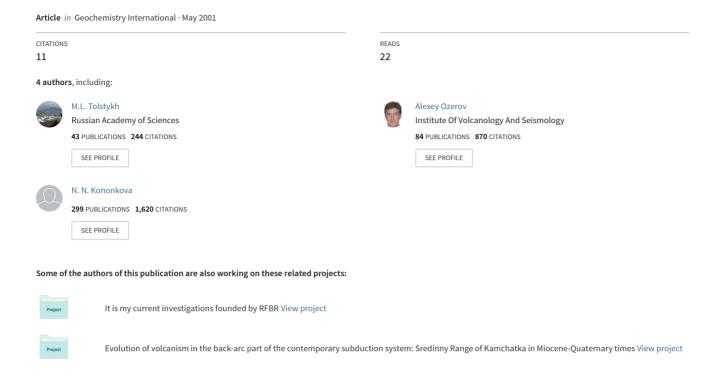
### Composition of magmas of the 1996 eruption at the Karymskii Volcanic Center, Kamchatka: Evidence from melt inclusions



# Composition of Magmas of the 1996 Eruption at the Karymskii Volcanic Center, Kamchatka: Evidence from Melt Inclusions

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**Abstract**—Melt inclusions were examined in phenocrysts of basalt from the Akademiya Nauk caldera (Novogodnii Fissure, Karymskoe Lake) and andesite (1996 eruption) from Karymskii volcano. The inclusions were studied by homogenization, and their glasses (more than 50) were analyzed on an electron microprobe. The  $SiO_2$  concentrations of melt inclusions in plagioclase and olivine from the basalt range from 47.4 to 57.1 wt %, and these values for plagioclase from the andesite are 55.7-67.1 wt %. The basaltic melts are characterized by usual concentrations of FeO (11.4–6.8%), MgO (6.1–2.3%), CaO (10.8–6.7%), and  $TiO_2$  (1.3–0.7%) and are enriched in  $Na_2O$  (7.4–2.9%, average 5.1%), with the highest  $Na_2O$  concentrations (7.4–5.3%) detected in the least silicic melts ( $SiO_2 = 47.4-52.0$ %). The  $K_2O$  concentrations vary from 0.4 to 1.7%. The basaltic melt was determined to contain 0.09% Cl and 0.14% S. The andesitic melts are characterized by high concentrations of FeO (average 6.5%) and CaO (5.2%) and usual concentrations of  $Na_2O$  (4.5%) and  $K_2O$  (2.1%). The Cl content of the melt was 0.26%, and that of S was 0.07%. The comparison of andesites from Karymskii volcano with the previously studied andesitic melts from the Shiveluch and Bezymyannyi volcanoes revealed their significant differences. The former are less silicic, higher in Fe, Ti, Ca, Mg, P, and Na but significantly lower in  $Na_2O$ . The Karymskii melts are most probably less differentiated than the melts of Bezymyannyi and Shiveluch volcanoes.

#### **INTRODUCTION**

Karymskii volcano, one of the most active in Kamchatka, belongs to the Karymskii volcanic group of nine eruption centers (which is referred to as the Karymskii volcanic center [1]) in the central part of the Eastern Kamchatka Volcanic Belt, at a distance of 30 km from the Pacific coast and 125 km north of the town of Petropavlovsk-Kamchatskii. Karymskii volcano has attracted much attention after its 1996 eruption, which was the strongest over a few recent years and noteworthy because of the fact that intermediate and mafic compositions were erupted simultaneously. A multitude of papers is devoted to the exhaustively documented dynamics of the eruption, petrography of the erupted rocks, and their genetic relationships [2–5 and others]. The homogenization temperatures of melt inclusions in apatite and plagioclase from the andesitedacite (as reported in [6-8]) were fairly high: 1440-1000°C. The composition of the melt was reported in a single paper [9], in which it was deduced from unusual magmatic inclusions, with evidence of liquid immiscibility in plagioclase from the andesite-dacite of Karymskii volcano.

Our study was centered on a detailed examination of melt inclusions in plagioclase from basalts and andesites of the latest, 1996, eruption of the Karymskii volcanic center with the aim of revealing the chemical composition of the melts and the possible genetic relations between rocks different in silicity. We also compared the chemistry of andesitic melts from Karymskii volcano and the previously studied andesites from Shiveluch and Bezymyannyi volcanoes, which led us to determine certain distinctive features of each of the volcanoes.

## OVERVIEW OF THE KARYMSKII VOLCANIC CENTER

Karymskii volcano in the central part of the Kamchatka Volcanic Zone is located in a Holocene caldera, which is overprinted on the Middle–Late Pleistocene volcanoes Dvor and Pra-Karymskii. The modern edifice is a cone, with a maximum elevation of 1536 m at the center of the caldera. The relative height of the cone is 600 m, with the crater attaining 200–250 m in diameter, and the caldera surface area as large as 12 km². In the north, the caldera is neighbored by the edifice of Dvor volcano, whose central part is filled with the lavas of the ancient volcano Karymskii. The floor of the caldera is made up of lavas from the young cone.

The caldera was produced 7700–7800 years ago by a series of eruptions of pumiceous material. After the development of the collapse caldera, the volcano remained quiescent for nearly 2000 years. A new active

Table 1. Chemical composition (wt %) of rocks and their groundmass glasses from the Karymskii volcanic center

Component	1	2	3	4	5	6	7
SiO <sub>2</sub>	52.00	52.38	62.45	61.54	66.59	74.80	75.28
${ m TiO_2}$	0.73	0.78	0.92	0.86	0.50	1.06	0.83
$Al_2O_3$	19.21	19.22	16.27	16.67	19.52	12.62	12.46
$Fe_2O_3$	_	2.32	_	2.43	_	_	_
FeO	8.30*	5.92	6.58*	5.12	1.78*	3.59*	3.14*
MnO	0.14	0.13	0.15	0.11	0.06	0.10	0.11
MgO	5.34	5.14	2.01	1.99	0.23	0.18	0.49
CaO	10.47	10.52	5.38	5.31	4.65	0.92	0.94
$Na_2O$	2.80	2.54	4.52	3.69	5.76	1.88	1.77
$K_2O$	0.58	0.78	1.57	1.58	1.64	3.50	3.44
$P_2O_5$	0.14	0.15	0.26	0.25	_	_	_
Cl	_	_	_	_	0.04	0.02	0.02
S	_	_	_	_	0.06	0.03	0.04
$H_2O$	_	0.11	_	_	_	_	_
Total	99.71	99.99	100.11	99.55	100.83	98.70	98.52

<sup>\*</sup> Total iron; (1) Sample K-2, (2) basalts (average of 20 analyses, data from [3, 4]), (3) Sample K-4, (4) andesites (average of 6 analyses [3]), (5–7) groundmass glasses: (5) Sample K-2, (6) Sample K-4, (7) Sample K-63.

episode of the volcanic center was related to the development of a young volcano in the caldera (~5300 years ago) and continued for nearly 3000 years. Massive eruptions of andesite-basaltic and andesitic pyroclastic material were interspersed by andesite lava outpouring. The most significant ejections of volcanic material occurred 5100 and 4200 years ago. After a period of ~500 years of quiescence, the volcanic activity was resumed in the form of pyroclastic eruptions and andesite lava outpourings. This episode of volcanic activity continues to the present.

The latest significant eruption of Karymskii volcano began on January 2, 1996 [3], and still proceeds. The eruption process may be subdivided into three stages. Over stage I (January 2–3), eruptions occurred at two volcanic centers at a distance of 6 km apart: at the summit of Karymskii volcano and in Karymskii Lake (northern sector) of Akademii Nauk volcano. The main crater continuously expelled a gas and ash column to heights of 500–1200 m, and tephra constantly fell down from a dark southward trail of the cloud. The trail attained 50–70 km in length, and the slopes of the volcano and its caldera walls were covered with thick ash deposits. Simultaneously, an underwater eruption took place at the eruption center in Karymskii Lake, at a 500-m distance from its shore. Powerful discrete phreato-magmatic explosions followed one another with intervals of 10-15 min, and vapor-gas clouds with an ash admixture were ejected to heights of a few kilometers. The strongest explosions produced numerous bombs, and waves in the lake were as high as 10 m. The

first stage of the eruption resulted in Novogodnii Peninsula (0.7 km² in area) in Karymskii Lake.

Stage II of the eruption (January 4–12, 1996) was characterized by eruptive activity only at the summit crater and a much lower frequency of explosions, which occurred with intervals of 10 min on average. The material was ejected to heights of 500–900 m, and ash trails extended for 50–60 km to the west and east.

During stage III (from January 13, 1996, to the present time), a succession of lava flows was outpoured from the main crater of Karymskii volcano. The thickest of them attained a length of 1.5 km and a thickness up to 25 m in its frontal part. The whole stage was characterized by explosive activity at the summit crater. Vapor–gas ejecta laden with volcanic ash rose to heights from 100 to 500–600 m and formed eruption clouds. The frequency of the ejections varies from a few minutes to several hours. The clouds developing during the strongest explosions (250 m and more) pervasively contained hot bombs (1–2 m across, more rarely up to 4–5 m) in their lower parts.

#### **PETROGRAPHY**

We examined three rock samples from the 1996–1997 eruption. Sample K-2 is a basaltic volcanic bomb from Novogodnii Peninsula. It was brought to the surface on January 2–3, 1996. The other two samples, K-4 and K-63, are andesite from lava flows that poured out of the summit crater of Karymskii volcano. The samples were taken in a hot state on September 22, 1996, and August 19, 1997, respectively. The compositions of

Component K-2 K-2 K-2 K-63 K-4 K-63 K-4 K-63 K-4\* 45.99 SiO<sub>2</sub> 44.79 47.64 47.28 47.58 52.85 51.97 55.07 57.38  $Al_2O_3$ 34.35 33.66 31.76 32.21 31.65 30.47 28.76 27.31 26.68 FeO 0.60 0.87 0.75 0.71 0.67 0.62 0.59 0.66 0.86 17.41 14.51 12.37 CaO 18.09 17.10 17.98 16.68 14.07 8.49 Na<sub>2</sub>O 0.99 1.56 2.23 1.78 2.65 3.36 4.31 4.64 5.86 K<sub>2</sub>O 0.03 0.01 0.05 0.05 0.08 0.11 0.13 0.15 0.29 Total 98.87 100.12 98.04 99.95 100.21 99.56 98.87 100.56 98.61 90.8 85.8 81.4 78.1 70.0 59.1 43.7 An83.6 63.9 Ab9.0 14.1 18.3 21.5 29.4 35.4 40.1 54.6 16.1 0.2 0.1 0.3 0.3 0.4 0.6 0.7 0.8 1.7 Or

Table 2. Representative analyses (wt %) of plagioclase from rocks of Karymskii volcano

the samples and the average compositions of the basalts and andesites of the 1996 eruption are reported in Table 1.

The basalt is a black vitreous rock with abundant plagioclase phenocrysts. Phenocrysts account for ~35% of the rock by volume and are composed of plagioclase, olivine, and pyroxene. The groundmass has a glassy texture and consists of glass and microlites of plagioclase, pyroxene, and opaque minerals. The composition of the groundmass glass is given in Table 1.

Plagioclase is the predominant phenocrystic mineral ( $\sim$ 80% phenocrysts), and its crystals vary from 0.3 to 3 mm. Large plagioclase phenocrysts contain thick inner zones with evidence of strong resorption. The plagioclase often occurs as glomerophyric aggregates. Its composition corresponds to bytownite-anorthite ( $An_{93-81}$ )

or labradorite ( $An_{75-62}$  [4]) in the margins. The composition of plagioclase with abundant melt inclusions is reported in Table 2 and Fig. 1a.

Olivine and pyroxene were found more rarely. The olivine is  $Fo_{72-83}$  or, rarely, is more magnesian, perhaps when occurring as a cumulative phase. The latter compose fragments of allivalite nodules, which are generally quite common in the pyroclastic rocks of the Karymskii volcanic center [5]. The basalts contain both ortho- and clinopyroxene, whose compositions are listed in Table 3.

The accessory minerals of the basalts are apatite and an opaque mineral. The former occurs exclusively as crystalline inclusions, whereas the latter was encountered in the form of both crystalline inclusions and microlites.

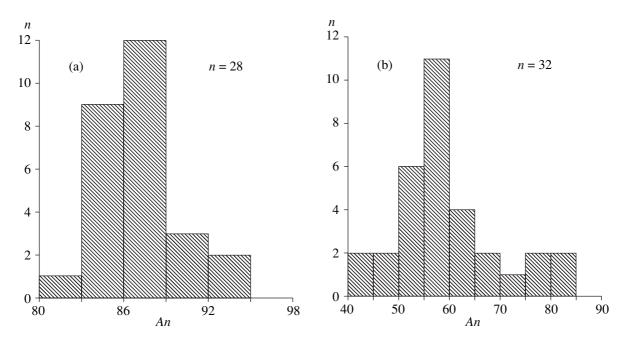


Fig. 1. Histograms for plagioclase composition from (a) basalt and (b) andesite of the Karymskii volcanic center.

<sup>\*</sup> K-4—microlite, others are phenocrysts.

Table 3.	Representative anal	yses (wt %) of mafi	c minerals from	rocks of Karymskii volcano	)
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Component	1	2	K-2	K-2	K-63	3	K-4	K-63
SiO <sub>2</sub>	38.45	39.58	37.93	53.58	52.35	52.19	50.76	52.08
$TiO_2$	-	_	0.00	0.49	0.34	0.47	0.63	0.53
$Al_2O_3$	_	_	0.04	1.33	1.11	2.75	1.88	1.54
FeO	22.20	17.53	20.24	19.55	20.37	8.21	10.40	10.94
MnO	0.57	0.42	0.03	0.44	0.71	0.07	0.49	0.49
MgO	38.22	43.11	39.18	20.80	23.24	15.50	13.89	14.75
CaO	0.11	0.15	0.17	2.24	1.92	20.71	20.98	19.78
$Na_2O$	_	_	_	0.13	_	0.48	0.31	0.35
$Cr_2O_3$	-	_	0.13	0.10	0.04	0.08	0.02	0.00
Total	99.55	100.79	97.72	98.66	100.08	100.46	99.36	100.46

Note: Analyses 1–3 are borrowed from [4].

The andesite is a low-porosity rock of dark gray color, with ~30–35% phenocrysts. The main rockforming mineral is plagioclase, which accounts for approximately 85% of all phenocrysts. The rock also contains olivine and pyroxene crystals (Table 3). The groundmass consists of glass, microlites of plagioclase, pyroxene, and ore minerals. The groundmass glass composition is demonstrated in Table 1. Plagioclase develops as grains of various sizes without any resorption traces, even in large phenocrysts. The compositional range of plagioclase from the andesite is wider than that of plagioclase from the basalt,  $An_{52-85}$  (Table 2, Fig. 1b). The accessory minerals of the andesites are the same as in the basalts. Table 4 reports the composition of the ore minerals.

#### **INCLUSIONS IN MINERALS**

Phenocrysts in the basalt and andesite carry crystalline, fluid, and melt inclusions. The crystalline inclusions are apatite and ore minerals (the same as in all phenocrysts). The fluid inclusions are bubbles of vari-

**Table 4.** Representative analyses (wt %) of ore minerals from rocks of Karymskii volcano

Com- ponent	K-2	K-4	K-63	K-4	K-4	K-4
FeO	52.25	78.05	78.09	81.86	93.26	92.90
$TiO_2$	40.13	12.87	11.80	10.23	3.88	3.17
$Al_2O_3$	0.43	3.35	3.26	3.12	1.66	1.30
MnO	0.29	0.42	0.45	0.53	0.45	0.45
MgO	3.18	1.91	2.69	2.04	1.18	1.11
CaO	0.04	0.06	0.13	0.03	0.03	0.06
$SiO_2$	0.03	0.06	0.18	0.06	0.04	0.19
$Cr_2O_3$	0.13	0.10	0.13	0.15	0.12	0.06
Total	96.48	96.82	96.73	98.02	100.62	99.24

ous sizes, dark, and nearly opaque. Because of their low densities, we failed to determine their composition cryometrically. The melt inclusions can be subdivided into three types in accordance with their appearance and position in host crystals.

The inclusions of type I are characteristic of phenocrysts in both basalts and andesites. These inclusions are most often opaque, elongated, or, more rarely, equant, have regular shapes, and range from a few to 30  $\mu m$ . Glassy inclusions are very rare. The inclusions of type II were detected only in the basalts. These are small opaque inclusions, whose location is clearly constrained to concentric zones around resorption zones ("riddled" plagioclase with glass embayments). The inclusions of type III were also found only in the basalt and compose nonzoned swarms in water-clear plagioclase grains.

The thermometry of melt inclusions was conducted in a micromuffle with a platinum heater. The accuracy was  $\pm 10^{\circ}$ C. We used the quenching technique [10]. The glasses of melt inclusions were analyzed on a Camebax Microbeam electron microprobe at an accelerating potential of 15 kV, 30 nA current, and rasters over 12 by 12, 5 by 5, or 2 by 2 μm when glasses were analyzed or 2 by 2 µm in the analysis of crystalline phases. The analytical accuracy was  $\pm 2\%$  at element concentrations of >10 wt %,  $\pm 5$ % at concentrations of 5-10 wt %, and  $\pm 10\%$  at concentrations of 1–5 wt %. It should also be mentioned that a significant Na loss was detected when inclusion glasses were analyzed by scanning over small areas. Because of this, we analyzed glasses in a number of large (30–50 μm) inclusions by scanning over distinct areas and calculated corrections for Na analyses in small inclusions. This coefficient was equal to 1.4.

After the heating of plagioclase phenocrysts to temperatures of 1100–1140°C and their subsequent rapid quenching, the samples were polished to expose melt inclusions at the surface, and the inclusions were then analyzed on a microprobe. Tables 5–7 list the results on

**Table 5.** Chemical composition (wt %) of glasses in melt inclusions in plagioclase and olivine from basalt (Sample K-2) of the Akademiya Nauk caldera

Component	1	2	3	4	5	6	7	8	9	10
SiO <sub>2</sub>	47.44	49.47	50.98	51.27	51.47	51.84	52.04	53.55	53.87	53.90
$TiO_2$	0.73	1.08	0.79	0.91	0.95	0.87	1.02	1.08	1.01	1.30
$Al_2O_3$	19.67	16.09	19.05	17.36	17.76	19.83	16.45	18.71	18.35	13.93
FeO	6.83	8.66	7.86	8.12	9.03	7.24	8.45	7.83	7.71	11.39
MnO	0.13	0.12	0.16	0.22	0.21	0.13	0.12	0.23	0.14	0.23
MgO	5.19	6.10	4.30	3.65	4.70	3.75	5.26	3.06	3.55	4.76
CaO	10.82	10.00	9.69	8.90	9.05	9.28	8.38	9.82	7.61	7.03
Na <sub>2</sub> O	7.40	5.96	6.21	5.33	6.38	5.91	7.07	4.02	5.56	3.88
K <sub>2</sub> O	0.44	1.13	0.66	1.07	0.66	0.74	1.40	0.92	0.94	1.25
$P_2O_5$	0.09	0.24	0.15	0.16	0.16	0.16	_	0.19	0.22	0.24
Cl	0.07	0.12	0.10	0.06	0.08	0.07	_	0.09	0.09	0.11
S	0.14	0.19	0.16	0.15	0.10	_	0.22	0.19	-	0.11
Total	98.95	99.16	100.11	97.20	100.55	99.82	100.41	99.69	99.09	98.13
T, °C	1140	1140	1120	1140	1120	1100	1130	1100	1100	20
An	93	81	89	84	92	85	91	89	88	84
Component	11	12	13	14	15	16	17	18	19	20
SiO <sub>2</sub>	54.11	54.68	54.87	55.44	55.44	55.47	55.62	55.75	57.14	53.30
$TiO_2$	0.85	1.00	0.83	1.19	0.86	1.03	0.91	1.17	0.88	0.97
$Al_2O_3$	16.42	17.30	14.41	16.23	17.67	17.62	18.59	16.05	17.97	17.38
FeO	8.90	7.70	8.98	8.96	5.45	8.08	6.85	9.79	7.29	8.17
MnO	0.21	0.15	0.14	0.15	0.09	0.21	0.16	0.19	0.17	0.17
MgO	4.63	3.68	6.59	3.92	3.72	3.63	3.61	5.10	3.50	4.35
CaO	8.16	8.12	8.21	6.66	8.15	7.24	7.90	7.34	7.46	8.43
Na <sub>2</sub> O	4.43	6.05	4.60	5.15	2.64	3.09	4.84	3.50	2.87	5.08
K <sub>2</sub> O	1.66	0.91	0.68	1.44	5.95	1.11	1.04	0.96	1.10	1.00
$P_2O_5$	0.14	0.13	0.24	0.19	0.11	0.17	0.21	0.16	0.15	0.17
Cl	0.07	0.08	0.09	0.11	0.01	0.11	0.09	0.09	0.11	0.09
S	0.17	0.14	0.10	0.15	0.03	_	0.10	0.07	0.10	0.14
Total	99.58	99.94	99.74	99.59	100.12	97.76	99.92	100.17	98.74	99.25
T, °C	1120	1140	1140	1100	1140	20	1120	1159*	1120	
An	86	87	86	83	82	83	83		83	

Notes: Numbers 1–17 and 19 are plagioclase, 18 is olivine  $(Fo_{76})$ , 20 is an average of 21 analyses.

inclusions in basalt and andesite, respectively. These data are also portrayed in variation diagrams in terms of  $SiO_2$  vs. major elements for the compositions of rocks, glasses in melt inclusions, and glasses in the ground-mass of the rocks (Fig. 2).

The  ${\rm SiO_2}$  concentrations of melt inclusions in plagioclase and olivine from the basalt vary from 47.4 to 57.15 (here and below, concentration values are given in wt %). The melts have usual concentrations of FeO (11.4–6.8%), MgO (6.1–2.3%), CaO (10.8–6.7%), and

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<sup>\*</sup> Calculated temperature for the olivine–melt equilibrium at  $K_d^{\mathrm{Fe-Mg}} = 0.30$ .

**Table 6.** Chemical composition (wt %) of glasses in melt inclusions in plagioclase from andesite (Sample K-4) of Karymskii volcano

Component	1	2	3	4	5	6	7	8
SiO <sub>2</sub>	55.70	56.67	58.33	61.68	62.26	63.01	63.60	64.13
$TiO_2$	1.27	1.47	1.40	1.47	1.52	1.52	1.17	0.92
$Al_2O_3$	15.87	15.36	15.09	14.20	14.44	14.48	15.37	15.38
FeO	8.15	8.54	7.54	7.75	7.41	7.69	6.18	5.60
MnO	0.14	0.46	0.21	0.21	0.24	0.22	0.16	0.17
MgO	2.74	2.70	2.15	2.00	1.87	1.77	1.86	1.57
CaO	6.45	6.81	6.60	5.34	5.02	5.30	4.55	5.07
$Na_2O$	5.82	5.71	5.94	4.65	4.29	3.24	4.39	4.06
$K_2O$	1.37	1.68	1.89	1.96	1.93	1.88	2.24	2.29
$P_2O_5$	0.32	0.36	0.45	0.33	0.36	0.45	0.34	0.32
Cl	0.27	0.26	0.35	0.26	0.28	0.26	0.30	0.21
S	0.10	0.07	0.09	0.06	0.05	0.08	0.06	0.08
Total	98.20	100.09	100.04	99.91	99.67	99.90	100.22	99.80
T, °C	1100	1100	1100	1110	1110	1110	1110	1110
An	80	78	78	65	65	65	69	64
Component	9	10	11	12	13	14	15	16
SiO <sub>2</sub>	64.30	64.70	64.73	65.21	65.46	65.75	65.78	62.69
$TiO_2$	0.69	1.39	0.83	1.02	1.04	0.94	0.96	1.21
$Al_2O_3$	16.30	14.06	15.46	14.64	15.70	14.13	15.05	15.09
FeO	4.08	6.03	4.72	4.48	4.65	4.93	5.33	6.27
MnO	0.12	0.20	0.14	0.20	0.11	0.18	0.20	0.20
MgO	1.05	1.48	1.07	1.06	1.26	1.18	1.39	1.70
CaO	4.97	4.40	4.97	3.66	4.47	3.62	4.39	5.08
Na <sub>2</sub> O	4.96	3.98	4.96	4.18	4.12	3.65	3.65	4.51
$K_2O$	3.07	2.77	2.00	2.03	2.05	2.54	2.55	2.13
$P_2O_5$	0.18	0.53	0.22	0.24	0.36	0.37	0.41	0.35
Cl	0.14	0.19	0.15	0.17	0.18	0.16	0.15	0.23
S	0.07	0.06	0.07	0.08	0.08	0.06	0.07	0.07
Total	99.93	99.79	99.32	96.97	99.48	97.51	99.93	99.53
<i>T</i> , °C	1110	1110	1110	1100	1100	1100	1100	
An	58	58	59	53	53	55	53	

Note: Numbers 1-15 are inclusions in plagioclase, 16 is an average of 16 analyses.

 $TiO_2$  (1.3–0.7%) but are enriched in  $Na_2O$  (7.4–2.9% at an average of 5.1%), with the highest  $Na_2O$  concentrations (7.4–5.3%) detected in the most mafic (least silicic) melts (47.4–52.0%  $SiO_2$ ). The  $K_2O$  concentrations vary from 0.4 to 1.7%. The only exception is an inclusion whose  $K_2O$  concentration (5.95%) is signifi-

cantly higher than that of  $Na_2O$  (2.6%). It is pertinent to note that this K-rich inclusion does not contain Cl, whereas all of the rest of the 20 inclusions have Cl concentrations of 0.06–0.12% at an average value of 0.09%. Previously, we determined analogous Cl concentrations in a K-rich melt from the volcanics of the Medvezh'ya

**Table 7.** Chemical composition (wt %) of glasses in melt inclusions in plagioclase from andesite (Sample K-63) of Karymskii volcano

Component	1	2	3	4	5	6	7	8
SiO <sub>2</sub>	56.89	57.26	58.21	59.26	59.45	59.55	60.39	60.64
$TiO_2$	2.25	1.71	1.70	1.33	1.47	2.11	1.60	1.29
$Al_2O_3$	13.60	15.76	15.15	16.34	16.58	16.03	14.86	16.42
FeO	8.98	7.82	7.84	6.73	6.29	6.89	8.16	5.94
MnO	0.26	0.26	0.20	0.23	0.18	0.25	0.23	0.15
MgO	2.43	2.15	1.97	1.62	1.63	1.67	1.99	1.67
CaO	6.17	6.33	6.44	6.00	5.53	5.52	5.47	5.35
Na <sub>2</sub> O	5.66	5.22	4.95	5.22	5.83	5.28	4.74	5.60
$K_2O$	1.80	1.79	1.74	1.75	1.84	1.81	1.77	1.67
$P_2O_5$	_	1.16	1.23	0.89	0.36	0.46	0.28	0.39
Cl	0.38	0.30	0.30	0.29	0.29	0.29	0.30	0.25
S	0.12	0.15	0.13	0.06	0.05	0.09	0.13	0.07
Total	98.54	99.91	99.86	99.72	99.50	99.95	99.92	99.44
T, °C	1110	1110	1110	1110	1120	1110	1110	1120
An	84	84	84	60	78	60	84	78
Component	9	10	11	12	13	14	15	16
SiO <sub>2</sub>	60.71	61.30	62.45	63.02	63.64	64.57	67.10	61.15
$TiO_2$	1.69	1.35	1.22	1.58	0.98	1.14	0.90	1.48
$Al_2O_3$	15.48	14.12	15.49	15.62	16.88	12.30	13.85	15.14
FeO	7.02	6.87	6.23	5.70	4.31	5.45	5.66	6.67
MnO	0.24	0.26	0.21	0.25	0.16	0.20	0.21	0.22
MgO	1.68	2.27	1.57	1.20	1.02	1.36	1.28	1.69
CaO	5.68	5.40	5.32	4.57	3.77	3.23	3.55	5.19
Na <sub>2</sub> O	4.42	5.02	3.88	3.84	4.84	4.86	4.22	4.68
$K_2O$	1.77	1.89	2.12	1.94	3.10	2.85	2.21	2.03
$P_2O_5$	0.59	1.16	0.46	0.45	0.59	0.47	0.33	0.62
Cl	0.33	0.33	0.29	0.21	0.31	0.21	0.20	0.29
S	0.06	0.09	0.06	-	0.07	0.04	0.08	0.08
Total	99.67	100.06	99.30	98.38	99.67	96.68	99.59	99.24
T, °C	1120	1110	1120	1120	1120	1120	1120	
An	70	84	70	78	58	52	59	

Note: Numbers 1–15 are inclusions in plagioclase, 16 is an average of 17 analyses.

caldera on Iturup Island, southern Kuriles [11], and in acid melts from the Verkhneural'sk mining district, Southern Ural [12]. The S concentration of the basaltic melt from the Karymskii volcanic center is relatively high: from 0.07 to 0.22% at an average of 0.14%.

The  $SiO_2$  concentrations (55.7–67.1%) of glasses in melt inclusions from our andesite samples is generally

9% higher than the analogous values for inclusions in the basalt sample. The andesitic melts are characterized by high concentrations of FeO (9.0–4.1%, average 6.5%) and CaO (5.2% on average) at normal concentrations of Na<sub>2</sub>O (4.5%) and  $K_2O$  (2.1%). The Cl concentration of the melt is significantly higher (0.26% on average), whereas the content of S is much lower (0.07% on average).

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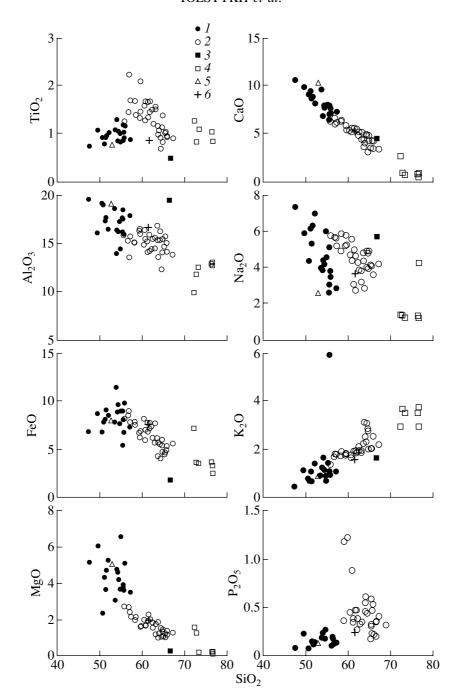


Fig. 2.  $SiO_2$  vs. major element variation plots.

(1, 2) Melt inclusions in phenocrysts from (1) basalt and (2) andesite; (3, 4) groundmass glasses of (3) basalt and (4) andesite; (5, 6) whole-rock compositions of (5) basalt and (6) andesite.

#### DISCUSSION

The most principal problems arising after the analysis of data on melt inclusions in samples from the Karymskii volcanic center can be summarized as follows:

(1) What is the genesis of the Na-enriched mafic melts detected in plagioclase from the basalts?

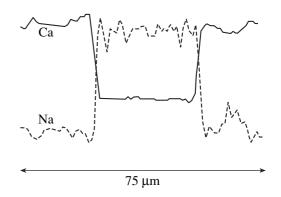
- (2) Are the andesitic melts of Karymskii volcano direct derivatives of basaltic melts?
- (3) What relationships existed between the melts of Karymskii volcano and those of other volcanoes in Kamchatka?
- (1) First of all, it is worth noting that the highest Na<sub>2</sub>O concentrations (7.4–5.3%) were encountered in the least silicic (47.4–52.0% SiO<sub>2</sub>) melts of Karymskii

volcano, and high-Na glasses were detected in calcic plagioclase ( $An_{81-92}$ ). No exchange reactions seem to have proceeded in the mineral–melt system after inclusion entrapment. This follows from microprobe profiles across a number of inclusions (Fig. 3), which reveal equal Ca and Na concentrations over the area of the inclusions and the absence of wide rims around the inclusions.

In addition to high Na concentrations, the basaltic melt is characterized by high Na<sub>2</sub>O/K<sub>2</sub>O ratios of 5.1 on average at K<sub>2</sub>O concentrations corresponding to the medium-K series (Fig. 4a). Equally high Na concentrations and similar Na2O/K2O ratios in melts were encountered earlier in xenoliths from Mongolia and Yemen [13, 14]. Glasses in peridotite xenoliths from alkaline basalts in Mongolia [13] contain 51.8–57.0%  $SiO_2$  and 6.8–10.6%  $Na_2O$ , and their  $Na_2O/K_2O$  ratio ranges from 4.5 to 17.2 at an average of 8.6 (19 analyses). The glasses detected in spinel lherzolites from Yemen [14] bear 50.0–55.8% SiO<sub>2</sub>, 5.9–8.9% Na<sub>2</sub>O<sub>3</sub> and their Na<sub>2</sub>O/K<sub>2</sub>O ratio is 7.5-14.1 at an average value of 9.7 (15 analyses). The genesis of such melts seems to remain problematic. Conceivably, a certain role in it is played by mantle metasomatism under the effect of sodic fluid, which was enriched in mediumincompatible trace elements (where the concentrations of these elements were analyzed, their relative enrichment was noted). When applied to the melts of the Karymskii volcanic center, this conclusion can be verified by analyzing several trace elements.

(2) An ambiguous situation arose during the consideration of the relationships between mafic and intermediate compositions in the products of the 1996 eruption. First, both melts affiliate with the same series of medium-K tholeiites (Fig. 4b). The clear-cut trends with negative correlations in the pairs SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>-FeO, SiO<sub>2</sub>-MgO, SiO<sub>2</sub>-CaO (Fig. 2), and SiO<sub>2</sub>-An (Fig. 5a), as well as the positive  $SiO_2$ – $K_2O$  correlation (Fig. 2), suggest close genetic links between these melts. However, other plots display distinct correlations. For example, the Ti concentration in most inclusions from the andesites is nearly 1.5 times higher than in the mafic glasses. Negative SiO<sub>2</sub>–Na<sub>2</sub>O correlations are atypical (Fig. 2), and the plot apparently has two branches, which characterize the basaltic and andesitic melts. An equally unexpected correlation was determined between CaO and Na<sub>2</sub>O (Fig. 5b). Hence, the genetic relationships between the andesitic and basaltic melts can be elucidated by additional research, primarily, analyses for trace elements.

(3) The comparison between the compositions of melt inclusion from the Karymskii andesites and melt inclusions from Shiveluch and Bezymyannyi volcanoes in Kamchatka (these inclusions were earlier analyzed by the same techniques and on the same equipment [15–17]) further highlights the peculiarity of Karymskii volcano (Fig. 6). The figure demonstrates the com-



**Fig. 3.** Electron microprobe profile across a melt inclusion in plagioclase from basalt (Table 5, analysis 6).

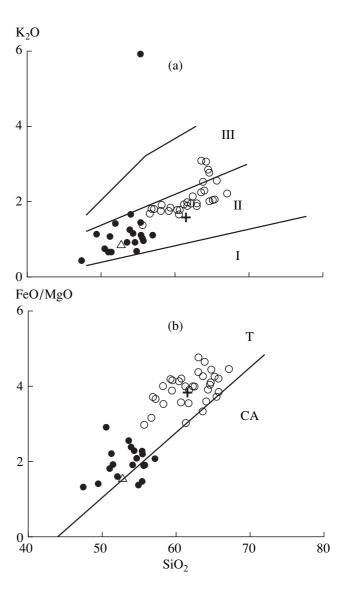


Fig. 4. Classification plots for volcanic series. (a) Based on the  $K_2O$  concentration: I, II, and III are low-medium-, and high-K series, respectively. (b) Based on the FeO/MgO ratio: T is the tholeittic and CA is the calc–alkaline series. See Fig. 2 for symbol explanations.

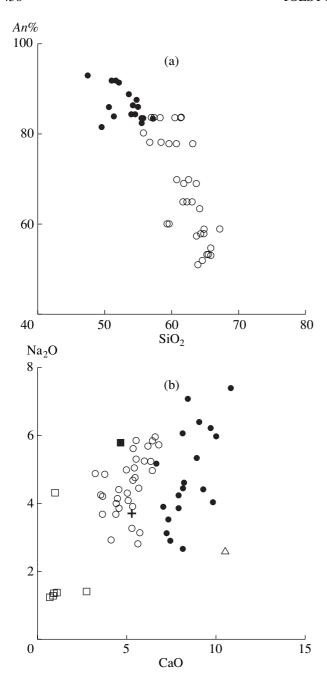


Fig. 5. Diagrams showing correlations between (a) the SiO<sub>2</sub> concentration of melt inclusions and the composition of their host plagioclase and (b) between the CaO and Na<sub>2</sub>O concentrations. See Fig. 2 for symbol explanations.

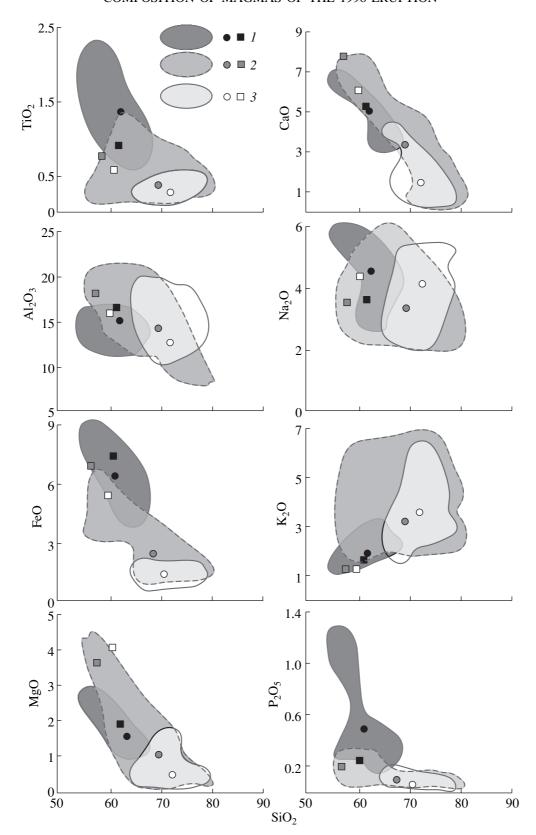
positional fields of melts from the three volcanoes, average values for each field, and the average compositions of the rocks. Apparently, the Karymskii melts are generally less silicic and higher in titanium, iron, magnesium, calcium, and phosphorus. At the same time, their  $Na_2O$  concentrations are commensurable with those of melts from Shiveluch and Bezymyannyi volcanoes, and the  $K_2O$  contents of the Karymskii melts are

much lower than those in melts from the other volcanoes. These data led us to conclude that the andesitic melts of Karymskii volcano are the least differentiated among the melts of the three volcanoes. This is also confirmed by the close spacing between data points for the melt and rock in Fig. 6, whereas the analogous distances for the other two volcanoes are very large.

Karymskii volcano is noted for the fact that its melts and rocks are practically identical in composition (this pertains to both mafic and intermediate rocks), except for the very high sodium concentrations of some melt inclusions in the basalts. The similarities between the compositions of melts and rocks and the absence of acid melts makes Karymskii volcano different from other Kamchatkan volcanoes discussed above. Another distinctive feature of Karymskii is its sodic melts of unusual composition contained in phenocrysts of calcic plagioclase from the basalt. The basaltic and andesitic melts of the Karymskii volcanic center are probably genetically related at the magma chamber level, although it is hardly possible to determine their exact relationships until trace-element concentrations are precisely analyzed in the two melt types.

#### **CONCLUSIONS**

- 1. The compositions of melt inclusions were analyzed in phenocrysts of basalt from the Akademii Nauk caldera (Novogodnii fissure and Karymskii Lake) and andesites of the latest, 1996, eruption of Karymskii volcano, Kamchatka. The basaltic melts (47.4-57.1 wt % SiO<sub>2</sub>, data on 21 inclusion) are characterized by usual concentrations of FeO (11.4–6.8%), MgO (6.1–2.3%), CaO (10.8–6.7%), and  $TiO_2$  (1.3–0.7%) but are significantly enriched in Na<sub>2</sub>O (7.4-2.9% at an average of 5.1%). The highest Na<sub>2</sub>O concentrations (7.4–5.3%) were detected in the least silicic (47.4–52.0% SiO<sub>2</sub>) melts. The  $K_2O$  concentrations range from 0.4 to 1.7%. The andesitic melts (55.7-67.1% SiO<sub>2</sub>, data on 33 inclusions) are characterized by high concentrations of FeO (6.5% on average) and CaO (5.2%) at usual concentrations of  $Na_2O$  (4.5%) and  $K_2O$  (2.1%).
- 2. The melts were analyzed for volatile components. The basaltic melt contains 0.09 wt % Cl and 0.14 wt % S on average, and the analogous values for the andesitic melt are 0.26 wt % Cl and 0.07 wt % S on average.
- 3. The compositions of andesitic melts from Karymskii volcano were compared with the previously studied (by analogous methods) andesitic melts from the volcanoes Shiveluch and Bezymyannyi, Kamchatka. The melts of these volcanoes were determined to be significantly different: the Karymskii melts are less silicic, higher in titanium, iron, magnesium, and calcium but much lower in potassium than the melts of Shiveluch and Bezymyannyi volcanoes. The melts of Karymskii



**Fig. 6.** Comparison between the compositions of rocks (andesites) and melt inclusions from the volcanoes (1) Karymskii, (2) Bezymyannyi, and (3) Shiveluch in Kamchatka.

Fields show the composition of melt inclusions, circles are the average composition of the melt inclusions, and squares present the average composition of the rocks (andesites).

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volcano seem to be less differentiated than the melts of the Bezymyannyi and Shiveluch volcanoes.

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#### **REFERENCES**

- Ivanov, B.V., *Izverzhenie Karymskogo vulkana v 1962–1965 gg. i vulkany Karymskoi gruppy* (The 1962–1965 Eruption of Karymskii Volcano and Other Volcanoes of the Karymskii Group), Moscow: Nauka, 1970.
- 2. Fedotov, S.A., On the 1996 Eruptions in the Akademii Nauk Caldera and Karymskii Volcano, Kamchatka, *Vulkanol. Seismol.*, 1997, no. 5, pp. 3–37.
- 3. Ozerov, A.Yu., Dynamics of the 1996 Eruption of Karymskii Volcano, Kamchatka, and the Composition of Its Products, *Vestn. Dal'nevost. Fil. Akad. Nauk*, 1997, no. 3, pp. 86–93.
- 4. Grib, E.N., Petrology of the January 2–3, 1996, Eruption in the Akademii Nauka Caldera, *Vulkanol. Seismol.*, 1997, no. 5, pp. 71–96.
- Vulkanicheskii tsentr: stroenie, dinamika, veshchestvo (Karymskaya struktura) (Volcanic Centers, Their Inner Structure, Dynamics, and Composition: An Example of the Karymskii Structure), Masurenkov, Yu.P., Ed., Moscow: Nauka, 1980.
- Bakumenko, I.T., Studies of Glassy and Recrystallized Inclusions in Magmatic Minerals, in *Problemy* petrologii i geneticheskoi mineralogii (Problems of Petrology and Genetic Mineralogy), Moscow: Nauka, 1970, vol. 2, pp. 259–272.
- Il'in, A.G. and Krasov, N.F., Crystallization Temperatures of Plagioclase Phenocrysts in Lavas of Karymskii Volcano with Different Gas Concentrations, in *Termobarogeokhimiya i geneticheskaya mineralogiya* (Studies of Inclusions and Genetic Mineralogy), Novosibirsk: Nauka, 1975, pp. 37–46.

- 8. Krasov, N.F., Crystallization of Lavas of the Andesite Association in Kamchatka: Evidence from Melt Inclusions in Minerals, in *Termobarogeokhimiya zemnoi kory i rudoobrazovanie* (Studies of Inclusions in Crustal Rocks and the Genesis of Ore Mineralization), Moscow: Nauka, 1978, pp. 68–72.
- 9. Krasov, N.F. and Clocciatti, P., Liquid Immiscibility in Silicate Melts and Its Possible Petrogenetic Role: Evidence from Melt Inclusions, *Dokl. Akad. Nauk SSSR*, 1979, vol. 248, no. 1, pp. 201–204.
- Naumov, V.B., Studies of Melt Inclusions in Quartz Phenocrysts from Quartz Porphyries, *Geokhimiya*, 1969, no. 4, pp. 494–498.
- 11. Tolstykh, M.L., Naumov, V.B., and Kononkova, N.N., Three Types of Melts Participated in the Formation of the Medvezh'ya Caldera, Iturup Island, South Kuriles, *Geokhimiya*, 1997, no. 4, pp. 391–397.
- Naumov, V.B., Karpukhina, V.S., Baranov, E.N., and Kononkova, N.N., Composition of Melts, Concentrations of Volatile and Trace Components, and Quartz Crystallization Temperatures in Acid Volcanics of the Verkhneural'sk Mining District, South Urals, *Geokhimiya*, 1999, no. 4, pp. 339–351.
- 13. Ionov, D.A., Hofmann, A.W., and Shimizu, N., Metasomatism-Induced Melting in Mantle Xenoliths from Mongolia, *J. Petrol.*, 1994, vol. 35, pp. 753–785.
- 14. Chazot, G., Menzies, M., and Harte, B., Silicate Glasses in Spinel Lherzolites from Yemen: Origin and Chemical Composition, *Chem. Geol.*, 1996, pp. 159–179.
- Tolstykh, M.L., Naumov, V.B., Babanskii, A.D., et al., Melt Composition and Crystallization Conditions of Shiveluch Volcano, Kamchatka: Evidence from Inclusions in Minerals, *Dokl. Ross. Akad. Nauk*, 1998, vol. 359, no. 5, pp. 676–679.
- Tolstykh, M.L., Naumov, V.B., Babanskii, A.D., et al., Chemical Composition, Trace Elements, and Volatile Components in Melt Inclusions in Minerals from Andesites of the Shiveluch Volcano, Kamchatka, Geokhimiya, 2000, vol. 38, suppl. 1, pp. S123–S132.
- 17. Tolstykh, M.L., Naumov, V.B., Bogoyavlenskaya, M.L., and Kononkova, N.N., Andesite–Dacite–Rhyolite Melts during the Crystallization of Phenocrysts in Andesites at Bezymyannyi Volcano, Kamchatka, *Geokhimiya*, 1999, no. 1, pp. 14–24.