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GEOCHEMISTRY

Geochemistry of Volcanic Glasses from the Paektusan Volcano

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The Paektusan Volcano (2744 masl) is situated at the North Korea/China border at 42°00′ N and 128°04′ E (Fig. 1). Mt. Paektusan is the only active volcano at the eastern margin of the Asian continent. It is a stratovolcano that is 10 km in diameter and is localized in the central part of the Shangbaishan basaltic plateau. The cone largely consists of lavas and pyroclastic rocks (trachyte, alkali trachydacite, pantellerite, and comendite).

Table 1. Major (wt %) and minor (ppm) element compositions of volcanic rocks from the Paektusan Volcano

Component	P-505/5	P-509/1	P-509/5	P-507/1	P-506/1	P-509	P-509/6	P-507/4	21B
	1	2	3	4	5	6	7	8	9
SiO_2	64.59	66.24	66.14	66.20	68.30	69.25	72.31	72.90	72.64
TiO_2	0.44	0.34	0.34	0.46	034	0.32	0.21	0.23	0.11
Al_2O_3	16.85	15.59	14.95	13.92	13.92	13.79	11.56	9.98	11.50
Fe_2O_3	1.97	2.10	3.12	2.62	2.20	1.04	2.20	0.03	2.15
FeO	2.17	2.44	2.30	2.28	2.48	3.25	2.03	4.13	0.97
MnO	0.12	0.13	0.12	0.12	0.11	0.12	0.07	0.08	0.03
MgO	0.36	–	–	0.38	0.95	–	–	0.24	–
CaO	1.26	0.89	0.90	0.92	0.33	0.49	0.33	0.33	2.20
Na_2O	5.81	6.30	6.27	6.25	5.74	6.01	5.62	5.38	3.70
K_2O	5.67	5.02	5.03	6.00	5.27	4.64	4.51	4.52	4.90
P_2O_5	0.13	0.13	0.04	0.15	0.06	0.05	0.11	0.06	
H_2O^-	–	–	0.03	–	0.04	0.05	0.03	0.17	0.50
L.O.I.	0.18	0.37	0.36	0.65	0.07	0.49	0.56	2.13	1.50
Total	99.55	99.55	99.60	99.95	99.81	99.50	99.54	99.62	100.20
Ni	2	3	2	3	3	3	2	3	
Co	3	–	–	–	–	–	–	–	
Cr	5	5	–	–	–	4	4	–	
V	5	7	3	2	–	2	3	–	
Cu	16	16	16	18	17	18	18	20	
Pb	24	40	40	21	44	58	63	45	
Zn	76	150	180	110	140	190	260	270	
Sn	7	11	11	7	12	15	17	14	
B	4	8	11	5	5	12	16	16	
F	734	1805	1565	651	992	1969	2986	2184	
Cl	660	1500	1610	660	30	2650	3160	2400	
S	95	95	210	115	25	75	25	55	

Note: (1–4) Alkali trachydacite; (5, 6) pantellerite; (7, 8) comendite; (9) trachyrhyolite. Major elements were determined by chemical analysis (L.I. Alekseeva, analyst); minor elements, by the XRF method on a VRA-30 scanning spectrometer at the analytical center of the Far East Geological Institute, Vladivostok (E.A. Nozdrachev, analyst). (–) Not detected. Gap means that the element was not analyzed.

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Table 2. Rare earth elements (ppm) in volcanic glasses from the Paektusan Volcano

Component	P-505/5	P-509/1	P-509/8	P-509/2	PV-1	PV-2	P-509	1-1	21B
	1	2	3	4	5	6	7	8	9
Sc	5.45	4.51	4.03	1.55	0.56	0.38	0.87	1.25	1.05
Sb	0.15	0.14	0.14	0.38	0.43	0.46	0.50	0.36	0.39
Cs	1.37	1.43	1.39	2.85	5.35	5.16	4.14	3.71	3.88
Rb	127	136	133	232	346	338	296	226	239
Ba	79	43	–	7	–	36	–	143	109
Sr	–	–	–	–	–	–	–	28	–
La	75.69	80.84	84.56	145.45	158.19	156.93	201.92	65.81	67.01
Ce	148.38	155.44	162.28	273.45	316.68	303.60	386.73	135.47	137.16
Nd	62.55	65.57	65.76	111.87	103.54	101.76	146.72	62.28	50.65
Sm	11.50	12.04	12.09	21.05	26.35	24.92	28.20	10.41	10.97
Eu	0.64	0.48	0.40	0.32	0.37	0.35	0.48	0.37	0.25
Tb	1.47	1.48	1.49	2.85	3.89	3.69	4.08	1.54	1.65
Dy	7.62	8.36	8.22	16.55	23.91	21.76	21.87	10.38	10.90
Yb	3.49	4.34	4.30	8.97	10.22	9.77	10.20	4.01	4.80
Lu	0.52	0.57	0.59	1.28	1.61	1.59	1.65	0.70	0.83
Ta	4.17	4.37	4.29	10.33	14.80	14.14	13.84	6.18	6.97
Zr	484	519	514	1467	1890	1882	1887	250	262.52
Hf	14.23	14.89	14.69	40.11	54.23	52.42	52.96	9.98	9.96
Th	12.27	12.94	12.76	26.42	45.92	44.31	38.24	27.05	27.51
U	4.86	5.00	5.71	12.19	15.42	15.15	15.12	3.65	4.47
Ce/Yb	42	36	37	30	31	31	38	22	29
Zr/Hf	34	34	34	36	35	36	35	25	26
Group	PNK3	PNK3	PNK3	PNK2	PNK2	PNK2		PNK1	PNK1

Note: (1–3) Alkali trachydacite; (4–7) pantellerite; (8, 9) trachyrhyolite. (PNK1, PNK2, and PNK3) Geochemical groups classified from statistical processing of analytical results (sample P-509 could not be classified). Trace elements were determined by the INAA method in the Research Reactor Center of the University of Missouri, Columbia, USA. (–) Not detected.

The summit caldera, 4×6 km^2 in area and partially occupied by Lake Tianchi, was formed around 940 B.C. as a result of a catastrophic directed explosion [1, 2] that produced 75–115 km^3 of comenditic tephra, as well as an enormous volume of gas (H_2O, Cl, F, and S). The most recent volcanic events at Mt. Paektusan were recorded in 1702 (within-caldera eruption of trachytic ignimbrites and tuffs) and 1898 (phreatomagmatic eruption in the crater lake resulting in the ejection of vapor, gas, and sand) [3].

Geochronological datings indicate that the volcano was formed over more than 3 Ma with a certain periodicity of catastrophic eruptions, particularly during the recent stage of its evolution [1, 2].

The study of this volcano is important for elucidation of the genesis of alkali silicic melts and their relation to vast plateau basalts. This may also provide insights into the mechanism of eruptions and their prediction. This issue becomes especially topical if we consider that the last eruption (more than 1000 yr ago) was catastrophic. Tephra and ash was ejected to a great height and reached Japan. The enormous amounts of gases (Cl, F, and S) released in this process [1] exerted a strong impact on the environment. Furthermore, the study of the products of volcanic eruptions, especially volcanic glasses (obsidians) from Mt. Paektusan [4], is helpful for solving geoarcheological problems related to the Holocene settling of mankind, its habitat in regions of volcanic activity, and so on. Obsidians were crucial to the development of the ancient stone industry. The search for sources of archaeological obsidian sites based on the geochemical correlation between artifacts and geological samples [5–7] makes it possible to trace the migration paths of ancient man in eastern Asia and adjacent islands.

The alkali silicic rocks make up a volcanic cone and surrounding fields of loose pumice deposits. In the caldera section, the pumices alternate with trachyte flows that build up the main edifice. The silicic rocks occur as glassy lava flows and sheets, as well as units of

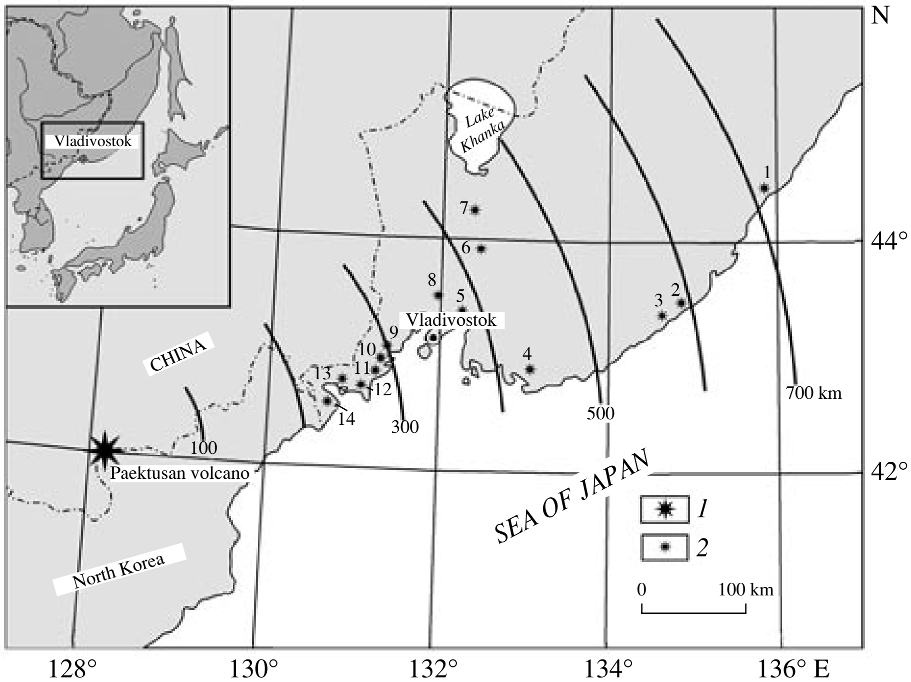

Fig. 1. Location of the Paektusan Volcano (source of volcanic glasses) and distribution of obsidian artifacts at archeological sites of Primorye, after [7, 12]. (*1*) Native source of volcanic glass; (*2*) archaeological sites (numbers in scheme): (1) Monastyrka, (2) Yevstafii, (3) Phusun, (4) Pereval, (5) Maikhe, (6) Gorelaya Sopka, (7) Firsanova Sopka, (8) Timofeevka, (9) Chernaya Sopka, (10) Rybak, (11) Boisman, (12) Troitsa, (13) Gladkaya, (14) Khansi.

ignimbrite, massive volcanic glass, tuff, and pumice. Ignimbrites contain fiamme and interlayers of volcanic glass with phenocrysts and rock fragments. The glassy varieties also contain numerous phenocrysts of arfvedsonite, aegirine, sanidine, fayalite, clinopyroxene, biotite, and sodic plagioclase. Zircon, apatite, monazite, and ilmenite are accessory minerals. Quartz, oligoclase, pyroxene, and ore minerals are rare.

The geochemical study of volcanic glasses from Mt. Paektusan was carried out at the analytical center of the Far East Geological Institute, Vladivostok (chemical analysis of major elements) and at the Research Reactor Center of the University of Missouri (neutron activation analysis of trace elements). The microelemental compositions of geological and archaeological samples were statistically processed with cluster and factor analyses using the methods described in [8, 9].

The chemical composition of volcanic rocks from Mt. Paektusan corresponded to alkali trachydacite, pantellerite, comendite, and trachyrhyolite (Table 1). In terms of water content, trachydacite–comendite volcanic glasses correspond to obsidians, while trachyrhyolitic glasses may be classified as obsidian–perlite and perlite. Alkali trachydacites are enriched in Na, K, F, and Cl. In pantellerite and comendite, the K content systematically decreases, while H_2O, F, Cl, and B concentrations increase. In trachyrhyolite, K prevails over Na. In general, all varieties of alkali silicic rocks are depleted in compatible elements (Ni, Co, Cr, and V). Concentrations of some ore elements, e.g., Sn, Pb, and Zn, increase from trachydacite to comendite. High HFSE, LILE (except Sr and Ba), and REE contents, typical of silicic volcanics, increase from trachydacite to comendite (Table 2; Fig. 2). In trachyrhyolite, the HFSE, LILE, and REE contents markedly decrease to the level of alkali trachydacite (Table 2). The volcanic rocks reveal a fractionated distribution of trace elements—high HFSE and LILE concentrations; maximal Cs, Rb, Th, U, Hf, and Zr concentrations; and minimal Sr and Ba contents. The REE patterns have a negative slope with an Eu minimum. The rocks demonstrate two trends on spidergrams (Fig. 2). The first trend characterizes alkali trachydacite and trachyrhyolite, whereas the second trend is related to pantellerite and comendite. The PM-normalized REE patterns are similar in alkali trachyte and trachydacite, except for Eu (Fig. 2).

The study of the chemical composition of volcanic glasses in order to elucidate the sources of archaeological obsidians is very topical at present [5, 6]. In the Russian Far East, we have conducted such investigations since 1992 [7, 11, 12]. Based on the geochemical study of basaltic and rhyolitic obsidians and perlites from Cenozoic volcanic complexes (Primorye and adjacent regions) and obsidian tools (artifacts) from archaeological sites, we were able to establish the following main sources of archeological obsidian in Primorye and Sakhalin: basalts of the Shkotovo Plateau in southern Primorye, the Paektusan (Baitoushan) Vol-

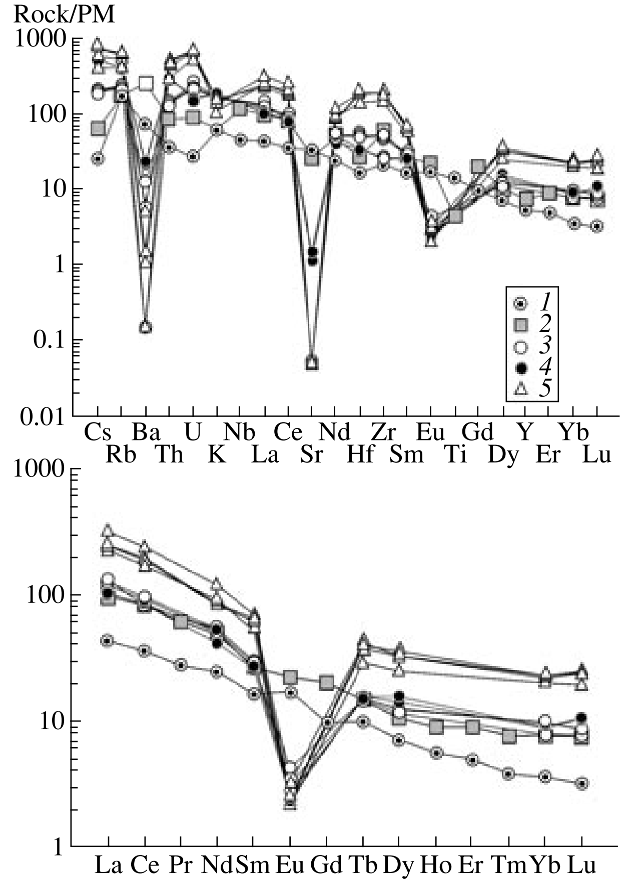

Fig. 2. Trace element contents in glasses of the Paektusan Volcano normalized to the primitive mantle (PM), after [10]. The distribution of elements in alkali basalt and trachyte of the Paektusan Volcano (authors' data) are given for comparison. (*1*) Basalt, (*2*) trachyte, (*3*) alkali trachydacite, (*4*) trachyrhyolite, (*5*) pantellerite and comendite.

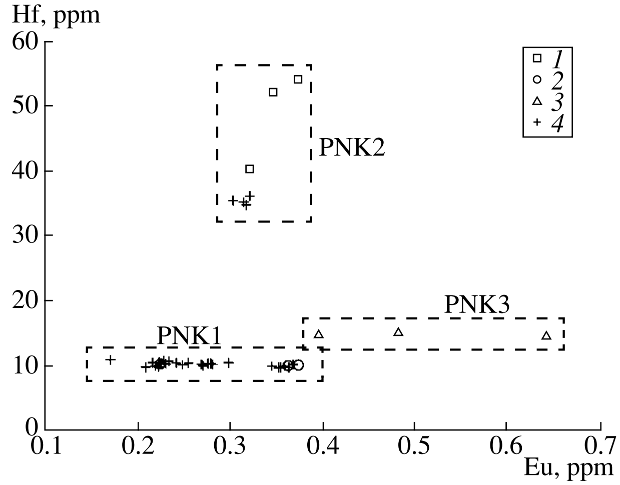

Fig. 3. Hf–Eu diagram for volcanic glasses of the Paektusan Volcano. Geochemical groups of obsidians: (PNK1) trachyrhyolite, (PNK2) pantellerite and comendite, (PNK3) alkali trachydacite. (*1–3*) Geological samples; (*4*) artifact.

cano at the North Korea/China border, and the Shirataki and Oketo volcanoes on Hokkaido Island [7, 11, 12].

The Paektusan source turned out to be the most interesting and controversial. Obsidian from this source was found over a distance of 230–700 km at many archaeological sites in Primorye (Fig. 1). However, up to now this conclusion has been based on results of the analysis of just two geological samples and has thus remained tentative [12]. Therefore, we decided to carry out an additional sampling of volcanic glasses from the volcano and obsidian artifacts. In 2002 and 2004, we conducted field works on the Chinese side of Mt. Paektusan and collected obsidian tools from two sites on the southern Korean Peninsula (Janghung-ri and Khavage-ri) [13, 14], which were dated at 24–13 ka B.P. by means of the ^{14}C method [15].

The statistical processing of analytical data revealed three geochemical groups of volcanic glasses from the Paektusan Volcano, and two of these groups were identified as sources of archaeological obsidian (Fig. 3).

The first group (PNK1), which is the most representative, comprises 2 geological and 35 archaeological samples, including obsidian artifacts from 14 archaeological sites in southern Primorye (34 samples) and from one site in South Korea (1 sample). The geological samples include trachyrhyolitic obsidian–perlite and perlite from the Korean (southern) side of Mt. Paektusan between peaks Khiando and Sanmuchjige. The volcanic glasses occur here as "obsidianite" layers, which are 1–5 m thick and interbedded with pumice units. The chemical composition of pumice [4] is completely identical to the obsidian composition (Table 1, sample 21C). According to paleomagnetic data, the age of obsidian is estimated at 50 ka B.P. [4]. The glass has good technological properties (massive texture and conchoidal fracture with sharp edges).

The second group (PNK2) includes three geological samples of pantelleritic obsidian taken from interlayers and lenses in glassy lava flows from the upper part of the volcanic cone and four archeological samples of the same composition from two sites in South Korea. This obsidian has a low technological quality owing to the presence of phenocrysts. Therefore, it was only rarely used for making stone tools.

The third group (PNK3) is represented by three alkali trachydacite obsidian samples taken from glass interlayers in ignimbrite and from pumice fragments on slopes of the volcano. Glass of this group is unsuitable for the preparation of tools because of its poor technological properties.

Results of the pioneer geochemical study of volcanic glasses at Mt. Paektusan indicated the existence of two obsidian sources that are different in chemical composition and technological properties. Volcanic glass of the first source (group PNK1) was used by ancient people for a long period [7], beginning in the early Paleolithic (~24 ka B.P.). In the interval from 24 to 10 ka B.P., the distance from the source of obsidian to the site of its processing reached 400–500 km. Obsidians from the second source (group PNK2) are not abundant among archaeological sites.

In conclusion, it should be emphasized that alkali silicic rocks of the Paektusan Volcano are products of trachytic melt fractionation. The study of artifacts, which remain rare if they are not exotic subjects of research for Russian geologists, allowed us to considerably supplement the geochemical database on natural volcanic glasses that serve as the medium with primary genetic information that is needed for the investigation of magma evolution.

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