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GEOCHEMISTRY

Geochemistry of Obsidian from Krasnoe Lake on the Chukchi Peninsula (Northeastern Siberia)

V. K. Popov[a] *, A. V. Grebennikov[a,b], Ya. V. Kuzmin[c, d], M. D. Glascock[e], E. A. Nozdrachev[a], S. Yu. Budnitsky[a], and I. E. Vorobey[f]

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Abstract—This report considers features of the geochemical composition of obsidian from beach sediments of Krasnoe Lake along the lower course of the Anadyr River, as well as from lava–pyroclastic rocks constituting the lake coastal outcrops and the surrounding branches of Rarytkin Ridge. The two geochemical types of obsidian, for the first time distinguished and researched, correspond in their chemical composition to lavas and ignimbrite-like tuffs of rhyolites from the Rarytkin area. The distinguished types represent the final stage of acidic volcanism in the West Kamchatkan–Koryak volcanic belt. It was assumed that the accumulation of obsidian in coastal pebble beds was caused by the erosion of extrusive domes and pyroclastic flows. The geochemical studies of obsidian artifacts from archeological sites of the regions of the Sea of Okhotsk, the Kolyma River, and the Chukchi Peninsula along with the correlation of geological and archeological samples show that Krasnoe Lake was an important source of "archeological" obsidian in Northeastern Siberia.

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Krasnoe Lake, located along the lower course of the Anadyr River (Northeastern Siberia, Chukotka Autonomous District), has long drawn the attention of geologists, geographers, and archeologists due to ambiguous opinions on the origination of the lake basin, the exposures of Cenozoic igneous rocks on the western and eastern coasts, and a considerable concentration of obsidian pebbles in the beach sediments. These pebbles have been used for a long time (from the Late Neolithic to the ethnologically current time) to produce the obsidian tools commonly found in archeological sites of the regions of the Sea of Okhotsk, the Kolyma River, and the Chukchi Peninsula along with those of Alaska [1–5].

The formation of the Krasnoe Lake basin (32 km in length and 18 km in width, Fig. 1) is ascribed to tectonic, volcanic, or thermokarst processes [1, 6]. The lake is surrounded on the west by the Chikaevo Mountains (absolute heights of 280–390 m) and on the east by the northern branches of Rarytkin Ridge (350–420 m) which are made up of Paleogene effusives. The effusive fields are considered as the Rarytkin area of the West Kamchatkan–Koryak volcanic belt [6, 7]. This area is characterized by widespread occurrence of acidic volcanic rocks (lavas, ignimbrites, and tuffs of rhyolites, rhyodacites, dacites, and, less commonly, andesites) constituting formations up to 270 m in thickness. This stratum completes the section of volcanic formations of the Late Eocene–Oligocene basalt–andesite–dacite–rhyolite series characterized in detail by [6, 7]. The effusive mass in coastal outcrops is presented by tuffs and ignimbrites of rhyolites and rhyodacites.

Studies of the petrology and geochemistry of Cenozoic volcanism in this region dealt mainly with basalts [6, 7]. No studies (excluding [1]) were carried out on the composition of dacite–rhyolitic rocks, and volcanic glasses in terms of petrogenesis. At the same time, geochemical studies of obsidian from Krasnoe Lake, as well as of acidic effusive formations, are of vital importance in terms of their genesis and the evolution of acidic volcanism of the Kamchatkan–Koryak volcanic belt, as well as for solving key problems of geoarcheology. The studies of obsidian based on the comparison of the geochemical composition of

[a] *Far Eastern Geological Institute, Far East Branch, Russian Academy of Sciences, Vladivostok, 690022 Russia*
[b] *Far Eastern Federal University, Vladivostok, Russia*
[c] *Sobolev Institute of Geology and Mineralogy, Siberian Branch, Russian Academy of Sciences, Novosibirsk, 630090 Russia*
[d] *Tomsk State University, Tomsk, Russia*
[e] *University of Missouri Research Reactor, Columbia, Missouri, USA*
[f] *Magadan Regional Museum of Local Lore, Magadan, Russia*
**e-mail: vladpov@fegi.ru*

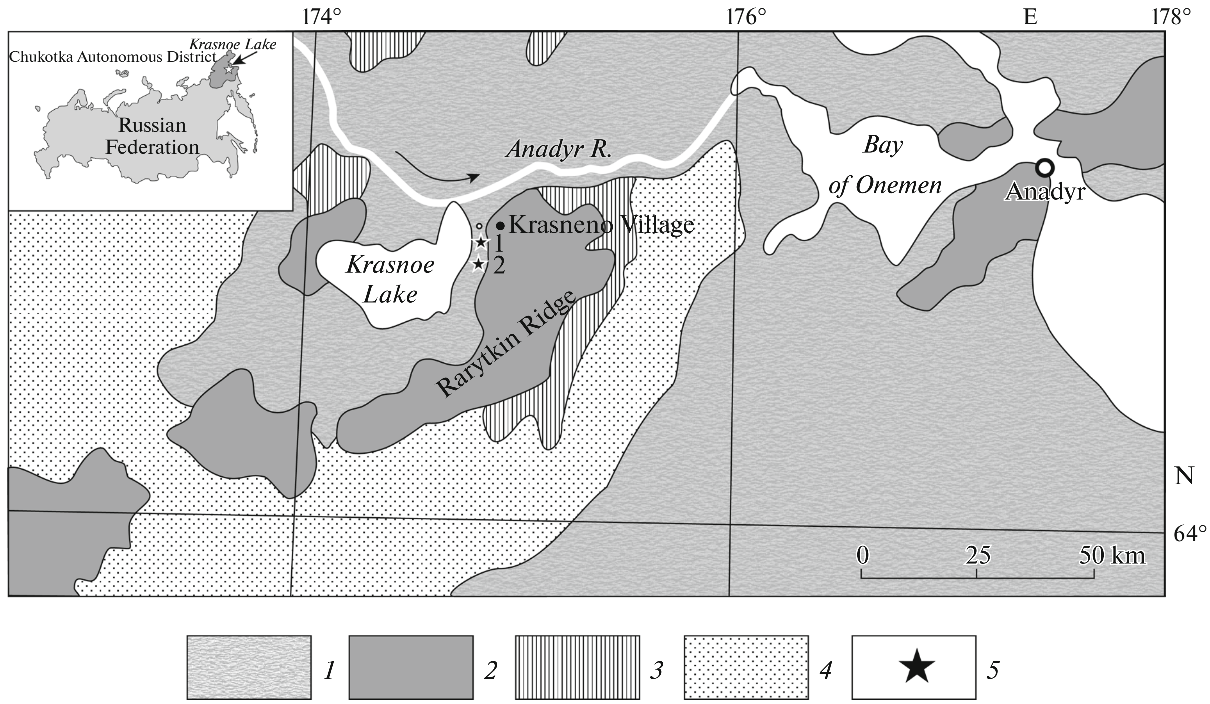

Fig. 1. Schematic geological map of Krasnoe Lake by [1] with modifications and additions. *1*, Quaternary terrigenous deposits; *2*, Late Eocene–Oligocene rocks of the West Koryak volcanic belt; *3*, Paleocene–Middle Eocene basalts; *4*, rocks of the Mesozoic basement; *5*, obsidian sampling sites: (1) Mysovoi Brook and (2) Cape Rybachii.

ancient artifacts and geological samples allows to characterize the use of obsidian from the late Paleolithic to ethnologically present times in the northern part of the Russian Far East and Northeastern Siberia. Ancient human routes of migration over this vast region including the time of existence of the Bering Land Bridge (11 000–20 000 years ago) may be reconstructed as well [8]. Formerly, the conclusion was drawn that obsidian from the Krasnoe Lake coasts was brought to Alaska across the Bering Strait about 3000–5000 years ago [2]. The reliability of this conclusion is testified by the first data on the composition and occurrence of obsidian over the northeastern part of Russia [4, 5]. Thus, final conclusions may be obtained exclusively by detailed geochemical studies of volcanic rocks and obsidians of Krasnoe Lake, as well as of obsidian objects from archeological sites of the northeastern regions of Russia, which is, in fact, the subject of the present study.

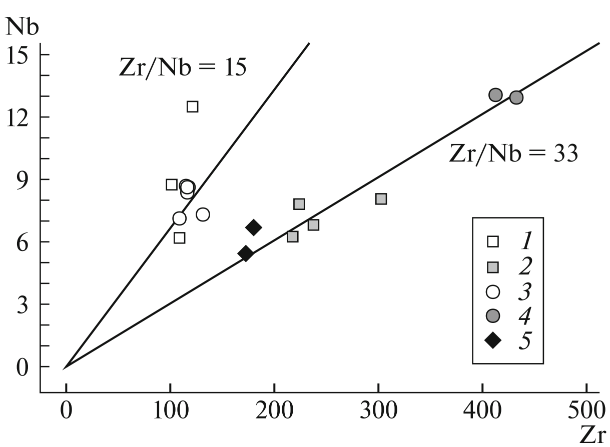

Fig. 2. The distribution of Zr and Nb in obsidian and volcanic rocks of Krasnoe Lake. *1*, Lavas and extrusive bodies of hialorhyolites; *2*, ignimbrites and tuffs of rhyolites and rhyodacites; *3* and *4*, obsidian of high-aluminous and subalkaline composition, respectively; *5*, andesites and dacites of the Krasnaya River system (authors' data).

To solve the problems mentioned, we studied the petrography and geochemistry of volcanic rocks constituting the exposures on the western and eastern coasts of Krasnoe Lake, along with the samples of obsidian from the beach sediments.

The section on the eastern shore of the lake began with heavily argillized rhyolite tuffs overlapped with voluminous flows of rhyolitic and dacitic ignimbrites, as well as with the intruded hyalorhyolites. Tuffs and ignimbrites contain coarse fragments (as large as 0.5 cm) of morion-like (smoky) quartz, plagioclase, and biotite. In hyalorhyolites, phenocrysts of smoky quartz (obsidian-like in color), plagioclase, biotite, orthopyroxene, and magnetite occur within the matrix consisting of light gray volcanic glass (perlite). In the axial part of Rarytkin Ridge (10 km from the coastline), the section is completed with flows of dacites and andesites (Fig. 1).

Table 1. Petrochemical (wt %) and microelemental (ppm) composition of representative samples of obsidian and volcanic rocks of Krasnoe Lake

Composition	AB-73/1	AB-74/1	AB-74/2	AB-72	AB-74/3	AB-74/5	AB-73/3	AB-75	AB-76	AB-76/3bl	AB-76/3sp	AB-75/1alk	AB-75/3alk
	1	2	3	4	5	6	7	8	9	10	11	12	13
SiO_2	72.02	70.76	73.62	75.37	76.21	74.85	77.05	76.75	76.98	77.16	77.40	77.14	77.01
TiO_2	0.35	0.38	0.27	0.16	0.15	0.12	0.07	0.07	0.09	0.07	0.07	0.10	0.11
Al_2O_3	13.72	14.64	13.44	12.09	13.22	12.20	12.12	12.17	12.22	12.33	12.27	11.81	11.78
Fe_2O_3 total	2.78	2.09	1.99	1.52	1.38	1.29	1.02	1.05	1.02	0.94	0.92	1.55	1.58
MnO	0.03	0.01	0.01	0.03	0.01	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.01
MgO	0.22	0.36	0.33	0.29	0.11	0.15	0.04	0.03	0.04	0.02	0.02	0.01	0.01
CaO	1.43	1.64	1.20	1.13	0.60	0.73	0.42	0.41	0.43	0.44	0.43	0.21	0.21
Na_2O	3.70	3.92	3.51	2.71	3.64	3.41	3.89	3.90	3.89	3.87	3.90	4.31	4.30
K_2O	4.14	3.89	4.14	4.43	4.31	4.49	4.59	4.58	4.58	4.50	4.39	4.29	4.36
P_2O_5	0.08	0.01	0.02	0.09	0.01	0.02	0.01	0.01	0.01	0.00	0.01	0.02	0.01
H_2O^-	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.12	0.14	0.05	0.18
LOI	0.91	0.87	0.92	2.38	0.87	2.45	0.21	0.30	0.30	0.32	0.14	0.25	0.09
Sum	99.38	98.58	99.45	100.19	100.52	99.73	99.44	99.28	99.57	99.79	99.69	99.74	99.65
Be	3.46	3.32	3.82	3.56	7.29	7.64	4.74	5.29	5.13	4.17	4.09	3.83	4.24
Sc	7.6	7.3	5.5	4.40	5.0	4.80	9.5	2.5	2.4	3.3	3.6	2.9	2.7
V	26.42	28.44	18.43	12.43	9.32	10.02	5.24	4.43	3.59	1.32	1.39	1.09	1.31
Cr	16.3	<2	<2	1.97	<2	12.20	<2	<2	13.1	4.53	2.74	4.47	3.82
Co	3.40	3.38	2.23	2.38	1.26	0.92	0.23	0.21	0.22	0.19	0.18	0.12	0.17
Ni	11	2.5	1.7	3.04	7.4	16.70	5.6	<1	17.2	2.9	1.2	1.0	1.6
Zn	50.8	46.8	39.7	37.90	37.8	42.10	50.6	49.2	51.4	47.9	46.5	97.8	95.8
Ga	20.94	22.07	21.31	17.62	25.09	22.77	22.27	21.81	21.33	22.52	23.14	26.14	27.09
Rb	125.1	124.3	149.6	161.38	259.2	252.69	197.1	196.6	193.3	186.4	179.1	126.6	137.1
Sr	102.7	120.3	85.4	123.22	26.8	27.19	3.8	3.4	3.2	3.0	2.9	0.9	2.5
Y	46.06	30.79	37.20	45.27	49.50	117.58	74.78	59.93	58.63	65.03	63.63	86.48	90.38
Zr	218.7	237.8	224.5	108.75	121.4	101.72	118.7	109.6	115.9	116.9	116.6	412.5	433.1
Nb	6.19	6.76	7.75	6.17	12.44	8.69	8.58	7.09	8.64	8.37	8.57	13.04	12.93
Mo	0.79	0.20	0.67	0.92	0.68	0.65	0.71	1.37	1.48	1.13	1.23	2.97	3.05
Sn	5.43	6.31	7.09	4.00	15.95	16.67	16.23	9.93	10.26	8.01	7.69	5.82	6.11
Cs	6.61	6.68	9.45	6.09	21.63	24.05	16.91	16.79	16.80	8.28	7.36	4.53	4.78
Ba	543.3	529.3	404.4	282.40	119.8	97.50	24.1	19.9	18.9	17.7	14.8	24.3	27.6

Table 1. (Contd.)

Composition	AB-73/1	AB-74/1	AB-74/2	AB-72	AB-74/3	AB-74/5	AB-73/3	AB-75	AB-76	AB-76/3bl	AB-76/3sp	AB-75/1alk	AB-75/3alk
	1	2	3	4	5	6	7	8	9	10	11	12	13
La	44.27	24.08	34.62	16.27	19.69	22.97	23.03	22.38	21.51	21.50	20.15	36.61	39.60
Ce	76.77	51.67	76.67	38.69	47.67	54.22	59.12	58.12	56.77	53.79	50.14	84.89	91.39
Pr	12.22	6.02	8.68	4.75	5.54	7.84	7.54	7.33	7.15	6.94	6.85	11.02	11.76
Nd	49.58	23.51	33.7	18.40	22.30	37.11	31.38	31.40	30.58	29.94	29.94	44.80	49.58
Sm	10.96	4.80	5.93	6.50	6.12	11.91	8.68	9.01	8.82	7.90	7.57	10.77	12.90
Eu	0.71	0.70	0.47	0.18	0.11	0.10	0.10	0.10	0.10	0.07	0.03	0.21	0.20
Gd	10.28	5.25	6.45	5.56	6.71	13.54	9.63	8.59	9.82	8.63	8.45	12.19	12.72
Tb	1.47	0.79	0.96	1.15	1.30	2.58	1.84	1.69	1.59	1.64	1.59	2.30	2.39
Dy	9.63	5.80	6.36	7.95	8.75	18.57	11.97	11.08	11.23	10.20	9.67	13.98	13.94
Ho	1.53	0.94	1.10	1.39	1.46	3.52	2.03	1.99	1.96	2.19	2.11	3.04	3.13
Er	5.00	3.18	3.70	4.26	5.29	12.58	6.58	6.35	6.44	6.72	6.57	9.49	9.04
Tm	0.66	0.42	0.51	0.55	0.83	1.73	0.88	0.85	0.81	0.93	0.90	1.32	1.24
Yb	4.58	2.95	3.47	3.26	5.11	11.69	6.59	6.01	5.27	5.62	5.41	8.42	8.12
Lu	0.66	0.46	0.50	0.48	0.73	1.56	1.07	0.79	0.85	0.87	0.86	1.20	1.28
Hf	7.22	8.02	7.52	3.72	5.66	5.94	6.52	5.68	5.96	5.55	5.58	12.36	13.18
Ta	0.68	0.71	0.97	0.51	1.81	1.23	1.15	1.07	1.28	0.72	0.75	0.82	0.98
W	1.16	1.27	0.99	4.28	2.51	4.00	2.31	2.23	2.83	2.95	2.89	2.10	1.83
Pb	15.42	14.38	17.33	14.78	23.36	22.52	23.09	23.25	21.99	22.81	24.13	23.38	22.85
Th	12.47	12.67	14.56	8.80	26.57	25.51	18.00	17.05	17.00	15.01	15.39	12.47	13.05
U	3.12	3.44	3.81	3.39	5.82	8.53	5.77	5.81	5.87	5.93	5.95	4.20	4.24
Na_2O/K_2O	0.89	1.01	0.85	0.61	0.84	0.76	0.85	0.85	0.87	0.86	0.89	1.00	0.99
K/Rb	275	260	230	228	138	147	193	193	188	200	203	281	264
Rb/Sr	1.22	1.03	1.75	1.31	9.66	9.23	51.46	57.32	60.42	61.51	61.76	134.68	53.98
Ba/Rb	4.34	4.26	2.70	1.75	0.46	0.38	0.12	0.10	0.10	0.09	0.08	0.19	0.20
Zr/Nb	35.33	35.17	28.97	17.63	9.76	11.7	13.83	15.46	13.41	13.97	13.61	31.63	33.5
Zr/Hf	30.29	29.65	30.96	29.23	21.45	17.12	18.21	19.3	19.44	21.06	21.9	33.37	32.86
FFFTh/La	0.28	0.53	0.42	0.54	1.35	1.11	0.78	0.76	0.79	0.7	0.76	0.34	0.33
Ba/La	12.27	21.98	11.68	17.36	6.08	4.24	1.04	0.89	0.88	0.82	0.73	0.66	0.70

1–3 are tuffs and ignimbrites of rhyolites and rhyodacites; 4–6 are lavas and extrusives of hyalorhyolites; 7–11 are high-aluminiferous obsidian samples; and 12–13 are subalkaline obsidian samples. The analyses were carried out at the Analytical Center of the Far Eastern Geological Institute. 1–9, The concentrations of petrogenous elements were determined with an S4 Pioneer spectrometer by E.A. Nozdrachev; 11–12, the concentrations of SiO_2, H_2O^-, and losses on ignition (LOI) were determined using gravimetry by L.I. Alekseeva and L.A. Avdevnina; the other oxides were determined by atomic absorption spectroscopy with inductively coupled plasma using an iCAP 6500 Duo spectrometer by G.A. Gorbach, E.A. Tkalina, and N.V. Khurkalo. The rare elements were determined by the ICP MS technique using an Aligent 7700 spectrometer by M.G. Blokhin. The “nd” is “not determined.”

Table 2. The results of anslysis by electron probe microanalyser of chemical composition (wt %) for glass matrix in hyalorhyolites and obsidians of Krasnoe Lake

Component		SiO_2	TiO_2	Al_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	S	Sum
AB-72	1	72.22	0.00	12.59	0.79	0.00	0.05	0.42	3.91	4.45	0.06	0.16	94.64
AB-72*	2	76.33	0.00	13.30	0.83	0.00	0.04	0.44	4.13	4.70	0.06	0.17	100.00
AB-74/5	3	74.16	0.08	12.00	0.45	0.04	0.06	0.35	3.28	5.31	0.07	0.03	95.83
AB-74/5*	4	77.41	0.08	12.52	0.47	0.04	0.06	0.36	3.42	5.54	0.07	0.03	100.00
AB-75/2	5	77.05	0.04	12.53	0.68	0.01	0.05	0.39	4.05	4.89	0.11	0.05	99.89
AB-75/4	6	76.93	0.06	12.35	0.81	0.02	0.03	0.41	4.01	4.90	0.10	0.07	99.69
AB-75/1alk	7	77.08	0.10	11.67	1.30	0.04	0.04	0.11	4.31	4.79	0.10	0.04	99.59
AB-75/3alk	8	77.01	0.14	11.97	1.34	0.00	0.08	0.23	4.33	4.70	0.13	0.00	99.93

1–4 are hyalrhyolites (*, recalculated for dry residue); 5–6 are high-aluminiferous obsidians; 7–8 are subalkaline obsidians. The analyses were carried out at the Analytical Center, Far Eastern Geological Institute, by E.A. Nozdrachev.

Table 3. Results of K–Ar dating of obsidian and ignimbrite samples from Krasnoe Lake

No.	Sample	Rock	Potassium, wt %	$^{40}Ar_{rad} \times 10^{-5}$, nmm^3/year	Atmospheric Ar, %	Age, Ma
1	AB-76/3bl.	Obsidian	3.77	10.43 ± 0.03	nd	39.5 ± 0.9
2	AB-74/1	Ignimbrite	3.23	8.65 ± 0.08	5.4	39.1 ± 1.2

The content of radiogenic Ar was determined by means of an MI 1201 IG mass spectrometer using isotope dilution with ^{38}Ar as a tracer in the sample AB-76/3 and by means of a MAT 253 mass spectrometer using the special CF–GC–IRMS procedure with laser melting [13] in the sample AB-74/1 by A.V. Lebedev at the Institute of Ore Geology and by S.Yu. Budnitskii at the Far Eastern Geological Institute, respectively. The content of potassium was determined using flame spectrophotometry; nd means "no data." The constants used in age calculations: $\lambda_K = 0.581 \times 10^{-10}$ year^{-1}, $\lambda_{\beta-} = 4.962 \times 10^{-10}$ year^{-1}, $^{40}K = 0.01167$ (at %).

It was noted in describing the volcanic glasses of Krasnoe Lake that obsidian was found as boulders and pebbles at the eastern and western coasts of the lake [1]; two varieties of obsidian were distinguished. First, this is black obsidian of weak whitish hue, swelling under heating. The other variety is presented by "dull" glass of black color, not swelling even at high temperatures (1150–1200°C). The field surveys confirmed the occurrence of these varieties of volcanic glass on the eastern coast of the lake southward of the settlement of Krasneno, with maximum concentrations in Mysovoi Brook and along Cape Rybachii (Fig. 1). The beach sediments contain most commonly obsidian pebbles (0.5–10 cm diameter) and less abundant boulders (up to 30 cm). These forms consist of black-colored (morion-like) glass, show typical conchoidal fracture, a pronounced vitreous luster in new chips, and a whitish hue on weathered surfaces. In isolated instances, obsidian of patch–banded texture was found, owing to the brick-red coloration of oxidized fragments developed irregularly over the black fluidal glass. In thin sections, transparent glass is rich in fine grains of ore minerals and inclusions forming thin band-shaped accumulations representing the melt flow. Some of the samples of obsidian contain fine crystal-like sanidine grains (0.2 mm or less in diameter), along with rare grains of zircon and amphibole. The surfaces of weakly rounded pebbles are covered with cohchoidal microcracks and contain the pressed marks of glass pieces. The features as such are characteristic of acidic volcanic glasses associated with hyaloclastites [9]. Pebbles and boulders of dull obsidian are of extremely rare occurrence. This obsidian is characterized by a cryptogranular structure.

The geochemistry of volcanic rocks was studied at the Analytical Center of the Far Eastern Geological Institute by means of Inductively Coupled Plasma—Mass Spectrometry and X-Ray Fluorescence, as well as at the University of Missouri Research Reactor (Neutron Activation and X-Ray Fluorescence analyses). Along with 11 samples of volcanic rocks, ten geological and 229 archeological samples of obsidian were examined. The data on the microelemental composition of geological and archeological samples of obsidian were treated statistically by means of cluster and factor analyses using the procedure in [10].

Tuffs and ignimbrites, as well as rhyolite and dacite lavas of the Rarytkin area, belong to the potassic–sodium calc–alkali high-aluminiferous series (Na_2O/K_2O = 0.8–1, ASI = 1.04–1.08). The agpaitic coefficient varies from 0.73–0.77 in ignimbrites and tuffs to 0.81–0.86 in the lavas of rhyolites. The volcanic rocks are characterized by a fractionated spectrum of the distribution of rare and trace elements. The concentrations of Rb, Th, U, and Y are increased and those of Nb, Ba, Sr, ant Tb are decreased in relation to the composition of the upper crust from [11]. The acidic effusives including hyalorhyolites and volcanic glasses constitute a unified trend in the distribution curves of rare-earth elements normalized by chondrite [12], with a weak negative slope from La to Eu. All the types of rocks are characterized by a europium minimum pronounced to the greatest degree in extrusive hyalorhyolites and volcanic glasses.

Volcanic glasses belong to potassic–sodium calc–alkali series (Na_2O/K_2O = 0.85–1.22) and are subdivided into two groups. The first (prevailing) group belongs to the high-aluminiferous petrochemical type (ASI = 1.00–1.03; Na_2O/K_2O = 0.85–0.89); the other group (rare samples) is of a subalkaline type (ASI = 0.97–0.98; Na_2O/K_2O = 0.99–1.22). The agpaitic coefficients amount to 0.89–0.94 and 0.99–1.00, respectively, in obsidians of the first and second groups. The latter are also characterized by higher concentrations of Na_2O and Fe_2O_3 and a lower content of Al_2O_3, CaO (Table 1, samples 12, 13; Table 2, samples 7, 8). The distinctions are most pronounced in microelemental compositions. Subalkaline obsidians are enriched in Zr, Nb, Hf, Y, and Dy and depleted in Rb, U, and Th in relation to high-aluminiferous rocks (Table 1). The latter are also characterized by deep minima for Ba and Sr. In terms of the geochemical composition, these types of volcanic glasses show the affinity to various facies of volcanic rocks. Thus, by the concentrations of rare (Rb, Zr, Cs, U, Th) and rare-earth elements, high-aluminiferous obsidians are close to the lavas and extrusive bodies of hyalorhyolites. Subalkaline obsidians are similar to ignimbrites and tuffs of rhyolites and rhyodacites (Table 1). This is expressed in the similar values of K/Rb, Zr/Nb, Zr/Hf and indicator values (Table 1, Fig. 2), which testify to the genetic affinity. The potassium–argon dates for the samples of high-aluminiferous obsidian and rhyolite tuff (Table 3) point as well to their synchronous formation.

The results of geochemical studies of microelemental compositions obtained at the University of Missouri Research Reactor for all the available obsidian samples from Krasnoe Lake along with those from archeological sites of Northeastern Siberia (229 obsidian artifacts from 59 archeological sites in the areas of the Sea of Okhotsk, the Kolyma River, and the Chukchi Peninsula) showed that 148 objects (about 65%) were made of raw material from the coast of Krasnoe Lake. The tools and flakes from archeological sites consist as a rule of high-aluminiferous obsidians, with only a few of subalkaline type.

Thus, the studies of volcanic glasses from Krasnoe Lake have revealed for the first time two geochemical variations of obsidian distinguished by the chemical compositions and characterized by a genetic relationship to various facies types of volcanic rocks. Since the Neolithic time, ancient humans used the prevailing high-aluminiferous obsidian for making tools. Obsidian tools of subalkaline glass are quite rare at archeological sites of Northeastern Siberia.

In conclusion, one must emphasize that the geochemical varieties of obsidian identified from Krasnoe Lake correspond to the composition of the Eocene acidic effusive rocks of the Rarytkin area. The accumulation of obsidian in coastal deposits is caused by the erosion of various facies types of volcanic rocks containing the quenching crusts and fragments of volcanic glass.

The results of studies of artifacts, being still uncommon and even "exotic" subjects for Russian geologists, have made it possible to supplement the bank of geochemical data on natural volcanic glasses as carriers of primary genetic information for studying the evolutionary processes of magmatic melts.

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