

LATERAL VARIATIONS IN ASH COMPOSITION DUE TO EOLIAN DIFFERENTIATION

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The ash deposited by Opala Volcano 1500 ¹⁴C years ago and the ash blown from Shiveluch during its eruption in 1964 have been studied to examine a relationship between the grain size and chemical composition of volcanic ash. The bulk mineral compositions of the ashes have been found to be different from the compositions of their individual size fractions. This fact points to the need for caution in using analytical data from a single sample of ash which reflects the effect of eolian differentiation in one sampling site of the air-fall area. It is advisable, therefore, to determine quantitatively the mineral composition of each size fraction, before using the analytical data, in order to account for lateral composition variations due to eolian differentiation.

The aim of this paper is to investigate a relationship between the grain size and the chemical composition of volcanic ash. The importance of undertaking this research was recognized during a study of the eolian differentiation of volcanic ashes. The air-fall deposition of pyroclastic fragments from an eruption cloud is affected by the wind: the particles are gravitationally sorted into fractions of quantitatively different mineral composition. In this connection a question arises whether single chemical analyses of the ash samples collected in one site can be taken to be representative of the composition of the lava and pyroclastic material erupted during a given event.

The process of eolian differentiation has been discussed by many investigators [3], [4], [5], [6], [13]. Murray and Renard [16] were among the first investigators who noticed this phenomenon in their study of the Krakatoa thephra deposited by the 1883 eruption. They found that the proportion of glass and minerals in the ash varied with distance from the vent and explained it by the fact that the ash rich in crystals fell close to the source and the more siliceous and more vesicular glass-rich dust and pumice rose to a greater height, stayed in suspension a longer time, and were blown by the wind for larger distances.

Later, Dubik and Menyailov [5] demonstrated that variation of a silica percentage in the material of one ash fall did not show any regular pattern. Clearly, this phenomenon is related to a nonuniform proportion of minerals in the size fractions and to the mechanism of settling of different ash fractions from an eruption cloud.

As an object of our study we chose the ashes of two large eruptions in Kamchatka: the eruption of Opala 1500 years ago and the eruption of Shiveluch on November 12, 1964.

ERUPTION OF OPALA VOLCANO

The bulk of the tephra ejected by a flank eruption of Opala Volcano in Baranii Amphitheater fell east of the volcano, on the coast and in the Pacific. The thickness of the ash layer deposited at a distance of 75 km from the vent in this direction is 12 cm. The ash deposit was traced northeastward as far as Lake Kronotskoe which is over 300 km from the source (Figure 1). The volume of the erupted tephra was determined by I.V. Melekestsev to be more than 8 km³ (minimum estimate).

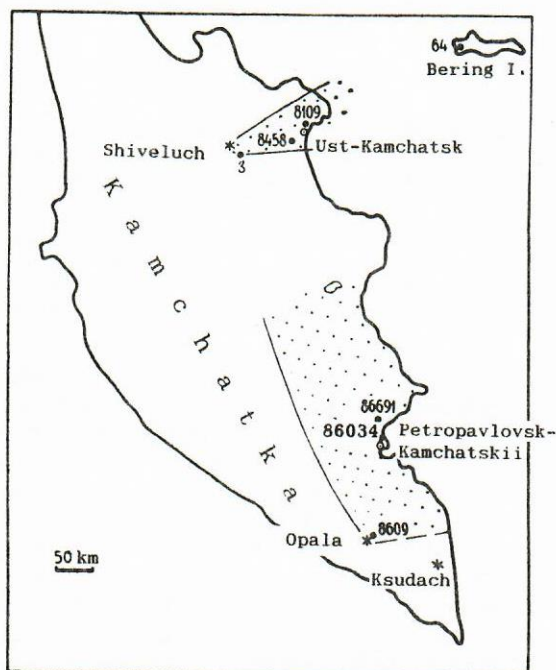


Figure 1 Distribution of tephra from the eruptions of Shiveluch (November 12, 1964) and Opala (1500 years ago) and location of sampling sites.

The components of the Opala tephra are pumice (containing minerals), glass, plagioclase, ore minerals, lithic fragments, biotite, and piroxenes. The tephra consist largely of light fragments dominated by glass (>80%) at all distances from the vent. The ash particles become smaller with increasing distances, the pumice fragments being replaced by colorless glass which dominates all size fractions (Figure 2). The chemical composition of the Opala tephra presented in Table 1 does not show a monotonic increase or decrease of major oxides with distance from the vent. Insignificant variability of the chemical composition of the Opala ash with distance can be explained by a low

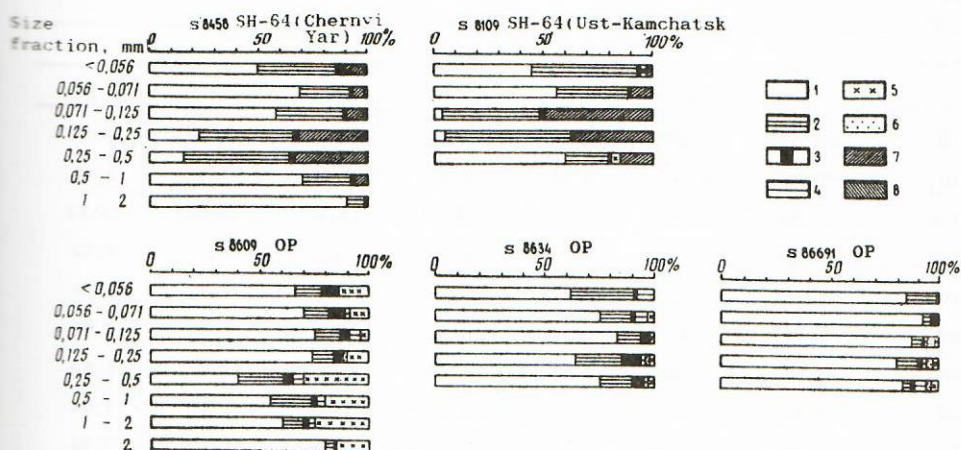


Figure 2 Quantitative mineral composition of different size fractions of the Shiveluch (SH-64) and Opala (OP) eruptions. 1 - glass; 2 - plagioclase; 3 - ore minerals; 4 - biotite; 5 - lithic fragments; 6 - pyroxenes; 7 - green hornblende; 8 - brown hornblende.

degree of magma crystallization. It is common knowledge that the settling velocities of heavy and light minerals differ greatly. Kittleman and Lawrence [14] have shown, however, that the proportion of heavy and light minerals in the Mazama tephra does not vary laterally over a distance of up to 400 km from the source, even though the size of the fragments decreases.

Figure 3 shows variations in the contents of five oxides as a function of the grain size for three Opala ash samples collected at different distances from the vent. Most pronounced are variations in the SiO_2 percentage even though they do not exceed 3%, the other oxide percentages being invariable or varying by less than 1% (Table 2). Earlier [6], one of the writers proved that the quantitative mineral composition of volcanic ash does not vary with distance if the content of one component (e.g., glass) is at least 80% and the percentages of the other components are 4 or 5% at most, that is, are within the accuracy of computation. So, the chemical and quantitative mineral composition of ash whose main component is glass remains invariable at any distance from the source.

ERUPTION OF SHIVELUCH VOLCANO

During the Shiveluch eruption in November 12, 1964, the ash-fall axis was directed SE from the volcano toward Ust-Kamchatsk and the Komandorskie Islands. The tephra cover was 26 cm thick at the foot

Table 1 Chemical composition of ashes produced by the Shiveluch eruption of November 12, 1964, and the Opala eruption 1500 years ago, wt. %.

Oxide	Specimen						
	1	2	3	4	5	6	7
SiO	63.08	52.80	61.87	73.00	73.02	74.57	73.32
TiO ₂	0.62	0.86	0.61	0.20	0.29	0.36	0.48
Al ₂ O ₃	15.92	19.92	16.23	14.37	14.18	14.54	15.16
Fe ₂ O ₃	2.75	2.82	2.68	2.49	3.25	2.12	0.52
FeO	2.51	3.53	2.62				1.57
MnO	0.14	0.12	0.12	n.d.	n.d.	n.d.	0.06
MgO	3.76	5.88	3.65	1.20	0.97	0.79	0.63
CaO	5.33	8.84	5.78	2.05	1.54	1.13	1.04
Na ₂ O	4.35	4.28	4.24	3.31	3.28	4.24	3.82
K ₂ O	1.54	0.76	1.90	2.80	2.78	3.41	3.27
P ₂ O ₅	-	0.20	0.30	0.09	0.10	0.15	0.13

Note. Samples of Shiveluch ash collected at different distances from the vent: 1 - sample 3 at 18 km, 2 - sample 8109 at 85 km, 3 - sample 64 at 300 km (analytical data after [4]). Samples of Opala ash: 5 - sample 8609 at 5.5 km, 6 - sample 86034 at 110 km, 7 - sample 86691 at 125 km; 4 - sample 8601 is a pyroclastic flow matrix from Opala. All data are calculated for anhydrous residue. Total Fe is given in specimens 4, 5 and 6. Analyses were made at the Central Chemical Laboratory of the Institute of Volcanology. Analyst N.A. Solov'eva.

of the volcano on the Bekesh River, 20 km to the southeast from the vent. The tephra consisted of pumiceous lapilli and bombs with a minor amount of volcanic sand. In Ust-Kamchatsk, 85 km from the volcano, the tephra layer was as thin as 2-3 cm and consisted of "salt-and-pepper" sand with particles averaging 0.27 mm and having a maximum size of 2 mm. Finely pulverized ash fell during the eruption on Bering Island. It was deposited as a 0.23 cm layer and consisted of particles having an average size of 0.02 mm and a maximum size of 0.1 mm. No traces of this ash have been discovered during recent surveys. The total volume of tephra produced by the eruption was estimated to be 0.3 km³. The tephra components are glass, plagioclase, ore minerals, green and brown hornblende, pyroxenes, and lithic fragments [1].

The mineral composition of the ash was studied as a function of grain size using the samples taken at 75 km (Chernyi Yar) and 85 km (Ust-Kamchatsk) from the volcano (see Figure 1).

Table 1 presents the results of the bulk chemical analysis of the ash samples collected at 18, 85 and 300 km from the vent. It is remarkable that the andesitic ash deposited at the foot of the volcano changed to basaltic in Ust-Kamchatsk and became andesitic again in the Komandorskie Islands. The ash showed a nonuniform grain-size

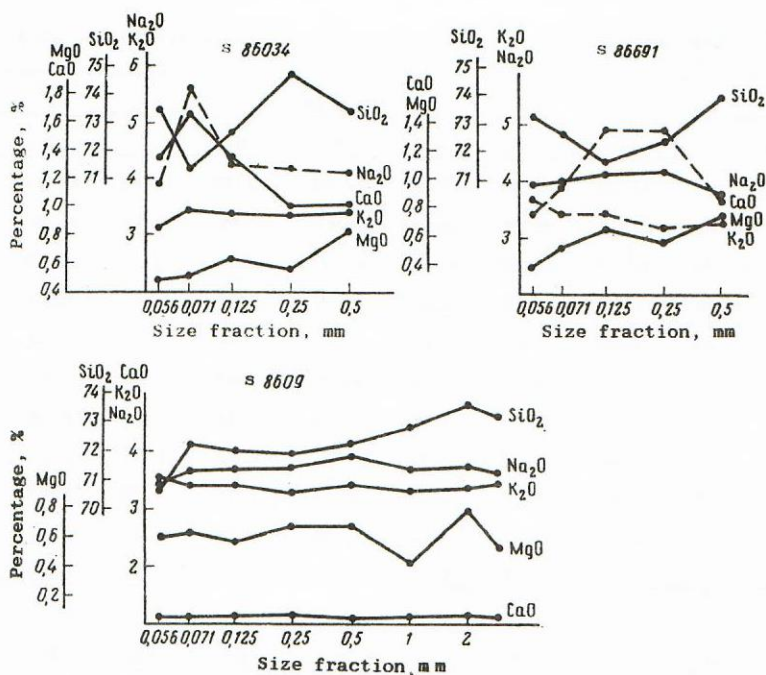


Figure 3 Variation of major oxide percentages in the Opala ash as a function of particle size fractions.

distribution [7]. For instance, the particles of 0.25 to 0.5 mm at sites 8458 and 8109 accounted for over 65 percent by weight of the bulk, whereas the particles of 0.125-0.25 mm and 0.25-0.5 mm taken together for over 85 percent (Table 3). A distinctive feature of the quantitative mineral composition of the Shiveluch ash is a large percentage (31 to 49%) of hornblende in the particles having a size > 0.125 mm and a < 10 percent hornblende content in the particles of smaller size. The particles of two size fractions, 0.125-0.25 mm and 0.25-0.5 mm, contain the smallest amounts of glass (Table 4). They are distinguished by the highest MgO content and the lowest SiO₂ percentage (Figure 4). Also, they show a high CaO content, which means that they are enriched in plagioclases. As seen in Table 4, the ashes of the above two size fractions are chemically identical in the sampling sites of 75 and 85 km from the volcano and are only different by the weight percentages of these size fractions in the bulk of the sample. Most of the hornblende and plagioclase crystals are equal to the grain sizes of these fractions. This is related to magma differentiation rather than to the desintegration of magma as it was shattered by explosion to produce ash.

The ashes rich in mafic minerals (green hornblende in our samples) fell at a certain distance from the vent. And it was not the size of the particles but the mineral composition (density) of the

crystal-rich ash that was ejected in the opening phase of the eruption and deposited at certain distance from the vent was abundant in plagioclase and hornblende. This affected the bulk chemical composition of the ash.

Table 3 Grain-size distribution of Opala ash (age 1500 years) and Shiveluch ash (1964 eruption).

Sample number	Size fraction, mm							
	<0.056	0.056-0.071	0.071-0.225	0.125-0.25	0.25-0.5	0.5-1	1-2	>2
Opala:								
9609	4.4	2.0	8.0	12.4	16.8	19.2	16.4	20.8
96034	13.4	4.2	10.5	25.7	29.4	5.3	1.3	0.2
96691	28.8	6.6	15.1	30.5	19.0	-	-	-
Shiveluch:								
9458	2.8	0.7	2.4	18.2	68.4	7.2	0.3	-
9109	1.0	0.4	22.8	65.2	10.4	0.2	-	-

Proceeding from the above considerations, the sequence of the air-fall deposition of the Shiveluch tephra is likely to be as follows. Coarse ejecta consisting of pumiceous bombs, lapilli, and coarse-grained sand of andesitic composition fell near the volcano. The amount of fine particles consisting largely of glass and plagioclase was insignificant. Next, at some distance from the volcano, 0.125 to 1 mm mafic crystals and ore minerals fell from the eruption cloud and the ash became essentially basaltic. At a large distance glass-rich dust, plagioclase crystal fragments, and ore dust fell on Bering Island where the ash was andesitic and chemically identical with the tephra deposited near the volcano.

Differences between the bulk mineral (and hence chemical) composition of the ash and the compositions of the individual size fractions indicate that a single sample of tephra is far from being representative of the composition of the magma from which it was derived because the single result reflects the effect of eolian differentiation in a given site of the ash-fall area. This fact need be remembered when ash layers of large eruptions are used as markers and correlated at great distances from the source. It is important, therefore, that ash samples are collected at several sites located at different distances from the volcano and that due allowance is made for the composition variations of the ash that fell away from the vent. When some ash layer need be identified as a product of a certain volcano, tephra samples should be collected at a minimum possible distance from the vent because the chemical composition of coarse ejecta (bombs, lapilli) is more representative of the matrix of pyroclastic flows or lavas of a given eruption (see Table 1) [11], [12].

Table 4 Chemical composition of Shiveluch Ash, November 12, 1964, wt. %.

Oxide	Specimen				
	1	2	3	4	5
SiO ₂	63.87	64.93	53.41	54.46	57.77
TiO ₂	0.75	0.78	0.98	0.81	0.82
Al ₂ O ₃	16.81	16.81	16.86	20.06	20.67
Fe ₂ O ₃	2.25	2.94	4.18	2.13	2.05
FeO	2.47	2.02	5.35	3.64	2.60
MnO	0.10	0.11	0.13	0.10	0.08
MgO	2.77	2.89	7.00	5.01	3.27
CaO	4.49	3.34	7.25	8.83	6.19
Na ₂ O	4.35	4.17	3.78	4.03	4.83
K ₂ O	1.79	1.63	0.89	0.75	1.49
P ₂ O ₅	0.33	0.38	0.15	0.18	0.24

Oxide	Specimen				
	6	7	8	9	10
SiO ₂	62.56	59.16	52.33	54.27	60.69
TiO ₂	0.75	1.00	1.00	0.78	0.71
Al ₂ O ₃	16.58	16.05	16.99	19.49	17.27
Fe ₂ O ₃	1.48	4.89	3.43	1.97	0.60
FeO	4.06	2.03	5.05	3.79	4.16
MnO	0.10	0.03	0.13	0.10	0.10
MgO	3.92	5.49	7.37	5.66	3.50
CaO	4.69	5.26	8.86	8.71	6.47
Na ₂ O	3.99	3.83	3.96	4.47	4.47
K ₂ O	1.57	2.03	0.68	0.61	1.84
P ₂ O ₅	0.29	0.23	0.19	0.15	0.18

Note. 1 thru 6 - sample 8458 collected in Chernyi Yar, 75 km from the vent, size fractions: 1 - 0.056 mm, 2 - 0.056-0.071 mm, 3 - 0.125-0.25 mm, 4 - 0.25-0.5 mm, 5 - 0.5-1 mm, 6 - 1-2 mm; 7 thru 10 - sample 8109 collected in Ust-Kamchatsk, 85 km from the volcano, size fractions: 7 - 0.071-0.125 mm, 8 - 0.125-0.25 mm, 9 - 0.25-0.5 mm, 10 - 0.5-1 mm. Analysis were made at the Institute of Volcanology (calculated for dry residue), analyst N.A. Solov'eva.

This conclusion is consistent with the observations of Japanese investigators [17] who use coarse pumice or cinders to determine the bulk chemical composition of tephra in order to minimize the effect of sorting and weathering. Kobayashi et al [15] studied acid, intermediate and basic rock types of volcanic ashes and did not find any essential

differences between the lavas and pyroclastics produced by one eruption.

Table 5 Chemical composition of Ksudach tephra (age 1800¹⁴C years), wt.%.
 Oxide

Oxide	Specimen						
	1	2	3	4	5	6	7
SiO ₂	71.49	68.03	70.93	70.39	69.58	70.73	69.73
TiO ₂	0.49	0.66	0.51	0.68	0.57	0.62	0.67
Al ₂ O ₃	14.81	16.29	15.25	15.13	15.51	15.17	14.98
Fe ₂ O ₃	1.23	1.83	1.30	1.20	1.13	0.99	1.67
FeO	2.45	2.48	2.15	2.50	2.62	2.60	2.72
MnO	0.09	0.09	0.09	0.08	0.08	0.08	0.09
MgO	0.28	0.65	0.64	0.39	0.23	0.33	0.44
CaO	3.03	4.34	3.20	3.22	3.68	3.31	3.35
Na ₂ O	4.57	4.20	4.28	4.87	5.02	4.68	4.83
K ₂ O	1.45	1.32	1.50	1.49	1.48	1.39	1.42
P ₂ O ₅	0.10	0.11	0.15	0.10	0.10	0.09	0.09

Oxide	Specimen						
	8	9	10	11	12	13	
SiO ₂	70.23	65.30	65.17	67.90	65.87	68.95	
TiO ₂	0.54	0.76	0.80	0.62	0.76	0.59	
Al ₂ O ₃	15.52	16.98	17.23	16.04	16.44	15.88	
Fe ₂ O ₃	0.76	0.80	1.78	0.87	1.81	0.60	
FeO	2.94	3.98	3.87	3.59	3.71	3.51	
MnO	0.04	0.23	0.18	0.14	0.14	0.12	
MgO	0.26	1.93	1.51	1.40	1.50	0.56	
CaO	3.29	4.28	4.20	3.42	4.09	3.43	
Na ₂ O	4.96	4.45	3.85	4.60	4.13	4.89	
K ₂ O	1.37	1.28	1.15	1.23	1.28	1.47	
P ₂ O ₅	0.10	-	0.26	0.18	0.30	-	

Note. 1 - sample 86039/4 collected at 7 km from the volcano; 2 - sample 86039/6, 7 km; 3 - sample 86038/3, 15 km; 4 - sample 86038/7, 15 km; 5 - sample 86038/20, 15 km; 6 - sample 86038/21, 15 km; 7 - sample 86037/15, 30 km; 8 - sample 86037/17, 30 km; 9 - sample 78361/1, 275 km; 10 - sample 3-86, 325 km; 11 - sample 8017a/1, 350 km; 12 - sample 11-83, 360 km; 13 - sample 8014/6, 375 km. Samples from O.A. Braitseva's collection. Analyses were made at the Institute of Volcanology (calculated for dry residue). Analyst G.V. Lets (specimens 1,2,4,5,-6,7,8,10,11,13) and G.P. Novoseletskaya (specimens 3 and 9).

Some of the basaltic ashes have been reported to be unaffected

by eolian differentiation [2]. This can be explained by the fact that ash particles often consist of interlocked crystals of two or more different minerals enclosed in volcanic glass and look like fragments of volcanic rocks. Such aggregates diminish in size with distance from the vent but their mineral composition remains invariable. So, the tephra produced by basaltic eruptions are chemically closer to their lavas [11]. Obviously, the compositional invariability of ashes, no matter how far from the vent they land, must also be characteristic of phreatic eruptions: the ash they produce is dominated by lithic fragments whereas juvenile material is absent.

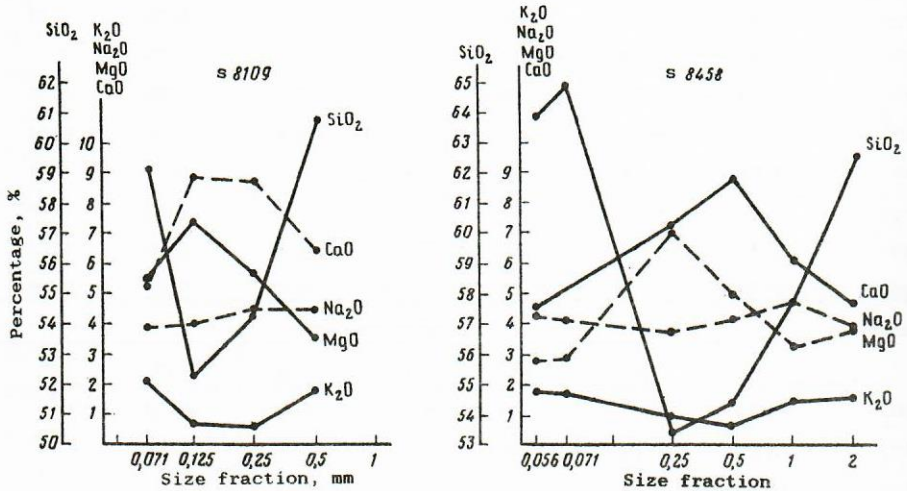


Figure 4 Variation of major oxide percentages in the Shiveluch ash as a function of particle size fractions.

In case of glass-rich ash, the chemical composition of any size fraction deposited at any distance from the vent represents rather closely the bulk ash composition and can be used to describe a given ash as a whole and to compare it in terms of chemistry with the other products of the eruption (lavas, pyroclastic flows, extrusive domes). Besides, the chemical composition of one ash size fraction can be used effectively where some of the ash size fractions are contaminated with land-derived and redeposited products of erosion. An example of interest is a study of ash samples collected in the European part of the Soviet Union, from a locality near Voronezh. The ash is believed to be blown from a catastrophic caldera-forming eruption that occurred in late Pleistocene time in the Phlegraeon Fields, Italy [10]. The study revealed that the particles larger than 0.25 mm in size consisted almost totally of rounded quartz grains of terrigenous origin. Contaminations of this kind may lead to a misleading interpretation of the bulk chemical composition of ash and the employment of the chemical compositions of smaller-size particles is justified in such

cases.

Differences between the chemical compositions of individual grain-size fractions and the bulk composition of the Shiveluch ash do not fall outside the limits of one and the same petrochemical series, whatever the distance from the vent. As follows from the $\text{Na}_2\text{O}+\text{K}_2\text{O}$ content (<7.5-8.1%), the ash belongs to a normal alkali series. On the basis of the K_2O percentages the Shiveluch tephra can be assigned to the type of moderately potassic rocks and the Opala tephra to potassium-rich types [8]. As the ashes erupted by certain volcanoes belong to the same petrochemical classes as the rocks that build up the volcanic cones, the ash produced by each eruption can be traced to a certain vent and the ash layers can be correlated from site to site, whatever their distances from the vents.

Table 6 Chemical composition of Ksudach tephra (age 6000¹⁴C years), wt. %.

Oxide	Specimen					
	1	2	3	4	5	6
SiO_2	62.42	62.57	63.93	62.90	62.39	61.15
TiO_2	0.79	0.78	0.70	0.79	1.14	0.94
Al_2O_3	16.59	16.51	16.42	16.95	18.70	18.01
Fe_2O_3	2.56	2.56	1.73	1.07	-	4.08
FeO	4.37	3.99	4.10	4.95	4.73	3.94
MnO	0.17	0.20	0.21	0.21	0.09	0.23
MgO	2.21	2.14	1.43	2.09	1.83	1.68
CaO	5.43	5.48	5.66	5.83	5.74	5.12
Na_2O	4.20	4.20	4.35	4.04	4.26	3.85
K_2O	1.08	1.15	1.22	0.90	0.96	0.98
P_2O_5	1.18	0.21	0.23	0.28	0.17	0.28

Note. 1 - sample 86039/12 collected at 7 km from volcano; 2 - sample 86039/15, 7 km; 3 - sample 86037/10, 30 km; 4 - sample 86608/6, 75 km; 5 - sample 86008/2, 125 km; 6 - sample 3-27, 290 km. Analyses were made at the Institute of Volcanology (calculated for dry residue). Analysts, L.A. Kartasheva (1,2,5), G.P. Novoseletskaia (3,4), and T.G. Osetrova (6).

Studies of tephra deposits have shown that eolian differentiation may lead to variations in composition comparable with those that result from magma differentiation in volcanic reservoirs (removal or accumulation of crystals): in both processes the products of differentiation remain within the limits of one petrochemical class [12].

The results obtained from the study of the ashes deposited from Opala and Shiveluch Volcanoes illustrate two "extreme" cases of potential variations in ash composition resulting from eolian differentiation. Examples of this kind are known from the ashes produced by

different events in the eruptive history of one volcano. For instance, the SiO_2 percentage in the ash blown from Ksudach Volcano in Kamchatka about 1800 years ago varies by more than 6 percent over a distance of 375 km from the vent (Table 5). At the same time, the chemical composition of the ash produced by the eruption of the same volcano that occurred approximately 6000[±]C years ago remains almost invariable with distance (Table 6). This can be explained by differences in the amounts of crystals in the ash and by the proportions of the various kinds of mafic minerals.

In view of the fact that ashes of most eruptions occupy an intermediate position in a composition variation series which is controlled by the content of crystals [6], [9], it is advisable to study quantitatively the mineral composition of the ash and examine variations in its composition caused by eolian differentiation before using analytical data.

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