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Compositions of Spinels from Cumulative Anorthites of the Mutnovskii, Ksudach, Golovnina, and Malyi Semyachik Volcanoes, in Kamchatka

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Abstract—Microprobe studies of unzoned plagioclases (An_{92-96}) from crystal tuff of Mutnovskii Volcano and allivalite nodules of rocks from the Ksudach, Malyi Semyachik, and Golovnina Volcanoes revealed small inclusions of a dark-colored mineral that was later identified as spinel. Microprobe analyses showed that the grains are unzoned and spinel inclusions of different chemical compositions may occur in one plagioclase crystal. The spinel compositions form a clear extended single trend corresponding to the solvus zone of a solid solution that has not been described in the literature. The existence of this spinel trend in the solvus zone might have been due to early capturing of spinel grains by growing plagioclase crystals and their rapid cooling soon after eruption, resulting in hardening of the metastable solution. These spinels are supposed to form synchronously with plagioclase crystallization. The diversity of spinel compositions is explained by thermo diffusive equalizing of originally zonal spinel crystals after they were captured by plagioclase crystals or by their growth in crystallization haloes of anorthite.

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INTRODUCTION

Studies of plagioclases from crystalloclastic tuff of Mutnovskii Volcano revealed small inclusions of a dark-colored mineral in some crystals, which was later identified as spinel. Microprobe analyses of these spinels showed that their compositions form a long single trend that was previously virtually unknown in the literature. In order to study it in more detail and for comparative analysis, plagioclases of analogous composition from Ol–An inclusions (allivalites) of the Ksudach, Golovnina, and Malyi Semyachik volcanoes were investigated. The study of spinels from allivalite plagioclases revealed that their compositions almost exactly fit the originally identified trend. Few analyses of such spinels are found in the literature [Grib, 2007, 2008; Barnes and Roeder, 2001]. Similar and somewhat different compositions of spinels included in olivine crystals from allivalites and basalts are found in [Grib, 2008; Plechov et al., 2008; Prikhod'ko et al., 1977; Krause et al., 2007] and were also obtained by the authors of this paper; however, they are not discussed here.

BRIEF GEOLOGICAL AND PETROGRAPHIC DESCRIPTIONS OF THE STUDIED SAMPLES

Coarse-bedded pyroclastic tuffs of Mutnovskii Volcano occur on the summit of the northeastern crest of the ridge coming from the cliff of the eastern crater. The tuffs are pyroclastic rocks consisting of fine ash material, slag fragments from 0.5 to 3–7 cm across, a great amount of plagioclase crystals 0.4–1 cm long, and some up to 4 cm long. The crystals are of flattened rectangular shape with chamfered corners, often twinned, with the wider side being the composition plane. Inclusions of similar large crystals and small olivines are found in slag fragments. The 2–3 m thick tuffs are underlain by low-potassium basalts.

Allivalites, i.e., cumulative olivine–anorthite inclusions, are widely known in low-potassium island arc tholeiites. Their geological position, as well as their mineral and chemical compositions, including those for Ksudach, Golovnina, and Malyi Semyachik volcanoes, have been described in many papers [Volynets et al., 1978; Prikhod'ko et al., 1977; Selyangin, 1987; Frolova and Plechov, 2001; Plechov et al., 2008; Shishkina et al., 2009]. The most complete review of hypotheses of the origin of allivalites is presented in [Plechov et al., 2008], so we will not discuss this problem in this paper. I share the view on cumulative genesis of allivalites from high-alumina, low-potassium melts. It's worth noting that the allivalite samples from Ksudach and Golovnina volcanoes occurred in pyroclastic deposits and those of Malyi Semyachik Volcano were found in a lava flow [Selyangin, 1979].

The samples chosen for analysis are coarse-grained Ol–An nodules with an average grain size of plagioclase of 0.5–1.5 cm and olivine below 0.5 cm; the black-colored groundmass in the intergranular space occupies a small volume compared with the crystals.

ANALYTICAL TECHNIQUE

Due to the fact that spinel inclusions in plagioclase crystals occur rather rarely and the direct study of them with a microprobe was difficult, we took a sample of plagioclase crystals weighing about 100 g (from Mutnovskii Volcano) and dissolved it in hydrofluoric acid following the technique of [Neuerburg, 1961, 1975]. A comparable amount of plagioclase was sampled from coarse-grained allivalites of Ksudach and Golovnina volcanoes and treated similarly. As a result, we separated 200 spinel grains in the first case and about 30–40 in the second and the third cases. As a rule, the grains were octahedral in shape with slightly rounded crystal edges that were 0.03–0.1 mm, or, rarely, up to 0.4 mm across. Spinels from allivalites of Malyi Semyachik Volcano were studied directly in plagioclase crystals.

Minerals were analyzed by this author using a Camebax microprobe (Institute of Volcanology and Seismology of the Far East Branch of the RAS). Concentrations were calculated on the basis of standard software. The accelerating voltage was 20 kV and the electric current was 40 nA. The etalons were Fe (ilmenite), Mn (rhodonite), Ni (synthetic Ni–Fe spinel), Zn (synthetic ZnO), Al, Mg, and Cr (chrome spinel). The concentration of Ni and Zn in all the spinels was practically zero,; therefore, it is not shown in the analyses. The Fe^{+3} concentration was calculated in accordance with spinel stoichiometry.

RESULTS OF ANALYSIS

The spinels studied here consisted of a series of solid solutions with wide variations in their ratios of hercynite, pleonaste, magnetite, and ulvospinel minals (Table 1). No zonality features were observed in the spinels with the exception of one irregularly shaped grain that was a fragment of a larger crystal (Table 2). No correlation between spinel grain size and spinel composition was found. One plagioclase crystal may contain spinel grains with greatly different compositions (Table 1, analyses 4 and 8). Structures of solid solution disintegration are observed in some spinel varieties occurring in plagioclase in Malyi Semyachik allivalites. In some spinel crystals melt inclusions occur that consist of glass that occasionally contain trapped minerals, such as high-alumina clinopyroxene and hornblende.

Plagioclases from Mutnovskii tuffs and allivalites are unzoned and have the composition An_{92-96}. At the crystal–matrix boundary (for allivalite samples) a very narrow margin (about 100 μ) may occur in which plagioclase composition gradually changes approximately up to An_{60} with an accompanying increase in the FeO content up to 2–3%. The plagioclases from tuffs occasionally contain fine (up to 0.3 mm) irregularly shaped inclusions of chromodiopside (Table 3). Olivine Fo_{75-81} and, more rarely, clinopyroxene are also found in allivalites.

DISCUSSION OF ANALYSIS RESULTS

The problem of typomorphism in minerals of the spinel group has been discussed in many papers. This is due to the fact that spinels form continuous (with a few exceptions) series of solid solutions whose compositions are controlled by temperature, oxygen fugacity, general pressure, and the composition of the source melt. A change in any of these factors (or a group of these) in a magmatic system results in certain changes in chemical composition of the spinel. Certain trends and fields of spinel compositions belonging to different rock types and different geological objects have been identified. Many of those constructions are based on or supported by experimental studies [Hill and Roeder, 1974; Muan, 1975; Sack and Ghiorso, 1991]. It is not possible to give a complete list of all works on which those constructions are based, because they are so numerous. Therefore, the analysis of our data will largely be based on [Barnes and Roeder, 2001], which used an extensive selection of analyses (more than 21000) and summed the data from many authors; fields and trends defining spinel typomorphism for different rocks and geological processes are identified in certain coordinate systems.

Consideration of spinel compositions in the Fe^{+3}–Cr^{+3}–Al^{+3} coordinates (formula units, that is, in ratios of concentrations, not percent) on a triple diagram (Fig. 1a) indicates that figurative points form a long trend involving spinels from the Mutnovskii, Ksudach, and Golovnina volcanoes. Spinels of Malyi Semyachik Volcano characteristic of higher chromium content are located somewhat aside in a separate group (Table 1, analyses 17–21). Spinels of Mutnovskii Volcano form the longest trend; analyses of zonal spinel (Table 2) completely correspond to the overall direction of the trend, continuing its most ferrous section. The spinel trend of Ksudach Volcano is somewhat shorter than the trend of Mutnovskii Volcano and completely coincides with it. The spinels of Golovnina Volcano divide into two separate groups, which also agree with the two previous trends. The general position of all spinel groups does not correspond to any one field of typomorphic compositions identified in the triple diagram in [Barnes and Roeder, 2001] (Fig. 2a). Our spinel groups occur in the solvus field, or "spinel gap," as these authors call it, i.e., an area where the solid solutions of spinel compositions are not stable and below certain temperature disintegrate into compositions that correspond to the points on the

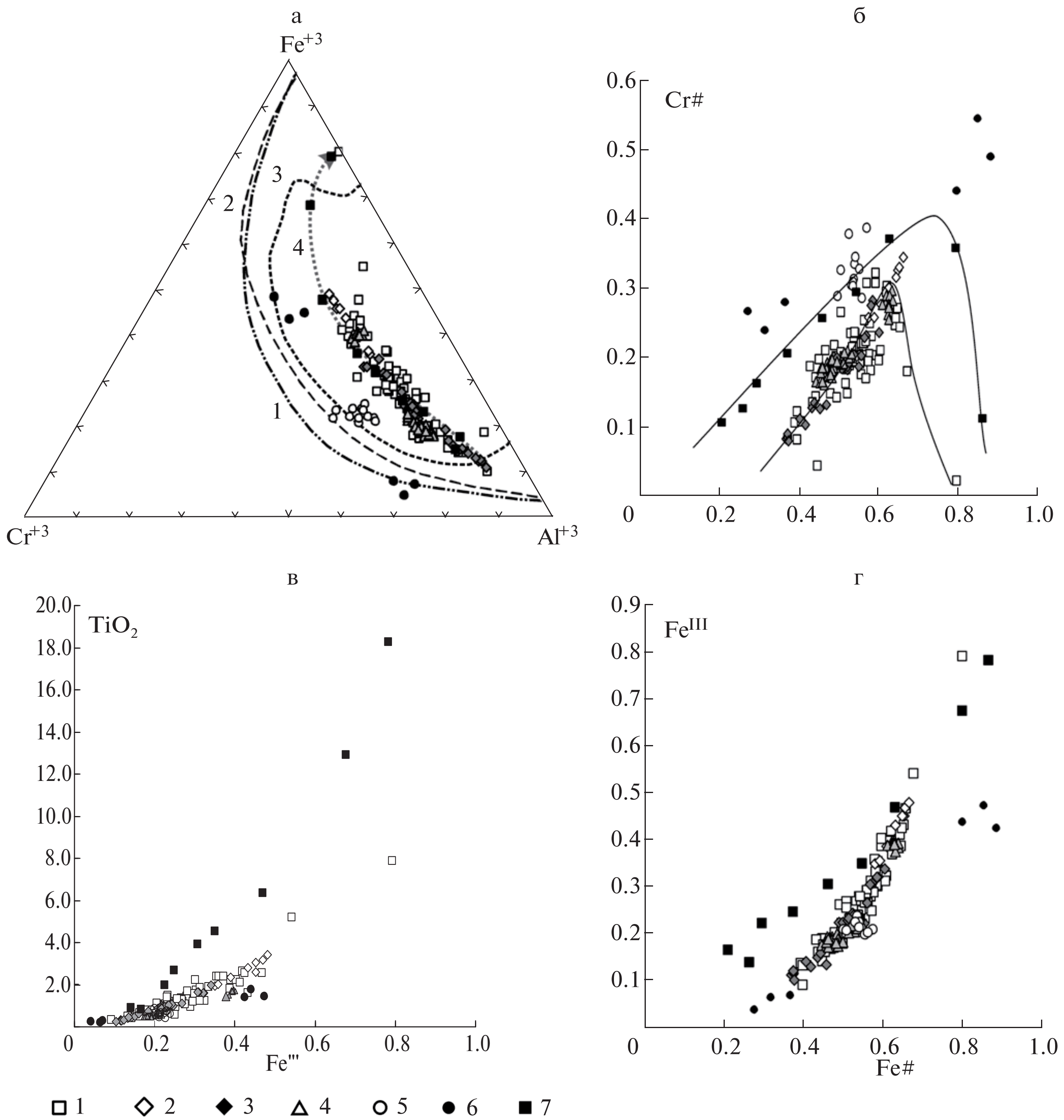

Fig. 1. Figurative points of spinel compositions based on results of this study, plotted on the diagram in accordance with [Barnes and Roeder, 2001]. (1) Mutnovskii Volcano; (2) Mutnovskii Volcano, zonal spinel (Table 2); (3) Ksudach Volcano; (4) Golovnina Volcano; (5) Malyi Semyachik Volcano; (6) compositions of spinel disintegration zone from Malyi Semyachik Volcano; (7) zonal spinel Sr157 [Ridley, 1977].
Numerals denote (triple diagram): *1* - solvus line for chromospinelides of the Stare Ransko layered peridotite-gabbro complex [Van der Veen and Maaskant, 1995], *2* - solvus line for chromospinelides of Uktusskii and Kytlymskii massifs [Pushkarev, 2000], 3 - generalized solvus line for chromospinelides of mafic rocks [Barnes and Roeder, 2001], 4 - trend of zonal spinel Sr157 [Ridley, 1977].
$Fe\# = Fe^{+2}/(Fe^{+2} + Mg^{+2})$; $Cr\# = Cr^{+3}/(Cr^{+3} + Al^{+3})$; $Fe^{III} = Fe^{+3}/(Fe^{+3} + Al^{+3} + Cr^{+3})$; TiO_2 in weight percent..

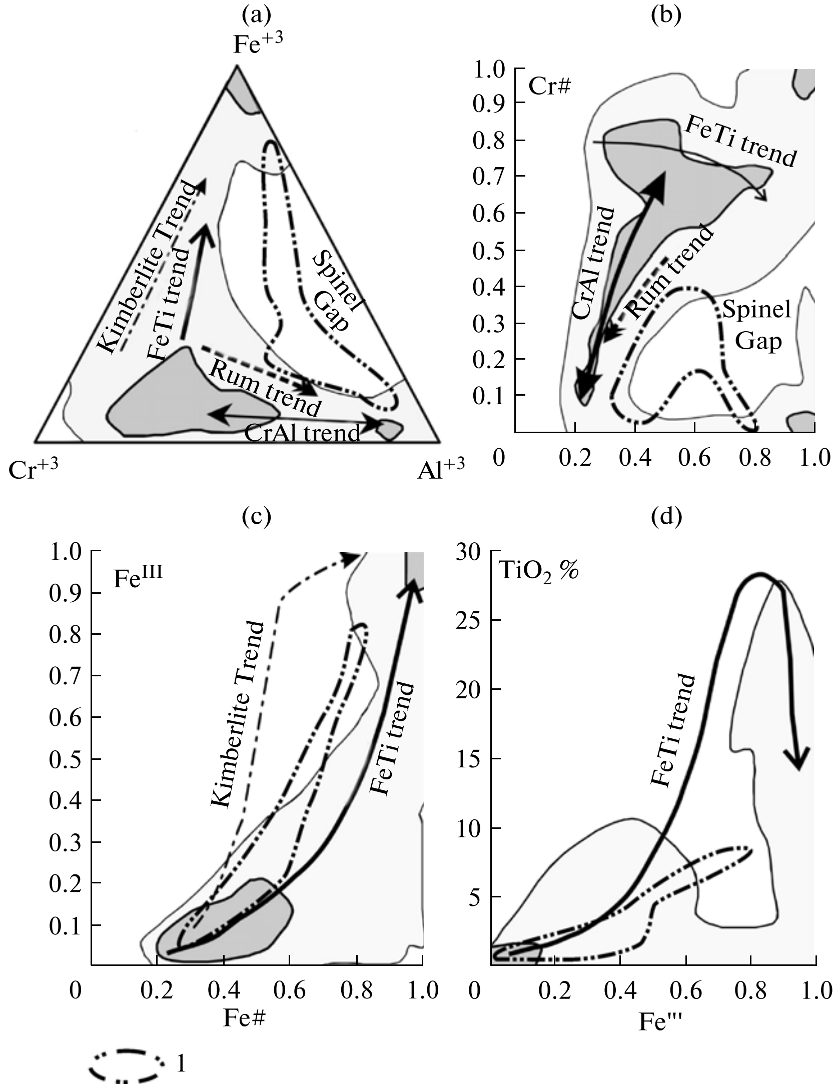

Fig. 2. Trends and spinel composition fields reported in [Barnes and Roeder, 2001] and those obtained in this study. (1) Field of spinel compositions obtained in this study.

solvus line where this is intersected by the tie line passing through an initial composition of spinel. Such fields of solid solution instability for spinel were obtained both in experiments [Muan, 1975; Sack and Ghiorso, 1991] and in studies of some geological objects [Evans and Frost, 1975; Pushkarev, 2000; Tamura and Arai, 2004] (Fig. 1a). In the chrome–iron (Cr# – Fe#) diagram the general trend of analyzed spinels also lies in the solvus field (Fig. 2b), which does not coincide with any of the identified fields. In the other two diagrams (Fig. 2c, d) the spinel composition fields approximately correspond to the Fe–Ni trend identified in [Barnes and Roeder, 2001]; accordingly, it shows a faster accumulation of Fe^{+3} and a slower accumulation of TiO_2. In the triple diagram (Fig. 1a) the spinel trend passes from the aluminum corner almost parallel to the Fe^{+3}–Al^{+3} side with insignificant increase of chrome content, suggesting some small changes in chrome concentration in the source melt during crystallization [Hill and Roeder, 1974]. In that case, the scatter of some chrome concentration values in spinel may be due to its local variations. The gradual decrease of aluminum presence in spinel may be explained by its decrease in the source melt [Dick and Bullen, 1984]. With accumulation of a considerable amount of Fe^{+3} (approximately up to 50 rel %) a tendency of Cr replacement by Fe^{+3} appears. A similar behavior of chrome is observed in the Cr#–Fe# diagram (Fig. 1b): with increasing iron content the total chrome increases at first, then abruptly drops practically to zero. This can probably be explained by a sharp increase of oxygen fugacity and drop of the temperature, which agrees with [Hill and Roeder, 1974]. As the total iron content in spinel increases, so does the concentration of TiO_2 (ulvospinel minal) and Fe^{+3} (Fig. 1c, d).

Table 1. Representative analyses of spinel

#	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21
Sample no.	M10-25	M12-12	M12-3	M12-9	M10-19	M10-15	M15-20	M14-803	K14-5	K15-5	K15-9	K15-11	G-11	G-36	G-47	G-18	S-2114	S-124	S-176	SS-6	SS-8
TiO_2	0.31	0.64	0.88	1.30	1.75	2.23	5.18	7.89	0.28	0.79	0.93	1.61	0.46	0.54	0.54	1.66	0.35	0.88	0.75	0.30	1.45
Al_2O_3	50.79	42.52	34.94	30.73	27.94	21.12	16.53	7.79	49.34	35.64	33.96	25.09	39.92	36.18	33.96	21.54	37.98	28.58	25.23	39.30	10.90
Cr_2O_3	6.90	10.08	13.04	12.19	12.69	14.17	5.51	0.30	6.85	12.55	12.91	14.90	11.97	13.02	13.45	13.26	14.95	19.46	23.89	23.08	19.68
Fe_2O_3	8.79	14.95	19.27	22.64	24.89	30.47	37.56	47.70	10.98	18.78	19.60	26.10	15.71	17.97	18.87	31.26	14.87	19.39	18.35	6.41	33.97
FeO	17.10	18.35	20.82	21.47	23.05	23.07	26.97	32.53	15.85	21.04	19.86	22.76	19.00	20.63	20.28	23.57	17.09	21.30	20.50	15.13	29.47
MnO	0.15	0.19	0.25	0.25	0.31	0.27	0.25	0.26	0.15	0.18	0.25	0.27	0.22	0.21	0.19	0.27	0.30	0.26	0.31	0.42	0.07
MgO	14.76	13.50	11.20	10.22	9.35	8.95	7.43	4.76	15.40	11.05	11.45	9.16	12.60	11.14	10.81	8.22	13.33	10.14	10.02	14.85	2.99
Total	98.80	100.23	100.40	98.80	99.98	100.28	99.43	101.23	98.85	100.03	98.96	99.89	99.88	99.69	98.10	99.78	98.87	100.01	99.05	99.49	98.53
Formula units per 32 oxygen atoms																					
Ti	0.05	0.11	0.16	0.24	0.33	0.43	1.04	1.66	0.05	0.14	0.17	0.31	0.08	0.10	0.10	0.32	0.06	0.16	0.14	0.05	0.31
Al	13.23	11.41	9.79	8.94	8.19	6.38	5.20	2.57	12.88	9.99	9.65	7.46	10.91	10.14	9.75	6.56	10.49	8.29	7.49	10.61	3.66
Cr	1.21	1.81	2.45	2.38	2.50	2.87	1.16	0.07	1.20	2.36	2.46	2.97	2.19	2.45	2.59	2.71	2.77	3.79	4.75	4.18	4.43
Fe^{+3}	1.46	2.56	3.45	4.20	4.66	5.88	7.55	10.04	1.83	3.36	3.56	4.96	2.74	3.22	3.46	6.08	2.62	3.59	3.48	1.11	7.28
Fe_{+2}	3.16	3.49	4.14	4.43	4.80	4.95	6.03	7.61	2.93	4.19	4.00	4.80	3.68	4.10	4.13	5.10	3.35	4.39	4.32	2.90	7.02
Mn	0.03	0.04	0.05	0.05	0.07	0.06	0.06	0.06	0.03	0.04	0.05	0.06	0.04	0.04	0.04	0.06	0.06	0.05	0.07	0.08	0.02
Mg	4.86	4.58	3.97	3.76	3.47	3.42	2.96	1.99	5.08	3.92	4.11	3.45	4.35	3.95	3.93	3.17	4.66	3.72	3.76	5.07	1.27
Total	24.00	24.00	24.00	24.00	24.00	24.00	24.00	24.00	24.00	24.00	24.00	24.00	24.00	24.00	24.00	24.00	24.00	24.00	24.00	24.00	24.00
Minals																					
Fe#	0.39	0.43	0.51	0.54	0.58	0.59	0.67	0.79	0.37	0.52	0.49	0.58	0.46	0.51	0.51	0.62	0.42	0.54	0.53	0.36	0.85
$MgCr_2O_4$	0.00	0.00	0.00	0.00	0.00	0.03	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$FeCr_2O_4$	0.08	0.11	0.15	0.15	0.16	0.15	0.03	0.00	0.08	0.15	0.15	0.19	0.14	0.15	0.16	0.17	0.17	0.24	0.30	0.26	0.28
$MgAl_2O_4$	0.61	0.57	0.50	0.47	0.43	0.40	0.33	0.16	0.64	0.49	0.51	0.43	0.54	0.49	0.49	0.40	0.58	0.47	0.47	0.63	0.16
$FeAl_2O_4$	0.22	0.14	0.12	0.09	0.08	0.00	0.00	0.00	0.17	0.13	0.09	0.04	0.14	0.14	0.12	0.01	0.07	0.05	0.00	0.03	0.07
Fe_3O_4	0.09	0.16	0.21	0.26	0.28	0.36	0.46	0.54	0.11	0.21	0.22	0.30	0.17	0.20	0.21	0.37	0.16	0.22	0.21	0.06	0.45
$MgFe_2O_4$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.08	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe_2TiO_4	0.01	0.01	0.02	0.03	0.04	0.05	0.13	0.21	0.01	0.02	0.02	0.04	0.01	0.01	0.01	0.04	0.01	0.02	0.02	0.01	0.04
$MnFe_2O_4$	0.00	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.00	0.00	0.01	0.01	0.01	0.01	0.00	0.01	0.01	0.01	0.01	0.01	0.00

Note: 1–8 Mutnovskii Volcano, 9–12 Ksudach Volcano, 13–16 Golovnina Volcano, 17–19 – spinel disintegration structures, 20—21 spinel involving a disintegration structure, Malyi Semyachik Volcano.

Table 2. Representative analyses of zonal spinel

#	1	2	3	4	5	6	7	8
Sample no.	M13-7a	M13-25a	M13-21a	M13-5a	M13-22a	M13-23a	M13-6a	M13-24a
TiO_2	1.95	2.02	2.37	2.60	2.79	3.05	3.19	3.43
Al_2O_3	24.70	24.10	21.82	17.68	19.14	17.80	16.82	15.73
Cr_2O_3	12.97	12.71	12.63	12.90	12.51	12.46	12.53	12.52
Fe_2O_3	28.24	28.45	30.21	33.98	32.79	33.83	35.07	35.12
FeO	22.63	22.99	23.49	24.70	24.27	24.95	25.35	25.58
MnO	0.27	0.24	0.29	0.29	0.30	0.26	0.30	0.23
MgO	9.45	9.08	8.65	7.59	8.19	7.81	7.65	7.38
Total	100.21	99.59	99.46	99.74	99.99	100.16	100.91	99.99
Formula units per 32 oxygen atoms								
Ti	0.37	0.39	0.46	0.52	0.55	0.60	0.63	0.69
Al	7.33	7.23	6.64	5.51	5.89	5.51	5.21	4.94
Cr	2.58	2.56	2.58	2.70	2.58	2.59	2.60	2.64
Fe^{+3}	5.35	5.45	5.87	6.76	6.44	6.69	6.93	7.05
Fe^{+2}	4.76	4.89	5.07	5.46	5.30	5.48	5.57	5.70
Mn	0.06	0.05	0.06	0.06	0.07	0.06	0.07	0.05
Mg	3.55	3.44	3.33	2.99	3.19	3.06	3.00	2.93
Total	24.00	24.00	24.00	24.00	24.00	24.00	24.00	24.00
Minals								
Fe#	0.57	0.59	0.60	0.65	0.62	0.64	0.65	0.66
$MgCr_2O_4$	0.00	0.00	0.00	0.03	0.03	0.04	0.05	0.06
$FeCr_2O_4$	0.16	0.16	0.16	0.14	0.13	0.12	0.11	0.11
$MgAl_2O_4$	0.44	0.43	0.41	0.34	0.37	0.34	0.33	0.31
$FeAl_2O_4$	0.01	0.02	0.00	0.00	0.00	0.00	0.00	0.00
Fe_3O_4	0.33	0.33	0.36	0.41	0.39	0.41	0.42	0.43
Fe_2TiO_4	0.05	0.05	0.06	0.06	0.07	0.08	0.08	0.09
$MnFe_2O_4$	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01

Such spinel trends are almost unknown in the literature. According to [Barnes and Roeder, 2001], some individual spinels from blanket and alkaline basalts occur in the solvus zone. Grib [2007] describes similar spinels found in anorthites from a basalt dyke in the rim of Karymskii caldera. A similar (but involving somewhat more chrome) trend of spinel compositions from dykes of olivine horblendites of Kos'va Mountain (Kytlyn massif, Northern Urals) was described in [Krause et al., 2007]. The analyses [Ridley, 1977] that were obtained from the study of a spinel grain trapped in an olivine crystal from intermediate alkaline olivine basalts of Ram Island are rather interesting (sample SR-157). The profile based on spinel compositions from the center to the margin lies precisely on the trend of our spinels (Fig. 1a). The only difference is that our trend was obtained from analyses of many grains of unzoned spinels of various compositions, while sample SR-157 consisted of a single grain with a composition gradually varying from the middle to the margins. In the other plots both trends are either parallel to each other (Figs. 1b, 1c) or intersect (Fig. 1d).

The spinels from Malyi Semyachik plagioclase form a compact group somewhat apart from the general trend; these spinels mostly differ in having a somewhat higher chrome content and presence of structures of solid solution disintegration (Fig. 3). It is clearly seen that the figurative points of spinel disintegration structures and those of non-disintegrated spinels lie on the same line (tie line) and form rather compact sets (Fig. 1a). The absence of disintegration structures in spinels from other geological objects may be due to the fact that allivalites and plagioclases of the Mutnovskii, Ksudach, and Golovnina volcanoes existed in pyroclastic deposits and after eruption cooled rather quickly, thus resulting in hardening of the metastable solid solution of spinel, while the allivalites of Malyi Semyachik Volcano occurred in a lava flow [Selyagin, 1979] and cooled for a long time, thus resulting in disintegration of the spinel solid solution through solid-phase thermal diffusion.

Ridley [Ridley, 1977] explains the appearance of zonality in spinels as a result of their interaction with an evolving basalt melt. This interaction leads to series of certain cation replacements due to composition changes in the residual liquid because of precipitation of crystals, changed f_{O_2} , and melt structure. On the other hand, spinel zonality might arise from successive overgrowth of non-equilibrium marginal zones by spinel envelopes that were in equilibrium with the melt [Plaksenko, 1989]. This is, in turn, supported by the existence of a trend of homogeneous unzoned spinels.

One may try to approximately estimate the composition of the initial melt from which the spinel crystallized on the basis of non-crystallized melt inclusions in this mineral. This author could not homogenize melt inclusions, so for the purpose of such estimation we selected analyses with the best sums and the least losses of sodium (due to peculiarities of microprobe analysis of this element in glasses). As seen from Table 4, the glass compositions are approximately those of a low-potassium high-alumina basalt. We obtained similar glass compositions earlier [Anan'ev and Shnyrev, 1984; Anan'ev, 1985] for melt inclusions in olivines of Ksudach Volcano. Similar results were obtained by other authors [Plechov et al., 2008; Shishkina et al., 2009] based on homogenization of melt inclusions in olivine from the same geological objects. The sum deficit in glass analyses is probably due to the presence of volatile components in the glass, largely water. Anan'ev and Maksimov [1989] carried out an experimental verification of the correlation of the sum deficit in microprobe analyses and the water content in synthetic glasses obtained by melting of natural material with the addition of certain amounts of H_2O. The results showed a nearly linear dependence and good agreement between the analyses and the concentrations in the 0–9% H_2O interval.

Table 3. Representative analyses of small clinopyroxene crystals in anorthites from tuffs of Mutnovskii Volcano

#	1	2
Sample no.	P_7V1	P_41E14
SiO_2	49.69	50.34
TiO_2	0.57	0.57
Al_2O_3	6.09	5.98
Cr_2O_3	0.29	0.30
FeO	6.91	6.25
MnO	0.12	0.21
MgO	13.29	14.06
CaO	21.87	21.84
Na_2O	0.24	0.16
Total	99.07	99.71
Formula units per 6 oxygen atoms		
Si	1.8552	1.8600
Ti	0.0160	0.0158
Al	0.2680	0.2604
Cr	0.0086	0.0088
Fe	0.2158	0.1931
Mn	0.0038	0.0066
Mg	0.7397	0.7745
Ca	0.8749	0.8646
Na	0.0174	0.0115
Total	3.9994	3.9953
Fe#	0.2259	0.1996
WOLL	0.4780	0.4719
EN	0.4041	0.4227
FS	0.1179	0.1054

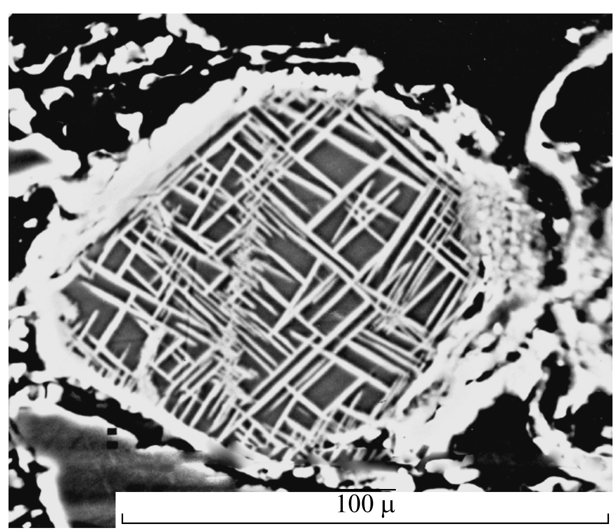

Fig. 3. Spinel with lamellas of solid solution disintegration from plagioclase Ol–An nodules, from the Malyi Semyachik Volcano (microprobe, back scattered electrons).

Table 4. Representative analyses of non-crystallized melt inclusions and of host spinels

#	1	2	3	4	5	6	7	8
Area	Mutnovskii Volcano						Ksudach Volcano	
Sample no.	2MU02GL	2MU02/14	MU016GL	MU01/7	G_353714	G_03/12	KS3	KS7
Mineral	Gl	Sp	Gl	Sp	Gl	Sp	Gl	Sp
SiO_2	48.42	–	51.34	–	50.76	–	50.26	–
TiO_2	0.96	1.70	0.84	2.37	1.00	1.20	0.73	0.87
Al_2O_3	17.17	27.24	17.44	19.29	18.95	35.14	18.58	35.00
Cr_2O_3	0.00	13.08	0.00	12.15	0.00	9.19	0.00	11.70
FeO	8.35	27.04	9.49	33.42	9.13	21.62	8.85	20.63
Fe_2O_3	0.00	22.03	0.00	23.43	0.00	21.44	0.00	20.45
MnO	0.19	0.26	0.21	0.27	0.17	0.23	0.16	0.25
MgO	4.68	10.27	5.43	8.38	4.21	10.84	4.53	11.41
CaO	10.35	–	9.64	–	9.46	–	10.00	–
Na_2O	2.50	–	2.00	–	2.61	–	2.91	–
K_2O	0.91	–	0.27	–	0.34	–	0.27	–
Total	93.53	101.62	96.66	99.31	96.61	99.66	96.29	100.31
Formula units per 8 and 32 oxygen atoms for Gl and Sp, respectively								
Si	2.4697	–	2.5132	–	2.4844	–	2.475	–
Ti	0.0368	0.3130	0.0309	0.4675	0.0366	0.2168	0.027	0.1561
Al	1.0324	7.8612	1.0062	5.9577	1.0930	9.9258	1.078	9.8023
Cr	0.0000	2.5313	0.0000	2.5164	0.0000	1.7420	0.000	2.1976
Fe^{+2}	0.3560	4.9816	0.3885	6.5908	0.3736	3.8987	0.364	3.6879
Fe^{+3}	–	4.5106	–	5.1341	–	4.2979	–	4.0630
Mn	0.0080	0.0544	0.0087	0.0591	0.0069	0.0465	0.007	0.0502
Mg	0.3560	3.7480	0.3963	3.2744	0.3073	3.8724	0.333	4.0428
Ca	0.5654	–	0.5056	–	0.4963	–	0.528	–
Na	0.2469	–	0.1898	–	0.2477	–	0.278	–
K	0.0590	–	0.0169	–	0.0213	–	0.017	–
Total	5.1302	24.0000	5.0561	24.0000	5.0670	24.0000	5.1067	24.0000
Fe#	0.5000	0.5462	0.4950	0.6106	0.5487	0.5260	0.5226	0.5012
$FeCr_2O_4$	–	0.1582	–	0.0369	–	0.1089	–	0.1374
$MgAl_2O_4$	–	0.4685	–	0.1203	–	0.4840	–	0.5054
$FeAl_2O_4$	–	0.0228	–	0.3724	–	0.1363	–	0.1073
Fe_3O_4	–	0.3045	–	0.4045	–	0.2379	–	0.2242
Fe_2TiO_4	–	0.0391	–	0.0584	–	0.0271	–	0.0195
$MnFe_2O_4$	–	0.0068	–	0.0074	–	0.0058	–	0.0063

CONCLUSIONS

The existence of the spinel trend in the solvus zone of solid solutions may be explained, as described above, by the early capture of spinel grains by growing plagioclase crystals and rapid cooling after eruption, which resulted in hardening of the metastable solution. The absence of zonality in spinel grains seems to indicate equilibrium conditions during the growth of a discrete crystal. A formed unzoned crystal is unlikely to occur under non-equilibrium conditions to acquire zonality. Preservation of a spinel grain in a plagioclase crystal may create such a situation. On the other hand, initially spinel grains might have a certain zonality corresponding to the identified trend, but being trapped in plagioclase crystals and with no contact with the melt, they underwent equilibration and averaging of composition by thermal diffusion of the components, resulting in the appearance of unzoned crystals. This process seems quite possible taking into account the small size of spinel grains and the high temperature of plagioclase crystallization estimated by [Frolova and Plechov, 2001] as 1050–1100°C. The finding of a spinel grain (an irregularly shaped fragment) with expressed zonality (Table 2) indirectly supports this supposition. Probably, in this case the crystal was included in plagioclase for a short time or incompletely and its composition had no time to be averaged; therefore, its marginal zones are in the most ferrous parts of the trend. In their turn, the diversity (or zonality) of spinel compositions may have been caused by local and long-living changes of initial melt composition related to plagioclase crystallization. It can therefore be hypothesized that plagioclase crystallized and grew in equilibrium quiet conditions, which is supported by the stable compositions, perfect forms, and large sizes of anorthite crystals (Mutnovskii Volcano). Spinel crystals might be initiated and grow in crystallization haloes (haloes of "scooping out") of plagioclase [Vorob'ev, 1990; Sobolev, 2009] and subsequently captured by them. Since the sizes of plagioclase crystals and spinel grains differ by several orders of magnitude and spinel volumes are negligible compared to plagioclase volumes, such a process seems to be quite possible. This is partly supported by the fact that the spinels found in plagioclases from tuffs usually occur in margins of crystals. Melts of crystallization haloes in large anorthite crystals must be impoverished in Al and Ca and consequently enriched in other elements of the source melt, in particular, iron and volatiles (water). Oxygen fugacity in these zones must also increase. The change in the amount of chrome will not be as large as for macroelements due to its low concentration in the source liquid. The process of the formation of crystallization haloes in crystals growing in silicate melts is not sufficiently understood, but for water solutions whose viscosity is significantly lower, it may reach the size of the crystal itself. The compositions of crystallization halos adjoining different crystallographic faces may differ [Vorob'ev, 1990; Sobolev, 2009]. Since the composition of melt in a halo follows the common trend in element accumulation, remaining stochastic to a considerable extent, spinel compositions crystallizing in these zones remain different, yet form a single genetically connected trend. The small chromodiopside inclusions (Table 3) in anorthites of Mutnovskii tuffs are probably of the same nature. Unfortunately, the last supposition on the genesis of such a trend has not thus far been supported in studies of non-crystallized melt inclusions in spinels and meets with difficulties in descriptions of a similar phenomenon for plagioclases of allivalite modules. The diversity of spinel compositions can be also possibly be explained by some inhomogeneity in the composition of the initial melt due to local fluctuations of fluid-phase composition related to the presence of some local sources.

REFERENCES

Anan'ev, V.V., Origin of Ol–An–Cpx Segregations in Volcanic Rocks Based on Studies of Spinels and Melt Inclusions, *Tezisy dokladov VI Vsesoyuznogo vulkanologicheskogo soveshchaniya* (Abstract of Papers of VI All-Union Volcanological Conference), Petropavlovsk-Kamchatskii, 1985, no. 2, pp. 124–126.

Anan'ev, V.V. and Shnyrev, G.D., Garnet in Melt Inclusions from Olivine Ol–An Segregations (Ksudach Volcano, Kamchatka), *Dokl. Akad. Nauk*, 1984, vol. 274, no. 2, pp. 402–406.

Anan'ev, V.V. and Maksimov, A.P., Indirect Determination of H_2O in Silicate Glasses by a Microprobe: Experimental Verification, *I Vsesoyuznaya shkola-seminar "Mikrozond i progres v geologii"* (1st All-Union School–Workshop "Microprobe and Progress in Geology"), April 21–28, 1989, Extended Abstracts of Papers, Suzdal': VIMS, 1989, pp. 81–82.

Barnes, S.J. and Roeder, P.L., The Range of Spinel Compositions in Terrestrial Mafic and Ultramafic Rocks, *J. Petrol.*, 2001, vol. 42, no. 12, pp. 2279–2302.

Dick, H.J.B. and Bullen, T., Chromian Spinel as a Petrogenetic Indicator in Abyssal and Alpine-Type Peridotites and Spatially Associated Lavas, *Contrib. Mineral. Petrol.*, 1984, vol. 86, pp. 54–76.

Evans, B.W. and Frost, B.R., Chrome-Spine1 in Progressive Metamorphism – a Preliminary Analysis, *Geochim. Cosmochim. Acta*, 1975, vol. 39, pp. 959–972.

Frolova, T.I., Plechov, P.Yu., Tikhomirov, P.L., and Churakov, S.V., Melt Inclusions in Minerals of Allivalites of Kuril–Kamchatka Island Arc, *Geokhimiya*, 2001, vol. 39, no. 4, pp. 336–346.

Grib, E.N., Spinels of the Karymskii Volcanic Center: A Petrogenetic Interpretation, in *Materialy konferentsii, posvyashchennoi Dnyu vulkanologa, 27–29 marta 2008 g* (Materials of the Conference Devoted to the Day of Volcanologist, March 27–29, 2008), Petropavlovsk-Kamchatskii, 2008, pp. 71–80.

Grib, E.N., Mineralogical Features of Olivine-Bearing Basalts of Karymskii Volcanic Center, *Vestnik KRAUNTs. Nauki o Zemle*, 2007, no. 2, no. 10, pp. 17–33.

Henderson, P., Reaction Trends Shown by Chrome-Spinels of the Rhum Layered Intrusion, *Geochim. Cosmochim. Acta*, 1975, vol. 39, pp. 1035–1044.

Hill, R. and Roeder, P., The Crystallization of Spinels from Basaltic Liquids as a Function of Oxygen Fugacity, *J. Geol.*, 1974, vol. 82, pp. 709–729.

Krause, J., Bruegmann, G.E., and Pushkarev, E.V., Accessory and Rock Forming Minerals Monitoring the Evolution of Zoned Mafic–Ultramafic Complexes in the Central Ural Mountains, *Lithos*, 2007, vol. 95, pp. 19–42.

Muan, A., Phase Relations in Chromisan Oxide-Containing Systems at Elevated Temperatures, *Geochim. Cosmochim. Acta*, 1975, vol. 39, pp. 781–803.

Neuerburg, G.J., A Method of Mineral Separation Using Hydrofluoric Acid, *Amer. Mineral.*, 1961, vol. 46, nos. 11–12, pp. 1498–1501.

Neuerburg, G.J., A Procedure, Using Hydrofluoric Acid, for Quantitative Mineral Separation from Silicate Rocks, *U.S. Geol. Survey*, 1975, no. 3, pp. 377–378.

Plaksenko, A.N., *Tipomorfizm aktsessornykh khromshpinelidov ul'tramafit-mafitovykh magmaticheskikh formatsii* (Typomorphism of Accessory Chromospineldes of Ultramafic–Mafic Magmatic Rock Associations), Voronezh: Voronezh. Univer., 1989.

Plechov, P.Yu., Shishkina, T.A., Ermakov, V.A., and Portnyagin, M.V., Formation Conditions of Allivalites, Olivine–Anorthite Crystal Inclusions, in Volcanics of the Kuril–Kamchatka Arc, *Petrologiya*, 2008, vol. 16, no. 3, pp. 1–30.

Prikhod'ko, V.S., Bekhtol'd, A.F., and Romanenko, I.M., Chromospinelides of Allivalite Inclusions and Their Petrologic Significance *Dokl. Akad. Nauk SSSR,* 1977, vol. 235, no. 4, pp. 918–920.

Pushkarev, E.V., *Petrologiya Uktusskogo dunit-klinopiroksen-gabbrovogo massiva (Srednii Ural)* (Petrology of the Uktusskii Dunite–Clinopyroxene–Gabbro Massif (Middle Urals)), Yekaterinburg: OOO "IRA UTK", 2000.

Ridley, W.I., The Crystallization Trends of Spinels in Tertiary Basalts from Rhum and Muck and Their Petrogenetic Significance, *Contrib. Mineral. Petrol.*, 1977, vol. 64, pp. 243–255.

Roeder, P.L., Chromite: from the Fiery Rain of Chondrules to the Kilauea Iki Lava Lake, *Canad. Mineralogist*, 1994, vol. 32, pp. 729–746.

Sack, R.O. and Ghiorso, M.S., Chromian Spinels As Petrogenetic Indicators: Thermodynamics and Petrological Applications, *Amer. Mineral.*, 1991, vol. 76, pp. 827–847.

Selyangin, O.B., Continuously Differentiated Lava Flows with Inclusions and a Possible Arrangement of Magma Differentiation Region beneath a Volcano, *Byul. Vulkanol. Stantsii*, 1979, no. 57, pp. 39–52.

Selyangin, O.B., *Petrogenezis bazal't-datsitovoi serii v svyazi s evolyutsiei vulkano-struktur* (Petrogenesis of Basalt–Dacite Series in Connection to Evolution of Volcanic Structures), Moscow: Nauka, 1987.

Shishkina, T.A., Plechov, P.Yu., and Portnyagin, M.V., Conditions of Formation of Olivine–Plagioclase Cumulates of Ksudach Volcano, Kamchatka, *Geoloiya i Razvedka*, 2009, no. 1, pp. 8–17.

Sobolev, R.N., Physical-Chemical Analysis of Melt Cooling Processes Paper 2. State Diagrams, Crystal Shapes and Formation of Rock Textures, *Byul. Mosk. Obshchestva Ispytatelei Prirody*, 2009, vol. 84, no. 6, pp. 28–35.

Tamura, A. and Arai, S., Inhomogeneous Spinel in Chromitite from the Iwanai-Dake Peridotite Complex, Hokkaido, Japan: Variations of Spinel Unmixing Texture and Chemical Composition, *Science Reports of the Kanazawa University*, 2004, vol. 48 nos. 1/2, pp. 9–29.

Van der Veen, A.H. and Maaskant, P., Chromian Spinel Mineralogy of the Stare Ransko Gabbro-Peridotite, Czech Republic, and Its Implications for Sulfide Mineralization, *Mineralium Deposita*, 1995, vol. 30, pp. 397–407.

Volynets, O.N., Sheka, S.A., and Dubik, Yu.M., Olivine–Anorthite Inclusions: Kamchatka and Kurils Volcanoes), in *Vklyucheniya v vulkanicheskikh porodakh Kurilo-Kamchatskoi ostrovnoi dugi* (Inclusions in Volcanic Rocks of the Kuril–Kamchatka Island Arc), Moscow: Nauka, 1978, pp. 124–168.

Vorob'ev, V.K., *Zakonomernosti rosta i evolyutsii kristallov mineralov* (Regularities of Growth and Evolution of Mineral Crystals), Moscow: Nauka, 1990.20