L/s occurring for hidden discharge.

Water-balance calculations (Table 4, Fig. 8) showed that the highest recharge of thermal waters (445 L/s) occurred in 2000. This parameter tended to decrease in 2005 and later. Since 2012 the old and new hydrothermal discharges of Cl–Na composition supplied approximately 140 L/s of hot water into the lake (Taran et al., 2013), which is 3 times the value before the 1996 eruption, and 2 and 3 times those in 1996 and 2000, respectively. Water-balance calculations for the

lake showed that the incoming and outgoing parts are in disagreement (see Table 4). Following the eruption, a tendency to a decrease in hidden water runoff for the lake occurred. The hidden runoff was less by a factor of nearly 10 compared with 1996.

After a period of 20 years from the eruption in Lake Karymskii, the lake–river system approached a comparative stability in water balance, both for its discharge/recharge and chemistry.

## CONCLUSIONS

The underwater eruption of 1996 was accompanied by the arrival of vast amounts of dissolved gases and chemical components of deep brine along with the erupted volcanogenic material. The result of the eruption was to make the lake, which had been a freshwater reservoir with neutral water, acidic (up to pH 3.2), to heat the water to 20–25°C in the entire lake, and to remove all dissolved  $O_2$ , and thus to kill all fauna and flora. The presence of helium in the gas sampled in 1996 in the northern part of Lake Karymskii probably indicated a mantle origin of the emanations along zones of seismotectonic faults.

The hydrochemical evolution of Lake Karymskii exhibited effects of fumarolic, postvolcanic, and hydrothermal activities simultaneously. A small local area in the northern sector of the lake was found to show, almost simultaneously, two sets of components dissolved in water: (1) fumarolic components (S, Ca, and Mg) which came into the lake along with erupted material and (2) hydrothermal components (Na, K, and Cl), which enriched the water as a result of

renewed activity on the part of older areas and the appearance of new ones where thermal waters were discharged from the hydrothermal system. The new and preexisting areas where hydrothermal Cl–Na discharges occurred with low values of  $\text{SO}_4^{2-}$ , Ca, and Mg have been the main agents that supplied Cl–Na hydrothermal components into the lake until recently.

Beginning in 1998, Lake Karymskii was observed to show the first signs of stratification in the water with regard to bulk salinity. The bottom water differed from the overlying mass in 2000 in having higher concentrations of  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$ , and  $\text{SO}_4^{2-}$ , which provided evidence of local supply of higher-salinity thermal waters, whose discharges were in fact detected both on the bottom of the lake itself and in the NE and SW walls of the Tokarev underwater crater edifice.

The alkalification of lake water that started in 2012 may be greatly accelerated, unless Karymskii Volcano resumes activity or other cataclysms occur in the area.

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