

The Ash Discharged by Sheveluch Volcano (Kamchatka, Russia) in April 2023 As a Source of Water-Soluble Salts

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Abstract—This paper considers the propagation of ash during the paroxysmal eruption of Sheveluch Volcano which occurred April 10–13, 2023, and its impact on the water resources of the affected area. We characterize ash thicknesses at various population centers and describe the grain-size composition of the ash. We show that the propagation of ash plumes is primarily driven by the eruption dynamics, but atmospheric circulation actually controls the spatial distribution of deposit thickness. The water-soluble salts contained in the ash and the dynamics of their washing out under natural conditions have been determined. The water-soluble part of fresh ash is dominated by calcium and magnesium sulfates, sodium chloride, with minor amounts of chlorides and fluorides of aluminum, potassium, and ammonium. The first substances to be washed out from ashes are well-soluble chlorides, to be followed by sulfates. As time goes on, the total concentration of soluble salts is decreasing, and their qualitative composition changes: hydrogen carbonates of calcium, magnesium, and sodium begin to dominate. Several months after the eruption, the impact of the ashfall on water resources of the settlements, including open springs at the ground surface, was leveled out.

Keywords: Sheveluch Volcano, eruption, volcanic ash, soluble salts

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INTRODUCTION

Volcanic ash is an indispensable product of eruptions. It transports onto the ground surface soluble salts and trace elements in the mobile water-soluble form; subsequently, as meteoric waters go through the deposits, soluble tephra components come into the atmosphere and in water streams (Basharina, 1974). The influence of volcanic ash on the quality of potable and household water is considered in (Wilson et al., 2010, 2012; among others). The main effects that are noted in the relevant studies include increased turbidity in water bodies, a lower pH in waters due to dissolution of acid eruptive products and increased concentrations (in the waters) of sulfates and chlorides of calcium, sodium, and magnesium, as well as fluorides. A study of the impact due to the 2008–2009 Koryaksky eruption on water bodies (Melekestsev et al., 2011) showed also that the water-soluble components of tephra led to a decreased pH (down to ~4–5), as well as increasing the concentrations of sulfates and chlorides of calcium, magnesium, and sodium, as well as of aluminum salts.

It was noted that the ash of Etna brings water-soluble forms of nickel, cadmium, and arsenic into the

environment, resulting in possible exceedance of the permissible concentrations of these elements in potable water at peak times of the eruption/ashfall (Barone et al., 2021). Water-soluble compounds of aluminum, fluorine, and sulfur that have arrived in the water reservoirs of New Zealand from the ash discharged by Tongariro Volcano in 2012 have caused health problems for the residents and did damage to agriculture (Cronin et al., 2014). The ash of Nyamuragira Volcano situated in Congo was a source, in 2010, of water-soluble sulfates, chlorides, and fluorides of sodium, calcium, and ammonium, as well as salts of aluminum, manganese, cadmium, and lead, and has caused acidification of potable water (Cuoco et al., 2013). These authors noted that the quality of potable water has considerably deviated from the acceptable standards owing to the impact of ash. The ash of Hekla Volcano in Iceland discharged in 1991 and in 2000 has led to increased concentrations of fluorides and aluminum in the meteoric waters in contact with the ash; at the same time the water streams received chlorine, iron, manganese, arsenic, cadmium, lead, and zinc, so that the waters were made thereby temporarily unfit for man. One interesting feature in the migration of toxic elements noted by the authors of this study consisted

in sorption of several harmful admixtures on settling hydroxides of aluminum and iron (III). That is to say, waters that have been contaminated with soluble salts of volcanic ash are as if were purifying themselves (Flaathen and Gislason, 2007). Stewart et al. (2006) report on increased turbidity and acidification of natural waters after the fallout of volcanic ash. These authors tried to model the dynamics of contamination affecting potable waters with soluble salts of ash deposits.

An integrated approach that relates rock type and the anion composition of water-soluble tephra salts was demonstrated in (Witham et al., 2005). It was noticed that andesitic rocks have higher relative concentrations of sulfates, while dacitic eruptive products show increased relative concentrations of chlorides and fluorides. They also noted the role of the grain-size distribution of tephra in the arrival of water-soluble salts into water streams. Naturally, the smaller the ash particles, the greater is the specific area of the surface where water-soluble salts are sorbed. Therefore, special hazard for ecosystems emanates from finer ash as carrying higher concentrations of salts.

Explosive eruptions of volcanoes constitute a natural environmental risk for Kamchatka. We study the tephra of the powerful Sheveluch eruption occurring in April 2023 and its water-soluble part for determining the potential impact on the intake and the quality of water used for human consumption and for household needs. The Sheveluch eruption affected several settlements, with those suffering the most including Klyuchi whose population is over 4400, Maiskoe with over 100 people, and Kozyrevsk with over 1100 residents. They were covered with a continuous ash layer whose thickness reached 8 cm, with over 5600 people occurring in the ashfall zone. The ashfall led to the death of some birds (Lobkov, 2023).

THE APRIL 10–13, 2023 ERUPTION OF SHEVELUCH VOLCANO

Sheveluch is the most active volcano of Kamchatka. It stands in the northern Central Kamchatka Depression at a distance of 50 km from the village of Klyuchi and 450 km from Petropavlovsk-Kamchatsky. The volcano is a major volcanic edifice in Kamchatka, with its base being 45–50 km across and its area at least 1300 km² (Melekestsev et al., 1991). The present-day edifice includes three main features: Stary Sheveluch (3283 m), an ancient caldera, and Molodoy Sheveluch (2800 m). The crater of Molodoy Sheveluch hosts a growing dome that appeared there since August 1980 whose activity includes extrusive, effusive, and explosive (Vulcanian-type) eruptions (Melekestsev et al., 1991; Ozerov et al., 2020). The larger explosive eruptions of this volcano related to the growth of the lava dome were observed in 2001, 2004, 2005, and 2010 (Girina et al., 2006, 2007; Fedotov et al., 2004; Ovsyannikov and Manevich, 2010).

Sheveluch was comparatively quiet in the beginning of 2022, but the intensity of the dome growth started increasing since June 10 in that the rate of incandescent avalanches hitting the dome slopes has increased. From October 21 until the start of the April 10, 2023 paroxysmal eruption one could observe a constant arrival of juvenile material onto the ground surface (Girina et al., 2023).

The paroxysmal eruption of Sheveluch lasted over three days. It began at 13:10 UTC April 10, 2023 (Girina et al., 2023). The powerful cyclone that occurred over all of Kamchatka pulled the ash plume westward, turned it southward, extended it northward, and generally pushed it east of the volcano.

Ash layers whose thickness varied between 0.1 and 8 cm were sampled at seven population centers in northern Kamchatka at distances of 50 to 220 km from the volcano in May 2023 after the eruption had ended. The amount of ash collected from 1 m² varied from between 8.92 and 16.62 g in residences farthest from the volcano (Atlasovo, Ezzo, Anavgai, and Dolinovka) to 48.4–58.4 kg in Klyuchi, Maiskoe, and Kozyrevsk.

Girina et al. (2023) showed the evolution of the eruption plume produced by the eruption using an animation based on a series of images acquired by the Himawari-9 satellite in the information system “Remote Monitoring of Volcanic Activity in Kamchatka and the Kuriles” (VolSatView) from 08:00 UTC April 10 to 07:00 UTC April 14 [http://d33.info-space.ru/jr_d33/materials/2023v20n2/283-291/168-3110898.webm]. The animation shows distinctly how the original eruption cloud was accompanied by a great amount of aerosols that were released as the explosions destroyed the lava dome which had been subjected to metasomatic processes during several decades. To take an example, the total amount of sulfur dioxide (SO₂) it contained as of 01:42 UTC April 11 was 214.46 thousand tons, while the concentration reached 471.9 Dobson units, which is equivalent to 210.6 mmol/m² (Girina et al., 2023).

Below we provide a detailed description of the movement of aerosol and eruption clouds over settlements.

— The aerosol cloud containing resurgent ash was above Anavgai from 19:50 UTC April 10 to 04:40 UTC April 11 (about 8 h); subsequently, from 14:10 to 16:10 UTC April 11 (about 2 h), juvenile ash was falling at the same location.

— The aerosol containing resurgent ash was above Ezzo from 19:50 UTC April 10 to 05:00 UTC April 11 (about 9 h); subsequently, from 14:50 to 16:40 UTC April 11 (about 1.5 h), juvenile ash was falling.

— Juvenile ash began to fall at Klyuchi from 18:20 UTC April 10, with the ashfall continuing unintermittedly until 04:10 UTC April 11; after a short stop, because of a turn of the eruption cloud, the ashfall was resumed and went on approximately from 09:00 to

19:30 UTC on April 11, and then from 23:00 UTC April 11 to 03:10 UTC on April 12. The total duration of these ashfalls was thus about 23 h.

— In Maiskoe, juvenile ash continued falling from 19:10 to 22:40 UTC on April 10 (about 3.5 h), this village afterwards being in the zone of the aerosol cloud charged with resurgent ash; juvenile ash was again falling in the village from 12:00 to 16:00 UTC April 11 (about 4 h); that is, the total duration of these ashfalls was about 7.5 h.

— In Kozyrevsk, juvenile ash had been falling from 20:20 UTC April 10 to 06:00 UTC April 11 (about 20 h 20 min); afterwards from 10:20 UTC to 16:20 UTC April 11 (about 6 h); that is, the total duration of these ashfalls was about 26.3 h.

— The eruption cloud containing juvenile ash moved from Klyuchi, Maiskoe, and Kozyrevsk to arrive at Atlasovo and to reside above the village from 21:20 UTC April 10 to 07:10 UTC April 11 (about 10 h), afterwards from 15:20 to 17:40 UTC April 11 (about 2 h 20 min); that is, the total duration of the ash cloud hanging above the village was about 12.3 h.

— The aerosol cloud containing resurgent ash moved from Anavgai and Esso to arrive to the village of Dolinovka and stay there from 23:00 UTC April 10 to 07:10 UTC April 11 (about 8 h); afterwards juvenile ash fell on the village between 16:50 and 19:20 UTC April 11 (about 2.5 h).

This propagation of aerosol-bearing and eruption-induced clouds was largely related to the violence of the Sheveluch paroxysmal eruption, and only secondarily was caused by high cyclone activity in this area of Kamchatka during April 10–14, 2023. The explosions during the eruption were not vertical, their angle of inclination was constantly varying (Girina et al., 2023), and so was the volume of the material ejected by the explosions. Bearing the above in mind, we can explain the higher intensity of the ashfall at Kozyrevsk (58.4 kg/m^2) compared with that at Klyuchi (48.4 kg/m^2) by the great ashfall duration at these villages, about 26.3 and 23 h, respectively. The dominance of fine fractions in the tephra is consistent with the evolution of the eruption: these villages mostly received juvenile ash, which arrived at the ground surface after the lava dome had been destroyed.

Fallen ash was not abundant at the villages that were the farthest from Sheveluch, but, according to the granulometric composition, the ash itself was coarser than, e.g., that at Klyuchi; also, the ash contained particles of rocks that had undergone metasomatic processes during the growth of the lava dome. The ash deposited at those population centers was likely to have been in part that produced by the first explosions that destroyed the lava dome.

THE METHODS EMPLOYED TO STUDY ASHES AND WATER SAMPLES

Ash was sampled during the field season at Klyuchi in April 10–20 and in August 2023. The samples were dried at a temperature of 105°C to remove free liquids. The elemental composition was studied using an S4-PIONEER (Bruker) dispersive X-ray fluorescence spectrometer. The concentrations of trace elements were estimated by a semiquantitative method using the MultiRes program, which is part of the software provided along with the S4-PIONEER dispersive X-ray fluorescence spectrometer. X-ray fluorescence analyses were performed at the Analytical Center of the Institute of Volcanology and Seismology (IVS) FEB RAS.

The mineral composition of the ash was determined by X-ray diffractometry using an XRD MAXima 7000 (Shimadzu) instrument, in the range $6\text{--}70^\circ 2\theta$, at step $0.1^\circ 2\theta$; the scanning rate was 4 deg/min , which is equivalent to a 1.5-s exposure time at a point. The unit cell parameters were determined by the Rietveld method in the PowderCell 2.4 program. The X-ray diffractometry was performed at the Analytical Center of the IVS FEB RAS.

Aqueous extracts were obtained by mixing 100.0 g ash in 1.0 L of distilled water; this was allowed to clarify during a long (up to a few days) time and then filtered to get a transparent solution to analyze using flame photometry, spectral photometry, titration, and potentiometry. Evaporation of the aqueous extract at a temperature of 105°C gave dry salt residues which were analyzed by X-ray diffractometry to determine the phase composition. The method we employed for obtaining aqueous extracts from ashes was tested for samples of products discharged during some eruptions of Klyuchevskoy Volcano for the period 1932–2017 (Kiryukhin et al., 2023a).

Water was sampled at Klyuchi in June–August 2023 from the central water supply network, from the intake of the town, from discharges of cold springs in the bed of the Kamchatka River, and from springs around the town to be analyzed in the same manner as for aqueous extracts.

The ash micromorphology and chemical composition were studied by scanning electron microscopy (SEM) using a VEGA3 LMH (Tescan) instrument. Ash particles $>0.5 \text{ mm}$ across were laid out in rows on a two-sided carbon scotch tape and sprayed with carbon. Pointwise semiquantitative energy dispersive X-ray microanalysis of the ash particles was conducted at an accelerating voltage equal to 20 kV. The microanalytical studies were performed at the Analytical Center of the IVS FEB RAS.

RESULTS OF CHEMICAL ANALYSES OF WATER AND ASH SAMPLES

Table 1 shows the concentrations of major and trace components in dacitic ash sampled in April 2023 at times close to each other. One notes increased concentrations of barium and strontium in the ash, which provides an indirect evidence for a high degree of rock transformation during gas–hydrothermal activity that accompanied the growth of the lava dome before the eruption. As well, one can note high concentrations of rubidium, zirconium, chromium, and cerium; that is, of a rather broad range of elements that migrate under different conditions. Their concentration in the ash provides evidence of a rather complex totality of chemical processes that were occurring during the growth of the lava dome prior to the eruption.

Figure 1 shows ash compositions in a classification diagram for igneous rocks. For comparison purposes we also plotted the compositions of the ashes and rocks discharged by earlier eruptions of Sheveluch as reported in (Girina et al., 2007; Zharinov and Demyanchuk, 2013; Gorbach, 2013; Simakin et al., 2019). By their composition, the April 2023 ashes are largely dacites at the boundary with andesites, which is typical of the Sheveluch tephra. One can note some displacement in the composition of fresh ash toward acid rocks compared with the data acquired during the previous years (see Fig. 1a). That means that Klyuchi, Kozyrevsk, and Maiskoe where a powerful ashfall occurred were covered with juvenile dacitic tephra. Anavgai, Esso, and Dolinovka were mostly covered with resurgent ash that resulted from the explosive destruction of the lava dome, and their composition is somewhat displaced toward low-alkaline dacites (see Fig. 1b).

The diffractometry of the ash showed that its main mineral phases are anorthoclase, plagioclase, and hornblende (Fig. 2). More accurate determination of unit cell parameters for the three rock-forming minerals has enabled us to find that the anorthoclase is similar to pure albite and has the composition $\text{Na}_{0.8-1}\text{K}_{0.2-0}\text{AlSi}_3\text{O}_8$, the plagioclase is like anorthite-bytownite, while the amphibole has unit cell parameters that make it similar to magnesium hornblende. Essentially, the elemental and mineral composition of the Sheveluch ash is similar to the composition of eruptive products discharged by its other eruptions (Zharinov and Demyanchuk, 2013; Simakin et al., 2019; Girina et al., 2007; Gorbach et al., 2013).

Consider ash particles sampled at Anavgai. They are altered, have corroded surfaces, and are frequently strongly “dusted” with particles of volcanic glass (Fig. 3a); as well, particles of “rounded” aspect are encountered (see Fig. 3b). According to the mineral composition of the ash as studied by SEM, it mostly consists of calcium amphiboles (actinolite and hornblende), with calcium pyroxene (augite) being present in lesser amounts. Of feldspars, the dominant species

are solid solutions of plagioclase that have compositions similar to anorthite, less frequently to albite; andesine has been detected in some tests. In addition, the ash particles were found to contain volcanic glass. The varieties encountered in lesser amounts include microcrystals of hematite and titanium-containing magnetite, and most likely of titanite. The most rare findings have been classified as ferrous globules (Sandimirova et al., 2003) (see Fig. 3c) and as zirconium. The crystals are not fritted, they are undeformed, untwisted, and more likely must have come from the destroyed lava dome of the volcano, and were subjected to the action of high temperatures and aggressive fluids. The overall aspect of the particles shows that the minerals in the rocks of the destroyed dome have been transformed during fumarolic activity prior to the eruption.

We analyzed soluble salts in ash by first obtaining the dry salt residue from an aqueous extract from the ash; the residue turned out to mostly consist of calcium sulfate—bassanite $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ and halite NaCl (see Fig. 2). The admixture is gypsum, which results from hydration of bassanite. The salt mixture includes carnallite $\text{KMgCl}_3(\text{H}_2\text{O})_6$, hexahydrate $\text{Mg}(\text{SO}_4)(\text{H}_2\text{O})_6$, and hydrates of calcium chloride like $\text{CaCl}_2(\text{H}_2\text{O})_4$. There are small amounts of magnesium chloride, glauberite, and vanthoffite. The dominance of calcium sulfate and sodium chloride is due to interaction between the rocks of the growing dome and acid volcanic fluids. Hydrogen chloride, which is invariably present in volcanic gases (Basharina, 1953a, 1953b), when it acts on minerals in the host rocks, leads to their destruction, with sodium, calcium, magnesium, aluminum, iron, and other elements being converted to their mobile forms. In the same way, sulfur, which is included in volcanic gases as part of various compounds, is oxidized when coming in contact with water and the oxygen of air, ultimately becoming sulfuric acid. This in its turn leads to corrosion of the minerals that compose the host rock, thus producing outward transport of elements.

Table 2 shows the ion and trace element composition of the aqueous extract from ash, that is to say, those elements which can go into water reservoirs, river network, and into the adjacent sea.

Kurlov’s formula for aqueous extracts from ash is $M0.96 \frac{\text{SO}_4 76 \text{Cl} 24}{\text{Ca} 72 \text{Mg} 16 \text{Na} 8}$ pH 4.09. The waters that wash out the ash are enriched in calcium sulfate, chlorides of magnesium and sodium, they are weakly acidic and magnesium-calcium chloride-sulfate ones. As to trace elements, one notes high concentrations of strontium and barium, manganese, cadmium, arsenic, zinc, copper, and several other elements. The aqueous extract from ash has a composition that correlates well with that for the dry salt residue. Appreciable amounts of iron and aluminum salts have gone into soluble salts because of alteration of the growing dome with acid

Table 1. Major and trace component composition of Sheveluch ash discharged in April 2023

Major component	Average, minimum and maximum concentration (10 samples)	Trace component	Average, minimum and maximum concentration (10 samples)	Detection limit
	Percentage, wt %		ppm	
SiO ₂	$\frac{64.69}{63.68-65.85}$	Sc	$\frac{12}{7-17}$	1.5
TiO ₂	$\frac{0.52}{0.50-0.56}$	V	$\frac{98}{88-116}$	1.6
Al ₂ O ₃	$\frac{15.35}{14.87-15.83}$	Cr	$\frac{87}{71-113}$	2.8
Fe ₂ O ₃	$\frac{2.4}{2.18-2.76}$	Ni	$\frac{30}{25-36}$	1.6
FeO	$\frac{1.50}{1.20-1.64}$	Cu	$\frac{37}{22-49}$	2.1
MnO	$\frac{0.09}{0.09-0.10}$	Zn	$\frac{113}{97-145}$	1.6
CaO	$\frac{5.04}{4.68-5.42}$	Rb	$\frac{19}{4-26}$	0.8
MgO	$\frac{2.86}{2.63-3.32}$	Sr	$\frac{374}{145-495}$	0.8
Na ₂ O	$\frac{4.22}{3.68-4.50}$	Y	$\frac{11}{4-15}$	0.9
K ₂ O	$\frac{1.48}{1.25-1.56}$	Zr	$\frac{87}{33-116}$	1.4
P ₂ O ₅	$\frac{0.16}{0.13-0.18}$	Nb	$\frac{5}{2-7}$	0.9
LOI	$\frac{0.95}{0.52-2.13}$	Ba	$\frac{426}{370-481}$	4.9
Total	$\frac{97.62}{92.95-99.98}$	La	$\frac{12}{9-16}$	4.5
S	$\frac{0.13}{0.02-0.47}$	Ce	$\frac{41}{36-45}$	4.6
Cl	$\frac{0.09}{0.02-0.24}$	Pb	$\frac{16}{7-29}$	1.4

The analyses were performed using an S4 PIONEER dispersive X-ray fluorescence spectrometer at the Analytical Center of the IVS FEB RAS. Analysts: E.V. Kartasheva, A.A. Kuzmina, N.I. Chebrova, and V.M. Ragulina. Ash was sampled by I.A. Nuzhdaev, D.V. Melnikov, V.I. Frolov, R.I. Cherkashin, R.A. Kuznetsov, and Yu.V. Demyanchuk in the environs of Klyuchi, Maiskoe, Ezzo, Kozyrevsk, Anavgai, Atlasovo, and Dolinovka; LOI stands for *loss on ignition*.

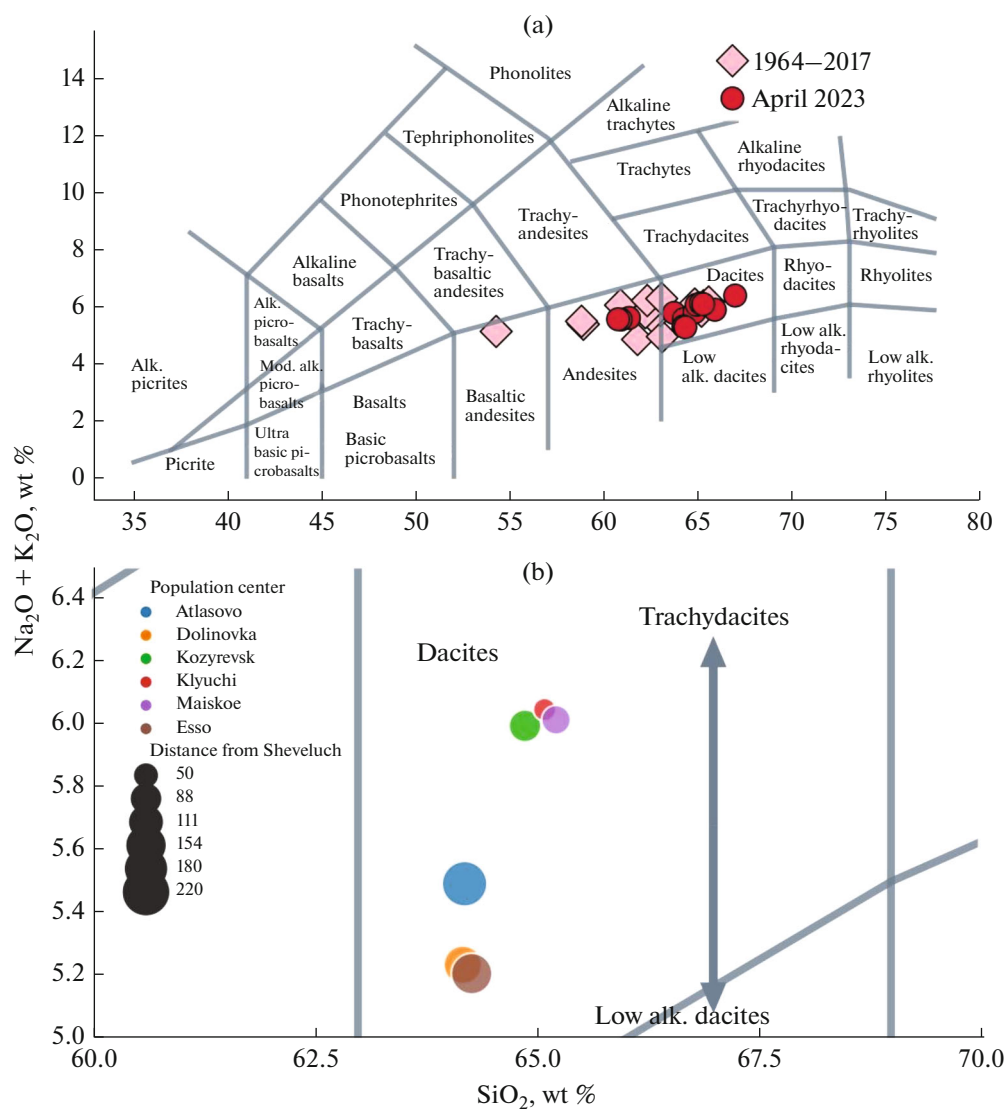


Fig. 1. The compositions of Sheveluch ashes discharged in April 2023 and during the period 1964–2017 based on data from (Zharinov and Demyanchuk, 2013; Simakin et al., 2019; Girina et al., 2007; Gorbach et al., 2013) (a); tephra composition at different distances from Sheveluch (b).

steam and gas jets. The Sheveluch lava dome edifice is like a giant chemical reactor where a large-scale process was occurring involving the action of hot acid fluid flows on minerals in the rocks. The presence of high sulfate concentrations provides evidence of surface waters penetrating the interior of the dome edifice where they were acidizing sulfur-containing compounds in volcanic gases with dissolved oxygen.

The salt composition of the dry soluble residue is shown in Table 3 where the concentration of soluble salts is per one kilogram of ash. The salt concentrations were calculated from data on the ion composition of the aqueous extracts from ash and refined using X-ray diffractometry. This was done in order to determine the arrival of concrete substances into the sea. The salt composition is dominated by calcium and

magnesium sulfates, and by magnesium and sodium chlorides. There are minor amounts of sulfates of ammonium and iron(III), as well as of aluminum chloride, hence fumarolic activity must be expected to produce iron–ammonium sulfates and minerals based on calcium and magnesium sulfates, as well as on chlorides. The latter are short-lived compounds and, like ammonium salts, will be comparatively rapidly removed by meteoric water. Poorly soluble double salts like sabieite $\text{NH}_4\text{Fe}(\text{SO}_4)_2$, minerals of the jarosite and alunite group, as well as calcium sulfates with varying amounts of crystallization water, and halite, were found on the surfaces of rootless solfataras in heated areas of fresh pyroclastic flows. Curiously enough, the major mineral composition of solfataras is controlled by soluble salts of ash.

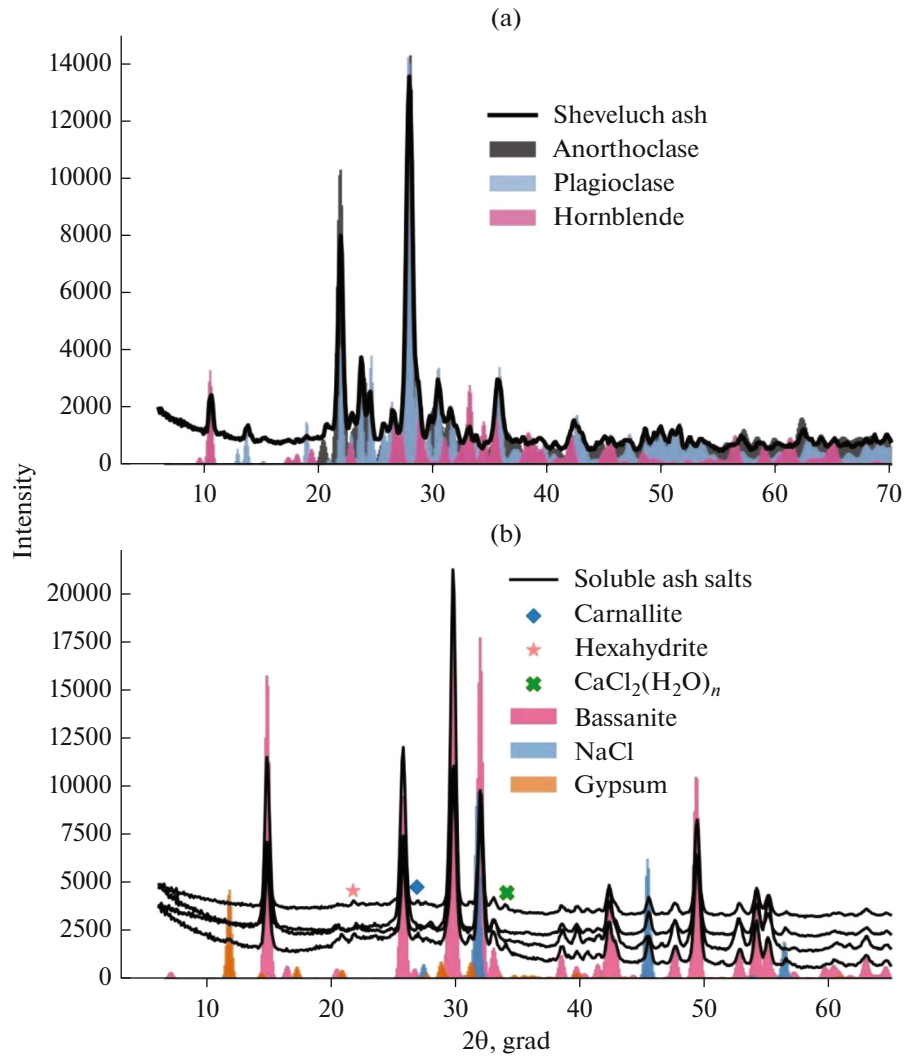


Fig. 2. Minerals (a) and soluble salts as dry salt residue (b) in diffractograms of the ash.

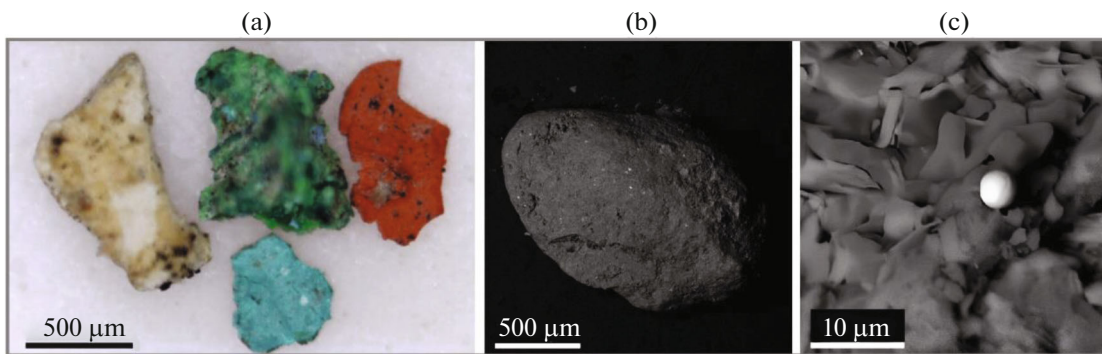


Fig. 3. Ash particles from the village of Anavgai: morphology of ash particles (a); a “rounded” ash particle composed of potassium feldspar, amphibole, and anorthoclase with impregnations of titanium-containing magnetite, photograph in backscattered electrons (b); a hematite ball on an amphibole ash particle, photograph in backscattered electrons (c).

Table 2. Major and trace component composition of the aqueous extract from fresh Sheveluch ash deposited in April 2023 converted to the soluble part per ash mass

pH			4.09		
Major component			Trace component		
	mg/L, extract	g/kg, ash		mg/L, extract	mg/kg, ash
Cl ⁻	95.71	0.96	Cu	0.0119	0.119
SO ₄ ²⁻	415.6	4.16	Zn	0.090	0.90
PO ₄ ³⁻	1.09	0.01	Pb	<0.005	
F ⁻	1.32	0.01	Ni	0.0374	0.374
Total cation	513.7	5.1	Co	0.0120	0.120
Li ⁺	<0.1		Mn	0.9203	9.203
Na ⁺	21.33	0.02	As	0.0265	0.265
K ⁺	5.52	0.06	V	0.0027	0.027
Ca ²⁺	160.00	1.60	Cd	0.0384	0.384
Mg ²⁺	21.85	0.22	Cr	0.0015	0.015
Fe ³⁺	0.20	0.002	Sr	0.4989	4.989
Al ³⁺	1.62	0.02	Hg	<0.0001	
NH ₄ ⁺	0.52	0.005	I	<0.1	
Total anion	211.0	2.11	Br	0.130	1.30
H ₃ BO ₃	2.00	0.002	Se	<0.005	
SiO ₂ p.	232.00	0.232	Ba	0.2290	2.290
Salinity of water samples	958.8	9.60	Ag	0.0012	0.012

The aqueous extract from ash was obtained by M.A. Nazarova; the analysis was performed by A.A. Kuzmina, E.V. Kartasheva, E.A. Yakhimova, S.M. Ivanova, L.A. Pozolotina, O.V. Belous, S.D. Kurdyukov, N.I. Chebrova, and V.M. Ragulina; SiO₂d. denotes the concentration of dissolved silicic acid as converted to SiO₂; Salinity means the total concentration of components in the solution.

Table 3. The salt composition of the dissolved part of the Sheveluch ash discharged in April 2023

Salt composition of dissolved part of ash, g/kg							
CaSO ₄	NaCl	MgCl ₂	MgSO ₄	KCl	AlCl ₃	NH ₄ Cl	FeCl ₃
5.43	0.54	0.54	0.40	0.11	0.08	0.02	0.01

The salt composition was calculated by A.V. Sergeeva based on the major component composition of aqueous extracts.

Table 4 lists the compositions of waters from the central water supply and from the Kamchatka River, as well as the composition of aqueous extracts from ashes that have been under the open sky until August 2023, and which have been subjected to natural effects due to meteoric waters. The waters became near neutral, the anion composition was dominated by hydrocarbonate, while chloride ion, which marks deep-seated components (Kiryukhin et al., 2023b), practically disappeared, and the concentration of fluoride decreased. The cation composition had an increasing amount of sodium and potassium, while the relative concentration of calcium decreased. The total salinity of aqueous extracts from ash that has been under the open sky

decreased by factors of 8–14 compared with the extract from fresh ash; that is to say, the Sheveluch ash has lost about 90% of soluble salts during a span of a few months.

Table 5 shows the compositions of waters from natural springs, from the central water supply, and from the intake at Klyuchi. These are fresh hydrocarbonate waters with near neutral pH, with the cation composition being dominated by sodium. The concentration of chloride ions, which are tracers of processes at depth, decreased down to detection threshold, that of fluorides also decreased, and biogenic components appeared, viz., nitrates and phosphates. It seems that the influence of soluble salts from ash on the Klyuchi

Table 4. The major component composition of aqueous extracts from Sheveluch ash that has lain in natural conditions under the open sky as converted to ash mass

	Klyuchi, August 22, 2023		Quarry at 30 km from Klyuchi, August 22, 2023		Klyuchi, May 15, 2023	
pH	6.90		6.40		6.38	
	mg/L	mg/kg ash	mg/L	g/kg ash	mg/L	g/kg ash
HCO ₃ ⁻	18.50	185.00	20.00	200.00	21.10	211.00
Cl ⁻	<10.0		<10.0		<10.0	
SO ₄ ²⁻	3.87	38.70	25.70	257.00	13.62	136.20
PO ₄ ³⁻	1.61	16.11	0.94	9.35	0.63	6.25
F	<0.15		0.16	1.60	0.17	1.70
Total A	23.98	239.81	46.8	467.95	35.52	355.15
Li ⁺	<0.1		<0.1		<0.1	
Na ⁺	1.18	11.82	1.44	14.40	2.88	28.78
K ⁺	0.67	6.65	0.50	5.05	0.48	4.81
Ca ²⁺	1.28	12.78	9.18	91.79	4.05	40.45
Mg ²⁺	0.47	4.73	0.41	4.06	0.74	7.39
Fe ³⁺	<0.1		<0.1		<0.1	
Fe ²⁺	<0.1		<0.1		<0.1	
Al ³⁺	<0.04		<0.04		<0.04	
NH ₄ ⁺	<0.1		<0.1		<0.1	
Total K	3.60	35.98	11.53	115.29	8.14	81.43
H ₃ BO ₃	2.29	22.90	6.29	62.90	11.44	114.40
SiO ₂ p.	1.81	18.10	2.03	20.30	6.03	60.30
SiO ₂ c.	<1.0		<1.0		<1.0	
Salinity of water samples	31.68	316.79	66.64	666.44	61.13	611.28

Ash was sampled by A.V. Sergeeva, P.O. Voronin, and N.B. Zhuravlev; the aqueous extract was obtained by A.V. Sergeeva and M.A. Nazarova; the analysis was performed by A.A. Kuzmina, E.V. Kartasheva, E.A. Yakimova, S.M. Ivanova, L.A. Pozolotina, O.B. Belous, S.D. Kurdyukov, N.I. Chebrova, and V.M. Ragulina; SiO₂d. denotes the concentration of dissolved silicic acid as converted to SiO₂; SiO₂c. denotes the concentration of colloid silicic acid as converted to SiO₂; Salinity is the total concentration of component in the solution.

waters has been short-lived. We show diagrams that display relative compositions for cations and anions of aqueous extracts from ash and natural springs (Fig. 4). One can clearly see the evolution in the composition of aqueous extracts toward fresh water: the cation composition has a decreasing relative concentration of calcium, while sulfate is being replaced with hydrocarbonate in the anion composition. The freshest extracts were dominated by calcium sulfate and sodium chloride; as the ash was being washed, the dominance passed to sodium and potassium hydrocarbonates, and the composition approached that at the Klyuchi intake and at discharges of underground water in the Kamchatka R. bed.

DISCUSSION

The Elemental and Grain-Size Composition of the Ash

The dacitic composition of ash (see Fig. 1a) is characteristic for Sheveluch, but we wish to note that the compositions of earlier eruptive products were frequently andesitic (Kiryanov, 1983; Simakin et al., 2019); that is, the more recent eruptive products have greater acidity. It is possible that the increasing concentration of silica over time is a reflection of the tendency toward greater acidity of the Sheveluch rocks, at least at the present time. Farther from the volcano we find ash whose composition is somewhat different from that of the ash which fell on Klyuchi, Maiskoe, and Kozyrevsk. As an example, the ash that fell at dis-

Table 5. The water composition for springs and the central water supply network at Klyuchi, mg/L

	Stromboli Hotel, 2023			Klyuchi, a spring in Kamchatka River	Klyuchi, a spring in Kamchatka River, intake	Klyuchi, a spring in Kamchatka River	Lake Kurazhechie
	15.06	22.08	24.08	56.32358° N 160.85818° E	56.32389° N 160.84333° E	56.32401° N 160.84381° E	56.38189° N 160.89612° E
				22.08.2023–24.08.2023			
pH	7.35	6.52	6.74	6.60	6.70	6.82	6.76
HCO ₃ ⁻	40.30	50.03	50.04	80.54	57.36	89.09	63.46
Cl ⁻	<10.0	<10.0	<10.0	<10.0	<10.0	14.18	<10.0
SO ₄ ²⁻	16.7	15.67	14.37	34.02	12.81	20.09	14.4
F ⁻	0.18	0.17	0.21	0.38	0.29	0.23	<0.15
NO ₃ ⁻	<0.02	3.30	3.20	4.00	4.00	5.00	7.20
PO ₄ ³⁻	3.72	0.34	0.38	0.64	0.60	0.80	0.63
Br ⁻	0.57	0.46	0.33	0.46	0.31	0.49	0.49
Total A	64.87	69.51	68.20	119.58	75.06	129.39	85.66
Li ⁺	0.013	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Na ⁺	13.19	12.82	12.65	25.22	13.70	20.22	14.93
K ⁺	<1.0	<1.0	<1.0	2.17	1.28	2.18	1.72
Ca ²⁺	9.31	9.19	9.05	14.07	9.63	14.10	10.42
Mg ²⁺	4.70	3.80	3.79	7.49	3.99	9.09	6.67
Fe ³⁺	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Fe ²⁺	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
NH ₄ ⁺	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Total K	27.21	25.81	25.49	48.95	28.60	45.59	33.74
H ₃ BO ₃	1.03	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
SiO _{2d} .	38.41	42.80	45.10	46.80	44.50	55.80	56.90
SiO _{2c} .	<1.07	2.10	<1.07	<1.07	<1.07	<1.07	<1.07
Salinity of water samples	131.52	138.12	138.79	215.33	148.16	230.78	176.30

Samples were taken by N.B. Zhuravlev, P.O. Voronin, A.V. Kiryukhin, V.I. Frolov, and A.V. Sergeeva. The analysis was performed by A.A. Kuzmina, E.V. Kartasheva, E.A. Yakimova, S.M. Ivanova, L.A. Pozolotina, O.V. Belous, S.D. Kurdyukov, N.I. Chebrova, and V.M. Ragulina; SiO_{2d} denotes the concentration of dissolved silicic acid as converted to SiO₂; SiO_{2c} denotes the concentration of colloidal silicic acid as converted to SiO₂; Salinity is the total concentration of components in the solution.

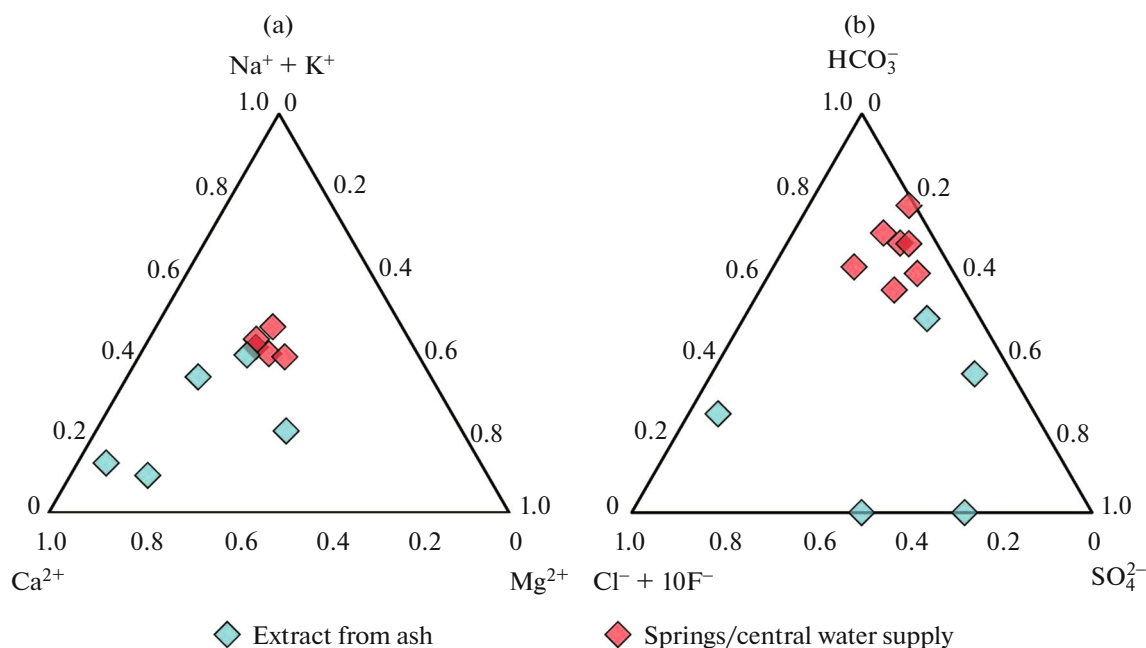


Fig. 4. The cation (a) and anion (b) compositions of aqueous extracts from ash at once after the eruption and after the lapse of a few months; natural springs and the central water supply system for Klyuchi, mg-equiv/L.

tances >100 km from the volcano has the concentration of $\text{Na}_2\text{O} + \text{K}_2\text{O}$ less than 5.6%, while in the ash that fell at distances <100 km of the volcano the concentration of $\text{Na}_2\text{O} + \text{K}_2\text{O}$ was greater than 5.7% (see Fig. 1b). As was shown above, the human settlements that were the nearest to the volcano (Klyuchi, Kozyrevsk, and Maiskoe) were covered by juvenile material, while cyclonic activity farther from the volcano operated to deposit resurgent ash that was formed by explosive destruction of the lava dome.

The mineral composition of the ash includes solid solutions of anorthoclase and plagioclase, as well as magnesian hornblende (see Fig. 2). Hornblende, which belongs to amphiboles, similarly to most members of this large set of ribbon silicates, is characterized by a great variety of cation composition and by wide limits where solid solutions can occur. The action of acid fluids on hornblende converts metals—magnesium, aluminum, calcium, and iron—to their mobile forms, which explains the rich salt composition of the ashes. In view of the large volumetric fraction of hornblende in the Sheveluch ashes one may be allowed to hypothesize that amphibole is one of the main sources of these elements. The aspect of hornblende crystals shows a high degree of corrosion due to fumarolic gases (see Fig. 3c).

With respect to grain-size composition, all tephra samples are fine ashes, because they are dominated by a fraction whose ash particles are <0.071 mm across, with this fraction being 76 to 90% of the sample mass (Figs. 5, 6). In addition, the amount of the 0.2–0.5-mm fraction in the tephra sampled at Dolinovka and

Atlasovo reaches 12–13%, with the respective figure for Esso and Atlasovo being 6–9%; for this reason they have pairwise similarity between the cumulative grain-size curves, and the former ashes are somewhat coarser than the latter (see Fig. 6b). The fraction distributions in ashes sampled in the farthest (from Sheveluch) population centers are fairly similar, unlike the Klyuchi tephra (see Fig. 6). The ashes sampled near the volcano contain, apart from the dominant <0.071 mm fraction (80%), the 0.071–0.125 mm fraction reaching 16%, while the 0.25–0.5-mm fraction is below 0.5% (see Fig. 6). In addition, the farther tephra contains individual large particles with varying coloration, in contrast to the ashes sampled at a distance of 50 km at Klyuchi where no such particles were found (see Figs. 3, 6b).

The differences in thickness, mass, and grain-size composition of the ash cover at the population centers are explainable by the evolution of the eruption (the initial destruction of the lava dome by explosions, and subsequent outward transport of juvenile material from it), as well as by the displacement of Sheveluch aerosol and eruption clouds driven by the cyclone during the April 10–13, 2023 eruption.

The Soluble Components of Sheveluch Ash

The composition of the tephra soluble part indicates a complex composition of the lava dome, which was destroyed during the eruption and deposited as ash on adjacent areas. There is abundant calcium sulfate, which indicates a long-continued alteration of

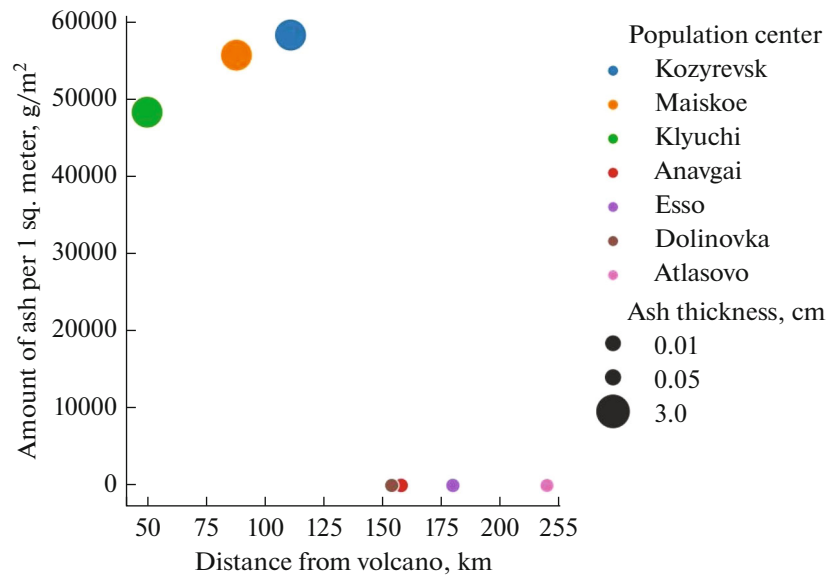


Fig. 5. The amount of ash (g/m^2) at different distances from Sheveluch after its eruption of April 10–13, 2023.

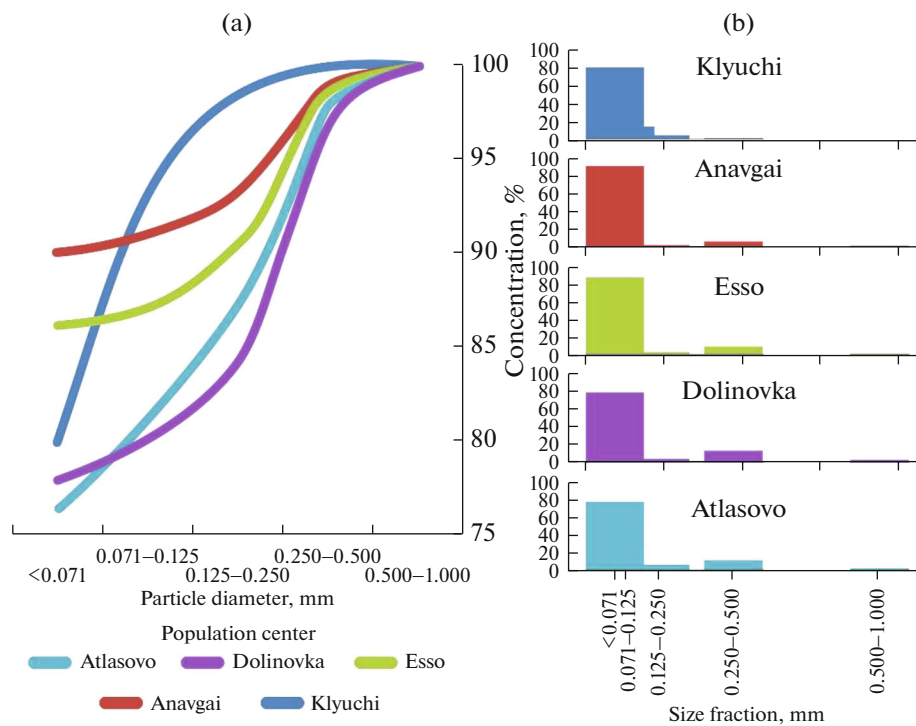


Fig. 6. Cumulative curves (a) and differential histograms (b) for the grain-size composition of the April 10–13, 2023 Sheveluch eruption tephra at various distances from the volcano.

the dome by fumaroles and/or steam–gas jets (Basharina, 1966; Basharina and Markhinin, 1971). As magmatic gases were released from the volcano, sulfuric compounds were oxidized, and interaction with the rocks resulted in leaching of calcium, magnesium, aluminum, iron, and several other elements. Sodium and magnesium chlorides were formed by interaction

between volcanic hydrogen chloride and minerals in the rocks; and, because the rocks are high in magnesium, also the interaction with volcanic gases converted this element to the mobile form. In the same manner aluminum chloride appeared among the salts. This chloride possesses appreciable volatility, and it seems most likely that it appeared as a result of subli-

mation of aluminum chloride, which was formed during interaction between the rocks and the hydrogen chloride of volcanic emanations. The waters that are washing the ash become low acidic, are enriched in sulfates of calcium, iron(III), ammonium, and chlorides of magnesium, sodium, potassium, and aluminum. The following trace elements were converted to their soluble mobile phases: copper, zinc, nickel, cobalt, manganese, arsenic, vanadium, cadmium, chromium, strontium, barium, bromine, and silver (see Tables 1, 2). The waters that were in contact with ash became chloride–sulfate and magnesium–calcium ones.

The main soluble compound that is extracted by meteoric waters from ash was calcium sulfate, which makes three minerals that have different degrees of hydration: anhydrite CaSO_4 , bassanite $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$, and gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. Calcium sulfate is deposited as gypsum under atmospheric conditions, is unlikely to travel through great distances, and is no toxic admixture taken by itself (see Table 2, Fig. 2).

Copper, zinc, nickel, cobalt, manganese, cadmium, silver. These are elements of ore minerals, they are encountered in rocks and in water in contact with these rocks in Kamchatka, as well as in the waters of present-day thermal fields. According to SanPiN no. 1.2.3685-21(2021)¹, the maximum allowable concentration (MAC) for copper in water-soluble form is 1.0 mg/L, with 0.1 for zinc, cobalt, and manganese, 0.02 for nickel, 0.001 for cadmium, and 0.05 mg/L for silver. In the aqueous extracts from ash prepared in the ratio 1 : 10 in mass, the MACs were exceeded for nickel, manganese, and cadmium. We note that in natural conditions the ratio between ash mass and washing water is controlled by the conditions of infiltration recharge, and must not necessarily be in the ratio 1 : 10.

Ash contains, in mobile water-soluble form, about 0.119 ppm copper, 0.90 ppm zinc, up to 0.4 ppm nickel, 0.12 ppm cobalt, 0.384 ppm cadmium, and over 9 ppm manganese. For soils and grounds there are their own MAC levels; as an example, the MAC for copper in water-soluble form is 3 ppm, with 5 ppm for Co, 60 ppm for Mn, 4.0 ppm for Ni, and 2.3 ppm for Zn. The MAC for the bulk concentration of cadmium in soil is about 0.5 ppm. If we compare the characteristics of ash and the maximum allowable concentrations for grounds, we find no significant excess.

¹ The decree of the Chief State Sanitary Doctor of the Russian Federation as of January 28, 2021 No. 2 “On the Approval of Sanitary Norms and Regulations SanPiN 1.2.3685-21 “Hygienic Norms and Requirements on the Ensuring the Safety and(or) Harmlessness of Environmental Factors for Man” (registered by the Ministry of Justice as of January 29, 2021, registration no. 62296). Published on February 3, 2021. Publishing number 0001202102030022. Accessible at <http://publication.pravo.gov.ru/Document/View/0001202102030022?index=1> 2021. 1029 pp.

At the same time, the observed exceedances over maximum concentrations of cadmium, nickel, and manganese in aqueous extracts from ash show that the peak times of the explosive eruption and ashfall posed a hazard of contaminating the intake with heavy metals. We note, however, that the very chemical nature of water-soluble salts in the ash discharged by Sheveluch favors immobilization of heavy metals by coprecipitation along with poorly soluble gypsum. The heavy metals indicated above are mobile in acid environments, while going into poorly soluble compounds like hydroxides and carbonates in near-neutral and alkaline environments.

The concentration of silver in water-soluble form in the ash is at the level 0.012 ppm, while in environments with high concentrations of chloride ions silver can be transported for great distances owing to the formation of soluble chloride complexes $[\text{AgCl}_n]^{n-1}$. In practice one can expect silver to be liberated at locations of chloride concentration, as, e.g., at the mouths of fumaroles/solfataras/steam-gas jets.

Barium and strontium. In water the MAC is 0.7 mg/L for barium and 7 mg/L for strontium. The concentrations of barium and strontium in aqueous extracts from ash did not exceed the MACs, being 0.50 and 0.23 mg/L, respectively, while the concentrations of barium and strontium in soluble form in the ash were at the levels 2.3 and 5.0 ppm. Overall, higher concentrations of barium and strontium are noted for deep waters in the present-day geothermal systems in Kamchatka (Sandimirova et al., 2022; Kalacheva et al., 2016). We note that the present-day geothermal systems of Kamchatka mostly contain barium and strontium in poorly soluble sulfates and/or carbonates (Sergeeva et al., 2023). In acid environments, the solubility of strontium and barium sulfates and carbonates is higher, so that their immobilization is to be expected at near neutral or alkaline pH. It is also possible that strontium and barium sulfates will coprecipitate with gypsum.

Arsenic, selenium, bromine, and iodine. These nonmetals are encountered in different environments both during fumarolic activity of volcanoes or in hydrothermal systems. As an example, arsenic forms minerals both in the Tolbachik fumaroles and in the mud-water pots of the Uzon caldera, as well as being encountered as a component in secondary deposits of the Pauzhetka hydrothermal system (Rychagov et al., 2012; Popova et al., 1985). The Sheveluch ash contains arsenic in mobile form at the level 0.265 ppm, while the MAC for ground is 2 ppm. The aqueous extract from ash contains arsenic in concentrations on the order of 0.03 mg/L, while the MAC for water is 0.01 mg/L. The concentration of arsenic in waters that wash fresh ash is controlled by naturally random relationships between the masses of ash and water, and can differ considerably from that in the aqueous extract from

ash, hence fresh ash can produce a short-lived contamination of natural water with arsenic.

The bulk of ash washed by meteoric waters can be for a long time a source of several elements, but in low concentrations. The concentration of selenium and iodine in the ash is below detection thresholds, hence is not considered here. Bromine enriches some thermal waters in Kamchatka, as well as being encountered in eruptive products of Kamchatka volcanoes (Basharina, 1966, 1974; Leonova et al., 2018; Anikin et al., 2018). It can be transported for great distances along with meteoric waters that wash the ash.

Variations in the Major Components of Aqueous Extracts from Ash

Cold water was sampled from the Klyuchi central water supply network at different times after the Sheveluch eruption (see Tables 4, 5). The water in the network has low salinity, it is sulfate–hydrocarbonate and calcium–sodium water. A similar composition was found for the waters at open springs in the town area and at the intake. No significant changes in the water composition due to the arrival of soluble salts from the Sheveluch ash have been detected. On the contrary, the contact waters of the tephra are gradually approaching the composition of natural cold springs at Klyuchi. It is possible that at peak times during the Sheveluch eruption, when the settlements were covered with a thick ash layer, the instant effect of the tephra on the composition of potable water might be noticeable, but rapidly decayed. For this reason the water in Klyuchi, including open springs at the ground surface, did not show noticeable changes due to ash-falls after a few months since the eruption (see Fig. 4).

Aqueous extracts from fresh ashes are chloride–sulfate, magnesium–calcium, with a dominant acid reaction of the environment. As the ash deposits were aging, which was due to successive washing of the tephra with meteoric water, the contact waters became progressively hydrocarbonate to increasing degrees, with dominantly neutral pH, and an aqueous extract from the ashes was approaching the composition of cold springs in the town and the water in the central water supply system. First of all, all soluble salts were washed out from the ashes, and the mineralization decreased by about an order of magnitude (see Tables 2–4). The washing-out of soluble ammonium and aluminum chlorides and sulfates is the most noticeable phenomenon, with these salts rapidly disappearing from contact solutions. The concentration of hydrocarbonates is increasing; the water in contact with tephra becomes a sulfate–hydrocarbonate sodium–calcium one instead of a chloride–sulfate magnesium–calcium one (see Fig. 4).

CONCLUSIONS

The ash discharged by Sheveluch Volcano in April 2023 fell on Klyuchi, Kozyrevsk, and Maiskoe, making a layer reaching 8 cm in thickness, while the other villages were less affected by the ashfall. The ash composition was dominantly dacitic, with the minerals being dominated by plagioclases whose compositions are similar to those of anorthite and andesine, and by hornblende and anorthoclase. With increasing distance from the volcano, the ash composition was slightly displaced toward low alkaline dacites, which is related to the dominance of resurgent material in the ash that has traveled the farthest.

According to the grain-size composition of the ash, it was dominated by the dust-size fraction, which favored a high concentration of water-soluble substances in the ash. The cause of this was the well-known fact that the specific area of the surface where soluble salts are sorbed increases with decreasing size of ash particles.

Freshly fallen ash contained high concentrations of calcium sulfate and sodium chloride, as well as chlorides, fluorides, and sulfates of ammonium, potassium, aluminum, and iron. As to the toxic elements detected in the aqueous extracts from the ash, these included copper, zinc, nickel, cobalt, manganese, arsenic, cadmium, strontium, and barium. Due to the wide range of admixtures for which norms have been prescribed, and a large amount of fallen ash, there was the threat, just after the paroxysmal eruption, that potable waters would be contaminated with several heavy metals, their concentrations could have exceeded MACs at certain locations. However, the tephra deposits were washed by meteoric waters after the eruption between April and August, resulting in the loss of about 90% of water-soluble salts; as well, their composition has been changed qualitatively: the concentrations of chlorides and fluorides decreased, giving way to hydrocarbonates (see Fig. 4). The cation composition has changed too, with the relative concentration of calcium gradually decreasing, hence the relative concentration of sodium was increasing.

As a matter of fact, as the tephra was being washed by meteoric waters, the composition of an aqueous extract from the ash was approaching the waters of natural springs at Klyuchi, and the concentration of toxic trace elements dropped below detection thresholds. As a matter of fact, the ash has been so thoroughly washed out by meteoric waters during a few months as to reduce it to a certain acceptable level, and has lost potentially toxic effects. No traces of toxic admixtures from volcanic ash were detected in the waters of the Klyuchi central water supply system and at natural springs around the town. We can therefore draw the conclusion that the contaminating effect of ash has been leveled out during the few months that have elapsed after the eruption.

ABBREVIATIONS AND NOTATION

RAS	Russian Academy of Sciences
IVS	Institute of Volcanology and Seismology
FEB	Far East Branch

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CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

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