Genesis of High-Alumina Basalts from Klyuchevskoi Volcano

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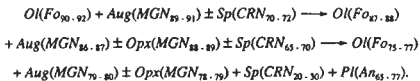
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Abstract – The mechanism and conditions of formation of the Klyuchevskoi high-alumina basalts were determined as a result of a comprehensive examination of 45 samples representing the rocks of 40 flank eruptions and a subsequent computer simulation of the generation of high-alumina basalt magmas from primary high-magnesia basalt melts. This petrological and geochemical study included a petrochemical and geochemical classification of the Klyuchevskoi basalts and an analysis of the compositions of minerals that coexist as glomerocrysts and mutual solid phase inclusions. The results suggested that the observed spectrum of compositions (from high-magnesia basalts to high-alumina varieties) represent a continuous igneous rock series that formed as a result of similar fractionation of the primary magmas, which approximated the composition of the high-magnesia basalts of the Bulochka Bocca. Analysis of the cotectic relations of the coexisting minerals yielded the following crystallization sequence:

$$Ol(Fo_{90-92}) + Aug(MGN_{89-91}) \pm Sp(CRN_{70-72}) \longrightarrow Ol(Fo_{87-88})$$

$$+ Aug(MGN_{86-87}) \pm Opx(MGN_{88-89}) \pm Sp(CRN_{65-70}) \longrightarrow Ol(Fo_{75-77})$$

$$+ Aug(MGN_{79-80}) \pm Opx(MGN_{78-79}) + Sp(CRN_{20-30}) + Pl(An_{65-77}).$$

A model of polybaric (*decompression*) basalt magma fractionation under hydrous conditions was developed using the COMAGMAT petrologic programs designed to simulate and evaluate the conditions of fractionation. Using this model, 600 calculations were performed for the isobaric and decompression fractional crystallization of the Klyuchevskoi primary magma (average high-magnesia basalt) for a pressure range of 1 atm - 20 kbar and an initial H_2O content of 0 - 2 wt %. The optimum model for the formation of this igneous rock series was determined to be polybaric primary magma fractionation at a pressure decline rate of 0.33 kbar per 1% crystallization with approximately 2 wt % H_2O in the initial melt. According to this model, magma crystallization starts with the separation of olivine and clinopyroxene (in the presence of spinel, according to natural data) at a pressure of approximately 19 kbar and temperature ~1350°C. High-Mg orthopyroxene crystallizes at around 15 kbar and ~1260°C. The accumulation of water in the melt results in a considerable delay of plagioclase crystallization and the formation of high-alumina differentiation products containing more than 18 wt % Al_2O_3. The line of alumina enrichment breaks as plagioclase appears at the liquidus at approximately 7 kbar, 1110°C, and ~3 wt % H_2O in the melt. By this time, the composition spectrum of the model liquidus corresponds to all varieties of the Klyuchevskoi lavas. Further crystallization involves rapid saturation of the system with water and subsequent degassing at about 1.5 kbar.

ORIGIN OF ISLAND-ARC HIGH-ALUMINA BASALT MAGMAS

Tilley (1950) was the first to identify high-alumina basalts as a separate type of basalt magma on the basis of elevated Al_2O_3 contents (up to 18 wt %) in some aphyric volcanic rocks of northern California. In his well-known paper, Kuno (1960) proposed some mineralogical and geochemical conditions for the separation of high-Mg basalts from associated tholeiitic and alkalic

rocks. He considered the former to be among the most widespread basalt types of the Japanese Islands. He was the first to raise the problem of the origin of high-alumina basalts, believing them to be primary magma generated by the partial melting of mantle peridotite. Later, Yoder and Tilley (1962) advanced a different view: Al_2O_3 accumulation in magmas can be caused by a delay in plagioclase crystallization from hydrous picrite-basalt magmas. During the following decades, the

question of whether high-alumina magmas are *primary or nonprimary* was the focus of discussions on the origin of high-alumina basalts (see reviews by Crawford *et al.*, 1987, and Kadik *et al.*, 1990).

Currently, there are several opposing hypotheses concerning this problem; these hypotheses interpret high-alumina basalts as the following: (1) products of the partial melting of subducted oceanic crust, including the incorporation of sedimentary material in melting (Marsh and Carmichael, 1974; Babanskii *et al.*, 1983; Baker and Eggler, 1983; Brophy and Marsh, 1986; Johnston, 1986); (2) residual melts that were formed as a result of high-magnesia mantle magma fractionation (Perfit *et al.*, 1980; Kay and Kay, 1985; Nye and Reid, 1986; Uto, 1986; Gust and Perfit, 1987; Kadik *et al.*, 1989, 1990; Draper and Johnston, 1992); (3) products of the reequilibration of primary melts and their derivatives with the rocks surrounding the magma channel (Kelemen and Ghiorso, 1986; Kelemen *et al.*, 1990); or (4) rocks formed by the mechanical accumulation of plagioclase crystals circulating in crystallizing magnesian magmas (Crawford *et al.*, 1987; Plank and Langmuir, 1988; Brophy, 1988, 1989; Fournelle and Marsh, 1991). One can see that the first two hypotheses admit the possibility of the generation of high-alumina melt proper, whereas the accumulation hypothesis offers an alternative mechanism to account for the wide spectrum of Al_2O_3 contents in the rocks of the tholeiitic and calc-alkaline series, caused by variations in the contents of plagioclase phenocrysts. Contradictions between researchers who advocate the view that high-alumina magmas are primary and those who support the opposing view have been resolved to a certain extent, as very primitive high-alumina melts coexisting with highly magnesian Ol^1 of the Fo_{90} composition have been discovered (Sobolev *et al.*, 1988). However, the rocks discovered were not island-arc rocks, but oceanic tholeiites.

In this context, results of geological observations indicating that high-alumina and high-magnesia basalts containing more than 10 wt % MgO (Perfit *et al.*, 1980) and *Fo*-enriched olivine phenocrysts (Fo_{88-92}) occur together in many large island-arc volcanic centers (Kay and Kay, 1985) are significant. Such associations have been found at Okmok and Makushin volcanoes in the Aleutian Islands (Nye and Reid, 1986; Gust and Perfit, 1987), at Klyuchevskoi Volcano in Kamchatka (Khrenov *et al.*, 1989; Ozerov and Khubunaya, 1992; Khubunaya *et al.*, 1993), and at Tolbachik in Kamchatka (Bol'shoe Treshchinnoe..., 1984). Despite their relative scarcity, high-magnesia basalts, derived from upper mantle peridotites, drew attention as potential parental magmas. This hypothesis was evolved through

a series of experiments intended to investigate the phase relations in samples of island-arc high-magnesia basalts at pressures of 1 atm - 20 kbar (Gust and Perfit, 1987; Kadik *et al.*, 1989, 1990; Draper and Johnston, 1992). The results of these experiments indicated that the products of high-magnesia magma fractionation at pressures above 8 kbar under anhydrous conditions were melts containing 16 - 18 wt % Al_2O_3 and resembling natural high-alumina basalts in many other petrochemical parameters. At the same time, in many respects (for instance, in terms of CaO and MgO proportions) the rocks of the island-arc series do not have analogs among experimental glasses (Draper and Johnston, 1992). Therefore, the conditions under which polybaric primary magma fractionation can occur remains an unanswered question.

The objective of this paper is to demonstrate, using a set of petrological and geochemical data and computer simulation, the feasibility of high-alumina-melt generation from primary high-magnesia magma by decompression fractionation (as it rises to the surface) under hydrous conditions (Barmina and Ariskin, 1992; Ariskin *et al.*, 1994). The model rocks were Klyuchevskoi lavas, whose series represents a continuous trend from high-magnesia to high-alumina basalts (Khrenov *et al.*, 1989; Kersting and Arculus, 1994).

STRUCTURE OF KLYUCHEVSKOI VOLCANO FROM GEOLOGICAL AND GEOPHYSICAL DATA

Klyuchevskoi Volcano is situated in the East Kamchatka volcanic belt, to which most of the active Kamchatkan volcanoes are restricted. It is the largest volcano of the Kuril-Kamchatka volcanic zone and is among the most active volcanoes of the world in terms of volume of erupted material (Fedotov *et al.*, 1987). This giant stratovolcano stands on the slope of the older Kamen Volcano, has a height of approximately 4800 m, and is about 7000 years old (Melekestsev *et al.*, 1992). Records of its eruptive activity from the 18th century to 1932 merely mention eruptions at the summit crater. Because those were mostly explosive and, occasionally, explosive–effusive events, the volume of pyroclastic material in its cone is substantially larger than that of lava flows. In 1932, a drastic change occurred in its activity: along with continued eruptive activity at the central crater, flank eruptions began to take place, once in every four years, on average (Fedotov *et al.*, 1987). Sixteen large flank eruptions have occurred since 1932 with the formation of extensive lava flows, ranging between hundreds of meters to 7 to 8 km in length. In addition, there are still more than 100 cinder cones on the slopes.

The cone of the volcano is built up of 90% aluminous basalts; the remaining 10% are magnesian and intermediate varieties (Khrenov *et al.*, 1989). Along with the lavas of summit eruptions, the material of fissure eruptions is a principal source of petrologic information. On the basis of tephrochronological data, the

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[1] Notation for minerals and end members: *Ab* – albite, *An* – anorthite, *Aug* – augite, *Cpx* – clinopyroxene, *Fa* – fayalite, *Fo* – forsterite, *Fs* – ferrosilite, *En* – enstatite, *Mt* – titanomagnetite, *Ol* – olivine, *Opx* – orthopyroxene, *Pig* – pigeonite, *Pl* – plagioclase, *Sp* – chrome spinel, and *Wo* – wollastonite.

flank eruptions have been classified into six groups (Bogoyavlenskaya *et al.*, 1985): (I) 1932 - 1991, (II) 150 - 1000 years ago, (III) 1500 - 2000 years ago, (IV) 2000 - 2500 years ago, (V) 2500 - 4000 years ago, and (VI) more than 4000 years ago. Flank eruptions have occurred mostly on the northeastern, eastern, and southeastern slopes (Fig. 1), usually from several radial fissures; central eruptions have been less common, and multivent eruptions were only recorded during two events. The fissures developed within a height range of 450 - 4000 m. Since 1984, magma has been recorded as standing high in the summit crater vent, with a simultaneous rise of flank eruptions: in 1987 - 1989, no boccas developed below 2800 m.

According to G.S. Gorshkov (1956), the Klyuchevskoi magma chamber is situated at a depth interval of 50 - 60 km and has the form of a flat lens, approximately 30 km across and at least 10 - 12 km thick. This view was evolved by other researchers who interpreted seismic shadows under the volcano as the combination of a mantle diapir and a vertical magma channel rising from the top of it at a depth of 60 - 70 km (Ermakov *et al.*, 1971). However, more reliable seismic data are currently available only for the upper 25 km of the Klyuchevskoi magma system (Fedotov *et al.*, 1988). According to these data, the most seismically active segment of this zone has a diameter of about 5 km, and the depth interval of 5 - 20 km contains an aseismic region that is about 3 km across (it is assumed to be a zone of plastic rocks surrounding the main magma channel). One important result of this work was that it was determined that the seismic zone does not contain aseismic regions that are larger than 5 km in size, which would be interpreted as large intermediate-depth magma sources. This is also supported by the uniform distribution of earthquake intensity in the depth interval of 0 - 25 km, which can also be interpreted to mean that there are no large inhomogeneities (magma reservoirs) at these depths of the magma system (Fedotov *et al.*, 1988). Therefore, the seismic data indicate that magma is supplied to the Klyuchevskoi system from the mantle, and that there are no large crustal or peripheral magma reservoirs in the conduit. As will be demonstrated below, this conclusion is borne out by the results of computer simulation of the phase equilibria and polybaric fractionation of the melt from which the Klyuchevskoi lavas were derived.

SAMPLE COLLECTION AND ANALYTICAL STUDIES

This study was performed using 45 samples that were collected in 1987 by A. Ariskin and G. Barmina from cinder cones and boccas in the height range of 500 - 2000 m on the Klyuchevskoi cone. The samples largely represent old cinder cones with an age of approximately 2000 years (24 samples) and a few cones from historical eruptions: Tuila (1932), Bilyukai (1938), Bylinkina (1951), Belyankin (1953), and Piip

(1966) (17 samples). Analytical work was performed at the Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences. Major elements were determined by XRF analysis; 15 representative samples were analyzed for REE and other trace elements. Ni, Co, Sr, Ba, and Li were determined by the ICP method; Cr and Cu were determined by atomic absorption analysis; Rb was determined by flame photometry; and REE and Sc, by neutron activation analysis.

As will be demonstrated below, this sample collection embraces almost the entire spectrum of basalt compositions and can be used as a basis for designing and testing computer models for the Klyuchevskoi magma differentiation. It should be noted that, until recently, there has been relatively little geochemical data on the Klyuchevskoi basalts (Leonova and Firsanov, 1974; Khrenov *et al.*, 1989). This paper, therefore, can be regarded as one of the first attempts, after Kerstig and Arculus (1994), to systematize the available evidence. In our petrochemical classification of the basalts, we used the most complete summary of basalts from the cinder cones and boccas, which was kindly given to us by A.P. Khrenov, as well as some analyses of lavas erupted from the summit crater from the collection of V.N. Andreev (Institute of Volcanology, Far East Division, Russian Academy of Sciences).

PETROCHEMICAL CLASSIFICATION OF BASALTS

The Klyuchevskoi basalts vary in composition from high-magnesia basalts (~12 wt % MgO, 13.5 wt % Al_2O_3) to high-alumina basalts (4 - 5 wt % MgO, 18 - 19 wt % Al_2O_3). They produce almost continuous trends for major and trace elements on variation diagrams (Khrenov *et al.*, 1989; Kersting and Arculus, 1994). Although breaks in the composition trends are smaller than 0.3 - 0.5 wt % (Fig. 2), this rock series has been conventionally subdivided into two members: magnesian and aluminous basalts. The transitional varieties were assumed to contain ~7% MgO and 16 - 17% Al_2O_3 (Khrenov *et al.*, 1989). Even though there are small (~0.2 wt %), but systematic, differences between the magnesian basalts of age group IV and the group-I and -II lavas of historic eruptions, different sources can hardly be postulated for the basalts of different ages, because they have identical Sr, Nd, and Pb isotope compositions (Kersting and Arculus, 1994a, 1994b).

The two-member subdivision of the Klyuchevskoi basalts was based on the use of one MgO–Al_2O_3 diagram (Fig. 2) and makes it difficult to compare them with rocks from other island-arc volcanic centers (Crawford *et al.*, 1987; Plank and Langmuir, 1988). To avoid terminological confusion, we systematized the information on the Klyuchevskoi basalts using a technique for multilevel petrochemical classification of igneous rocks that was developed by A.A. Yaroshevskii
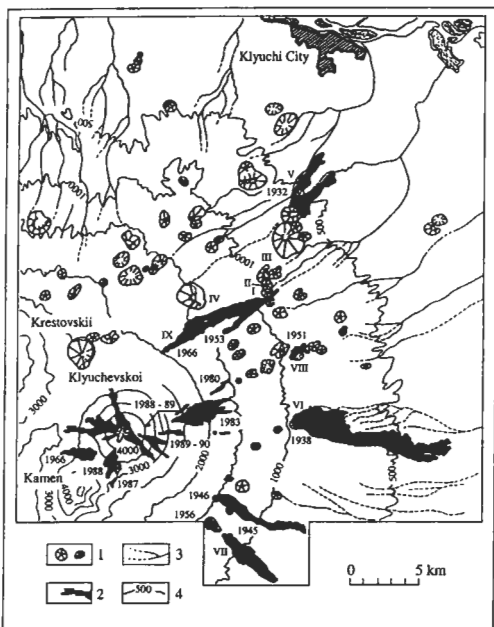
Fig. 1. Location map of Klyuchevskoi boccas, modified after V.N. Dvigalo (Institute of Volcanology).
1 – Cinder cones (I – Bulochka, II – Novograblenov, III – Luchitskii, IV – Slyunin); 2 – 1932 - 1990 lava flows and the years of eruptions (V – Tuila, VI – Bilyukai, VII – Zavaritskii, VIII – Bylinkina, IX – Piip); 3 – dry river beds; 4 – contour line.

and coworkers, Department of Geochemistry, Moscow State University. An example of its application was described by Barmina *et al.* (1989). We wrote a program, PETROTYP, to use this classification on a computer. The program identifies regions of composition clusters in a dimensional space corresponding to the number of petrogenic oxides specified for the classification.

We performed this classification for a data set containing 242 compositions of Klyuchevskoi basalts, using 10 petrogenic oxides as the basic parameters. Table 1 demonstrates that the compositions were grouped into four types, which are uniformly distributed over the composition space: highly magnesian (15 samples), magnesian (46), aluminous (50), and

high-alumina (131) basalts. The average compositions of these types are given in Fig. 2. The group of highly magnesian basalts includes lavas from the old cones Bulochka, Malysh, Luchitskii, Nezametnyi, and Novograblenov. The typical magnesian basalts are represented by a system of 1932 boccas (Tuila, Kirgurich, and Biokos') and by the lavas of the Slyunin cone and some other cones. Aluminous and high-alumina basalts are the abundant products of old and recent flank eruptions; the more aluminous compositions are restricted to the near-summit fissure and summit eruptions of the last decade. Approximately two-thirds of the Bilyukai samples (1938) are aluminous; the rest are magnesian basalts.

Table 1. Chemical compositions and norms of the petrochemical types of Klyuchevskoi Basalts

Component	Petrochemical type			
	I. High-magnesia basalt	II. Magnesian basalt	III. Aluminous basalt	IV. High-alumina basalt
	15*	46	50	131
SiO_2	51.76 (0.34)	53.39 (0.55)	53.22 (0.78)	53.50 (0.48)
TiO_2	0.86 (0.07)	0.84 (0.11)	0.95 (0.13)	1.09 (0.07)
Al_2O_3	13.86 (0.33)	15.29 (0.55)	16.79 (0.66)	18.26 (0.50)
FeO^*	8.83 (0.18)	8.52 (0.24)	8.83 (0.47)	8.67 (0.33)
MnO	0.17 (0.01)	0.17 (0.02)	0.17 (0.04)	0.16 (0.02)
MgO	11.55 (0.43)	8.58 (0.65)	6.89 (1.00)	5.24 (0.34)
CaO	9.73 (0.20)	9.41 (0.30)	8.91 (0.46)	8.22 (0.38)
Na_2O	2.47 (0.18)	2.72 (0.24)	3.11 (0.32)	3.45 (0.20)
K_2O	0.63 (0.09)	0.90 (0.15)	0.96 (0.19)	1.20 (0.10)
P_2O_5	0.15 (0.02)	0.18 (0.03)	0.18 (0.04)	0.20 (0.04)
$Mg/(Mg + Fe)$	0.699	0.641	0.580	0.517
$Ca/(Ca + Al)$	0.561	0.528	0.491	0.450
CIPW, wt %				
Or	3.72	5.32	5.67	7.09
Ab	20.90	23.01	26.31	29.19
An	24.88	26.86	29.02	30.80
Di	18.18	15.24	11.54	7.20
Hy	17.93	25.04	21.96	21.15
Ol	12.42	2.52	3.28	2.02
Ilm	1.63	1.60	1.80	2.07
Ap	0.36	0.43	0.43	0.47

Note: The compositions are dry-base converted. The norms have been calculated without separation into FeO and Fe_2O_3. The figures in the parentheses are standard deviations (1σ). FeO^* — all iron recast to FeO.

* The number of compositions.

Generally, the change from high-magnesia to high-alumina basalts is marked by a regular increase in the SiO_2, TiO_2, Al_2O_3, Na_2O, K_2O, and P_2O_5 contents with a monotonic decrease in the MgO and CaO concentrations. Because the contents of FeO remain approximately constant, the $MGN = Mg/(Mg + Fe)$ value declines monotonically from 0.7 to 0.5 in the more aluminous rocks. These features indicate that the most important process controlling the formation of the Klyuchevskoi lava series might be primary high-Mg magma fractionation through mafic mineral crystallization, without or with insignificant plagioclase crystallization. In this context, it is of interest to compare the norms presented in Table 1 for the identified petrochemical types. The most significant feature in the norm variation from high-magnesia to high-alumina basalts is the systematic accumulation of plagioclase components with a decline in the olivine and diopside constituents. Assuming that the petrochemical types represent the evolution of the melt during the primary high-magnesia magma fractionation, it can be con-

cluded that the main crystallizing phases were Ol and Cpx. During the early fractionation stages, the crystallizing material was dominated by olivine; when closer to a more aluminous composition, the proportion of crystallizing augite might increase, and small amounts of Opx might separate. These conclusions are supported by the compositional evolution of phenocrysts and mineral inclusions.

It is also of interest to compare the standard deviations (1σ) presented in Table 1 for the identified petrochemical types. It can be seen that the change from high-magnesia basalts to high-alumina varieties is marked by a systematic increase in the 1σ value for all 10 petrogenic components; the high-alumina basalts form a more compact group than the aluminous basalts (Fig. 2). This suggests that, along with general fractionation, the evolution of the Klyuchevskoi magma compositions was influenced by some other processes that introduced an extra dispersion into the compositions of the rocks. Such processes might be the accumulation of crystals and/or the mixing of fractionation products.
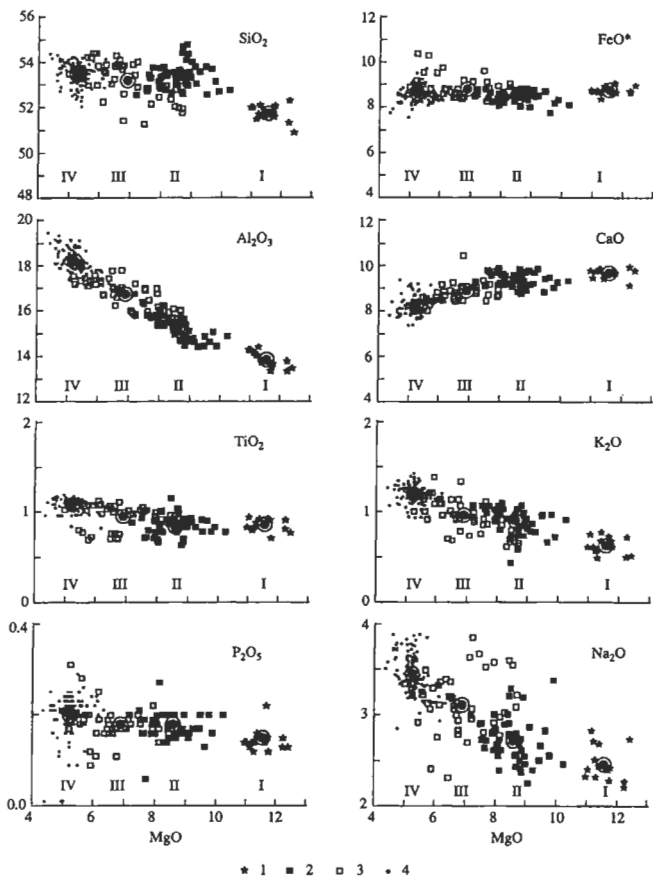
$\star$ 1 $\blacksquare$ 2 $\square$ 3 $\cdot$ 4

Fig. 2. Variation diagrams of Klyuchevskoi basalts, wt %.

The data set includes 242 analyses comprising the data of the authors, A.P. Khrenov, and V.N. Andreev (Institute of Volcanology). The samples have been grouped using the PETROTYP multilevel classification program into the following: 1 – high-magnesia basalts, 2 – magnesian basalts, 3 – aluminous basalts, and 4 – high-alumina basalts. The large solid circles are the average compositions of the petrochemical types; they are marked below by roman numbers in accordance with Table 1.

The effect of crystal accumulation during the formation of the general petrochemical trend appears to have been insignificant, as indicated by geophysical data on the structure of the Klyuchevskoi magma system (Fedotov et al., 1988) and the distinct, clear character of the trends (Fig. 2). The mineralogic indications that mixing was another factor influencing magma evolution will be considered in another section. Here, it can be mentioned that the group of aluminous basalts that are less compact than the more evolved high-alumina basalt (Table 1) suggests that the latter was one of the important end components that participated in magma mixing during the long eruptive history of this volcanic center.

EVOLUTION OF TRACE-ELEMENT CONCENTRATIONS

Table 2 presents the contents of major and trace elements in 15 samples that represent the main petrochemical types of the Klyuchevskoi basalts: Samples KL-3, 5, 9, and 12 are high-magnesia basalts; KL-28 and KL-45 are magnesian basalts; KL-6, 15, 19, 34, 35, and 40 are aluminous basalts; and KL-1,18, and 31 are high-alumina basalts. As in the case of the major components, these data indicate regular (though more variable) changes in trace-element concentrations as the high-magnesia basalts change to the high-alumina varieties: a monotonic decrease in Ni, Co, Cr, and Sc, elements that are usually distributed in olivine and pyroxenes, and the simultaneous accumulation of incompatible elements (Ba, Rb, Li, and light REE). The behavior of Sr is indicative of the composition variations: it also accumulates in the high-alumina basalts too, but not as actively as the typical incompatible elements. Heavy REE (Lu and Yb, Table 2) are even less accumulative. This trace-element distribution is in satisfactory agreement with the hypothesis of fractionation, which, as indicated by the degree of K, P, Li, and La accumulation, accounts for 50% of the primary magma volume. Apparently, the evolution of the Sc, Sr, and heavy REE concentrations was controlled by the crystallization of pyroxenes.

At the same time, these geochemical data are at variance with the previously advanced hypothesis that the magnesian basalts were derived from aluminous magma (Leonova and Kirsanov, 1974; Khrenov et al., 1989). For instance, the five-fold increase in the content of Ni and the ten-fold enrichment in Cr from high-alumina to high-magnesia basalts (Table 2; Fig. 3) would have required 80 - 90% crystallization of the primary magma, with plagioclase as the only liquidus phase. Experimental data on the phase relations of high-alumina basalts prohibited this (Babanskii et al., 1983; Baker and Eggler, 1983; Johnston, 1986). Moreover, as a result of the long-lasting plagioclase crystallization, the end differentiates would have exhibited abnormally

high Sc and incoherent element concentrations, without perceptible changes in the Mg-number of the system. Data on the evolution of the phenocryst compositions also disprove the idea that the primary Klyuchevskoi magma was of an aluminous basalt composition (see below).

Figure 3 shows variation in the contents of some trace element as a function of Ni concentration (as a fractionation index). Except for Cu, the contents of these elements vary little with the fairly uniform Ni concentrations. This indicates a relatively narrow range of variation in the magma composition, independent of the time at which corresponding basalt eruptions took place. These plots provide more support in favor of the genetic affinity of the Klyuchevskoi lavas with respect to both the primary magma composition and the mechanism of its differentiation. It seems important that some of the elements, e.g., Sc and Yb, exhibit no linear correlation with the Ni content, but have gently curving geochemical trends. This feature was first discovered for the Klyuchevskoi basalts by Kersting and Arculus (1994), who plotted trace-element contents against TiO_2 concentrations. This implies that the transitional basalt varieties could not have been formed by simple mixing of the end components, the high-magnesia and high-alumina basalt magmas.

Copper is an element that does not show an explicit dependence on the MgO or Ni contents or on other fractionation parameters. The Cu contents vary little in the high-magnesia basalts, but they exhibit a fan pattern embracing the enrichment and depletion regions in the less magnesian and more aluminous varieties (Fig. 3). A similar pattern was observed for the V distribution in the Klyuchevskoi basalts (Kersting and Arculus, 1994). In terms of fractionation, this means that, in the course of the primary and derivative magma crystallization, the bulk coefficients of the Cu and V distribution between the solid phase and the melt $(D_{Cu,V}^{S/L})$ varied around one: the melt was depleted in these elements when this value was greater than one, and they accumulated in the differentiation products when $D_{Cu,V}^{S/L} < 1$. This conclusion agrees with the properties of Cu and V, which existed in magma systems as the heterovalent forms Cu^+/Cu^{2+} and $V^{3+}/V^{4+}/V^{5+}$, whose proportions in the liquid phase (hence the bulk coefficients of crystal − melt distribution) are strongly dependent on oxygen fugacity (Borisov, 1986). Therefore, the Cu and V distribution in the rocks suggests that there were no stable oxidation-reduction conditions throughout the evolution (fractionation) history of this magma-generating system. This conclusion is indirectly supported by the wide compositional range of spinels that crystallized in the Klyuchevskoi basalts.

Table 2. Concentrations of major and trace elements in Klyuchevskoi basalts

Component	KL-3	KL-5	KL-9	KL-12	KL-28	KL-45	KL-19	KL-15	KL-40	KL-34	KL-35	KL-6	KL-18	KL-1	KL-31
SiO_2	50.90	51.40	50.84	50.90	52.65	52.24	51.73	51.80	52.42	53.46	53.83	53.55	53.07	53.10	53.23
TiO_2	0.80	0.70	0.83	0.79	0.83	0.88	0.96	0.88	0.95	1.01	1.04	1.01	1.10	1.12	1.13
Al_2O_3	13.70	13.50	14.19	14.00	14.44	14.41	15.63	15.80	15.22	15.90	16.76	16.93	17.92	17.70	17.96
FeO*	8.70	8.60	8.61	8.70	8.37	8.38	8.75	9.00	8.54	9.08	8.66	8.76	8.38	8.70	8.38
MnO	0.17	0.17	0.16	0.17	0.15	0.16	0.16	0.16	0.16	0.16	0.15	0.16	0.15	0.15	0.15
MgO	12.10	11.60	11.11	11.00	9.87	8.98	8.37	8.20	7.83	7.01	6.50	5.62	5.21	5.10	4.81
CaO	9.90	9.60	9.74	9.70	9.29	9.57	9.33	9.30	9.08	8.98	8.84	8.17	7.91	7.80	7.77
Na_2O	2.20	2.40	2.29	2.80	3.37	2.83	3.58	3.00	3.54	2.68	3.36	3.45	3.82	3.60	3.72
K_2O	0.50	0.60	0.57	0.60	0.72	0.85	0.66	0.60	0.88	0.72	0.68	0.90	0.92	1.20	1.15
P_2O_5	0.13	0.12	0.14	0.13	0.16	0.16	0.17	0.14	0.18	0.17	0.18	0.19	0.20	0.23	0.23
LOI	0.91	1.24	1.06	1.11	0.72	1.06	0.85	0.99	1.26	0.95	0.82	1.36	1.24	1.11	0.65
Total	100.02	99.93	99.54	99.94	100.55	99.55	100.17	99.87	100.07	100.08	100.78	100.08	99.89	99.80	99.19
Ni	210	210	170	190	160	110	96	96	82	46	52	44	32	28	40
Co	52	51	49	44	42	39	43	37	40	37	38	44	36	34	34
Cr	580	570	470	520	370	320	310	270	350	170	165	110	42	54	58
Sc	40	41	41	41	37	39	36	38	38	39	32	31	30	30	27
Cu	70	72	71	78	69	87	91	63	74	40	78	60	68	87	102
Sr	260	260	260	260	320	320	300	320	320	330	325	340	370	380	400
Ba	220	230	230	230	280	310	240	240	330	300	235	390	380	450	420
Rb	10	10	10	9	13	17	9	18	18	12	12	15	17	16	17
Li	6.8	6.3	7.2	7.6	11.0	9.4	8.0	7.0	10.0	8.7	8.3	12.0	11.0	14.0	12.0
La	4.4	4.7	5.0	4.8	6.7	6.2	5.3	5.5	6.7	6.8	6.4	7.7	7.2	9.0	9.8
Ce	9.8	11.3	10.1	10.4	14.0	13.3	10.9	11.6	15.0	14.5	14.8	16.4	15.5	17.9	18.7
Nd	6.8	7.7	6.8	7.1	8.7	8.6	7.7	7.8	8.7	9.3	8.6	9.8	9.4	11.8	10.8
Sm	2.1	2.2	2.2	2.2	2.1	2.4	2.3	2.5	2.7	2.6	2.5	2.7	3.0	3.8	3.0
Eu	0.96	0.92	1.05	0.87	0.93	–	0.96	1.01	–	1.04	1.01	1.36	1.20	1.27	1.17
Gd	3.1	3.2	3.2	3.0	3.0	3.6	3.3	3.3	3.6	3.6	3.6	4.2	3.9	5.4	3.9
Yb	1.6	1.9	1.6	1.9	1.6	1.9	1.9	1.8	2.0	2.2	1.8	2.5	2.0	2.6	1.9
Lu	0.31	0.32	0.26	0.32	0.25	0.31	0.31	0.29	0.34	0.37	0.29	0.42	0.33	0.45	0.32

Note: Analyses were made at the Central Analytical Laboratory, Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences. Major elements were determined by XRF; Ni, Co, Sr, Ba, and Li, by ICP; Cr and Cu, by atomic absorption analysis; Rb, by flame photometry; REE and Sc, by neutron activation analysis. Major elements are given in wt %, trace elements, in ppm. The figures in the sample indexes denote the boccas: 3 and 5 – Bulochka, 9 and 12 – Novograblenov, 28 – Maleev, 45 – Tuila, 19 – Menyailov, 15 – Tsirk, 40 – Bilyukai, 34 and 35 – Lepeshka, 6 – Belyankin, 18 – Kulakov, 1 – Piip, 31 – Bylinkina.

VARIATION OF ROCK-FORMING MINERAL COMPOSITIONS IN GLOMEROCRYSTS AND SOLID-PHASE INCLUSIONS

Petrography. The Klyuchevskoi lavas are vesicular or massive basalts containing phenocrysts of olivine, clinopyroxene, plagioclase, and orthopyroxene. The phenocrysts range between 0.1 and 1 mm in size, occasional equant grains of olivine and pyroxene amount to 5 - 7 mm across. All the rock types contain glomerocrysts, which may be as large as 10 mm. The olivine–clinopyroxene association of the phenocrysts and glomerocrysts is dominated by olivine in the high-magnesia basalts and by clinopyroxene in the magnesian and aluminous basalts, and it tends to be enriched in plagioclase in the high-alumina basalts. Occasional grains of plagioclase may be found in the magnesian basalts, but the systematic occurrence of this mineral as phenocrysts or in the glomerocrysts is generally recorded in the aluminous and high-alumina varieties. Occasional orthopyroxene grains, sometimes interlocked with plagioclase or clinopyroxene, have been found only in the aluminous and high-alumina basalts. In a microprobe analysis, orthopyroxene was identified as solid-phase inclusions in *Ol* and *Cpx* in all the rock
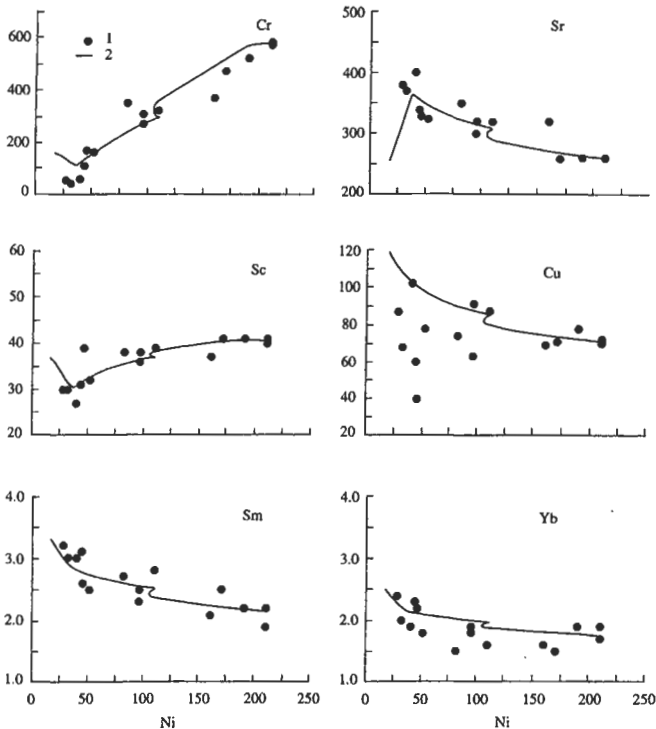
Fig. 3. Observed and computed variations of trace element abundances in Klyuchevskoi basalts, ppm.
1 – Natural samples (plotted from data listed in Table 2), 2 – magma composition evolution during decompression fractionation of hydrous primary high-Mg magma (computed by COMAGMAT program; for the values of the optimum model see Figs. 8e, 8f, and 9).

types (Ozerov, 1993; Khubunaya *et al.*, 1993). Cr-rich spinel (picotite) occurs as inclusions in olivines, especially in olivines from the high-magnesia basalts of the Bulochka and Novograblenov boccas and from the magnesian basalts of Tuila (Table 2). The high-alumina basalts are distinguished by a dissemination of fine tita-nomagnetite particles, sometimes interlocked with *Ol*

or *Cpx*; inclusions of low-Cr spinel are fairly numerous in the plagioclase.

The total amount of phenocrysts (glomerocrysts) varies between 3 and 7 vol % in the high-magnesia and magnesian rocks and may be as high as 20 vol % in the high-alumina basalts. It is important to note that, as they are generally typical porphyritic rocks with 0.5- to

1-mm plagioclases, the high-alumina basalts may include microphyric or even subaphyric varieties, often within the same bocca. The groundmass of the basalts varies from vitrophyric to intersertal. It is dominated by thin plagioclase laths and fine intergrowths of olivine, clinopyroxene (augite and pigeonite), and titanomagnetite. The mesostasis consists of slightly altered or devitrified glass, which has an andesite-dacite composition in the aluminous basalts (Ozerov, 1993).

Previous microprobe studies. The chemistry of rock-forming minerals from the Klyuchevskoi lavas has been comprehensively studied and reported by Ozerov and Khubunaya (1992), Ozerov (1993), Khubunaya et al. (1993), and Kersting and Arculus (1994). The chemical data reported revealed a few points of interest. First, there is a fairly magnesian association of clinopyroxene ($MGN = 87 - 90$) and olivine ($MGN = 88 - 92$), whose crystals contain numerous inclusions of Cr-, Al-, and Mg-rich spinel and occasional orthopyroxene. A maximum MGN value of approximately 89 was found in orthopyroxene trapped in olivines from the basalts of the Zavaritskii Bocca (Ozerov, 1993). Grains of high-Mg minerals are most abundant in the high-magnesia and magnesian basalts, and they also occur in the aluminous and high-alumina rocks.

Second, the compositions of the cores of the phenocrysts and mineral inclusions indicate a great variation in the Ol, Cpx, and Opx compositions, ranging from $MGN \sim 90$ to $MGN = 65 - 70$ with a simultaneous change in the coexisting spinel chemistry toward depletion in chromium and enrichment in titanomagnetite (e.g., Ozerov, 1993). Significantly, the most magnesian clinopyroxenes (with $MGN \sim 90$) were found as inclusions in the most magnesian olivines, and they are virtually absent in phenocrysts or intergrowths (Khubunaya et al., 1993).

Third, many olivine and pyroxene phenocrysts exhibit a normal zoning manifested in the more ferroan outer zones, though these differences generally do not exceed a few mol %. Some samples, e.g., those from the Bilyukai bocca, showed a more complex zoning, from normal to reversed and vice versa, which is particularly distinct in the clinopyroxene grains (Kersting and Arculus, 1994). This pattern is interpreted as an indication of magma composition heterogeneity produced by the mixing of liquid fractionation products prior to the eruptive phase (Sakuyama, 1981). The distinct bimodal distribution of the Cpx compositions in the Bilyukai lavas is supportive of mixing (Khubunaya et al., 1993). The wide spectrum of phenocryst compositions in some samples, which indicates the heterogeneity (nonequilibrium) of the coexisting minerals and magma, is suggestive not only of magma mixing, but also of the possibility of long-lasting circulation of early, refractory crystals in the low-temperature derivatives of the primary magma.

The composition of the plagioclase phenocrysts varies from $An_{94 - 85}$ to An_{60}. Such phenocrysts occur in the aluminous and high-alumina basalts, often in intergrowths with mafic minerals. The fact that the MGN value of olivine and pyroxene inclusions in the plagioclase is not higher than 72 - 76 (Ozerov, 1993) suggests that the latter crystallized from the late products of the primary high-magnesia magma fractionation, possibly during or immediately before the magma eruption. To support this conclusion, we present new evidence on the compositional evolution of minerals that coexist in intergrowths and solid-phase inclusions.

Analysis of coexisting mineral phases. To investigate the compositions of the minerals, we collected samples from 10 basalt flows representing high-magnesia basalts (KL-3 and KL-12), aluminous basalts (KL-35 and KL-40), and high-alumina basalts (KL-2, 8, 25, 27, 30, 31, and 33). Analyses were performed at the Microprobe Laboratory, University of Oregon, using thin sections that had previously been scanned with an express-probe to identify polymineral intergrowths. This procedure distinguished our study from the other analytical works, the principal objectives of which were to determine the general spectrum of the phenocryst compositions (Kersting and Arculus, 1994) or to concentrate on the mineral inclusions (Ozerov, 1993; Khubunaya et al., 1993). It was assumed that the crystals of the glomerocrysts represented cotectic associations of coexisting phases that had crystallized from the primary and derivative magmas. Where inclusions of silicate or oxide mineral phases were found, their compositions were also assumed to be cotectic. This work yielded approximately 700 analyses: 266 for olivine, 187 for augite, 104 for plagioclase, 107 for spinel, and 33 for orthopyroxene.

It should be noted that our work was hampered by the crystal zoning, the scope of which was usually 2 to 3 mol % in femic minerals (Ozerov, 1993; Kersting and Arculus, 1994). To minimize this problem, we analyzed mainly the crystal zones near the contacts of mineral grains and inclusions, assuming that this procedure would ensure that the most equilibrium compositions were determined. As seen in the plots that follow, this technique proved to be efficient for reliably identifying the evolutionary trends of coexisting mineral compositions.

Figure 4 illustrates the observed composition range of individual phenocrysts and glomerocrysts and inclusions for pyroxenes, olivine, spinel, and plagioclase. High-Ca clinopyroxene is represented here by augite with 37 - 45 mol % Wo, with MGN values varying from 91 to 67. The subcalcic varieties and pigeonite have an elevated Fe/Mg ratio and occur in the margins of the augite crystals; some of these varieties occur as microphenocrysts, but the groundmass was not investigated in detail in this study. The orthopyroxene contains 2 to 3 mol % Wo and has $MGN = 85 - 68$. The most magnesian composition ($MGN = 85$) was found in one
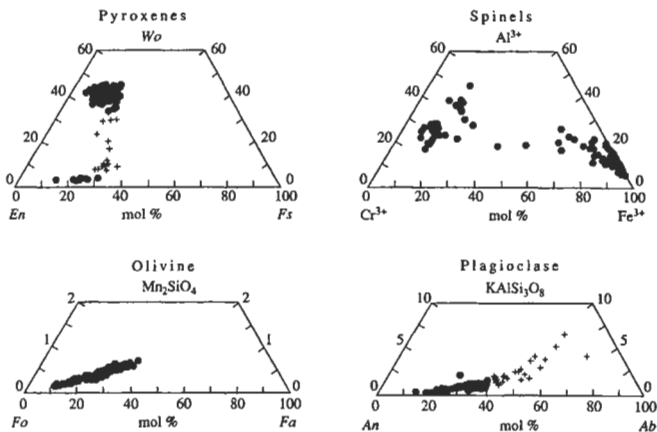
Fig. 4. Compositions of rock-forming minerals in Klyuchevskoi basalts (from microprobe analyses).
The circles are separate phenocrysts, intergrowths, and mineral inclusions; the crosses are compositions of pyroxenes and plagioclase in the margins of crystals and in the mesostasis.

orthopyroxene inclusion that we discovered in augite from the high-magnesia basalt, Sample KL-12; the other orthopyroxene compositions characterize the aluminous and high-alumina basalts.

The spinel compositions vary greatly, from Mg- and Al-rich chromites to Mg- and Al-poor titanomagnetites, which vary significantly in their magnetite and ulvospinel proportions (some titanomagnetite inclusions contain about 16 wt % TiO_2). The fact that these compositions show an obvious bimodal distribution suggests that one type of spinel composition was rapidly replaced by another (Ozerov, 1993). The occurrence of varieties with intermediate Cr^{3+} and Fe^{3+} proportions indicates that the spinels belong to the same solid solution series, and that the sudden change in their composition reflects a fairly great change in the (oxidation-reduction?) crystallization environment.

The olivine and plagioclase compositions form distinct trends: the Fo content in the olivine varies from 90 to 60%, with monotonous enrichment in Mn and CaO accumulation approximately from 0.12 to 0.25 wt %; the An content in large, perfectly bounded plagioclase crystals ranges between 85 and 58%, with simultaneous potassium accumulation. The margins of the plagioclase crystals are enriched in albite, and the microphenocrysts are of the An_{20-40} composition.

The direction of the composition trends shown in Fig. 4 does not contradict the hypothesis that fractional crystallization was the main mechanism responsible for the formation of the observed composition spectrum. However, given for individual minerals, these data cannot be treated as evidence in support of large-scale fractionation; they reflect the general, well-known features of mineral composition evolution under the declining temperature of basalt magma systems. Based on this analysis of the petrochemical data, we concluded that the series of Klyuchevskoi lavas may have been formed as a result of simultaneous olivine and pyroxene fractionation. The plausibility of this process can be proved more convincingly by using the paired evolution of mineral compositions (for all phases of the polymineral association) and correlating these relations with the experimental data available for phase equilibria. The numerous intergrowths of olivine and high-Ca pyroxene provide perfect petrologic material for this purpose.

Figure 5 compares the MGN values of the coexisting olivines and augites of the Klyuchevskoi basalts and those obtained by various authors in experiments on the melting of natural samples (see explanation given in the caption). Both plots show trends that almost overlap in the MGN range of 65 - 90. However, in the case of the natural data, the MGN dispersion in the augites is notably higher at the same Fo contents, which seems natural
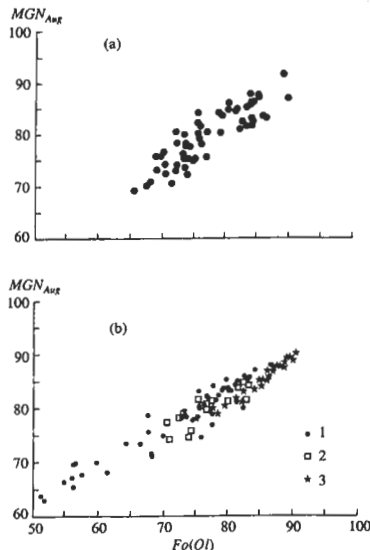
Fig. 5. Compositions of coexisting olivines and augites observed in Klyuchevskoi basalts and experiments.

(a) – natural samples (authors' data); (b) – experimental data obtained at: 1 – atmospheric pressure, 2 – 2 - 9 kbar, 3 – 10 - 20 kbar.

Experimental data on the compositions of Ol and Aug have been extracted from the INFOREX data base (Ariskin et al., 1992), the latest version of which contains comprehensive information on the conditions of quenching experiments and mineral compositions, reported in 120 references (papers, books, dissertations, and personal communications). The data sample used included the results of 20 works, 55 runs at $P = 1$ atm and 44 runs at $2 \leq P \leq 20$ kbar, that were conducted in systems of low and medium alkalinity ($Na_2O + K_2O \leq 5$ wt %). The search procedure selected low-pressure experiments that lasted no less than 48 hours; in the case of higher temperature and high-pressure experiments, the minimum duration was 12 hours.

considering the problem of zoning and the more complicated cooling history of real lavas as compared to products of experimental quenching.

We believe that the distribution of experimental data as a function of pressure is of principal importance. As seen in Fig. 5b, most of the experiments performed at atmospheric pressure fall in the region of more ferroan compositions, reflecting the fact that, at low pres-

sures, clinopyroxene crystallizes third after Ol and Pl at temperatures below 1180°C (more magnesian augites crystallized in low-pressure experiments on basalts enriched in pyroxene phenocrysts, containing not less than 12 wt % CaO and about 10 wt % MgO). At pressures of 2 - 9 kbar, the clinopyroxene compositions overlap the MGN range of 74 - 85; augites with MGN values above 80 have been synthesized during high-temperature experiments ($T > 1200°C$) at pressures of 8 to 9 kbar. Most of the more magnesian clinopyroxenes (with MGN about 90) were obtained in high-pressure experiments at $P = 10 - 20$ kbar. In all experiments, the highly magnesian association of olivine and augite was found to be at equilibrium with a high-magnesia basaltic melt containing >10 wt % MgO.

The nature of the observed and experimental evolutionary trends of olivine and clinopyroxene compositions can, therefore, be regarded not only as another argument in favor of the primary high-magnesia magma fractionation, but also as a sufficient basis for requiring preliminary estimates of the pressure during the Klyuchevskoi magma crystallization. Judging from the real composition range of the coexisting olivine and augite, the process of fractional crystallization obviously proceeded under nonisobaric conditions: the pressure varied approximately from 20 to 2 kbar. We will provide independent confirmations of these estimates while discussing the results of the computer simulation of the phase relations and fractional crystallization of the high-magnesia magma. Let us now consider the paired evolution trends for the other phases of this cotectic association.

Because olivine and clinopyroxene are the main crystallizing phases in terms of their abundance and the lengths of their evolution trends, data on the other coexisting minerals are given as a function of the Fo contents of Ol and the MGN value of augite (Fig. 6). To create a more complete picture, we used the results obtained by Ozerov (1993) for the compositions of solid-phase inclusions during his microprobe study of the high-alumina basalts of the Zavaritskii Bocca.

The upper pair of plots in Fig. 6 demonstrates the evolution of the orthopyroxene compositions. The distinct trends embracing the range of MGN (Opx) 89 - 72 indicate with certainty that this mineral had been in the crystallizing association from the early, if not the initial phase of the primary magma fractionation. In this context, the low content of orthopyroxene is a problem; according to our estimates, it composes not more than 1 to 2% of the magnesian and most of the high-alumina basalts. The distribution of the plagioclase compositions is of interest: with wide variation in An, this mineral does not show any significant correlation with the compositions of the coexisting femic phases. The average MGN value of Ol, Cpx, and Opx in the intergrowths and inclusions in the plagioclases is usually ~75 and never exceeds 78. These values obviously mark the first appearance of Pl as a crystallizing phase. The more
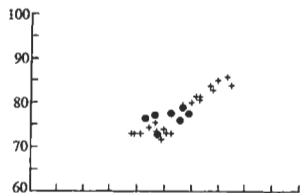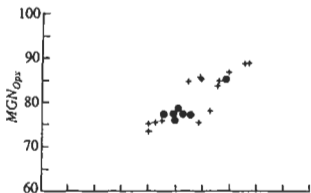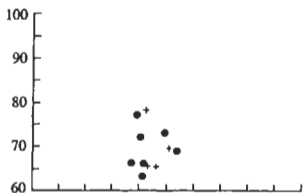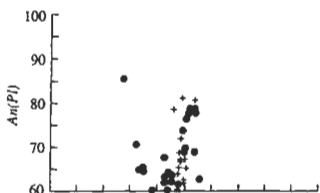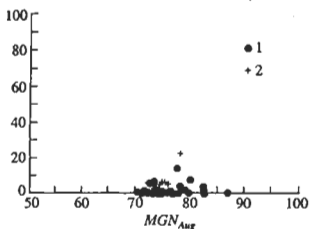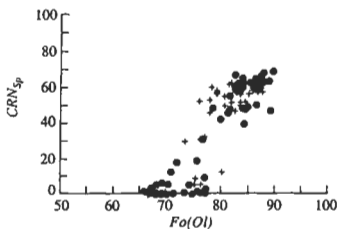
Fig. 6. Compositions of orthopyroxenes, plagioclases, and spinels found as intergrowths or inclusions in olivines and clinopyroxenes from Klyuchevskoi basalts.

1 – Authors' data, 2 – Ozerov's (1993) data on mineral inclusions in high-alumina basalts of Zavaritskii Bocca. $MGN = 100Mg/(Mg + Fe^{2+})$, $An = Ca/(Ca + Na + K)$, $CRN = Cr^{3+}/(Cr^{3+} + Al^{3+} + Fe^{3+})$.

ferroan compositions with $MGN \sim 65$ indicate the closing phase of fractionation in this system. It follows that the observed spectrum of the plagioclase compositions demands a new explanation other than the model of long-lasting Pl fractionation. This may be due to the variation in volatiles, especially water in the magma.
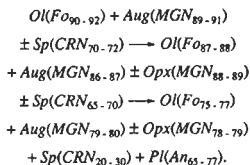
Interesting information can be derived from the comparison of the compositions of the spinel inclusions

in olivine and clinopyroxene (bottom pair of plots in Fig. 6). The spinel from the olivine exhibits a fairly systematic decrease in Cr concentration with declining Fo content [$70 > CRN > 0$, $CRN = Cr^{3+}/(Cr^{3+} + Al^{3+} + Fe^{3+})$], which agrees with the concept of primary magma fractionation. As for the clinopyroxene, we did not find inclusions with $CRN > 25$, even in the most magnesian grains. This observation seems to be the

gravest contradiction to the fractionation model: spinel inclusions in coexisting Ol and Cpx must have identical or similar compositions. A tenable explanation for the "magnetitic" composition of the spinel in the host mineral seems to be the high Cr solubility in the clinopyroxene and the resulting complete reequilibration of the chromite-inclusion compositions through the exchange reaction $Cr^{3+} \longrightarrow Fe^{3+}$. Indications of such reequilibration of the primary compositions of minerals have been extensively discussed in recent works. Regarding the $Sp–Cpx$ equilibrium, however, this assumption obviously needs to be tested experimentally.

No chromite inclusions have been found in the plagioclases. In this case, however, cotectic relations are likely to exist between Pl and ferroan spinellid. This is supported by our discovery of several pyroxene-plagioclase-magnetite intergrowths in the high-alumina basalt. Significantly, the abrupt change from Cr-rich spinels to titanomagnetites occurs in the same MGN range of the coexisting Ol that records the beginning of Pl crystallization: 75 - 77% Fo (Fig. 6). This justifies the conclusion that the copious separation of plagioclase and magnetite in the derivatives of the primary magma commenced almost simultaneously during the final phase of its fractionation.

The results of our study of the coexisting (cotectic) mineral intergrowths and mutual mineral inclusions can be summarized as two principal conclusions on the origin of the Klyuchevskoi basalts. First, the broad range of mafic mineral compositions indicates that, by the time of the eruption, these basalts represented radically nonequilibrium associations of the magma and the minerals suspended in it. This suggests that the melt was mixed in the conduit with crystals that had been produced during various stages of the primary magma fractionation. Second, the regular paired variations of the mineral compositions indicate that, irrespective of the time the flank eruptions took place, the processes of magma fractionation were identical, and the general sequence of mineral crystallization from the inferred high-MgO primary magma was as follows:

$$Ol(Fo_{90-92}) + Aug(MGN_{89-91})$$
$$\pm Sp(CRN_{70-72}) \longrightarrow Ol(Fo_{87-88})$$
$$+ Aug(MGN_{86-87}) \pm Opx(MGN_{88-89})$$
$$\pm Sp(CRN_{65-70}) \longrightarrow Ol(Fo_{75-77})$$
$$+ Aug(MGN_{79-80}) \pm Opx(MGN_{78-79})$$
$$+ Sp(CRN_{20-30}) + Pl(An_{65-77}).$$

The sign "±" corresponds to the situation in which the minerals do not form cotectic intergrowths and are identified only as mineral inclusions, in other words, when their contents in the crystallizing material are as small as fractions of a percent. The conditions under which crystallization succession of this kind is plausible have been determined using computer simulation.

P–T PHASE DIAGRAMS FOR ANHYDROUS AND HYDROUS HIGH-MAGNESIA MAGMA

For determining the origin and evolution of magmatic systems, evaluating the depths at which primary magma fractionation takes place is of great importance. The fulfillment of this task demands knowledge of the pressures that controlled the crystallization sequence and compositions of mineral phases. Conventional barometry of basalts consists in projecting their real compositions onto pseudoternary diagrams plotted from the results of high-pressure quenching experiments in natural silicate systems. It was by using this approach and $Ol–Cpx–SiO_2$ diagrams that Kersting and Arculus (1994) obtained the first estimates of the Klyuchevskoi magma crystallization pressure: 5 - 9 kbar. This technique, however, has disadvantages related to the fact that the projection procedure itself (1) incorporates a substantial convolution of the chemical information on the target by recalculating natural and experimental compositions to systems of smaller dimensions and (2) requires visual pressure evaluation using various nomograms and pregraduated diagrams. The use of computer models of polybaric magma crystallization opens up new opportunities in this line of research (Ariskin et al., 1990, 1991).

COMAGMAT System
as a Basis for Thermodynamic Computer Simulation

In our calculations, we used the high-pressure COMAGMAT version developed at the Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences (Ariskin et al., 1993). This petrological software package was implemented on an IBM PC and designed to compute mineral sequences and the chemical evolution of basalt magma as it underwent equilibrium or fractional crystallization. The basis of the software is the solution of systems of mineral–melt (geothermometer) equilibrium equations for the major phases of the basalt system with the given degree of its crystallization (Frenkel and Ariskin, 1984). We calibrated geothermometers for olivine, plagioclase, pyroxenes, and magnetites using the results of experiments described in the literature. They ensured the accuracy of crystallization temperature measurement within 10 - 15°C at atmospheric pressure and within 20 - 30°C at pressures to ~15 kbar. The compositions of minerals were calculated with an accuracy of 1 - 3 mol %. The COMAGMAT program simulates magma crystallization step by step as the amount of crystallizing material is increased, and it allows one to modify the oxidation-reduction potential under the conditions of a system that is open or closed (12 buffers) with respect to oxygen.

In its present state of development, the COMAGMAT software has the following limitations: a lack of chrome spinel crystallization; insufficient stability of the scheme during the simulation of peritectic relations
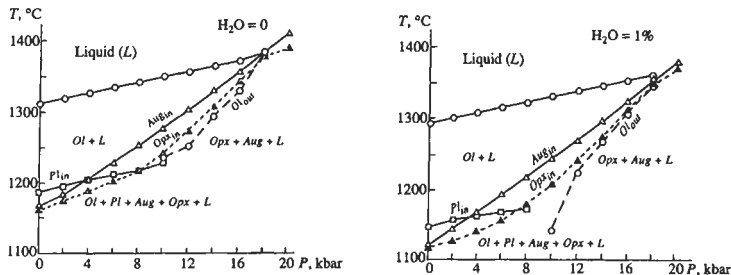
Fig. 7. $P–T$ diagrams of anhydrous and hydrous high-magnesia magma computed by the COMAGMAT program under QFM-buffer conditions (equilibrium crystallization).
The initial composition corresponds to the average Klyuchevskoi high-magnesia basalt (Type I in Table 1).

between Opx, Ol, and Aug (especially at high pressures); and a lack of garnet in high-pressure calculations (15 - 20 kbar). Nevertheless, it seems justified to use this software in tholeiitelike systems dominated by Ol, Cpx, and Pl crystallization (Ariskin et al., 1990, 1991; Barmina et al., 1989; Ariskin et al., 1993).

Equilibrium Crystallization of Anhydrous High-Magnesia Magma

As an initial hypothesis, we assumed that the average composition of the Klyuchevskoi high-magnesia basalts (Table 1) is a sufficiently reliable approximation of the parental magma. This assumption is justified by the petrochemical and geochemical features of the Klyuchevskoi lavas discussed above. The results of calculating the compositions of olivine on the high-magnesia basalt liquidus provide more support in its favor. For instance, Khubunaya et al. (1993) used olivine geothermometers by Ford et al. (1983) to calculate at atmospheric pressure the composition of olivine in equilibrium with the parental magma of the high-magnesia basalt from the Bulochka Bocca (Table 2); the value $Fo_{89.7}$ was obtained. Using the COMAGMAT model, we calculated the composition of olivine on the average high-magnesia basalt liquidus (Table 1) for a pressure range of 1 atm - 15 kbar and oxygen fugacity corresponding to the QFM buffer and obtained similar values: $Fo_{89.3 - 90.0}$. These values are slightly lower than the most magnesian Ol ($Fo_{91.5}$) found in the Klyuchevskoi lavas, but it almost coincides with the peaks of olivine composition distribution in the high-magnesia basalts of the Bulochka, Luchitskii, and Malysh boccas (Khubunaya et al., 1993). This justifies the conclusion that, despite the high probability of the existence of a more magnesian parental (or primary) magma, the

average composition of the Klyuchevskoi high-magnesia basalts can be used to simulate the origin of the transitional and high-alumina basalts.

The model anhydrous $P–T$ phase relations of the primary high-magnesia magma are displayed in Fig. 7 (left plot). These are the results of COMAGMAT computation of a series of isobaric paths of the equilibrium high-magnesia basalt magma crystallization at pressures of 1 atm - 20 kbar. The crystallization sequence was computed for each pressure from complete liquidus to total degree of crystallization $F = 50$ mol %, with the crystallization step $dF = 1$ mol %. The resultant diagram reflects the known properties of basalt systems related to the expansion of pyroxene crystallization regions at the expense of olivine and plagioclase with increasing total pressure.

Regarding the accuracy of the calculation, the line of orthopyroxene appearance is the most problematic. In experiments with magnesian basalts, Opx emergence to the liquidus is identified over a wide pressure range. This precludes the development of an optimum model for this mineral. Nevertheless, an important result of the computer simulation is that, at a pressure of about 18 kbar, the initial melt appears to be saturated with olivine ($Fo_{90.3}$) and augite ($MGN = 89.8$), that is, with the phases that correspond to the most magnesian mineral association discovered in the Klyuchevskoi lavas (Fig. 5). Close to the liquidus is the field of model orthopyroxene with $MGN = 89.7$ at this pressure. These relations can be interpreted as an indication that primary magma fractionation began at pressure of at least 20 ... is, at a depth consistent with the depth of the Klyuchevskoi magma source as it was located by geophysical data (Gorshkov, 1956).

*Equilibrium Crystallization
of Hydrous High-Magnesia Magma*

A *P–T* diagram for high-magnesia basalt magma that initially contained 1 wt % H_2O is shown in Fig. 7 (right). These data were obtained as a result of the first attempt to numerically model phase relations in the presence of water using the updated, hydrous version of the COMAGMAT system. This empirical model takes into account the varying degree of water effect on the liquidus temperatures of olivine, plagioclase, and pyroxenes and is based on a comparison of computed dry liquidus temperatures with temperatures observed in experiments, when the H_2O content is known to coexist in glass with another mineral. Dividing the difference between the anhydrous and hydrous liquidus temperatures by the content of water in the magma, we find a temperature drop due to 1 wt % H_2O for each mineral phase in this experiment. While applying the COMAGMAT hydrous version, we used the average values computed for several experimental series for individual minerals. The INFOREX data base (for explanation see Fig. 5) contained 45 such experiments for *Pl*, 7 for *Ol*, 28 for *Aug*, and 2 for *Opx*. These experiments were performed at pressures 1 - 5 kbar, temperatures 800 - 1350°C, and with the H_2O contents of magma ranging from 1.7 to ~8 wt %. The respective water effect coefficients were 42.2 ± 4.8°C for *Pl*, 17.5 ± 4.9°C for *Ol*, 27.4 ± 6.4°C for *Aug*, and 14.2 ± 4.1°C for *Opx*. Because the value for *Opx* was obviously underestimated since the data sample was too small, we used a value of 22.4°C, intermediate between the coefficients for *Ol* and *Aug*.

In our simulation of hydrous systems, we assume water to be an incompatible component, accumulating monotonically in fractionation products: potential mineral crystallization temperatures are computed for anhydrous magma and are then corrected by decreasing them in proportion to the found coefficients and H_2O concentrations. This rough approach should be considered as a first approximation, though it satisfactorily reconstructs the known regularities of the displacement of phase regions in hydrous systems (Yoder and Tilley, 1962; Baker and Eggler, 1983). As seen in Fig. 7, in the case of hydrous magma, the region of olivine grows notably larger, and that of plagioclase grows smaller, as the liquidus temperature declines. The intersection of the *Ol* and *Aug* liquidus surfaces shifts approximately 0.5 kbar higher.

Because the concentration of water in magma cannot surpass the solubility limit, an equation of the water saturation of the system had to be added in the model. For this purpose, experiments on the direct measurement of water solubility in basalt and andesite melts were processed. The basic information contained the results of 20 experiments performed at temperatures 1100 and 1200°C and pressures 1 - 6 kbar (Hamilton, 1964; Kadik *et al.*, 1971). These data were processed by the least square method for a linear model of solu-

bility variation with pressure, temperature, and melt composition. The final equation has the following form:

$$C_{H_2O} = -2787(\pm 935)/T \ (K)$$
$$+ 0.610(\pm 0.030)\ln P \ (bar) + 3.107(\pm 0.873)C_{SiO_2} \ (1)$$
$$- 6.282(\pm 1.785)C_{Al_2O_3} - 67.65(\pm 18.03),$$

where C_{H_2O}, C_{SiO_2}, and $C_{Al_2O_3}$ are the concentrations of the components in the melt (wt %). This equation reproduces the experimental solubility values (varying from 3.1 to 11.1 wt % H_2O) with an accuracy of about 0.3 wt %.

In the course of COMAGMAT simulation of hydrous magma crystallization, the computed water content in the liquid is compared after each crystallization step with the solubility limit computed by equation (1). Computation ends when the model H_2O content exceeds the limit. It is assumed that the previously homogeneous melt loses a considerable amount of water during degassing.

SIMULATION OF POLYBARIC FRACTIONATION OF ANHYDROUS PRIMARY MAGMA

Some Methodological Aspects of Computer Simulation

The plausibility of the phase relations and mineral compositions computed for the average high-magnesia basalt provided a basis for using a new COMAGMAT version in the computer simulation of the Klyuchevskoi magma fractionation. The main objective of this simulation was to determine whether it is possible to prescribe (find) the fractionation conditions under which the model evolution trends of major and trace element concentrations in minerals and magma would fit the real geochemistry of a given igneous rock series. The method of investigation consists in carrying out a series of COMAGMAT computations of primary magma fractionation using a given "net" of external conditions (pressure, f_{O_2}, H_2O content) and searching for an optimum variant that would best fit the observed geochemical and mineralogical features. The principal measure of the optimum character of the model (crystallization conditions) is the correspondence of the computed and natural trends of the petrogenic elements.

The interpretation of the results obtained in this way is based on two main assumptions. First, in the case of an exact identification of the primary magma, the compositions of the model fractionation products can be compared, strictly speaking, only with the compositions of natural glasses, aphyric rocks, or melt inclusions in minerals. In this context, the Klyuchevskoi lava series is certainly not ideal, but it is still acceptable, because the total amount of crystal intergrowths and separate phenocrysts is rarely greater than 5 - 10 vol %. Second, the computed crystallization sequences and composition evolution lines are functions of the extent

and time of fractionation (for dynamic models), that is, every subsequent differentiate can be obtained from the previous one within a strictly defined interval. The Klyuchevskoi eruptions do not provide a distinct time sequence for basalts of various petrochemical types: with the general tendency of the lavas to grow more acid and aluminous with time (Ozerov, 1993), there were instances in which magnesian basalts were erupted after aluminous ones (Khrenov *et al.*, 1989). For this reason, we do not consider the Klyuchevskoi lavas to be products of a simple one-stage fractionation of the same primary magma; we believe that the insignificant composition variation relative to the general petrochemical and geochemical trends (Figs. 2 and 3) reflects the stability of the primary magma compositions and their fractionation conditions throughout the eruptive history of this volcanic center. This approach does not contradict the mixing of differentiates that correspond to different fractionation stages or different times of formation; in any case, the bulk compositions of the mixed basalts in terms of petrogenic and trace elements must not deviate much from the main cotectic control line (Nielsen, 1990).

Isobaric Anhydrous Magma Fractionation

Our first step was to compute a series of isobaric high-magnesia magma fractionation paths at pressures of 1 atm and 1, 2, 3, ..., 20 kbar. Computation was performed for dry magma and an oxygen fugacity corresponding to the *QFM* buffer, using the estimates of Khubunaya *et al.*, (1994). The model sequences of mineral appearances on the liquidus were close to those shown in Fig. 7. The computed evolution trends of the magma are presented in Figs. 8a and 8b. For comparison, we used three oxides, Al_2O_3, CaO, and MgO, as the main barometric components of basalt systems (Ariskin *et al.*, 1990, 1991). The plots indicate that at pressures above 8 kbar high-alumina basalt magma might be derived from the primary high-magnesia magma, but its CaO content is systematically 1.5 - 2 wt % lower than that of the natural samples. Significantly, the greatest deviation of the computed trends from the natural ones was observed at 16 - 20 kbar, that is, near the point of cotectic saturation of the primary magma with olivine (Fo_{90}) and augite ($MGN \sim 90$) (Fig. 7).

The discrepancy between the calculated high-pressure and the observed CaO–MgO trends is not an artefact of the model. It was demonstrated experimentally for the first time by Draper and Johnston (1992) with reference to the calc-alkalic series of the Aleutian Island. The authors explained it by the potential effect of water but did not provide concrete arguments to support this view. We offer a different explanation.

Decompression Anhydrous Magma Fractionation

The fact that the natural CaO–MgO trends intersect the experimental and calculated lines of isobaric crystallization is an indication that a lower proportion of clinopyroxene crystallized under the real conditions. This might be caused by the contraction of the *Cpx*

crystallization field as fractionation proceeded, for example, due to a pressure decline as magma moved toward the surface. To test this hypothesis, we carried out an additional computation simulating the primary anhydrous high-magnesia magma crystallization at pressures ranging from ~19 kbar (corresponding to the *Ol–Aug* cotectic) to ~1 to 2 kbar. We modified the rate of decompression dP/dF, that is, the pressure decline per 1% of magma crystallization. The results of the computation are presented in Figs. 8c and 8d. The computed paths suggest that, at a decompression rate of ~0.4 kbar/mole, the model evolution of the magma composition fairly well reproduces most of the natural Al_2O_3–MgO and CaO–MgO trends. However, at the final fractionation stages, notable deviations are observed: the Al_2O_3 content ceases to grow, whereas CaO increases slightly.

Assuming that the Klyuchevskoi magma fractionation proceeded in accordance with the decompression mechanism, these deviations can be explained by assuming that during the final stages of the natural magma crystallization some new factor was operating, which influenced the phase relations. This factor might be the presence of volatiles, e.g., water (Yoder and Tilley, 1962; Baker and Eggler, 1983). This assumption is supported by studies on the compositions of fluid and melt inclusions in olivines and clinopyroxenes from the Klyuchevskoi lavas (Khubunaya *et al.*, 1994; Sobolev and Chaussidon, 1995). The results of these studies indicated that the fluid dissolved in the magma had a substantially hydrocarbonate composition; direct measurements of H_2O concentration in the homogenized melt inclusions with an ion probe yielded ~2.5 wt % H_2O with approximately 9 wt % MgO in the melt.

SIMULATION OF DECOMPRESSION FRACTIONATION OF HYDROUS PRIMARY MAGMA

The hypothesis of the decompression fractionation of hydrous magma was also investigated by computer simulation using the hydrous version of the COMAG-MAT program. To find the optimum conditions of fractional crystallization, computation was performed using a more compressed net of parameters ($-0.50 \le dP/dF \le -0.30$ kbar/mole, with an interval of 0.02 kbar/mole) and initial concentrations ($0.25 \le H_2O \le 2.00$ wt %, with an interval of 0.25 wt %). In many instances, we had to use a closer net of initial data: because of the intricate reaction relations between *Ol*, *Aug*, and *Opx* at high pressures, the system appeared to be extremely sensitive even to the smallest modifications of the input parameter values, which resulted in the loss of a phase in the crystallization sequence. This impairs the prediction capacity of the model, and the simulation procedure acquires the character of an optimization procedure with a great number of geochemical and mineralogical criteria. We analyzed more than 600 combinations of parameter values. The most important results are presented in Figs. 8e, 8f, and 9.
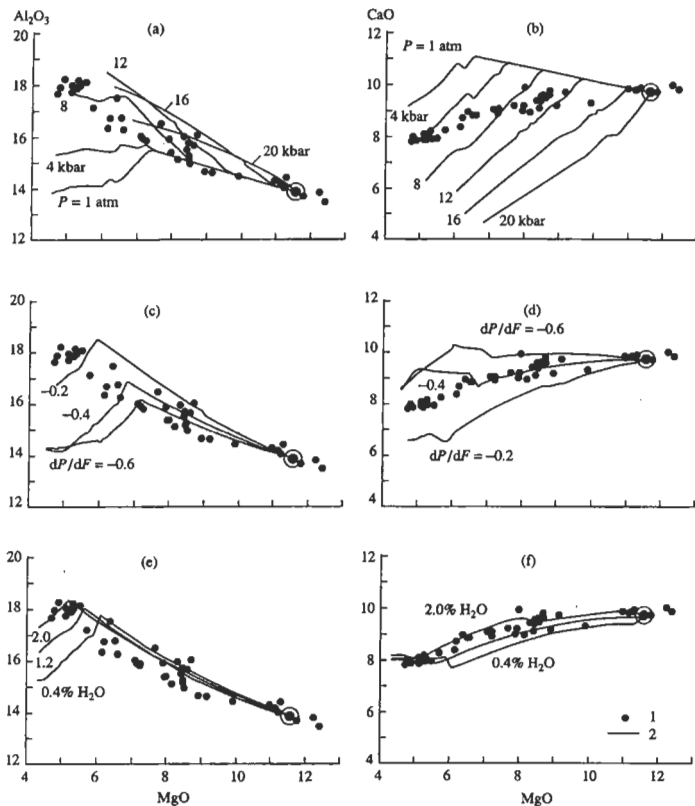
Fig. 8. Computer-simulated composition evolution trends (wt %) of liquid during the polybaric fractionation of anhydrous and hydrous high-magnesia basalt.

1 – natural samples (authors' data), 2 – computation results. The initial composition corresponds to the average Klyuchevskoi high-magnesia basalt (Type I in Table 1); it is denoted by a large solid circle. Computation was performed by the COMAGMAT model with a crystallization interval of 1 mol % under QFM-buffer conditions:

(a), (b) – isobaric fractionation in dry system (the figures on the lines indicate crystallization pressure);

(b), (c) – decompression fractionation in dry system (initial pressure P_i = 18 kbar; final pressure P_f = 1 kbar; parameter dP/dF characterizes decline of pressure P for 1 mol % increase of magma fractionation degree F);

(e), (f) – decompression fractionation in the presence of water (initial pressure P_i = 19.3 kbar; decompression rate dP/dF = –0.33 kbar/mole; the figures on the lines indicate initial water contents; at $P \sim 1.5$ kbar and 3.6 - 3.8 wt % H_2O in the magma the model predicts its water saturation).

Crystallization Sequence and Composition Evolution of Magma

According to the results of the computer simulation, the best model of the primary high-magnesia basalt magma fractionation corresponds to an initial water content of 1.2 - 2.0 wt % with a decompression rate of $dP/dF = -0.33$ kbar/mole. With these values, the computed fractionation lines, plotted in the Al_2O_3–MgO and CaO–MgO diagrams, fit the best with the observed petrochemical trends (Figs. 8e and 8f). The line of 0.4% H_2O shows a small but systematic deviation from the natural CaO–MgO trend and lags notably behind the typical high-alumina basalts in Al_2O_3 and MgO contents. Figure 9 presents the computed crystallization sequence and mineral composition variation with declining temperature and pressure for a water content of 2 wt % in the primary magma. The right-hand side of the plot compares the compositions of the average high-alumina basalt (HAB-1 in Table 1) and the model differentiate (HAB-2) at the onset of plagioclase crystallization.

It follows that the crystallization of the primary high-magnesia magma starts with the *Ol–Aug* cotectic at a pressure of approximately 19 kbar and a temperature of about 1350°C. Olivine and augite fractionate as 1 : 1.5 up to 1260°C (~15 kbar, fractionation degree $F = 15$ wt %), when magnesian orthopyroxene ($MGN = 87.8$) appears on the liquidus. The subsequent fractionation of these minerals is distinguished by the amount of crystallizing augite attaining 90 wt %, the proportion of olivine decreasing to 15 - 10 wt %, and that of orthopyroxene being as low as 2 wt %. More active augite separation results in the CaO–MgO trend bending (Fig. 8f) toward a greater decline in Ca content. Note that with declining pressure the proportion of clinopyroxene increases along with the diminishing of its crystallization field. This seemingly paradoxical feature of crystallization in basalt systems was discussed previously by Ariskin *et al.* (1990).

Plagioclase begins to crystallize at a pressure of ~7 kbar, a temperature of 1110°C, and about 3 wt % H_2O in the magma. The degree of system fractionation at this temperature is 36% of the initial magma weight; the composition of olivine as it appears on the liquidus is somewhat more magnesian (Fo_{79}) than that given by the results of microprobe measurements (Fo_{75-77}). Generally, the model compositions of mafic minerals closely fit the observed trends (Fig. 4), but they deviate to a greater degree from the equilibrium relationships (Figs. 5 and 6) below 1150°C. This suggests that, in the low-temperature computation of hydrous magma systems, the COMAGMAT program fails to attain complete agreement between the compositions of the coexisting olivine and pyroxenes (moreover, the effect of water on the plagioclase composition is not considered). Nevertheless, the main conclusion concerning the formation of high-alumina melt, identical to natural magmas, at the high-pressure stage seems to be justified (compare HAB-1 and HAB-2 in Fig. 9). In response to a decrease in the initial water content in the high-Mg magma, the point at which *Pl* crystallization begins shifts to a lower pressure but never descends below 5 kbar at the optimum values of 1.2 - 2.0 wt % H_2O with the decompression rate $dP/dF = -0.33$ kbar/mole.

The model crystallization sequences, displayed in Fig. 9, are cut off at a temperature of ~1050°C and a pressure of 4 kbar, which corresponds to 46% fractionation of the primary magma. This was done deliberately, because at lower temperatures and a high water content, the COMAGMAT program does not ensure that the computation results will be realistic. Generally, the fractionation interval after the appearance of plagioclase is characterized by a great predominance of the latter in the crystallizing material (70 - 75 wt %), with a simultaneously increasing amount of orthopyroxene. Of interest may be the computation result indicating that, in the case of the optimum model 2.0% H_2O, an andesitelike melt with 3.6 - 3.8 wt % H_2O is saturated with water at approximately 1000°C and 1.6 kbar [see equation (1)].

Evolution of Trace-Element Abundances

Figure 3 compares the natural and computed trends for the optimum model of the evolution of trace-element abundances in melts representing differentiates of primary high-magnesia magma. These computations were performed using fixed values or temperature-composition relations for crystal–melt partition coefficients (Barmina *et al.*, 1989; Ariskin *et al.*, 1993). For the specified conditions of decompression fractionation, the model lines reproduce the entire spectrum of compositions that characterizes the transition from high-magnesia to high-alumina basalts. The great decrease in Sr concentration during the final fractionation stages is related to abundant plagioclase crystallization, that is, the inflection point is a function of the initial water content and may be shifted to the region of realistic values in a more detailed computer simulation. The Cr and Sc accumulation toward the end of the process is caused by an abrupt decrease in the amount of crystallizing augite at temperatures below 1100°C; this appears to be a consequence of the inadequacy of computations in the low-temperature region. For lack of experimental data on the effect of oxygen fugacity on the partition of copper between minerals and basalt magma, the model line for this element describes only some of the natural compositions.

A small disturbance in the central segments of the model trends is caused by the insufficiently stable operation of the computation scheme when it deals with reaction relations between several minerals at once; it is not informative. Thus, the results of simulating the evolution of trace-element abundances can be regarded as another argument in favor of decompression fractionation.
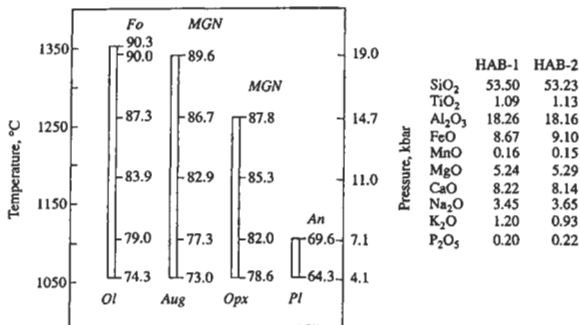
Fig. 9. Computer-simulated crystallization sequences and mineral compositions under decompression fractionation of hydrous high-MgO magma (optimum model for the generation of the Klyuchevskoi high-alumina magma).

Initial composition corresponds to the average Klyuchevskoi high-magnesia basalt (Type I in Table 1). Computation was performed by the COMAGMAT model with a crystallization step of 1 mol % under QFM-buffer conditions: decompression rate $dP/dF = -0.33$ kbar/mole, initial water content 2 wt % H_2O. HAB-1 — average composition of Klyuchevskoi high-alumina basalt (Type IV in Table 1); HAB-2 — composition of model differentiate after 36-percent fractionation of primary magma ($P = 7$ kbar, $T = 1110°C$, 3.0 wt % H_2O).

PROBLEM OF THE Ca/Al RATIOS IN CLINOPYROXENES

The conclusion that the association of phenocrysts, crystal intergrowths, and mineral inclusions observed in the Klyuchevskoi lavas represents considerably high-pressure formations is one of the most important outcomes of this analysis. The accuracy or details of the computer model used are irrelevant; this conclusion is based primarily on a detailed analysis of experimental data on the compositions of high-magnesia clinopyroxenes and olivines that coexist at pressures above 10 - 15 kbar (Fig. 5). Fairly high values have been obtained for the crystallization pressure of the Klyuchevskoi magmas (5 - 9 kbar) by the method of graphic projection (Kersting and Arculus, 1994). The densities of carbon dioxide fluid from inclusions entrapped in magnesian olivine crystals yielded lower values: 5 to 6 kbar (Khubunaya et al., 1994). There is, however, one mineralogical peculiarity of the Klyuchevskoi lavas that casts doubt upon their high-pressure origin.

Analysis of a large amount of experimental data on the compositions of augites, synthesized in experiments with basalt and peridotite samples, revealed that at pressures above 5 kbar pyroxenes have $CAN = 100CaO/Al_2O_3$ (wt %) < 400; the CAN value for low-pressure pyroxenes ranges between 500 and 1000 (Nesterenko and Ariskin, 1993). According to this measure, most of the pyroxenes from the Klyuchevskoi lavas exhibit typical low-pressure characteristics:

with the average contents of 19.7 ± 2.0 wt % CaO and 3.5 ± 1.4 wt % Al_2O_3, the average CAN value is 558 ($n = 187$). Representative analyses of coexisting high-magnesia Aug and Opx are presented in Table 3 (Ozerov, 1993). Also given in this table are the compositions of experimental Aug and Opx that were synthesized at 15 kbar and 1125°C (Meen, 1990) and 1250°C (Draper and Johnston, 1992). Both clinopyroxenes contained more than 7 wt % Al_2O_3 and had CAN < 300 in these experiments.

In attempting to solve this problem, we turned to the INFOREX data base (Ariskin et al., 1992), paying particular attention to the results of experiments at high pressures and in the presence of volatiles. Pyroxenes have been subdivided into high-pressure and low-pressure minerals on the basis of CAN using data obtained in anhydrous systems (Nesterenko and Ariskin, 1993). The studies of melt and fluid inclusions in minerals from the Klyuchevskoi basalts indicate that their primary magmas contained considerable amounts of water and carbon dioxide (Khubunaya et al., 1994; Sobolev and Chaussidon, 1995). Despite the scarcity of data on the compositions of pyroxenes that crystallized in hydrous magmas, we were lucky to find a few such experiments. Their results indicate that the Al_2O_3 content in clino- and orthopyroxenes drops rapidly at high pressures under hydrous conditions, as compared to anhydrous systems; this involves a considerable increase in the CAN value. Typical compositions of such

Table 3. Experimental, natural, and computed compositions of high-pressure melts and coexisting pyroxenes

Component	(Mysen, Boettcher, 1975) H_2O = 20.4 wt % P = 15 kbar T = 1120°C t = 13 hours			(Meen, 1990) H_2O = 0.0 wt % P = 15 kbar T = 1125°C t = 96 hours			(Draper, Johnston, 1992) H_2O = 0.0 wt % P = 15 kbar T = 1250°C t = 170 hours			(Ozerov, 1993) (Opx inclusion in Aug) T_c = 1206°C		Results of simulation H_2O = 2.0 wt % P = 14.7 kbar T_{mod} = 1261°C		
	L	Aug	Opx	L	Aug	Opx	L	Aug	Opx	Aug	Opx	L	Aug	Opx
SiO_2	59.60	52.67	57.20	53.20	50.90	55.50	47.50	48.60	49.60	53.25	55.89	52.59	52.62	56.14
TiO_2	0.60	0.10	0.06	1.08	0.33	0.20	0.95	0.77	0.32	0.16	0.08	0.95	0.19	0.10
Al_2O_3	18.10	2.00	1.20	15.00	7.41	1.58	20.03	7.33	6.01	1.99	1.63	15.24	6.83	3.27
FeO	2.10	2.79	3.80	9.37	6.58	11.20	9.12	10.14	15.15	4.69	9.01	8.99	4.25	7.36
MnO	0.10	0.06	0.14	–	–	–	0.15	0.24	0.28	0.02	0.11	0.18	–	–
MgO	4.20	19.20	34.80	4.91	13.50	28.70	5.63	15.21	23.42	16.84	30.59	8.85	15.56	29.80
CaO	14.50	20.80	1.30	7.22	20.30	1.95	6.46	14.60	2.50	21.25	1.56	9.50	20.55	3.33
Na_2O	0.60	–	0.01	3.25	1.24	0.26	3.76	0.74	0.20	0.37	0.01	2.81	–	–
K_2O	0.10	–	–	4.77	–	–	2.65	–	–	0.01	–	0.72	–	–
P_2O_5	–	–	–	1.13	–	–	1.13	–	–	–	–	0.17	–	–
MGN	78.1	92.5	94.2	48.3	78.5	82.0	52.4	72.8	73.4	86.5	85.8	63.7	86.7	87.8
CAN	80	1040	108	48	274	123	32	199	42	1068	96	62	301	102

Note: T_c is temperature calculated on the basis of CaO solubility in orthopyroxene at a pressure of 15 kbar (Sachtleben, Seck, 1981); $MGN = 100MgO/(MgO + FeO)$, mol %; $CAN = 100CaO/Al_2O_3$, wt %.

high-pressure pyroxenes with low-pressure characteristics are given in Table 3 (Mysen and Boettcher, 1975).

The data presented here demonstrate that, in their chemical features, the high-pressure pyroxenes that crystallize in the presence of water approximate the real pyroxenes observed in the Klyuchevskoi basalts. A more convincing argument in favor of the high-pressure origin of the Klyuchevskoi pyroxenes and the validity of the petrologic model derived on this basis would have been a comparison with experimental data obtained in a hydrous system at pressures above 15 kbar and temperatures between 1300 and 1350°C (Fig. 9). Unfortunately, we have not found such data in the literature. It is obvious that the problem of the influence of water and carbon dioxide, dissolved in magma, on the compositions of mafic minerals crystallizing at high temperatures and pressures is an urgent task.

CONCLUSIONS

1. The new data presented here on the geochemistry and mineralogy of the Klyuchevskoi lavas were used, along with systematized data from the literature, to substantiate the conclusion that the high-alumina magmas were formed as a result of high-pressure fractionation of magmas compositionally similar to high-magnesia basalts.

2. To specify the mechanism and conditions of this process, a model was derived on the basis of the COMAGMAT package of petrologic programs for the

isobaric and nonisobaric (decompression) fractionation of basalt magmas under hydrous conditions.

3. A new, hydrous version of the COMAGMAT system has been used to simulate the isobaric and decompression fractional crystallization of the primary Klyuchevskoi magma (an average high-magnesia basalt) over a pressure range of 1 atm - 20 kbar and initial water contents of 0 - 2 wt %. The optimum model of the formation of this magmatic series was found to correspond to polybaric fractionation of the primary magma at a decompression rate of −0.33 kbar per 1% of crystallization with an initial water content of about 2 wt %.

According to this model, crystallization of the magma begins with the separation of olivine and clinopyroxene (in the presence of spinel, as indicated by natural data) at a pressure of about 19 kbar and a temperature of ~1350°C. High-magnesia orthopyroxene begins to separate at a pressure of about 15 kbar and a temperature of ~1260°C, but its proportion in the composition of the crystallizing association is less than 2 wt %, and it does not have any significant effect on the cotectic control lines. The accumulation of water in the magma results in a considerable delay of plagioclase crystallization and the formation of high-alumina differentiation products containing more than 18 wt % Al_2O_3. The alumina enrichment line terminates at the point of plagioclase appearance on the liquidus at a pressure of about 7 kbar, a temperature of 1110°C, and a water content of ~3 wt % in the magma. By this time, the spectrum of model liquid compositions represents all of the varieties of Klyuchevskoi lavas, and further

crystallization results in rapid water saturation of the system with subsequent degassing at a pressure of about 1.5 kbar.

In view of the fact that this model does not take into account the multiphase processes of fractionation, mixing, degassing dynamics, etc., it cannot be regarded as an all-embracing model of the magmatic evolution of Klyuchevskoi Volcano. As an essentially thermodynamic model, it shows the external conditions under which the magma system passed from one state, corresponding to the observed features of high-magnesia magmas, to another state, corresponding to the real compositions of the high-alumina basalts. The dynamics of the fractionation process are incorporated implicitly through a parameter characterizing the decompression rate dP/dF. It is obvious that the optimum dP/dF values are related to the speed at which magma rises to the surface. For this reason, the degree of pressure decline per 1% of magma crystallization needs to be taken into account when deriving more rigorous dynamic or geophysical models of the evolution of volcanic systems.

Because the thermodynamic values presented in this paper were obtained by computer simulation, they must be treated with caution for potential computation uncertainties (Ariskin et al., 1993). Strictly speaking, the reproduction of natural processes in all their detail is not the main goal of modeling geochemical systems (Frenkel, 1992). The intention of this publication was to draw the attention of petrologists to the still inadequately studied *mechanism of decompression fractionation* and to the possibilities offered by modern computer-simulated phase-equilibria models.

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REFERENCES

Ariskin, A.A., Bouadze, K.V., Meshalkin, S.S., and Tsekhonya, T.I., INFOREX: A Data Base on Experimental Studies of Phase Relations in Silicate Systems, *Am. Mineral.*, 1992, vol. 77, pp. 668 - 669.

Ariskin, A.A., Barmina, G.S., and Meshalkin, S.S., Computer Simulation of Polybaric Fractionation of Mafic Magmas, *Abstr. Int. Volcanol. Congr.*, Ankara, 1994, p. 78.

Ariskin, A.A., Frenkel, M.Ya., Barmina, G.S., and Nielsen, R.L., COMAGMAT: A Fortran Program to Model Magma Differentiation Processes, *Comput. Geosci.*, 1993, vol. 19, pp. 1155 - 1170.

Ariskin A.A., Frenkel, M.Ya., and Tsekhonya, T.I., Fractional Crystallization of Tholeiitic Magmas under High-Pressure Conditions, *Geokhimiya*, 1990, no. 2, pp. 172 - 183.

Ariskin, A.A., Tsekhonya, T.I., and Frenkel, M.Ya., Computer Barometry and the Genetic Interpretation of Basalt Glasses from the Central Atlantic, *Geokhimiya*, 1991, no. 7, pp. 1038 - 1047.

Babanskii, A.D., Ryabchikov, I.D., and Bogatikov, O.A., *Evolyutsiya Shchelochno-Zemel'nykh Magm* (Evolution of Calc-Alkalic Magmas), Moscow: Nauka, 1983.

Baker, D.R. and Eggler, D.H., Fractionation Paths of Atka (Aleutians) High-Alumina Basalts: Constraints from Phase Relations, *J. Volcanol. Geotherm. Res.*, 1983, vol. 18, pp. 387 - 404.

Barmina, G.S., Ariskin, A.A., and Frenkel, M.Ya., Petrochemical Types and Crystallization Conditions of Plagiodolerites from the Kronotskii Peninsula, East Kamchatka, *Geokhimiya*, 1989, no. 2, pp. 192 - 206.

Barmina, G.S. and Ariskin, A.A., Decompression Mechanism of the Formation of High-Alumina Lavas at Klyuchevskoi Volcano, *10aya Mezhd. Shkola po Morskoi Geologii* (10th Int. Seminar on Mar. Geol.), Gelendzhik, 1992, vol. 2, pp. 151 - 152.

Bogoyavlenskaya, G.E., Braittseva, O.A., Zharinov, N.A., et al., Klyuchevskoi Volcano, *Activnye Vulkany i Gidrotermal'nye Systemy Kamchatki* (Active Volcanoes and Hydrothermal Systems of Kamchatka), Petropavlovsk-Kamchatskii, 1985, pp. 6 - 69.

Bolshoe Treshchinnoe Tolbachinskoe Izverzhenie (1975 - 1976, Kamchatka) (The Great Tolbachik Fissure Eruption, 1975 - 1976, Kamchatka), Fedotov, S.A., Ed., Moscow: Nauka, 1984.

Borisov, A.A., *Vliyanie Letuchesti Kisloroda na Sootnoshenie Raznovalentnykh Form Zheleza, Khroma, Vanadiya, Nikelya i Medi v Magmaticheskikh Rasplavakh* (Effect of Oxygen Fugacity on the Proportion of Heterovalent Forms of Iron, Chromium, Vanadium, Nickel, and Copper in Magmatic Melts), *Cand. Sci. (Geol.) Dissertation*, Moscow: GEOKHI, Akad. Nauk SSSR, 1986.

Brophy, J.G., Basalt Convection and Plagioclase Retention: A Model for the Generation of High-Alumina Basalt, *J. Geol.*, 1988, vol. 97, pp. 319 - 329.

Brophy, J.G., Can High-Alumina Arc Basalt Be Derived from Low-Alumina Arc Basalt?: Evidence from Kanaga Island, Aleutian Arc, Alaska, *Geology*, 1989, vol. 17, pp. 333 - 336.

Brophy, J.G. and Marsh, B.D., On the Origin of High-Alumina Arc Basalt and the Mechanics of Melt Extraction, *J. Petrol.*, 1986, vol. 27, pp. 763 - 789.

Crawford, A.J., Falloon, T.J., and Eggins, S., The Origin of Island Arc High-Alumina Basalts, *Contrib. Mineral. Petrol.*, 1987, vol. 97, pp. 417 - 430.

Draper, D.S. and Johnston, A.D., Anhydrous PT Phase Relations of an Aleutian High-MgO Basalt: An Investigation of the Role of Olivine-Liquid Reaction in the Generation of Arc High-Alumina Basalts, *Contrib. Mineral. Petrol.*, 1992, vol. 112, pp. 501 - 519.

Ermakov, V.A., Firstov, P.P., and Shirokov, V.P., Petrogenesis of the Klyuchevskoi Group of Volcanoes, *Vulkanizm i*

Glubiny Zemli (Volcanism and the Earth's Interior), Moscow: Nauka, 1971, pp. 152 - 156.

Fedotov, S.A., Khrenov, A.P., and Zharinov, N.A., Klyuchevskoi Volcano: Eruptive Activity in 1932 - 1986 and Predictive Evolution, *Vulcanol. Seismol.* 1987, no. 4, pp. 3 - 16.

Fedotov, S.A., Zharinov, N.A., and Gorel'chik, V.I., Deformation and Earthquakes at Klyuchevskoi Volcano: A Model for Its Eruptive Activity, *Vulkanol. Seismol.*, 1988, no. 2, pp. 3 - 42.

Ford, C.E., Russel, D.G., Craven, J.A., and Fisk, M.R., Olivine - Liquid Equilibria: Temperature, Pressure and Composition Dependence of Crystal/Liquid Cation Partition Coefficients for Mg, Fe^{2+}, Ca and Mn, *J. Petrol.*, 1983, vol. 24, pp. 256 - 265.

Fournelle, J. and Marsh, B.D., Shisalkin Volcano: Aleutian High-Alumina Basalts and the Question of Plagioclase Accumulation, *Geology*, 1991, vol. 19, pp. 234 - 237.

Frenkel, M.Ya. and Ariskin, A.A., An Algorithm for the Computer Solution of Crystallizing Basalt Melt Equilibrium, *Geokhimiya*, 1984, no. 5, pp. 679 - 690.

Frenkel, M.Ya., On the Thermodynamics, Dynamics and Mathematical Modeling of Geochemical Systems, *Geokhimiya*, 1992, no. 10, pp. 1401 - 1411.

Gorshkov, G.S., The Depth of the Magma Source of Klyuchevskoi Volcano, *Dokl. Akad. Nauk SSSR*, 1956, vol. 106, no. 4, pp. 703 - 705.

Gust, D.A. and Perfit, M.R., Phase Relations in a High-Mg Basalt from the Aleutian Island Arc: Implications for Primary Island Arc Basalts and High-Al Basalts, *Contrib. Mineral. Petrol.*, 1987, vol. 97, pp. 7 - 18.

Hamilton, D.L., Burnham, C.W., and Osborn, E.F., The Solubility of Water and Effect of Oxygen Fugacity and Water Content on Crystallization in Mafic Magmas, *J. Petrol.*, 1964, vol. 5, pp. 21 - 39.

Johnston, A.D., Anhydrous *P–T* Phase Relations of Near-Primary High-Alumina Basalt from the South Sandwich Islands: Implications for the Origin of Island Arcs and Tonalite-Trondhjemite, *Contrib. Mineral. Petrol.*, 1986, vol. 92, pp. 24 - 38.

Kadik, A.A., Lebedev, E.B., and Khitarov, N.I., *Voda v Magmaticheskikh Rasplavakh* (Water in Magmatic Melts), Moscow: Nauka, 1971.

Kadik, A.A., Rosenhauer, M., and Lukanin, O.A., Experimental Investigation of Pressure Effect on the Crystallization of Magnesian and Aluminous Basalts of Kamchatka, *Geokhimiya*, 1989, no. 12, pp. 1748 - 1762.

Kadik, A.A., Lukanin, O.A., and Lapin, I.V., *Fiziko-Khimicheskie Usloviya Evolyutsii Bazaltovykh Magm v Pripoverkhnostnykh Ochagakh* (Physico-Chemical Conditions of Basalt Magma Evolution in Near-Surface Chambers), Moscow: Nauka, 1990.

Kay, S.M. and Kay, R.W., Aleutian Tholeiitic and Calc-Alkaline Magma Series: I. The Mafic Phenocrysts, *Contrib. Mineral. Petrol.*, 1985, vol. 90, pp. 276 - 296.

Kelemen, P.B. and Ghiorso, M.S., Assimilation of Peridotite in Zoned Calc-Alkaline Plutonic Complexes: Evidence from the Big Jim Complex, Washington Cascades, *Contrib. Mineral. Petrol.*, 1986, vol. 94, pp. 12 - 28.

Kelemen, P.B., Reaction between Ultramafic Rock and Fractionating Basaltic Magma: I. Phase Relations, the Origin of Calc-Alkaline Magma Series, and the Formation of Discordant Dunite, *J. Petrol.*, 1990, vol. 31, pp. 51 - 98.

Kersting, A.B. and Arculus, R.J., Klyuchevskoi Volcano, Kamchatka, Russia: The Role of High-Flux Recharge, Tapped, and Fractionated Magma Chamber(s) in the Genesis of High-Al_2O_3 from High-MgO Basalt, *J. Petrol.*, 1994a, vol. 35, pp. 1 - 41.

Kersting, A.B. and Arculus, R.J., Pb Systematics of Klyuchevskoi Volcano, Kamchatka and North Pacific Sediments: Implications for Magma Genesis and Crustal Recycling in the Kamchatkan Arc, *Mineral. Mag.*, 1994b, vol. 58A (Abstr. Goldschmidt Conf., Edinburg), pp. 473 - 474.

Khrenov, A.P., Antipin, V.S., Chuvashova, L.A., and Smirnova, E.V., Petrochemical and Geochemical Features of Klyuchevskoi Basalts, *Vulkanol. Seismol.*, 1989, no. 3, pp. 3 - 15.

Khubunaya, S.A., Bogoyavlenskii, S.O., Novgorodtseva, T.Yu., and Okrugina, A.I., Mineralogical Features of Magnesian Basalts: Evidence of Fractionation in the Magmatic Chamber of Klyuchevskoi Volcano, *Vulkanol. Seismol.*, 1993, no. 3, pp. 46 - 68.

Khubunaya, S.A., Sobolev, A.V., and Novgorodtseva, T.Yu., Petrology of Basalts from Klyuchevskoi Flank Eruptions (Kamchatka), *Abstr. Int. Volcanol. Congr.*, Ankara, 1994, p. 112.

Kuno, H., High-Alumina Basalt, *J. Petrol.*, 1960, vol. 1, pp. 121 - 145.

Leonova, L.L. and Kirsanov, I.T., Geochemistry of Klyuchevskoi Basalts, *Geokhimiya*, 1974, no. 6, pp. 875 - 894.

Meen, J.K., Elevation of Potassium Contents of Basaltic Magmas by Fractional Crystallization: The effect of Pressure, *Contrib. Mineral. Petrol.*, 1990, vol. 104, pp. 309 - 331.

Melekestsev, I.V., Khrenov, A.P., and Kozhemyaka, N.N., The Tectonic Setting and General Description of North Kamchatka and Sredinnyi Range Volcanoes, *Deistvuyushchie Vulkany Kamchatki* (Active Kamchatkan Volcanoes), Moscow: Nauka, 1992, vol. 1, pp. 74 - 78.

Mysen, B.O. and Boettcher, A.L., Melting of a Hydrous Mantle: II. Geochemistry of Crystals and Liquids Formed by Anatexis of Mantle Peridotite at High Pressures and High Temperatures as a Function of Controlled Activities of Water, Hydrogen, and Carbon Dioxide, *J. Petrol.*, 1975, vol. 16, pp. 549 - 593.

Nesterenko, G.V. and Ariskin, A.A., Depths of Basalt Magma Crystallization, *Geokhimiya*, 1993, no. 1, pp. 77 - 87.

Nielsen, R.L., Simulation of Igneous Differentiation Processes, *Reviews in Mineralogy*, Nicholls, J. and Russel, J.L., Eds., *Mineral. Soc. Am.*, 1990, vol. 24, pp. 65 - 105.

Nye, C.J. and Reid, M.R., Geochemistry of Primary and Least Fractionated Lavas from Okmok Volcano, Central Aleutians: Implications for Arc Magma Genesis, *J. Geophys. Res.*, 1986, vol. 91, pp. 10271 - 10287.

Ozerov, A.Yu. and Khubunaya, C.A., Olivine and Pyroxene Chemistry as Evidence of a Genetic Relationship between the Aluminous and Magnesian Basalts of Klyuchevskoi Volcano, *Posteruptivnoe Mineraloobrazovanie na Aktivnykh Vulkanakh Kamchatki* (Posteruptive Mineral Formation at Active Kamchatkan Volcanoes), Vladivostok, 1992, part 2, pp. 37 - 61.

Ozerov, A.Yu., Eruptive Dynamics and the Petrochemistry of Aluminous Basalts of Klyuchevskoi Volcano, *Cand. Sci. (Geol.) Dissertation*, Moscow: Inst. of the Lithosphere, 1993.

Perfit, M.R., Gust, D.A., Bence, A.E., *et al.*, Chemical Characteristics of Island-Arc Basalts: Implications for Mantle Sources, *Chem. Geol.*, 1980, vol. 30, pp. 227 - 256.

Plank, T. and Langmuir, C.H., An Evaluation of the Global Variations in the Major Element Chemistry of Arc Basalts, *Earth Planet. Sci. Lett.*, 1988, vol. 90, pp. 349 - 370.

Sachtleben, T. and Seck, N.A., Chemical Control of Al-Solubility on Orthopyroxene and Its Application in Pyroxene Geothermometry, *Contrib. Mineral. Petrol.*, 1981, vol. 78, pp. 157 - 165.

Sakuyama, M., Petrological Study of the Myoko and Kurohime Volcanoes, Japan: Crystallization Sequence and Evidence for Magma Mixing, *J. Petrol.*, 1981, vol. 22, pp. 553 - 583.

Sobolev, A.V. and Chaussidon, M., H_2O Concentrations in Primary Melts from Island Arcs and Mid-Ocean Ridges: Implications for H_2O Storage and Recycling in the Mantle, submitted for publication in *Nature*.

Sobolev, A.V., Danyushevskii, L.V., Dmitriev, L.V., and Sushchevskaya, N.M., High-Al Magnesian Tholeiite – A Primary Magma of MOR Basalts, *Geokhimiya*, 1988, no. 10, pp. 1522 - 1528.

Tilley, C.E., Some Aspects of Magmatic Evolution, *Quart. J. Geol. Soc.*, London, 1950, vol. 106, pp. 37 - 50.

Uto, K., Variation of Al_2O_3 Content in Late Cenozoic Japanese Basalts: A Reexamination of Kuno's High-Alumina Basalt, *J. Volcanol. Geotherm. Res.*, 1986, vol. 29, pp. 397 - 411.

Yoder, H.S. and Tilley, C.E., Origin of Basalt Magmas: An Experimental Study of Natural and Synthetic Rock Systems, *J. Petrol.*, 1962, vol. 3, pp. 342 - 352.