ISSN 0869-5911, Petrology, 2008, Vol. 16, No. 1, pp. 1–18. © Pleiades Publishing, Ltd., 2008.
Original Russian Text © V.B. Naumov, M.L. Tolstykh, E.N. Grib, V.L. Leonov, N.N. Kononkova, 2008, published in Petrologiya, 2008, Vol. 16, No. 1, pp. 3–20.

Chemical Composition, Volatile Components, and Trace Elements in Melts of the Karymskii Volcanic Center, Kamchatka, and Golovnina Volcano, Kunashir Island: Evidence from Inclusions in Minerals

V. B. Naumov[a], M. L. Tolstykh[a], E. N. Grib[a], V. L. Leonov[b], and N. N. Kononkova[a]

[a] *Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences, ul. Kosygina 19, Moscow, 119991 Russia*

e-mail: naumov@geokhi.ru

[b] *Institute of Volcanology and Seismology, Far East Division, Russian Academy of Sciences, bul'v. Piipa 9, Petropavlosk-Kamchatskii, 683006 Russia*

e-mail: gen@ksnet.ru

Received October 1, 2006

Abstract—Melt inclusions were examined in phenocrysts in basalt, andesite, dacite, and rhyodacite from the Karymskii volcanic center in Kamchatka and dacite form Golovnina volcano in Kunashir Island, Kuriles. The inclusions were examined by homogenization and by analyzing glasses in more than 80 inclusions on an electron microscope and ion microprobe. The SiO_2 concentrations in the melt inclusions in plagioclase phenocrysts from basalts from the Karymskii volcanic center vary from 47.4 to 57.1 wt %, these values for inclusions in plagioclase phenocrysts from andesites are 55.7–67.1 wt %, in plagioclase phenocrysts from the dacites and rhyodacites are 65.9–73.1 wt %, and those in quartz in the rhyodacites are 72.2–75.7 wt %. The SiO_2 concentrations in melt inclusions in quartz from dacites from Golovnina volcano range from 70.2 to 77.0 wt %. The basaltic melts are characterized by usual concentrations of major components (wt %): TiO_2 = 0.7–1.3, FeO = 6.8–11.4, MgO = 2.3–6.1, CaO = 6.7–10.8, and K_2O = 0.4–1.7; but these rocks are notably enriched in Na_2O (2.9–7.4 wt % at an average of 5.1 wt %, with the highest Na_2O concentration detected in the most basic melts: SiO_2 = 47.4–52.0 wt %. The concentrations of volatiles in the basic melts are 1.6 wt % for H_2O, 0.14 wt % for S, 0.09 wt % for Cl, and 50 ppm for F. The andesite melts are characterized by high concentrations (wt %) of FeO (6.5 on average), CaO (5.2), and Cl (0.26) at usual concentrations of Na_2O (4.5), K_2O (2.1), and S (0.07). High water concentrations were determined in the dacite and rhyodacite melts: from 0.9 to 7.3 wt % (average of 15 analyses equals 4.5 wt %). The Cl concentration in these melts is 0.15 wt %, and those of F and S are 0.06 and 0.01 wt %, respectively. Melt inclusions in quartz from the dacites of Golovnina volcano are also rich in water: they contain from 5.0 to 6.7 wt % (average 5.6 wt %). The comparison of melt compositions from the Karymskii volcanic center and previously studied melts from Bezymyannyi and Shiveluch volcanoes revealed their significant differences. The former are more basic, are enriched in Ti, Fe, Mg, Ca, Na, and P but significantly depleted in K. The melts of the Karymskii volcanic center are most probably less differentiated than the melts of Bezymyannyi and Shiveluch volcanoes. The concentrations of water and 20 trace elements were measured in the glasses of 22 melt inclusions in plagioclase and quartz from our samples. Unusually high values were obtained for Li concentrations (along with high Na concentrations) in the basaltic melts from the Karymskii volcanic center: from 118 to 1750 ppm, whereas the dacite and rhyolite melts contain 25 ppm Li on average. The rhyolite melts of Golovnina volcano are much poorer in Li: 1.4 ppm on average. The melts of the Karymskii volcanic center are characterized by relative minima at Nb and Ti and maxima at B and K, as is typical of arc magmas.

DOI: 10.1134/S0869591108010013

INTRODUCTION

The Karymskii volcanic center in the southwestern flank of the central part of the Eastern Volcanic Belt in Kamchatka has sizes of 55×65 km and is slightly elongated northeastward, along the strike of the volcanic belt. The Karymskii volcanic center has a complicated structure (Fig. 1) and consists of numerous volcanic edifices of differentiated composition and a series of caldera structures, which dynamically evolved starting in the Pliocene (Vlodavets, 1947; Ivanov, 1970; Grib, 1997; Ozerov, 1997; Fedotov, 1997; and others). The development of the calderas (Stena, Sobolinaya, and Polovinka calderas) began in the Middle Pleistocene 180–150 ka BP (*Volcanic Center…*, 1980) and was associated with powerful eruptions of pyroclastic material of intermediate and acid composition ~280 km^3 in volume, which corresponds to ~100 km^3 when recalcu-

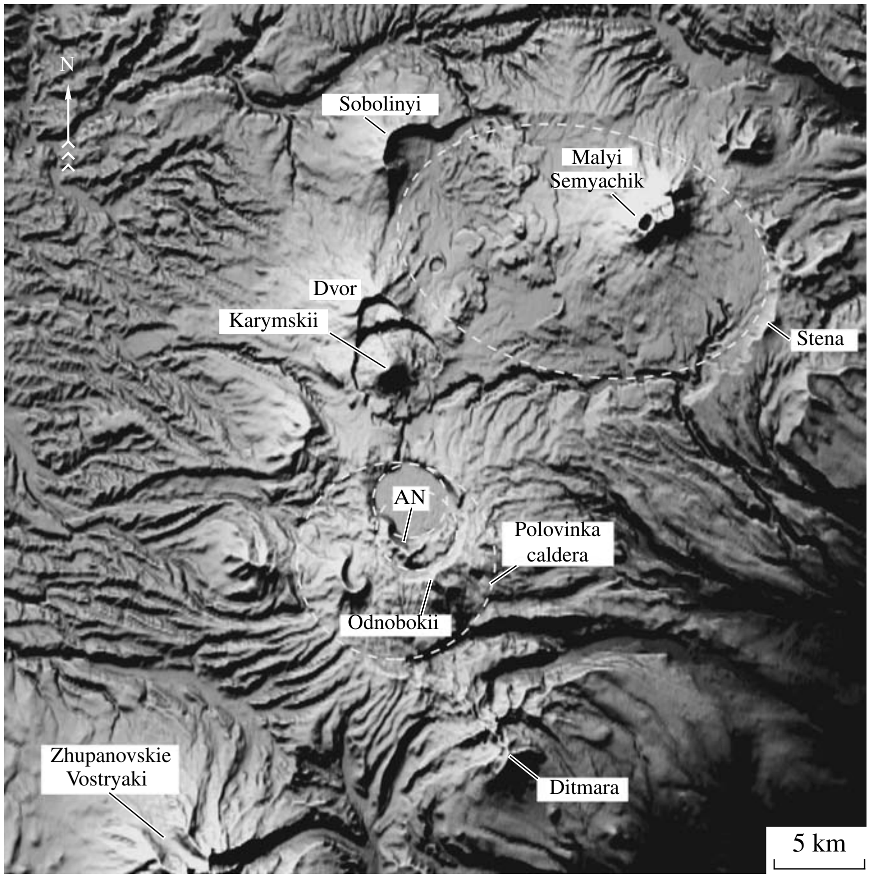

Fig. 1. Satellite image of the central part of the Karymskii volcanic center. Dashed lines outline calderas, AN is the volcano and caldera of Akademii Nauk (the caldera houses Lake Karymskoe). The oval in the northern part of the image outlines the Stena–Sobolinaya caldera system.

lated into magma (Grib and Leonov, 2001a, 2001b). After the origin of the middle Pleistocene calderas, volcanic activity was restricted exclusively to them. During this time span in the initial Late Pleistocene, such volcanoes were formed as Odnobokii, Dvor, Pra-Semyachik, and Pra-Karymskii. Their lavas were of predominantly basalt, basaltic andesite, and andesite composition. The volume of the products erupted during that period was estimated at 80 km^3 (*Volcanic Center…*, 1980). Younger calderas developed later on some of the volcanoes (Odnobokaya and Malyi Semyachik), then new volcanoes (Akademii Nauk and Malyi Semyachik) started to form within these calderas in the Late Pleistocene, and eventually new calderas were produced (Akademii Nauk and Karymskaya). Volcanism in the Late Pleistocene–Holocene produced compositionally more diverse products of various facies types.

The inner structure, tectonics, eruption dynamics, the petrography of the magmatic rocks, and their possible genetic links were discussed in numerous publications. However, data on the chemical composition of the magmatic melts that formed the Karymskii center and on their volatile and trace components are still scarce. However, the genesis of the rocks and more general problems of the regional magmatic history cannot be studied comprehensively enough without this information. Because of this, our research was centered on the detailed study of melt inclusions in minerals from compositionally diverse rocks (from basalts to rhyodacites) to elucidate the chemical composition of the magmatic melts and the possible genetic relations between magmatic rocks of various silicity. The first data of these studies were published in (Tolstykh et al., 2001). In order to compare our results on the chemical composition of melts of the Karymskii volcanic center, we also studied inclusions in quartz crystals from dacites of Golovnina volcano in Kunashir Island.

BRIEF PETROGRAPHIC CHARACTERIZATION OF THE KARYMSKII VOLCANIC CENTER

The Karymskii volcanic center started to attract close attention of researchers after eruptions in it in 1996. These eruptions were characterized by simultaneous activity at two sites, so that the melts simultaneously poured at the surface had an intermediate and basic composition. The eruption process can be subdivided into three stages. During the first of them

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

Component	K-2	K-4	K-63	K-41	K-35	K-31	K-23	K-2a	K-4a	K-63a
SiO_2	52.00	62.45	62.05	64.80	65.41	66.32	69.00	66.59	74.80	75.28
TiO_2	0.73	0.92	0.88	0.72	0.56	0.38	0.43	0.50	1.06	0.83
Al_2O_3	19.21	16.27	16.60	16.00	16.39	14.99	14.35	19.52	12.62	12.46
Fe_2O_3	–	–	–	1.79	2.77	1.19	1.26	–	–	–
FeO	8.30*	6.58*	6.95*	3.45	2.27	2.27	1.94	1.78*	3.59*	3.14*
MnO	0.14	0.15	0.12	0.18	0.16	0.03	0.16	0.06	0.10	0.11
MgO	5.34	2.01	2.00	1.62	0.90	0.94	0.94	0.23	0.18	0.49
CaO	10.47	5.38	5.39	3.90	4.41	3.28	1.76	4.65	0.92	0.94
Na_2O	2.80	4.52	4.08	3.72	4.12	3.91	3.66	5.76	1.88	1.77
K_2O	0.58	1.57	1.58	1.86	1.48	1.98	2.46	1.64	3.50	3.44
P_2O_5	0.14	0.26	0.25	0.03	0.19	0.09	0.06	–	–	–
LOI	–	–	–	2.40	1.48	4.10	3.80	–	–	–
Total	99.71	100.11	99.90	100.47	100.14	99.48	99.82	100.73	98.65	98.46

Note: Here and in Tables 2–5, sample K-2 is basalt of the 1996 eruption, Novogodnii peninsula, Akademii Nauk caldera; samples K-4 and K-63 are andesites from lava flows of the 1996 and 1997 eruption from the summit crater of Karymskii volcano; sample K-41 is dacite from the eastern wall of the Odnobokaya caldera; sample K-35 is tuff of dacitic composition from the western wall of the Polovinka caldera; sample K-31 is pumice of dacitic composition from the left-hand bank of the Karymskaya River eastern wall of the Karymskaya caldera; sample K-23 in pumice of rhyodacitic composition from the eastern slope of Akademii Nauk volcano; and samples K-2a, K-4a, and K-63a are groundmass glasses of the respective samples. * is total iron.

(on January 2–3, 1996), two volcanic centers spaced 6 km apart erupted: the summit crater of Karymskii volcano and the northern segment of Lake Karymskoe, which is the Akademii Nauk caldera (Fedotov, 1997). The main crater was characterized by a continuous ascent of a gas–ash column to a height of 500–1200 m. The dark trail of the ascending column extended southward for up to 50–70 km, and tephra continuously fell from it. At the same time, subaquatic eruptions of basalt occurred in Lake Karymskoe from the eruption center at a distance of 500 m from its shore (Grib, 1997). Powerful discrete phreatomagmatic explosions occurred one after another with time intervals of 10–15 min, and vapor–gas ejecta with ash rose to a height of a few kilometers. The most powerful explosions ejected numerous bombs, and the waves induced in the lake reached a height of 10 m. During the first stage of the eruption, Novogodnii Peninsula (0.7 km^2 in area) was formed in Lake Karymskoe.

The second stage of the eruption on January 4–12, 1996, was characterized by eruptive activity only at the summit crater of Karymskii volcano, with a much lower frequency of the explosions. The height of the ejecta was 500–900 m, and ash trails extended for 50–60 km, mostly in the western and eastern directions. During the third stage (from January 13, 1996, until present), a series of lava flows was erupted from the main crater of Karymskii volcano. The length of the thickest of them reached 1.5 km, and the height of its frontal part was 25 m. The lava eruptions were associated with explosions. The vapor–gas ejecta loaded with ash rose to heights from 100 to 500–600 m and produced eruption clouds. During the most powerful explosions (250 m and more), their lower parts persistently included bombs 1–2 m in diameter, occasionally up to 4–5 m (Ozerov, 1997).

We examined three samples selected from among products of the 1996–1997 eruption, whose composition is reported in Table 1. The first sample (K-2) is a basaltic volcanic bomb from Novogodnii Peninsula. It is a black porous vitreous rock with numerous plagioclase phenocrysts 0.3–3 mm in size. The composition of the phenocrysts varies from $An_{94–80}$ in cores to $An_{75–62}$ in marginal parts. The composition of plagioclase with abundant melt inclusions is shown in Table 2. The olivine ($Fo_{83–72}$) and pyroxenes (orthopyroxene and clinopyroxene, Table 3) occur more rarely. The accessory minerals of the basalt are apatite and an ore mineral. The former was found as crystalline inclusions and the latter as both crystalline inclusions and microlites (Table 4).

The other two samples (K-4 and K-63, Tables 1–4) are andesite from lava flows from the summit crater of Karymskii volcano. The samples were taken in a hot state on September 22, 1996, and August 19, 1997, respectively. These are weakly porous dark gray rocks with 30–35 vol % phenocrysts. Their major rock-forming mineral is plagioclase, which accounts for ~85% of

Table 2. Representative analyses (w%) of plagioclase in rocks from the Karymskii volcanic center

Component	K-41	K-2	K-2	K-4	K-63	K-41	K-41	K-31	K-23	K-35
SiO_2	45.00	44.79	47.64	47.58	52.85	53.39	57.66	58.26	60.40	62.15
Al_2O_3	33.02	34.35	33.66	31.65	30.47	28.03	24.99	24.74	23.54	21.59
FeO	0.55	0.62	0.59	0.75	0.66	0.40	0.35	0.44	0.33	0.07
CaO	19.29	18.09	17.10	17.41	14.51	13.13	9.92	9.65	7.36	5.31
Na_2O	0.82	0.99	1.56	2.65	3.36	4.25	6.15	5.83	7.42	8.22
K_2O	0.01	0.03	0.01	0.08	0.11	0.10	0.20	0.25	0.36	0.93
Total	98.69	98.87	100.56	100.12	98.04	99.30	99.27	99.17	99.41	98.27
An	92.7	90.8	85.8	78.1	70.0	62.7	46.6	47.1	34.7	24.5
Ab	7.2	9.0	14.1	21.5	29.4	36.7	52.3	51.5	63.3	69.9
Or	0.1	0.2	0.1	0.4	0.6	0.6	1.1	1.4	2.0	5.2

Table 3. Representative analyses (w%) of pyroxenes in rocks from the Karymskii volcanic center

Component	K-2	K-63	K-63	K-4	K-41	K-41	K-35	K-35	K-23	K-31
SiO_2	53.58	52.35	52.08	50.76	53.63	52.53	51.97	52.97	53.12	52.48
TiO_2	0.49	0.34	0.53	0.63	0.21	0.16	0.10	0.13	0.10	0.26
Al_2O_3	1.33	1.11	1.54	1.88	1.26	0.87	0.35	0.74	0.40	0.89
FeO	19.55	20.37	10.94	10.40	19.41	11.63	21.39	8.96	22.95	10.62
MnO	0.44	0.71	0.49	0.49	0.59	0.44	1.49	0.58	1.48	0.40
MgO	20.80	23.24	14.75	13.89	23.74	13.63	22.92	14.11	21.30	13.83
CaO	2.24	1.92	19.78	20.98	1.69	20.36	1.11	21.88	1.02	20.44
Na_2O	0.13	0.00	0.35	0.31	0.00	0.20	0.00	0.15	0.00	0.29
Total	98.56	100.04	100.46	99.34	100.53	99.82	99.33	99.52	100.37	99.21
Fs	32.9	31.7	17.5	16.8	30.4	18.8	33.6	14.4	36.9	17.3
En	62.3	64.5	42.0	39.9	66.2	39.2	64.2	40.5	61.0	40.1
Wo	4.8	3.8	40.5	43.3	3.4	42.0	2.2	45.1	2.1	42.6

Table 4. Representative analyses (w%) of ore minerals in rocks from the Karymskii volcanic center

Component	K-2	K-63	K-4	K-4	K-41	K-41	K-35	K-31	K-31	K-23
FeO	52.25	78.09	78.05	92.90	52.04	85.63	55.31	55.52	86.26	85.60
TiO_2	40.13	11.80	12.87	3.17	43.61	10.15	40.72	40.52	9.25	8.89
Al_2O_3	0.43	3.26	3.35	1.30	0.43	2.14	0.05	0.33	1.59	1.54
MnO	0.29	0.45	0.42	0.45	0.70	0.48	0.74	0.09	0.04	0.61
MgO	3.18	2.69	1.91	1.11	2.86	1.69	2.10	1.86	1.40	0.58
CaO	0.04	0.13	0.06	0.06	–	–	–	–	–	–
SiO_2	0.03	0.18	0.06	0.19	–	–	–	–	–	–
Total	96.35	96.60	96.72	99.18	99.64	100.09	98.92	98.32	98.55	97.22

all phenocrysts. The plagioclase occurs as grains of various sizes, with none of them (even large phenocrysts) showing resorption zones. The composition of the plagioclase ranges from An_{85} to An_{52}. The mafic minerals are orthopyroxene, clinopyroxene, and rare olivine, which displays reaction relations with the pyroxenes. The groundmass consists of glass and microlites of plagioclase, pyroxene, and an ore mineral.

Karymskii volcano is spatially restricted to the central part of the Karymskii caldera, which was produced by a catastrophic explosive eruption of Pra-Karymskii volcano at 7600–7700 years BP (*Volcanic Center…*, 1980). The pyroclastic deposits related to its origin consist of pumice tuffs of dacite composition (sample K-31, Tables 1–4). Pumice fragments of beige color have psephitic to agglomerated sizes, are submerged in fine-grained material, and sometimes compose strata with numerous pumice lapilli. The other samples examined in the course of this research were from pyroclastic deposits form the southern sector of the Karymskii volcanic center consisting of three calderas telescopically nested in one another. The Polovinka caldera is the oldest. The bulk of its pyroclastic deposits (close to 42 km^3) consists of agglomerated ash–pumice tuffs of rhyodacite and dacite composition (sample K-35, Tables 1–4). Later, Odnobokii volcano was formed in the Polovinka caldera, and the lavas of this volcano completely filled the caldera. The evolutionary history of the volcano involved two episodes of catastrophic explosive eruptions with a period of volcanic activity in between. These process formed the Odnobokaya caldera at 110–80 ka (*Volcanic Center…*, 1980; Grib and Leonov, 2004a, 2004b). The pyroclastic flows consist mostly of ash–pumice tuffs and are zonal, with their composition systematically varying from rhyodacite in the bottom of the flows to dacite in their upper parts. The pumice tuffs (sample K-41, Tables 1–4) consist of angular pumice fragments of psephitic and agglomerate size submerged in finer grained material. The pumices are dense, finely porous and have beige or gray color. They contain 10–20 vol % crystalline phase.

In the Late Pleistocene, Akademii Nauk volcano was formed near the southern boundary of the Odnobokaya caldera. The pyroclastic deposits of an explosive eruption of this volcano consist of agglomerate pumice tuffs of rhyodacite composition (sample K-23, Tables 1–4) and cover the southern slopes of the volcano. The tuffs are white, their pumice fragments are no larger than 5–10 cm, and their porosity is approximately 30–50%. The upper portions of the stratigraphic sequences are rewashed, which suggests that the tuffs were deposited in a lake. There is still no consensus about the genesis of the Akademii Nauk caldera in its modern form because it does not contain significant volumes of pyroclastic deposits related to its origin. It is thought that the caldera was formed in the Late Pleistocene–Early Holocene as a consequence of basaltic eruption in the zone of the submeridional fault in the northern part of Lake Karymskoe. This eruption was similar to the event in 1996. Basalt injections into the bottom part of the upper crustal chamber resulted in the mobilization of acid melt in it and a nearly synchronous eruption at Akademii Nauk volcano, its destruction, and the collapse of the walls of the already existing Odnobokaya caldera. The thorough investigation of the pyroclastic deposits related to calderas in the southern sector of the Karymskii volcanic center has demonstrated that basaltic tephra strata (sometimes in association with weakly compacted tuffs) are quite common in them starting in the terminal Middle Pleistocene deposits. This suggests that the events analogous to the 1996 eruption also occurred in this area previously (Grib and Leonov, 2004a, 2004b). The basaltic tephra of the Late Pleistocene and Holocene eruptions composes terraces along the northern shore of Lake Karymskoe that fills the Akademii Nauk caldera.

Phenocrysts in the pyroclastic deposits are plagioclase, orthopyroxene, clinopyroxene, and ore minerals, whose compositions often reflect the unequilibrated state of the melt during its crystallization. The early products in each caldera contain hornblende, and the earliest agglomerated tuffs of the Polovinka caldera contain quartz and biotite. A distinctive feature of the pyroclastic deposits of the Odnobokaya caldera is the presence of holocrystalline clusters (perhaps, cumulates). The pumice agglomerated tuffs of the first stage contain these clusters composed of plagioclase, clinopyroxene, and titanomagnetite that form poikilophitic intergrowth textures. This association sometimes also contains high-Al hornblende. The second-stage tuffs and ignimbrites typically contain olivine–anorthite nodules and their crystalline fragments, which are very unevenly distributed in the rocks. The agglomerated tuffs of andesite composition bear olivine microphenocrysts with skeletal growth structures.

Plagioclase dominates in all types of the pyroclastic deposits. Its phenocrysts range from 0.6 to 1.5 mm in size and occasionally reach 2–3 mm. The composition of the plagioclase is determined mostly by the composition of the pyroclastic deposits. For example, the rhyodacite pumice tuffs are dominated by oligoclase–andesine ($An_{28–42}$), and the predominant plagioclase of the dacitic tuffs is andesine ($An_{42–52}$). Some of the phenocrysts contain corroded calcic cores ($An_{52–55}$, more rarely $An_{75–85}$). The plagioclase contains melt inclusions, apatite, and, more rarely, magnetite and ilmenite. The holocrystalline aggregates are dominated by bytownite–anorthite ($An_{68–94}$). The basaltic tephra contains plagioclase phenocryst of bytownite composition ($An_{85–90}$) with crystalline inclusions of clinopyroxene and melt inclusions. The marginal zones of these plagioclase grains are characterized by a progressive decrease in the anorthite concentration and corresponds to $An_{68–66}$.

The mafic minerals of all of the pyroclastic deposits are dominated by orthopyroxene and clinopyroxene. They were found in the form of phenocrysts (0.6–

1.5 mm), microphenocrysts (100–300 μm), as polymineralic aggregates, and, more rarely, as crystalline inclusions in other minerals. The pyroxenes contain crystalline inclusions of magnetite, ilmenite, apatite, and rare plagioclase, along with melt inclusions. Amphibole occurs in the early products of each caldera in the southern sector of the Karymskii volcanic center. These minerals occur as black elongated columnar crystals from 1.5 to 2.5 mm long. The crystals are euhedral and are not altered. Hornblende in the rhyodacite pumice deposits of the Odnobokaya caldera and Akademii Nauk volcano are compositionally similar and correspond to moderately aluminous (6.0–8.0 wt % Al_2O_3) ordinary hornblende. The phenocrysts contain crystalline inclusions of titanomagnetite, ilmenite, apatite, and occasional plagioclase ($An_{42–48}$), as well as melt inclusions. The pumice tuffs of the Odnobokaya caldera sometimes contain aluminous amphibole (9–11, occasionally up to 12–13 wt % Al_2O_3). Biotite is the only mafic mineral in the most evolved rocks, namely, in the tuffs and ignimbrites ejected early during the development of the Polovinka caldera.

The ore minerals are titanomagnetite and ilmenite, whose contents vary from a few fractions of a percent to 1.5–2.0%. Their contents are the lowest in the pyroclastics of rhyodacite composition and are much higher in the dacitic rocks. They occur as crystalline inclusions in pyroxene and amphibole phenocrysts (and, more rarely, also in plagioclase and quartz) and as polymineralic aggregates. The sizes of the phenocrysts vary from 100 to 300 μm, and those of the crystalline inclusions are from a few micrometers to 100–150 μm.

In addition to the samples listed in Table 1, we also studied large quartz crystals from a buried pyroclastic flow found at the western wall of the complex of southern calderas of the Karymskii volcanic center. In an artificial exposure in a pyroclastic flow related to the Polovinka caldera, these deposits include a buried layer of coarse-grained sand, which is, in turn, overlain by younger ignimbrite. The quartz and plagioclase crystal-lapilli from this layer are 2–3 mm in size, and melt inclusions in them can be discerned even under a binocular magnifier.

As was mentioned above, for comparison we also examined melt inclusions in quartz crystals from Golovnina volcano. This volcano is situated in the southern part of Kunashir Island and has a caldera and central extrusion dome of Holocene age (Gorshkov, 1967; Frolova et al., 1985). The dacites of this volcano are porphyritic and contain phenocrysts of plagioclase ($An_{72–43}$) and orthopyroxene and large quartz crystals.

INCLUSIONS IN MINERALS

Melt inclusions were prepared for studying and analyzed on a Camebax Microbeam microprobe using the technique that we previously applied to study andesites from some volcanoes in the Kuriles and Kamchatka (Tolstykh et al., 2003) and trachybasalts from eastern Tuva volcanic highland (Naumov et al., 2003). The concentrations of H_2O, F, and trace elements in the melt inclusions were determined by secondary-ion mass spectrometry on an IMS-4f ion microprobe at the Institute of Microelectronics, Russian Academy of Sciences, in Yaroslavl by the method described in detail in (Sobolev, 1996; Nosova et al., 2002; Portnyagin et al., 2002).

We have examined more than 70 melt inclusions in plagioclase and quartz from various rocks of the Karymskii volcanic center and a few inclusions in quartz from dacites of Golovnina volcano. Our data on the chemical composition of the glasses of the melt inclusions are presented in Tables 5–7. The SiO_2 concentrations in inclusions in plagioclase phenocrysts from basalt from the Karymskii volcanic center vary from 47.4 to 57.1 wt %, inclusions in plagioclase phenocrysts from the andesites contain 55.7–67.1 wt % SiO_2, inclusions in plagioclase phenocrysts from the dacites and rhyodacites contain 66.1–72.5 wt % SiO_2 (Table 5), and quartz phenocrysts from the rhyodacites contain inclusions with 72.2–75.7 wt % SiO_2 (Table 7). The SiO_2 contents in quartz from the dacites of Golovnina volcano vary from 70.2 to 77.0 wt % (Table 7).

The basaltic melts (Table 5) contain usual concentrations (wt %) of TiO_2 (0.7–1.3), FeO (6.8–11.4), MgO (2.3–6.1), and CaO (6.7–10.8) but are significantly enriched in Na_2O (2.9–7.4 wt % at an average of 5.1%), with the highest Na_2O concentrations detected in the most basic melts (SiO_2 = 47.4–52.0 wt %). The K_2O concentrations range from 0.4 to 1.7 wt %. The only exception was one melt inclusion that contained much more K_2O (5.95 wt %) than Na_2O (2.64 wt %). Note that this K_2O-rich inclusion contains very little Cl (0.01 wt %), whereas the other 19 inclusions in sample K-2 are much richer in Cl (0.06–0.12 wt % at an average of 0.09 wt %). This feature of potassic melts in terms of Cl concentration was noted earlier in the melts of volcanics from the Medvezh'ya caldera in Iturup Island, southern Kuriles (Tolstykh et al., 1997) and in acid melts of the Verkhneuralsk mining districts in the Southern Urals (Naumov et al., 1999). The S concentrations in the basaltic melts are also relatively high (0.07–0.22 wt %, 0.14 wt % on average, in 17 inclusions). Two inclusions were determined to contain as much as 0.7 and 2.4 wt % H_2O (Table 6).

The SiO_2 concentrations in the glasses of melt inclusions in the andesite sample vary from 55.7 to 67.1 wt %, i.e., is 9 wt % on average higher than in the glasses in melt inclusions in the basalt sample (Table 5). The melts in plagioclase from the andesite are characterized by high concentrations of FeO (9.0–4.1 wt %, 6.5 wt % on average) and CaO (5.2 wt % on average) at usual concentrations of Na_2O (4.5 wt %) and K_2O (2.1 wt %). The Cl concentration in the andesite melt is much higher than in the basalt melt (up to

Table 5. Chemical composition (wt %) of glasses in melt inclusions in plagioclase from rocks from the Karymskii volcanic center

Inclusion no.	Component												Total	T, °C	An
	SiO_2	TiO_2	Al_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	Cl	S			
Sample K-2															
1	47.44	0.73	19.67	6.83	0.13	5.19	10.82	7.40	0.44	0.09	0.07	0.14	98.95	1140	93
2	49.47	1.08	16.09	8.66	0.12	6.10	10.00	5.96	1.13	0.24	0.12	0.19	99.16	1140	81
3	50.71	0.99	18.93	8.01	0.19	3.20	9.93	4.64	0.73	0.25	0.07	0.13	97.79	20	88
4	50.92	1.05	15.69	8.77	0.22	4.95	9.08	6.90	1.24	0.18	0.10	0.16	99.26	20	84
5	50.98	0.79	19.05	7.86	0.16	4.30	9.69	6.21	0.66	0.15	0.10	0.16	100.11	1120	89
6	51.27	0.91	17.36	8.12	0.22	3.65	8.90	5.33	1.07	0.16	0.06	0.15	97.20	1140	84
7	51.47	0.95	17.76	9.03	0.21	4.70	9.05	6.38	0.66	0.16	0.08	0.10	100.55	1120	92
8	51.84	0.87	19.83	7.24	0.13	3.75	9.28	5.91	0.74	0.16	0.07	–	99.82	1100	85
9	52.04	1.02	16.45	8.45	0.12	5.26	8.38	7.07	1.40	–	–	0.22	100.41	1130	91
10	53.55	1.08	18.71	7.83	0.23	3.06	9.82	4.02	0.92	0.19	0.09	0.19	99.69	1100	89
11	53.87	1.01	18.35	7.71	0.14	3.55	7.61	5.56	0.94	0.22	0.09	–	99.09	1100	88
12	53.90	1.30	13.93	11.39	0.23	4.76	7.03	3.88	1.25	0.24	0.11	0.11	98.13	20	84
13	54.11	0.85	16.42	8.90	0.21	4.63	8.16	4.43	1.66	0.14	0.07	0.17	99.58	1120	86
14	54.68	1.00	17.30	7.70	0.15	3.68	8.12	6.05	0.91	0.13	0.08	0.14	99.94	1140	87
15	54.87	0.83	14.41	8.98	0.14	6.59	8.21	4.60	0.68	0.24	0.09	0.10	99.74	1140	86
16	55.44	1.19	16.23	8.96	0.15	3.92	6.66	5.15	1.44	0.19	0.11	0.15	99.59	1100	83
17	55.44	0.86	17.67	5.45	0.09	3.72	8.15	2.64	5.95	0.11	0.01	0.03	100.12	1140	82
18	55.47	1.03	17.62	8.08	0.21	3.63	7.24	3.09	1.11	0.17	0.11	–	97.76	20	83
19	55.62	0.91	18.59	6.85	0.16	3.61	7.90	4.84	1.04	0.21	0.09	0.10	99.92	1120	83
20	57.14	0.88	17.97	7.29	0.17	3.50	7.46	2.87	1.10	0.15	0.11	0.10	98.74	1120	83
Sample K-63															
21	56.89	2.25	13.60	8.98	0.26	2.43	6.17	5.66	1.80	–	0.38	0.12	98.54	1110	84
22	57.26	1.71	15.76	7.82	0.26	2.15	6.33	5.22	1.79	1.16	0.30	0.15	99.91	1110	84
23	58.21	1.70	15.15	7.84	0.20	1.97	6.44	4.95	1.74	1.23	0.30	0.13	99.86	1110	84
24	59.26	1.33	16.34	6.73	0.23	1.62	6.00	5.22	1.75	0.89	0.29	0.06	99.72	1110	60
25	59.45	1.47	16.58	6.29	0.18	1.63	5.53	5.83	1.84	0.36	0.29	0.05	99.50	1120	78
26	59.55	2.11	16.03	6.89	0.25	1.67	5.52	5.28	1.81	0.46	0.29	0.09	99.95	1110	60
27	60.39	1.60	14.86	8.16	0.23	1.99	5.47	4.74	1.77	0.28	0.30	0.13	99.92	1110	84
28	60.64	1.29	16.42	5.94	0.15	1.67	5.35	5.60	1.67	0.39	0.25	0.07	99.44	1120	78
29	60.71	1.69	15.48	7.02	0.24	1.68	5.68	4.42	1.77	0.59	0.33	0.06	99.67	1120	70
30	61.30	1.35	14.12	6.87	0.26	2.27	5.40	5.02	1.89	1.16	0.33	0.09	100.06	1110	84
31	62.45	1.22	15.49	6.23	0.21	1.57	5.32	3.88	2.12	0.46	0.29	0.06	99.30	1120	70
32	63.02	1.58	15.62	5.70	0.25	1.20	4.57	3.84	1.94	0.45	0.21	–	98.38	1120	78
33	63.64	0.98	16.88	4.31	0.16	1.02	3.77	4.84	3.10	0.59	0.31	0.07	99.67	1120	58
34	64.57	1.14	12.30	5.45	0.20	1.36	3.23	4.86	2.85	0.47	0.21	0.04	96.68	1120	52
35	67.10	0.90	13.85	5.66	0.21	1.28	3.55	4.22	2.21	0.33	0.20	0.08	99.59	1120	59
Sample K-4															
36	55.70	1.27	15.87	8.15	0.14	2.74	6.45	5.82	1.37	0.32	0.27	0.10	98.20	1100	80
37	56.67	1.47	15.36	8.54	0.46	2.70	6.81	5.71	1.68	0.36	0.26	0.07	100.09	1100	78
38	58.33	1.40	15.09	7.54	0.21	2.15	6.60	5.94	1.89	0.45	0.35	0.09	100.04	1100	78
39	61.68	1.47	14.20	7.75	0.21	2.00	5.34	4.65	1.96	0.33	0.26	0.06	99.91	1110	65
40	62.26	1.52	14.44	7.41	0.24	1.87	5.02	4.29	1.93	0.36	0.28	0.05	99.67	1110	65

Table 5. (Contd.)

Inclusion no.	Component												Total	T, °C	An
	SiO_2	TiO_2	Al_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	Cl	S			
41	63.01	1.52	14.48	7.69	0.22	1.77	5.30	3.24	1.88	0.45	0.26	0.08	99.90	1110	69
42	64.13	0.92	15.38	5.60	0.17	1.57	5.07	4.06	2.29	0.32	0.21	0.08	99.80	1110	64
43	64.30	0.69	16.30	4.08	0.12	1.05	4.97	4.96	3.07	0.18	0.14	0.07	99.93	1110	58
44	64.70	1.39	14.06	6.03	0.20	1.48	4.40	3.98	2.77	0.53	0.19	0.06	99.79	1110	58
45	64.73	0.83	15.46	4.72	0.14	1.07	4.97	4.96	2.00	0.22	0.15	0.07	99.32	1110	59
46	65.21	1.02	14.64	4.48	0.20	1.06	3.66	4.18	2.03	0.24	0.17	0.08	96.97	1100	53
47	65.46	1.04	15.70	4.65	0.11	1.26	4.47	4.12	2.05	0.36	0.18	0.08	99.48	1100	53
48	65.75	0.94	14.13	4.93	0.18	1.18	3.62	3.65	2.54	0.37	0.16	0.06	97.51	1100	55
49	65.78	0.96	15.05	5.33	0.20	1.39	4.39	3.65	2.55	0.41	0.15	0.07	99.93	1100	53
Sample K-41															
50	47.27	0.67	18.93	6.34	0.16	5.56	10.56	7.07	0.25	0.15	0.04	0.09	97.09	1150	93
51	50.69	0.74	16.42	7.99	0.15	5.80	9.22	6.62	0.47	0.11	0.03	0.12	98.36	1150	93
52	65.93	0.37	13.77	2.02	0.12	0.63	2.29	3.64	2.55	0.09	0.17	0.01	91.59	20	49
53	66.05	0.40	13.80	2.21	0.00	0.59	2.10	4.54	2.40	0.12	0.19	0.01	92.41	20	47
54	66.76	0.32	13.89	2.31	0.11	0.64	2.23	4.40	2.46	0.00	0.15	0.00	93.27	20	63
55	68.24	0.46	14.00	2.59	0.14	0.66	2.26	4.20	2.56	0.06	0.19	0.01	95.37	20	63
56	68.32	0.21	13.93	2.32	0.11	0.64	2.15	4.48	2.46	0.08	0.19	0.01	94.90	20	47
57	69.95	0.47	13.73	2.94	0.03	0.89	2.23	4.44	2.47	0.10	0.19	0.02	97.46	20	63
Sample K-35															
58	71.76	0.21	13.16	0.94	0.03	0.27	0.83	4.97	3.32	0.00	0.20	0.01	95.70	1150	25
Sample K-31															
59	70.78	0.23	12.25	1.59	0.08	0.31	1.49	4.18	3.33	0.06	0.22	0.01	94.53	20	43
60	71.74	0.30	12.45	1.58	0.06	0.37	1.40	4.25	3.43	0.09	0.24	0.01	95.92	20	43
61	71.85	0.29	12.36	1.38	0.06	0.26	1.25	4.21	3.15	0.03	0.17	0.00	95.01	20	43
62	72.09	0.35	12.48	1.57	0.03	0.33	1.41	2.99	3.26	0.01	0.19	0.01	94.72	20	47
63	72.13	0.32	11.67	1.44	0.08	0.30	1.28	3.89	3.19	0.01	0.19	0.00	94.50	20	41
64	72.18	0.28	12.42	1.67	0.01	0.34	1.30	3.80	3.29	0.02	0.18	0.02	95.51	20	41
65	72.35	0.27	12.09	1.39	0.10	0.25	1.27	3.86	3.26	0.04	0.16	0.00	95.04	20	41
Sample K-23															
66	72.42	0.18	12.40	1.16	0.07	0.24	1.20	3.60	3.06	0.01	0.20	0.01	94.55	20	35
67	72.54	0.18	11.93	1.13	0.00	0.21	1.20	3.63	3.05	0.00	0.20	0.02	94.09	20	35
68	73.09	0.28	12.50	1.20	0.09	0.27	1.28	2.80	2.91	0.06	0.19	0.01	94.68	20	35

0.26 wt % on average), and the S concentration is lower (up to 0.07 wt % on average).

The glasses of melt inclusions in plagioclase ($An_{63–25}$) from the dacite and rhyodacite samples are characterized by usual concentrations (wt %) of SiO_2 (65.9–73.1), FeO (1.1–2.9), MgO (0.2–0.9), Na_2O (2.8–5.0), and K_2O (2.4–3.4). The Cl concentration of these melts is as high (0.19 wt % on average) as in the andesite melts, but the S concentration is much lower: 0.01 wt %. Ion microprobe analyses of nine melt inclusions allowed us to determine the water concentrations during the crystallization of the plagioclase (Table 6). These concentrations turned out to be very high: from 3.1 to 7.3 wt % at an average of 5.5 wt %. It should be noted that dacite sample K-41 contained a plagioclase

Table 6. Concentrations of water (wt %) and trace elements (ppm) in melt inclusions in plagioclase from rocks from the Karymskii volcanic center, Kamchatka

Component	Inclusion no. in Table 5											
	50	3	4	53	54	56	60	61	62	65	67	58
H_2O	0.69	2.44	–	7.27	4.64	4.97	5.14	5.87	3.12	4.96	6.65	4.75
Li	1750	284	118	25.2	22.3	23.2	14.8	14.6	16.0	15.8	22.2	73.7
Be	0.19	0.69	0.56	1.07	1.25	1.34	1.13	1.18	0.95	1.04	1.11	0.95
B	5.98	7.90	6.32	36.0	26.9	14.9	32.6	32.7	32.0	35.1	41.6	58.4
F	6.79	142	6.32	533	508	814	801	569	948	587	324	14.0
Cr	–	36.3	70.6	–	–	–	–	–	–	–	–	0.81
Rb	–	12.0	30.0	–	–	–	–	–	–	–	–	91.8
Sr	531	418	449	255	285	363	107	105	188	102	107	57.2
Y	8.90	15.2	19.3	19.8	16.1	9.19	18.6	21.5	22.4	22.9	16.9	8.15
Zr	17.5	55.9	64.1	134	107	58.2	183	177	204	209	140	57.2
Nb	0.42	1.88	1.87	2.89	2.53	1.46	4.05	4.31	6.30	4.96	3.71	3.69
Ba	88.1	187	236	413	481	461	629	629	734	685	606	1070
La	1.81	4.88	7.17	8.19	8.07	7.44	10.8	11.3	12.8	11.6	10.3	12.4
Ce	3.35	12.8	17.7	23.8	20.1	24.0	27.6	28.6	29.8	30.2	24.0	21.5
Nd	4.28	8.87	13.0	10.9	10.0	7.08	12.2	13.1	14.4	13.4	10.6	7.54
Sm	0.87	2.37	3.41	3.52	2.56	2.57	3.11	3.50	3.42	3.78	2.71	1.32
Eu	0.42	0.86	1.27	0.57	0.91	0.72	0.68	0.99	0.70	0.72	0.76	0.31
Gd	1.13	2.84	3.35	3.80	2.51	2.99	2.24	4.41	3.17	3.77	2.51	0.64
Dy	1.15	2.53	3.56	3.76	2.71	2.70	2.85	3.63	3.36	4.15	2.52	1.24
Er	0.77	1.83	2.59	2.87	2.08	2.09	2.17	2.68	2.61	3.08	2.00	1.04
Yb	0.79	2.03	2.35	2.86	2.00	1.80	2.62	2.97	2.72	3.32	2.26	1.25
Hf	–	1.69	2.17	–	–	–	–	–	–	–	–	1.78
Th	0.14	0.90	0.59	1.63	1.42	0.80	2.32	2.11	2.42	2.44	2.76	3.76
U	0.05	0.47	0.36	1.11	0.85	0.54	1.52	1.49	1.78	1.88	1.66	2.17
Th/U	2.80	1.91	1.64	1.47	1.67	1.48	1.53	1.42	1.36	1.30	1.66	1.73
La/Yb	2.29	2.40	3.05	2.86	4.04	4.13	4.12	3.80	4.71	3.49	4.56	9.92

phenocryst (An_{93}) with melt inclusions of composition analogous to those of inclusions in basalt sample K-2. They were also determined (Table 5) to bear high concentrations (wt %) of Na_2O (6.6–7.1), MgO (5.6–5.8), and FeO (6.3–8.0) at low concentrations of K_2O (0.2–0.5). It is pertinent to recall that sample K-2 is basalt erupted in 1996 at Novogodnii peninsula in the Akademii Nauk caldera, and sample K-41 was taken from the eastern wall of the Odnobokaya caldera (Fig. 1).

The SiO_2 contents in the glasses of melt inclusions in quartz from the buried pyroclastic flow (Table 7) are even lower: from 72.2 to 75.7 wt %. These acid melts bear usual concentrations (wt %) of TiO_2 (0.09–0.31), FeO (0.5–1.3), MgO (0.06–0.27), CaO (0.6–1.2), Na_2O (3.3–4.0), K_2O (2.8–4.1), and Cl (0.10–0.15). The water concentration in the melt varied from 0.9 to 4.9 wt % (at an average of 3.3 wt % of six analyses).

In order to compare them with the compositions of acid melts from the Karymskii volcanic center, we examined melt inclusions in quartz from dacite from Golovnina volcano. These inclusions (Fig. 2) are large, up to 100–140 μm and are either partly recrystallized (Figs. 2a, 2b) or contain only glass and small gas bubbles (Fig. 2c). The complete homogenization temperatures of these inclusions are 820–850°C, and the inclusions usually homogenized for no more than 5–10 min. The melts heterogenized with the separation of numerous gas bubbles (Fig. 2d) at temperatures of 700–780°C for 15–30 s, which testifies that the melt has a low vis-

Table 7. Chemical composition (wt %) of melt inclusions in (1–6) quartz from a buried pyroclastic flow in the Karymskii volcanic center, Kamchatka, and (7–10) quartz in dacites from Golovnina volcano, Kunashir Island

Component	1	2	3	4	5	6	7	8	9	10
SiO_2	72.15	72.83	73.28	74.02	74.91	75.67	70.18	72.12	74.05	77.02
TiO_2	0.24	0.11	0.12	0.09	0.31	0.11	0.24	0.19	0.16	0.16
Al_2O_3	12.82	12.51	12.98	12.44	12.95	12.83	10.95	11.78	11.02	9.29
FeO	1.30	0.51	0.57	0.54	1.25	0.67	1.57	1.25	1.18	0.90
MnO	0.04	0.06	0.07	0.13	0.15	0.11	0.00	0.15	0.08	0.04
MgO	0.27	0.12	0.16	0.06	0.24	0.10	0.27	0.21	0.20	0.19
CaO	1.23	0.66	0.88	0.62	1.19	0.68	1.43	1.35	1.04	0.98
Na_2O	3.89	3.32	3.60	3.72	4.03	3.64	5.81	4.79	4.46	4.10
K_2O	2.82	3.82	3.74	3.92	3.12	4.12	1.78	1.83	1.84	1.69
P_2O_5	0.02	0.04	0.00	0.06	0.01	0.04	0.02	0.02	0.04	0.10
Cl	0.14	0.11	0.10	0.11	0.15	0.10	0.28	0.26	0.26	0.19
H_2O	4.89	4.88	4.20	3.41	0.90	1.64	6.68	5.73	4.98	5.10
Total	99.81	98.97	99.70	99.12	99.21	99.71	99.21	99.68	99.31	99.76
Li	18.2	13.6	21.0	18.9	16.9	24.0	0.16	0.59	0.27	4.42
Be	1.04	0.94	0.76	0.94	0.99	0.93	0.70	0.58	0.58	0.49
B	30.0	55.4	37.1	54.6	43.5	57.5	105	110	100	70.9
F	605	269	223	274	644	163	539	925	765	401
Cr	2.26	0.74	1.13	0.73	2.38	1.09	1.10	2.00	2.50	1.46
Rb	–	–	–	–	–	–	25.7	39.3	43.4	23.8
Sr	123	50.6	113	54.9	121	59.1	74.0	68.2	56.5	45.2
Y	15.8	11.5	7.20	9.62	26.6	8.65	37.8	29.8	27.8	20.6
Zr	163	64.0	63.2	59.9	237	56.5	148	121	117	95.3
Nb	3.22	5.44	2.90	4.14	4.19	3.85	1.35	1.44	1.46	1.10
Ba	563	843	782	933	556	778	464	575	554	323
La	11.6	14.7	9.82	12.5	14.7	10.7	8.02	9.12	8.29	5.87
Ce	28.0	22.2	19.2	25.0	36.8	20.9	21.9	20.4	21.1	13.6
Nd	13.9	10.3	7.24	8.91	21.1	7.42	12.7	12.5	12.3	8.25
Sm	2.87	1.52	1.40	2.15	5.12	1.48	3.84	3.43	3.27	2.25
Eu	0.77	0.74	0.47	0.11	1.12	0.21	0.43	0.61	0.81	0.49
Gd	2.78	1.45	1.08	1.60	5.19	1.82	4.89	5.01	4.76	2.14
Dy	2.64	1.44	1.09	1.57	4.31	1.44	5.35	4.83	4.52	2.96
Er	1.69	1.27	0.92	1.34	3.13	1.02	4.47	3.89	3.48	2.32
Yb	1.91	1.35	0.95	1.53	3.19	1.20	5.45	4.29	9.35	2.84
Hf	4.28	2.21	1.85	1.96	5.26	1.63	4.94	4.79	4.75	3.08
Th	1.99	4.66	2.54	4.52	2.28	3.53	2.77	2.49	2.34	1.84
U	1.38	2.90	1.73	2.77	1.48	2.19	1.27	1.31	1.17	0.82
Th/U	1.44	1.61	1.55	1.63	1.54	1.61	2.18	1.90	2.00	2.24
La/Yb	6.07	10.9	10.3	8.17	4.61	8.92	1.47	2.12	0.89	2.07

Note: Oxides are given in wt %, trace elements are in ppm.

Table 8. Average La and Yb concentrations (ppm) and the La/Yb ratio of melt inclusions in minerals of volcanic rocks from Kuriles and Kamchatka

Volcano	Rock	Mineral	*n*	La	Yb	La/Yb
Kurile Islands						
Golovnina, Kunashir Island	dacite	quartz	4	7.8	5.5	1.4
Kudryavyi, Iturup Island	basaltic andesite	plagioclase	2	4.9	4.0	1.2
Men'shoi Brat, Iturup Island	basaltic andesite	plagioclase	2	9.4	5.3	1.8
Cjikurachki, Paramushir Island*	basalt	olivine	19	6.9	2.8	2.5
Kamchatka						
Karymskii	basalt	plagioclase	3	4.6	1.7	2.7
″	dacite	plagioclase	9	10.3	2.4	4.3
″	rhyodacite	quartz	6	12.3	1.7	7.2
Klyuchevskoi**	basalt	olivine	78	5.1	1.9	2.7
Avachinskii***	avachite	olivine	5	6.9	1.5	4.6
Avachinskii	andesite	plagioclase	2	7.3	1.2	6.1
Bezymyannyi	andesite	plagioclase	3	11.8	1.5	7.9
Dikii Greben'	dacite	plagioclase	2	11.8	1.4	8.4
Shiveluch	andesite	plagioclase	7	9.1	0.7	13.0

Note: * Data from (Gurenko et al., 2005), ** data from (Mironov and Portnyagin, in press), *** data from (Portnyagin et al., 2005); *n* is the number of analyses.

cosity. This behavior of the inclusions in our thermal experiments definitely indicates that the melt contained much water, which also follows from ion microprobe analyses of the inclusions (5.0–6.7 wt % H_2O at an average of 5.6 wt % of six analyses; Table 7). Compared to the acid melts of the Karymskii volcanic center, these melts are richer in Na_2O (4.1–5.8 wt %) and Cl (0.19–0.28 wt %) but poorer in K_2O (1.7–1.8 wt %).

DISCUSSION

Microprobe analysis of glasses in inclusions reveals very interesting compositional features of the melts of the Karymskii volcanic center. When plotted in a SiO_2 vs. (Na_2O + K_2O) diagram, most of the melts correspond to alkaline varieties from tephrite to trachyte, although some melts have lower alkalinity (Fig. 3). The rocks (Table 1) do not, however, contain elevated concentrations of alkalis. Another noteworthy feature is that the compositional trend in the diagram is nearly parallel to the abscissa, i.e., an increase in the silicity of the melts is not associated with an increase in the sum of alkalis, whereas crystallization differentiation should have resulted a simultaneous increase in both silica and alkalis.

The evolution of the melt is illustrated more comprehensively in Fig. 4. The behavior of various major components can be provisionally classified into the following three types:

(1) The concentrations of Al_2O_3, MgO, and CaO systematically decrease with increasing SiO_2, and the concentration of K_2O simultaneously increases. The trends have no bends and are typical of crystallization differentiation processes.

(2) The concentrations of TiO_2 and FeO systematically decrease with increasing SiO_2 only until SiO_2 > 57 wt % because of the precipitation of ore components in the course of crystallization differentiation. In more basic melts, which were found in inclusions in plagioclase from sample K-2 (basalt of the 1996 eruption at the Akademii Nauk caldera), the TiO_2 concentration even slightly increases (from 0.7 to 1.3 wt %). Much higher TiO_2 concentrations were detected in inclusions in plagioclase from samples K-4 and K-63 (andesite of the 1996 and 1997 eruptions of Karymskii volcano). TiO_2 concentrations higher than 1.3 wt % were found in 17 melt inclusions. The FeO concentration remains practically unchanging (7–9 wt %) at SiO_2 < 57 wt % (sample K-2, Fig. 4).

The most unexpected behavior shows Na_2O, whose content decreases with increasing silicity, and the plot (Fig. 4) displays two compositional trends. In one of them, the Na_2O concentration varies from 7.5 to 3 wt % within a relatively narrow range of SiO_2 (47–57 wt %), whereas the other trend has a gentler slope, with Na_2O varying from 6 to 3 wt % at SiO_2 changing from 57 to 73 wt %. The former trend was obtained for basalt

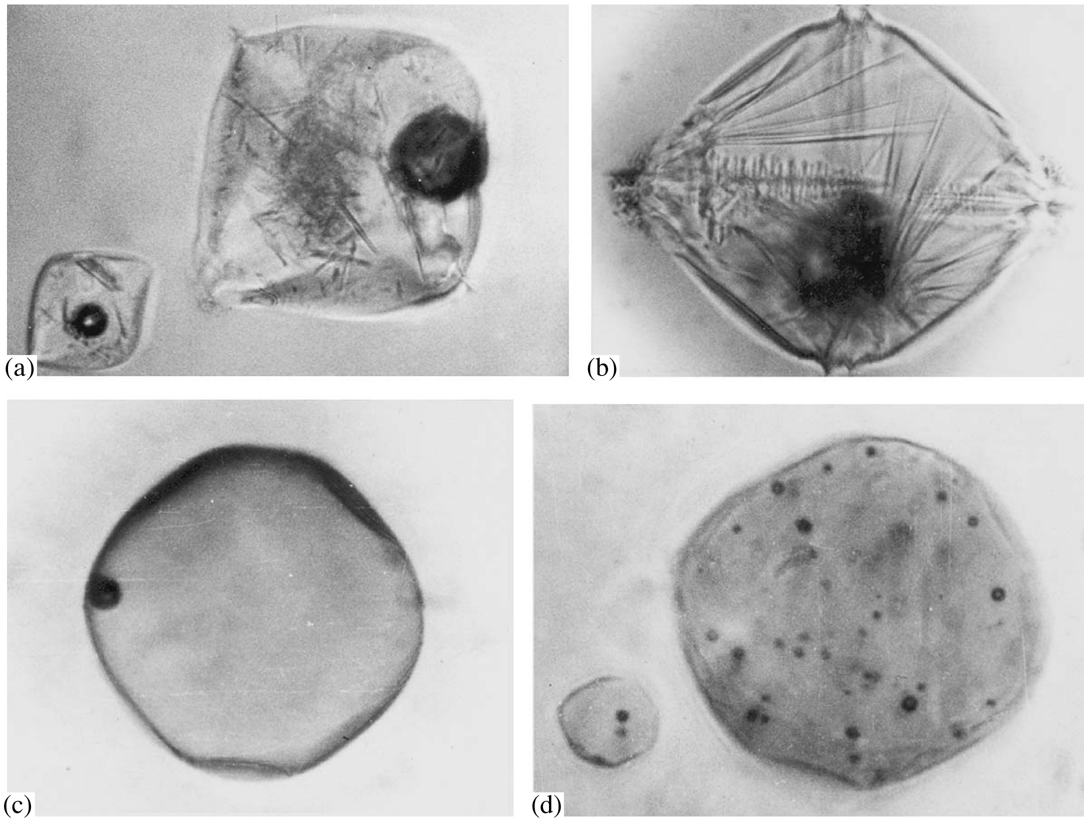

Fig. 2. Melt inclusions in quartz from dacite of Golovnina volcano. Sizes of inclusions: (a, c) 100 μm; (b, d) 50 μm.

(sample K-2), and the latter is for andesite (samples K-4 and K-63) and dacite (samples K-41 and K-31).

The basaltic melts of the Karymskii volcanic center (SiO_2 = 47–57 wt %) are characterized, along with high Na_2O concentrations, also by high Na_2O/K_2O ratios,

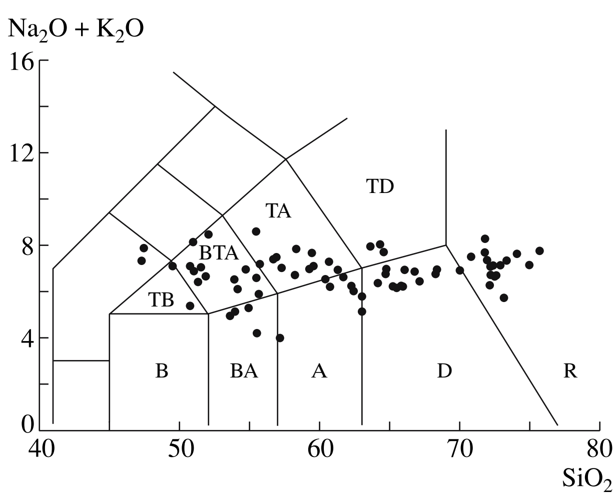

Fig. 3. SiO_2–($Na_2O + K_2O$) classification diagram (Le Bas et al., 1986) for the composition of melt inclusions.

Rocks: B—basalt, TB—trachybasalt, BA—basaltic andesite, BTA—basaltic trachyandesite, A—andesite; TA—trachyandesite, D—dacite, TD—trachydacite, R—rhyolite.

which is equal to 8.0 on average (average of 23 analyses). Equally high Na_2O concentrations and similar Na_2O/K_2O ratios were previously detected in xenoliths from Mongolia and Yemen (Ionov et al., 1994; Chazot et al., 1996). Glasses in peridotite xenoliths form alkaline basalts from Mongolia (Ionov et al., 1994) contain 51.8–57.0 wt % SiO_2 and 6.8–10.6 wt % Na_2O and have Na_2O/K_2O = 4.5–17.2 at an average of 8.6 (19 analyses). The glasses found in spinel lherzolites from Yemen (Chazot et al., 1996) contain 50.0–55.8 wt % SiO_2 and 5.9–8.9 wt % Na_2O at Na_2O/K_2O = 7.5–14.1 (average 9.7 of 15 analyses). The authors of these publications considered the genesis of such melts problematic and thought it could have been affected by mantle metasomatism under the effect of sodic mantle fluid.

The comparison of the compositional fields of the melts (Fig. 5) form various volcanoes (Karymskii volcanic center, Bezymyannyi, and Shiveluch) demonstrates that the volcanics of the Karymskii volcanic center show the broadest spectrum of melt compositions (including basic varieties enriched in Fe, Mg, and Ti). At the same time, the compositional trends of these melts are pronounced much more clearly in the variation diagrams, and the paired correlations of major components are stronger than those of the products of Bezymyannyi and Shiveluch volcanoes.

The distributions of incompatible elements in the basaltic and dacite-rhyolitic melts of the Karymskii

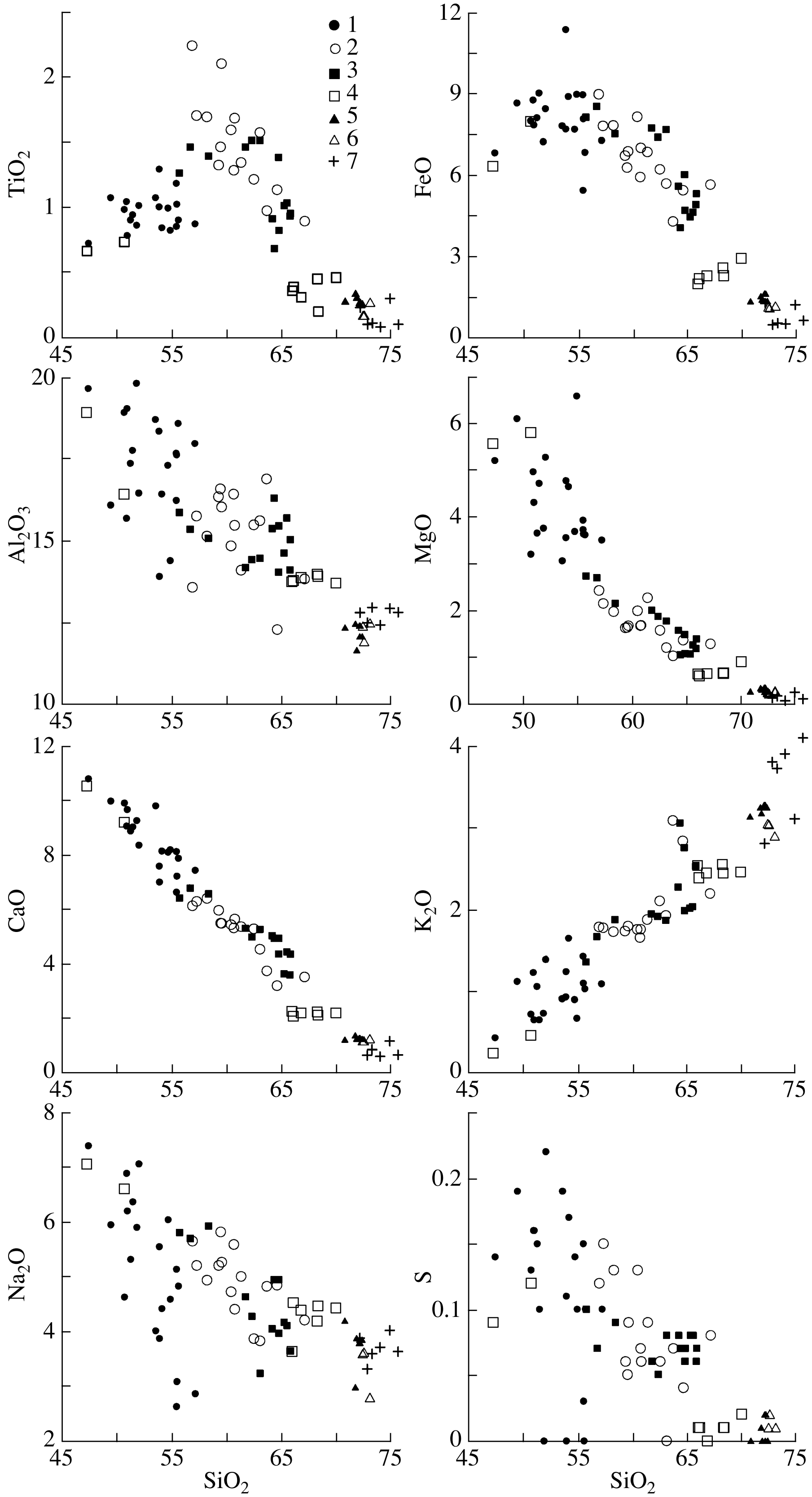

Fig. 4. Variation diagrams SiO_2–major element and SiO_2–S (wt %) for the compositions of melt inclusions in (1–6) plagioclase and (7) quartz from the Karymskii volcanic center.
Samples: (1) K-2; (2) K-63; (3) K-4; (4) K-41; (5) K-31; (6) K-23.

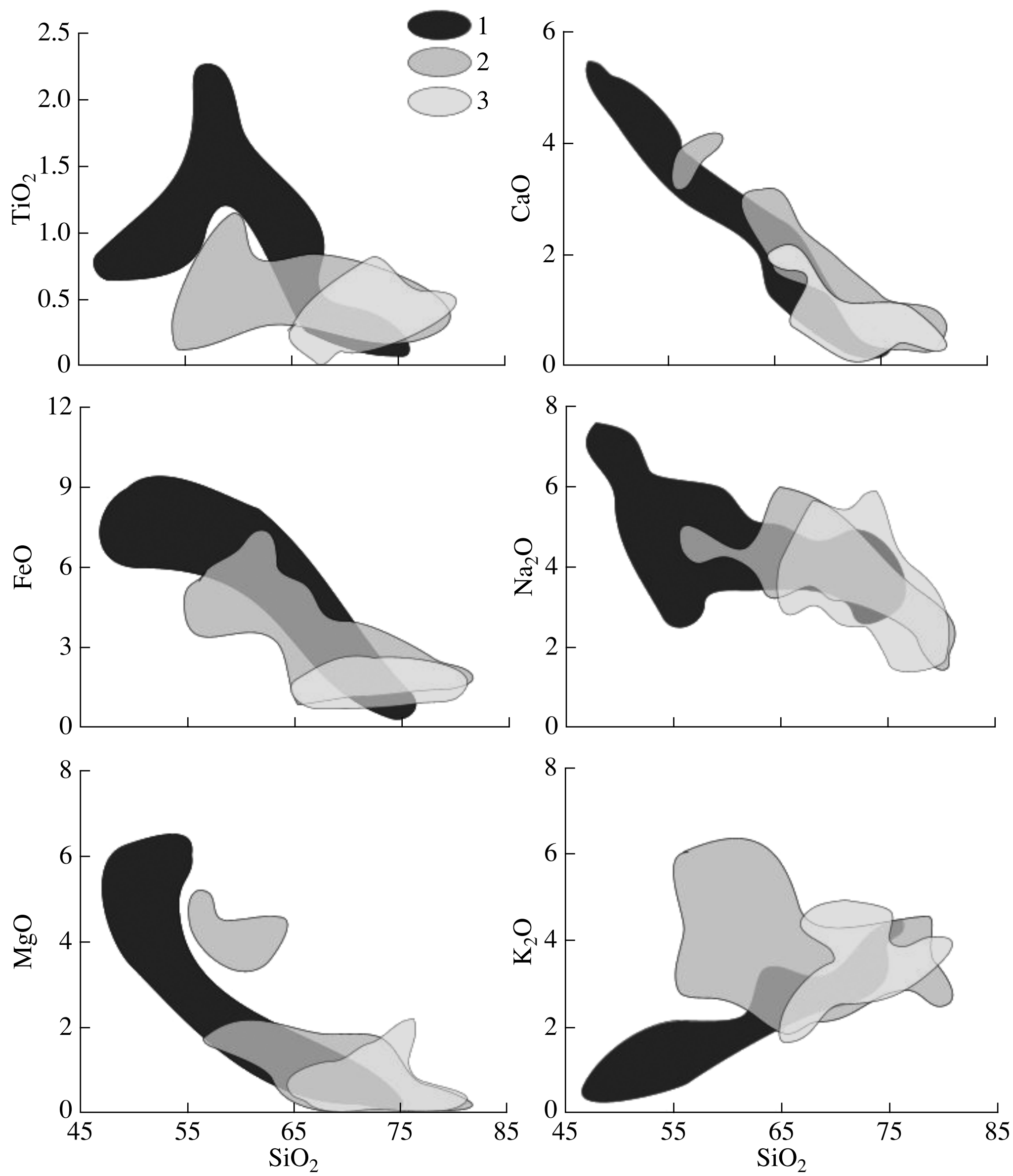

Fig. 5. Comparison of the composition (wt %) of melt inclusions in phenocrysts in volcanic rocks from (1) the Karymskii volcanic center, (2) Bezymyannyi, and (3) Shiveluch volcanoes.
Number of analyses of inclusions: Karymskii volcanic center—73, Bezymyannyi volcano—47, Shiveluch volcano—38.

volcanic center and in the rhyolitic melts of Golovnina volcano (Fig. 6) suggest an arc provenance of all of these melts. Inasmuch as the most strongly incompatible elements practically do not fractionate one relative another during crystallization, their bulk concentrations can provide information on the magmatic source of the volcanic center. The arc characteristics of the melts of the Karymskii volcanic center include, for example, Nb minima and high Ba/Th ratios relative to those in MORB. These features are characteristic of both the most primitive and the most differentiated melts. This points to a state of the mantle source, which was probably metasomatized by a fluid component enriched in LREE and relatively depleted in Nb. The magmatic source of the Karymskii volcanic center shows some distinctive features, first of all, relative enrichment in Li, which is pronounced particularly conspicuously in comparison with the melts of Golovnina volcano. Note that the enrichment in Li relative to HREE and Y compared to MORB is typical of many basic arc magmas (Portnyagin et al., 2007). However, the absolute concentrations of this element usually do not exceed 5–6 ppm, whereas the basic melts of the Karymskii volcanic center contain 19 to 290 times more Li, and the acid melts contain 2–12 times more this element. The difference for acid arc melts is even more significant (Fig. 6). Note that Li-rich melts are also noted for elevated Na

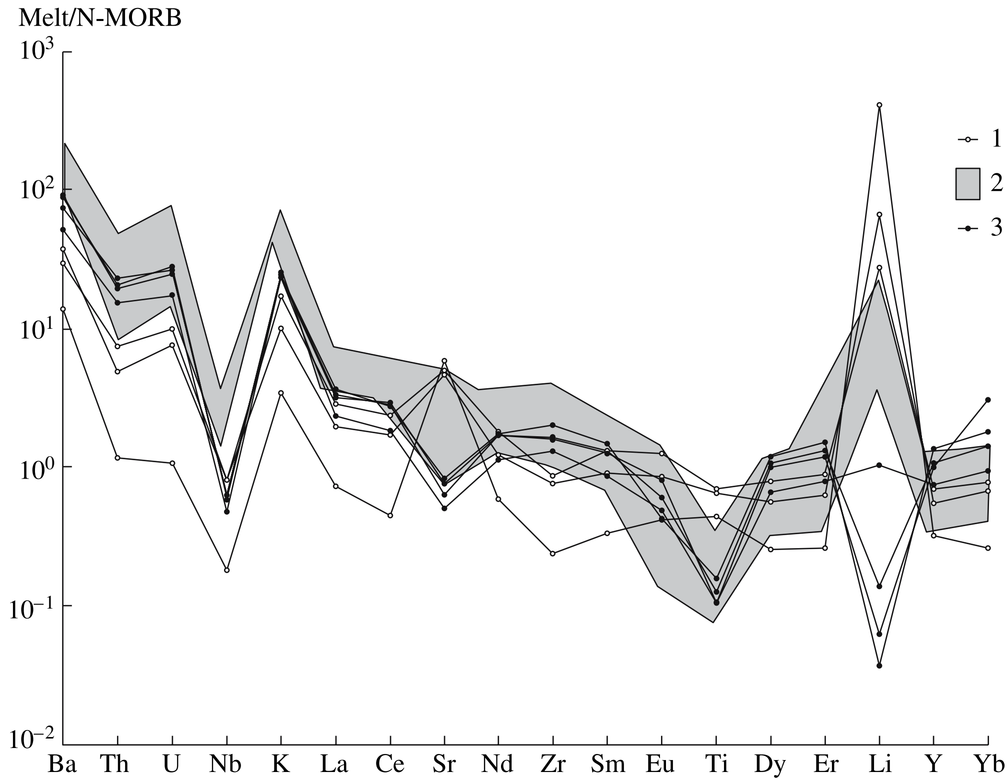

Fig. 6. N-MORB (Sun and McDonough, 1989) normalized trace-element composition of the melt inclusions. (1, 2) Karymskii volcanic center: (1) basaltic melts, (2) rhyodacitic melts; (3) rhyolitic melts of Golovnina volcano.

concentrations (up to 7.5 wt %). These values are generally atypical of basic melts.

It is interesting that, according to the analyses reported in (Portnyagin et al., 2007), some inclusions in olivine from Karymskii volcano correspond to basic melts with an average Na_2O concentration of 2.9 wt % and 5.23 ppm Li. The concentrations of incompatible elements reported by these researchers and ourselves were analyzed on the same equipment and with the use of the same standards, which rules out analytical errors. Thus, the relatively primitive melts of the Karymskii volcanic center (basic melts depleted in incompatible elements, including LREE) or some of them differ from most analogous basic magmas elsewhere in having elevated concentrations of Na and Li. The reasons for this enrichment remain uncertain. As one of the possible explanation variants, it could have been melt contamination with crustal minerals, for example, zeolites of the natrolite group, which were formed in the source from the material of ancient basalts of the volcanic center. The absence of information on these minerals makes it hard to draw any more specific conclusions.

Note that one of the samples in which the melt inclusions with high Na and Li concentrations were found was taken from a wall of the ancient caldera, and the other two samples were collected during the 1996 eruption. This led us to conclude that either the assimilation processes of crustal material were multiple over a long time period or the residence time of phenocrysts that crystallized from the melt was very long in shallow sitting chambers.

It is also difficult to reproduce the process because all minerals containing appreciable Li concentrations are either secondary (zeolites) or crystallize from differentiated melts late in the crystallization process of magmatic bodies (pegmatite minerals). Thus, as follows from available mineralogical data, the melt could enrich in these elements only near the surface via the reworking of crustal material.

A secondary nature of the Li- and Na-enriched phase can be ruled out: first, the inclusions are primary (as follows from their morphology); second, the rocks were not affected by secondary alterations because all of them were collected when still hot during the 1996 eruption; and, third, the features listed above are also inherited by more acid (i.e., more differentiated) melts of the volcanic center. Thus, relative enrichment in Li is characteristic of all melts of the Karymskii volcanic center.

Li behavior in melts of the Karymskii volcanic center should be considered anomalous, because this element should enrich melts in compliance with the classic differentiation scheme. In our situation, more acid melts have lower Li concentrations than more basic varieties. Because of this, we cannot rule out the mixing

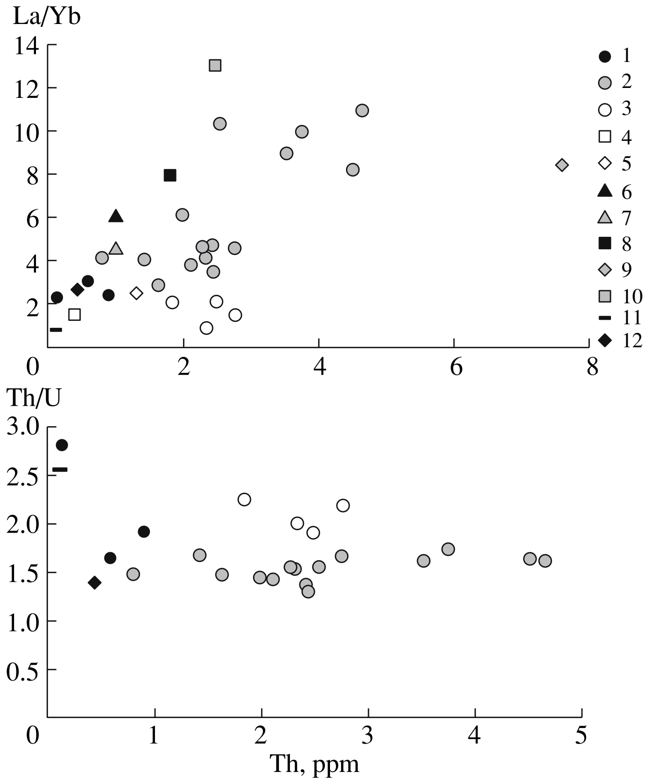

Fig. 7. Th–La/Yb and Th–Th/U diagrams for melt inclusions in minerals from volcanic rocks of Kamchatka and the Kurile Islands.

(1, 2) Karymskii volcanic center: (1) basalts, (2) andesites and dacites; (3) Golovnina volcano, Kunashir Island; (4) Medvezh'ya caldera, Iturup Island (Kovalenko et al., 2004); (5) Chikurachki volcano, Paramushir Island (Gurenko et al., 2005); (6, 7) Avachinskii volcano: (6) according to (Tolstykh et al., 2003), (7) according to (Portnyagin et al., 2007); (8) Bezymyannyi volcano; (9) Dikii Greben' volcano; (10) Shiveluch volcano; (11) N-MORB (Sun and McDonough, 1989); (12) Klyuchevskoi volcano (Portnyagin et al., 2007).

of basic melts with high Li concentrations with acid melts and the resultant enrichment of the latter in Li.

Figure 7 shows the La/Yb–Th and Th/U–Th relations for various volcanics from the Kurile–Kamchatka island arc and depleted MORB. As can be seen, the La/Yb ratio of the melts suggests their different degrees of differentiation. The melts of Golovnina volcano have La/Yb = 1.4, which is very close to the values of MORB (Table 8, Fig. 7). In this diagram (Fig. 7), other melts similar to MORB are from Kudryavyi and Men'shoi Brat volcanoes in Iturup Island, Kuriles, and the basaltic melts of the Karymskii volcanic center and Klyuchevskoi volcano in Kamchatka. The andesite–dacite melts of Karymskii and Avachinskii volcanoes (inclusions in olivine and plagioclase) plot slightly farther away from N-MORB. The melts of the southern sector of the Karymskii volcanic center, Bezymyannyi, Dikii Greben', and Shiveluch volcanoes are differentiated even more strongly.

The Th/U ratio in melts from the Karymskii volcanic center (Fig. 7) almost does not vary for all of the compositions and lies within the range of 1.3–1.9. At the same time, a basaltic melt with a remarkably higher Th/U ratio (equal to 2.8) was found. This melt is characterized by the highest Li concentration (1750 ppm) and a very high concentration of Na_2O (7.1 wt %) and the lowest content of K_2O (0.25 wt %). Acid melts from Golovnina volcano have Th/U ratios from 1.9 to 2.2.

Interpreting the analyses, it can be concluded that the Karymskii volcanic center was produced as a result of the fairly complicated evolution of the melts. The most primitive of them exhibit anomalously high concentrations of Na and Li. The genesis of these unusual melts should be further elucidated. The possible sources of the Li–Na complex could be zeolites of the natrolite group or Li micas. In any event, the melts should have been contaminated with crustal material. It is necessary to determine the composition of rock-forming melts in inclusions in mafic minerals: pyroxenes, olivine, and amphiboles and to examine the trace-element composition of the secondary minerals that developed in the Karymskii volcanic center.

CONCLUSIONS

(1) We have examined more than 80 melt inclusions in phenocrysts from basalt, andesites, dacites, and rhyodacites from the Karymskii volcanic center, Kamchatka, and dacites from Golovnina volcano, Kunashir Island, Kuriles. The SiO_2 concentrations in melt inclusions in phenocrysts from the Karymskii volcanic center range from 47 to 57 wt % in plagioclase phenocrysts from basalts, from 56 to 67 wt % in plagioclase phenocrysts in andesites, from 66 to 73 wt % in plagioclase phenocrysts from dacites and rhyodacites, and from 72 to 76 wt % in quartz phenocrysts from dacites and rhyodacites. The SiO_2 concentration in melt inclusions in quartz from dacites of Golovnina volcano varies from 70 to 77 wt %.

(2) It was determined that basaltic melts of the Karymskii volcanic center are significantly enriched in Na (Na_2O = 2.9–7.4 wt % at an average of 5.1 wt % of 23 analyses), with the highest Na_2O concentrations found in the most basic melts (SiO_2 = 47–52 wt %). These melts are characterized by very high Na_2O/K_2O ratios equal to 8.0 on average.

(3) Concentrations of volatile components were determined in the basaltic melts of the Karymskii volcanic center (1.6 wt % H_2O, 0.14 wt % S, 0.09 wt % Cl, and 50 ppm F) and in dacitic and rhyodacitic melts (0.9–7.3 wt % H_2O at an average of 4.5 wt % of 15 analyses; 0.15 wt % Cl; 600 ppm F; and 100 ppm S). The H_2O concentrations in melt inclusions in quartz from dacites of Golovnina volcano are higher (5.0–6.7 wt % at an average of 5.6 wt %), the Cl concentrations are also high (0.19–0.28 wt %), and the F concentrations are 660 ppm.

(4) The comparison of the composition of melts from the Karymskii volcanic center with those of the previously examined melts of Bezymyannyi and Shiveluch volcanoes revealed their significant differences. The former are more basic and are enriched in Ti, Fe, Mg, Ca, Na, and P but are notably depleted in K. The melts of the Karymskii volcanic center are likely less differentiated than the melts of Bezymyannyi and Shiveluch volcanoes.

(5) Concentrations of 20 trace elements were measured on an ion microprobe in the glasses of 22 melt inclusions in plagioclase and quartz. An unusual feature is the very high Li concentrations (along with high concentrations of Na) in the basaltic melts of the Karymskii volcanic center (118–1750 ppm), whereas the dacitic and rhyolitic melts contain 25 ppm Li on average. The rhyolitic melts of Golovnina volcano contain much less Li: 1.4 ppm on average. The La/Yb, Th–La/Yb, and Th–Th/U relations of the melts suggest their different degrees of differentiation. The melts of the Karymskii volcanic center are characterized by relative Nb and Ti minima and Ba and K maxima, as is typical of arc magmas.

ACKNOWLEDGMENTS

The authors thank A.A. Kadik (Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences) for quartz phenocrysts from dacite from Golovnina volcano provided for this research and A.V. Sobolev (Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences) and V.V. Yarmolyuk (Institute of the Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry, Russian Academy of Sciences) for constructive criticism of the text. This study was financially supported by the Russian Foundation for Basic Research (projects 04-05-65123, 05-05-64730, and 07-05-00497), Project 06-III-A-08-329 of the Far East Division, Russian Academy of Sciences, Program for the Support of Leading Research Schools (project 2006-RI-112.0/001/008), and a program of the Division of Earth Sciences of the Russian Academy of Sciences.

REFERENCES

1. G. Chazot, M. Menzies, and B. Harte, "Silicate Glasses in Spinel Lherzolites from Yemen: Origin and Chemical Composition," Chem. Geol., 159–179 (1996).

2. S. A. Fedotov, "Study and Mechanism of the 1996 Akademii Nauk Caldera and Karymsky Volcano Eruptions in Kamchatka," Vulkanol. Seismol., No. 5, 3–37 (1997).

3. T. I. Frolova, I. A. Burikova, A. V. Gushchin, et al., *Origin of the Island Arc Series* (Nedra, Moscow, 1985) [in Russian].

4. G. S. Gorshkov, *Volcanism of the Kuril Island Arc* (Nauka, Moscow, 1967), pp. 178–180 [in Russian].

5. E. N. Grib and V. L. Leonov, "Evolution of the Caldera Magmatic Chambers in the Southern Sector of the Karymsky Volcanic Center. Part 1. Geology, Structure, and Composition of Pyroclastic Flows," Vulkanol. Seismol., No. 4, 21–40 (2004a).

6. E. N. Grib and V. L. Leonov, "Evolution of the Caldera Magmatic Chambers in the Southern Sector of the Karymsky Volcanic Center. Part 2. *PTf*-Crystallization Conditions of Ignimbrite-Forming Melts, Magmatic Evolution," Vulkanol. Seismol., No. 5, 23–37 (2004b).

7. E. N. Grib and V. L. Leonov, "Different Evolution Trends of the Upper Crustal Magmatic Chambers of the Caldera Complexes of Eastern Kamchatka. Part 1. Structure of Pyroclastic Flows: Comparative Mineralogy," Vulkanol. Seismol., No. 4, 3–17 (2001a).

8. E. N. Grib and V. L. Leonov, "Different Evolution Trends of Upper Crustal Magmatic Chambers of the Caldera Complexes of Eastern Kamchatka. Part 2. Physicochemical Crystallization Conditions of the Ignimbrite-Forming Melts," Vulkanol. Seismol., No. 4, 18–28 (2001b).

9. E. N. Grib, "Petrology of the Products of Akademii Nauk Caldera Eruption on January 2–3, 1996," Vulkanol. Seismol., No. 5, 71–96 (1997).

10. A. A. Gurenko, A. B. Belousov, R. B. Trumbull, and A. V. Sobolev, "Explosive Basaltic Volcanism of the Chikurachki Volcano (Kurile Arc, Russia): Insights on Pre-Eruptive Magmatic Conditions and Volatile Budget Revealed from Phenocryst-Hosted Melt Inclusions and Groundmass Glasses," J. Volcanol. Geotherm. Res. **147**, 203–232 (2005).

11. D. A. Ionov, A. W. Hofmann, and N. Shimizu, "Metasomatism-Induced Melting in Mantle Xenoliths from Mongolia," J. Petrol. **35**, 753–785 (1994).

12. B. V. Ivanov, *1962–1956 Karymsky Volcano Eruption and the Karymsky Volcanic Group* (Nauka, Moscow, 1970) [in Russian].

13. V. I. Kovalenko, V. B. Naumov, M. L. Tolstykh, et al., "Composition and Sources of Magmas in Medvezh'ya Caldera (Iturup Island, Southern Kuriles) from a Study of Melt Inclusions," Geokhimiya, No. 5, 467–487 (2004) [Geochem. Int. **42**, 393–413 (2004)].

14. M. J. Le Bas, R. V. Maitre, A. Streckeisen, and B. A. Zannettin, "A Chemical Classification of Volcanic Rocks Based on the Total Alkali–Silica Diagram," J. Petrol. **27**, 745–750 (1986).

15. V. B. Naumov, M. V. Portnyagin, M. L. Tolstykh, and V. V. Yarmolyuk, "Composition of Magmatic Melts from the Southern Baikal Volcanic Region: A Study of Inclusions in Olivine from Trachybasalts," Geokhimiya, No. 3, 243–253 (2003) [Geochem. Int. **41**, 213–223 (2003)].

16. V. B. Naumov, V. S. Karpukhina, E. N. Baranov, and N. N. Kononkova, "Melt Compositions, Contents of Volatile Components and Trace Elements, and Temperatures of Quartz Crystallization in Silicic Volcanic Rocks of the Verkhneural'sk Ore District (Southern Urals)," Geokhimiya, No. 4, 339–351 (1999) [Geochem. Int. **37**, 289–301 (1999)].

17. A. A. Nosova, L. V. Sazonova, V. V. Narkisova, and S. G. Simakin, "Minor Elements in Clinopyroxene from Paleozoic Volcanics of the Tagil Island Arc in the Central

Urals," Geokhimiya, No. 3, 254–268 (2002) [Geochem. Int. **40**, 219–232 (2002)].

18. A. Yu. Ozerov, "Dynamics of the 1996 Karymsky Volcano Eruption and composition of Its Products," Vestnik DVO RAN, No. 3, 86–93 (1997).

19. M. Portnyagin, K. Hoernle, P. Plechov, et al., "Constraints on Mantle Melting and Composition and Nature of Slab Components in Volcanic Arcs from Volatiles (H_2O, S, Cl, F) and Trace Elements in Melt Inclusions from the Kamchatka Arc," Earth Planet. Sci. Lett. **255**, 53–69 (2007).

20. M. V. Portnyagin, N. L. Mironov, S. V. Matveev, and P. Yu. Plechov, "Petrology of Avachites, High-Magnesian Basalts of Avachinsky Volcano, Kamchatka: II. Melt Inclusions in Olivine," Petrologiya **13**, 358–388 (2005) [Petrology **13**, 322–351 (2005)].

21. M. V. Portnyagin, S. G. Simakin, and A. V. Sobolev, "Fluorine in Primitive Magmas of the Troodos Ophiolite Complex, Cyprus: Analytical Methods and Main Results," Geokhimiya, No. 7, 691–699 (2002) [Geochem. Int. **40**, 625–632 (2002)].

22. A. V. Sobolev, "Melt Inclusions in Minerals as a Source of Principle Petrological Information," Petrologiya **4**, 228–239 (1996) [Petrology **4**, 209–220 (1996)].

23. S.-S. Sun and W. F. McDonough, "Chemical and Isotopic Systematics of Oceanic Basalts: Implications for Mantle Composition and Processes," in *Magmatism in the Ocean Basins*, Ed. by A. D. Saunders and M. J. Norry, Geol. Soc. London Spec. Publ. **42**, 313–345 (1989).

24. M. L. Tolstykh, V. B. Naumov, A. D. Babanskii, et al., "Chemical Composition, Volatile Components, and Trace Elements in Andesitic Magmas of the Kurile–Kamchatka Region," Petrologiya **11**, 451–471 (2003) [Petrology **11**, 407–425 (2003)].

25. M. L. Tolstykh, V. B. Naumov, A. Yu. Ozerov, and N. N. Kononkova, "Composition of Magmas of the 1996 Eruption at the Karymskii Volcanic Center, Kamchatka: Evidence from Melt Inclusions," Geochem. Int. **39** (5), 447–458 (2001).

26. M. L. Tolstykh, V. B. Naumov, and N. N. Kononkova, "Three Types of Melt in the Basaltic Andesite from the Medvezh'ya Caldera, Iturup, Southern Kuril Islands" Geokhimiya, No. 4, 391–397 (1997) [Geochem. Int. **35**, 339–345 (1997)].

27. V. I. Vlodavets, "Volcanoes of the Karymsky Group," Tr. Kamchat. Vulkanost., No. 3, 3–48 (1947).

28. *Volcanic Center: Structure, Dynamics, and Composition (Karymsky Structure)*, Ed. by Yu. P. Masurenkov (Nauka, Moscow, 1980) [in Russian].