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Rodingites from the Alkaline Ultramafic Volcanics of the Valaginsky Range, Eastern Kamchatka: Petrologic Implications

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New data are reported on the geologic setting, structural relations, and composition of calc-silicate metasomatites (rodingites) found, in association with alkali-ultramafic volcanics, in the northern Valaginsky Range, Eastern Kamchatka. Unique conclusions were derived as to the general formation mechanism of rodingite mineral composition using the example of these high-temperature rocks. The new data were used as a basis for deriving a paligenetic-metasomatic model which extends the thermodynamic range of rodingite genesis. The universal nature of calcium metasomatism in mafic-ultramafic rocks of various associations is demonstrated.

INTRODUCTION

A particular problem in the general "ultramafic" problem is the secondary mineral transformation of initial mafic-ultramafic rocks, caused by a combination of magmatic, metamorphic, and metasomatic processes with the petrogenesis imprinting the physico-chemical environments that preceded or were contemporary with the emplacement of these rocks. A particular position among these products, widely developed in ultramafics of various rock associations, is occupied by rodingites. Conventionally included into this group of rocks are calc-silicate ($\text{CaO} > 20.0 \text{ wt\%}$) metasomatic formations which are believed to have been formed as a result of contact reactions between serpentinites and

basic igneous rocks, and also as a result of the transformation of small lenses, boudins, veins, and xenoliths of plagiogranites, volcanics, sediments, and metamorphics, consumed during the tectonic intrusion of ultramafics into ophiolite complexes [1], [4], [5], [6], [9], [12], [16], [26], [27], [28], [29], [33], [34], [37]. The estimates of the thermodynamic conditions of rodingite formation vary greatly, though the bulk of researchers agree that the upper temperature limit of rodingite genesis does not exceed 450-550 °C [15], [36].

Rodingites, unique in terms of their geologic setting and degree of preservation, were found for the first time, in association with volcanic rocks of the alkaline ultramafic rock association, in the northern segment of the Valaginsky Range in Eastern Kamchatka [18]. Using these high-temperature rocks as an example, we derived unique conclusions of the formation mechanism of the mineral composition of rodingites, which were proved by a further research to be applicable to the rodingites of the plutonic (ophiolite and dunite-clinopyroxenite-gabbro) associations. These conclusions were used as basis for deriving a palingentic-metasomatic model of rodingite genesis [21], some aspects of which are discussed in this paper.

GEOLOGIC SETTING

Cretaceous ultramafic volcanics occur in various regions of Eastern Kamchatka [11], [22], [23], [32]. It has been proved that the ultramafics are the members of a differentiated volcanic rock complex which combines several rock varieties, from low-alkaline meymechites to potassic and potassic-sodic alkaline ultramafic and mafic rocks. This provided a basis for referring the volcanic ultramafics of Eastern Kamchatka and the rocks associated with them to the alkaline ultramafic volcanic rock association.

We investigated the rocks, classed with the alkaline ultramafic volcanic rock association, in the northern segment of the Valaginsky Range west of the Kronotsky Lake (Fig. 1) in the drainage area of the Uzkii Creek and in the upper reaches of the Ozernyi Creek (Mt. Savulch area). The rocks are constituents of the Valaginsky Group of Campanian-Danian age and are represented mainly by meymechite tuffs which are replaced by lavas of the same composition. Upward the meymechites are replaced by sodic and potassic alkaline basic rocks which accumulated during the Maestrichtian. Lamproite-like potassic ultramafic tuffs and dikes are widely developed among the Valaginsky meymechites [20]. The tectonic setting of this rock complex is controlled by its occurrence in a zone of deep faults which control the trends of the ultramafic (ophiolite) belts of Eastern Kamchatka [17].

The rodingites locally occur as substantial constituents of the sequence of the Valaginsky volcanics producing a pudding structure of the rocks. They make up 3-5 to 30% of the rock volume in some strata. The size of rodingite inclusions ranges between a few centimeters and 30-35 cm, the dominant size being 8-12 cm. They may be

rounded, irregular, sometimes flattened, or angular in form. Because of their whitish, occasionally yellowish, greenish, or light gray colors the rocks are well seen against the background of the dark-colored meymechite tuff enclosing them. Single rodingite inclusions were found in the alkaline lavas. As a rule the rodingites have pronounced contacts with the meymechite tuff.

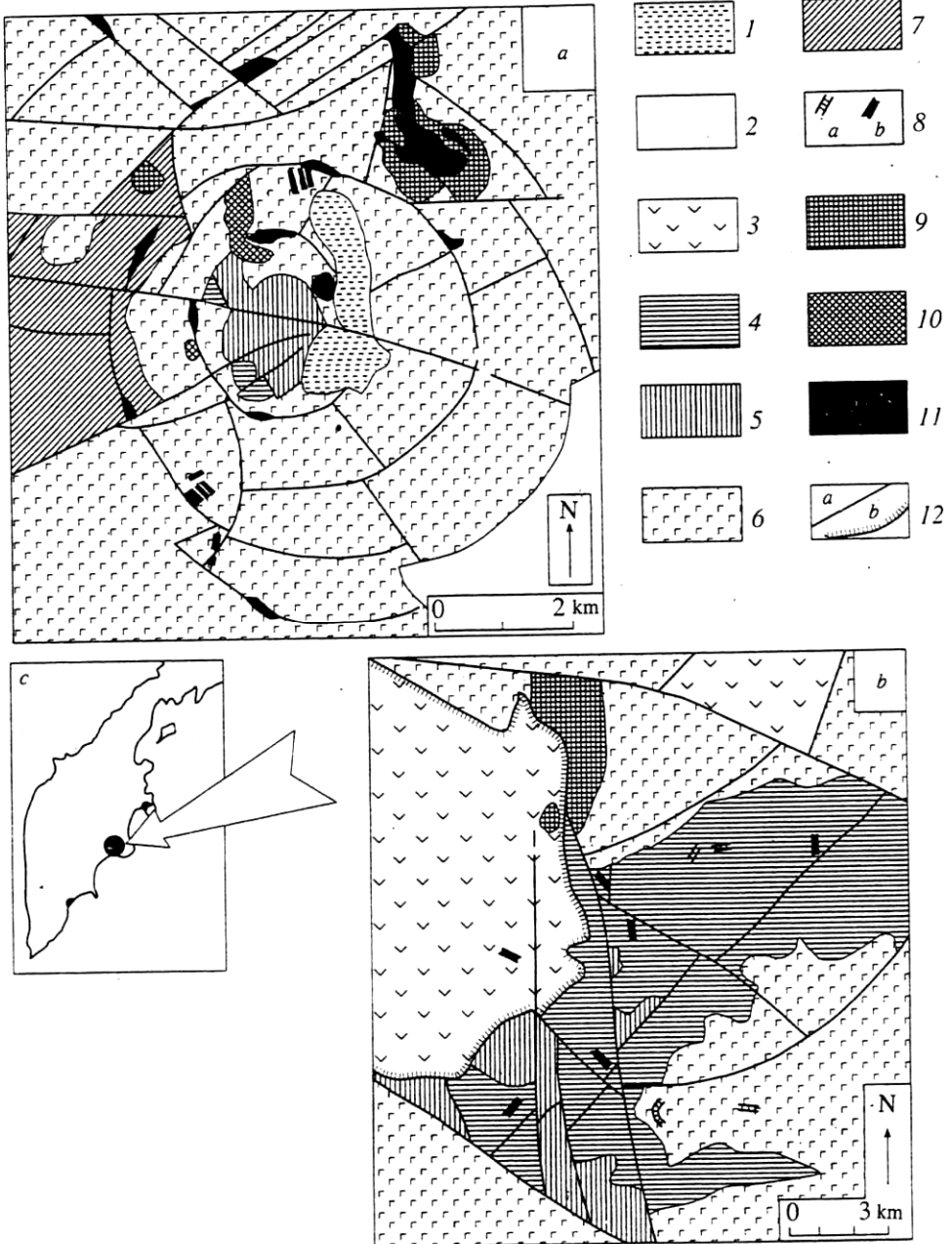
METHODS OF STUDY

Our mineralogical studies mainly consisted of the petrographic examinations of thin sections and the microprobe determinations of the chemical compositions of the major rock-forming minerals, using thin sections, polished sections, and mineral specimens. Most of the analyses were made on a Camebax microprobe equipped with a Kevex energy-dispersion detector in the Institute of Volcanology (Petropavlovsk-Kamchatsky) and some on an MS-46 Cameca microprobe in the Institute of Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry (IGEM RAN) in Moscow. The experimental conditions were conventional: accelerating voltage 20 kV, current 40 nA, exposure time 100 s, the usual size of the target 3-10 μm . Synthetic or natural minerals with known chemical compositions were used as standards. The crystal chemistries of the minerals were calculated using conventional techniques. The bulk compositions of the rocks were determined by chemical methods in the chemical laboratories of the Kamchatgeologiya Association and the Institute of Volcanology, both in Petropavlovsk-Kamchatsky. Trace and rare earth elements were determined by neutron activation, atomic absorption, XRF, and ICP-MS analyses. Analyses were made in the Institute of Volcanology, Institute of Geology and Geophysics (Novosibirsk), Union College (Schenectady, USA), and University of Southern Florida (Tampa, USA). The isotopic compositions of oxygen and carbon were studied in the Geological Institute (GIN RAN, Moscow).

TEXTURES, STRUCTURES, AND MINERAL COMPOSITIONS

Based on the degree of initial rock transformation, rodingites are classified into rodingitized rocks and rodingites proper, which have different structures and textures.

Rodingitized rocks are represented by meymechite and lamproite fragments and crusts of pillow lavas and volcanic pipes. Their important feature is that they preserved all of the textural and structural features of the meymechites [18], the rocks with an amygdaloidal structure, a porphyritic texture, and a glassy groundmass. Their phenocrysts consist of variably serpentinized olivine (40-60 vol.%). The groundmass is usually crystallized and contains clinopyroxene microlites of tabular, acicular, trunk, and other skeleton forms. The groundmass glass usually contains small biotite laths and apatite needles. The amygdules are commonly filled with serpentine-chlorite or clay material.



Rodingites differ from the rodingitized rocks by the total or partial reworking of the primary textures and structures of their protoliths, the result of this reworking being the structural homogenization of the rock. Rodingites usually have a vesicular texture, the vesicles being often empty. Where the vesicles are filled, the rock acquires an amygdaloidal structure.

The rodingites have a porphyritic texture, their groundmass varying from glassy, microlitic to fine-granular noncrystalline. The groundmass consists of brownish, almost isotropic, highly refractive glass or products of its devitrification and a varying amount of clinopyroxene microlites. The glass has an ultrabasic, high-Ca and low-alkali composition. The glass composition is fairly persistent in different samples, the low analytical sums indicating saturation with dissolved volatiles.

Most of the clinopyroxene phenocrysts, enclosed in the isotropic groundmass, have perfect crystallographic forms and a composite structure, consisting of a relict resorbed core and a regeneration rim. The clinopyroxenes of the other variety are acicular-prismatic crystals of metasomatic diopside filling the amygdules and pseudomorphs after olivine. The chemical analyses of both clinopyroxene generations are listed in Table 1. The ternary Wo-En-Fs diagram of Fig. 2, *a* shows that the data points of the clinopyroxenes lie in the fields of diopside and salite and that the relict and regeneration clinopyroxenes from the groundmass and the acicular crystals filling the amygdules have the same composition, except that the relict cores are significantly higher in Al_2O_3 than the secondary clinopyroxenes and than the coexisting regeneration rims. In the Ca-Al (form, units) diagram of Fig. 2, *b* the newly formed pyroxene filling the amygdules resides in the field of extremely low Al_2O_3 and the highest CaO values. The clinopyroxenes of this generation are somewhat lower in Cr_2O_3 , TiO_2 , and Na_2O than the relict magmatic clinopyroxenes. Worthy of mention is the high MnO content in the acicular crystals and the occurrence of trivalent iron in the tetrahedral positions of the relict pyroxene cores (an. 1 to 4 in Table 1).

The rocks that had experienced multiphase rodingitization contain newly formed yellowish-green (to dark brown) garnet. Its relatively large crystals usually occur in voids where garnet fills the interstices between the clinopyroxene needles. Some of the

Figure 1 Schematic geological maps of alkaline ultramafic rocks in some areas of the Valaginsky Range, Eastern Kamchatka: *a* - Ozernyi Creek upper reaches, *b* - Uzkii Creek drainage area [20], *c* - location of study area. 1 - recent landslide breccia; 2 - Tyushevsky Group (N^{1-2}_1), clastic flysch; 3-7 - Valaginsky Group ($K_2 - P_1$): 3 - Temnorechinskaya Formation shoshonite and latite lavas and tuffs; 4, 5 - alkaline ultramafic volcanics: alkaline basalt tuff and meymechite tuff and lavas, respectively; 6 - Poputnovskaya Formation basalt tuffs and lavas; 7 - Golubovskaya Formation tuffs and tuffaceous siltstones; 8 - meymechite (*a*) and lamproite (*b*) dikes; 9 - gabbrosyenite intrusions (K_2); 10 - diabase and gabbro intrusions (K_2); 11 - serpentinite sheets and lenses ($K_2?$); 12 - faults (*a* - normal and reverse, *b* - thrust faults).

Table 1 Representative chemical compositions of clinopyroxenes from the volcanic rodingites of the Valaginsky Range (Eastern Kamchatka), wt%.

Oxide	Newly formed Cpx							Relict Cpx cores		
	inclusions				groundmass					
	1*	2	3	4	5	6	7	8	9	10
SiO ₂	52.25	53.05	52.85	53.95	52.66	54.24	53.48	47.59	49.54	51.44
TiO ₂	0.00	0.00	0.02	0.14	0.12	0.06	0.00	1.04	0.38	0.37
Al ₂ O ₃	0.07	0.13	0.09	0.00	0.44	0.12	0.12	6.24	2.69	2.54
FeO**	8.32	5.23	8.00	5.66	7.66	3.58	7.60	8.90	10.32	6.31
MnO	1.41	1.31	1.03	0.31	0.28	0.27	0.54	0.11	0.68	0.07
MgO	12.26	14.32	13.41	15.22	13.72	16.01	13.48	13.97	11.55	15.67
CaO	24.66	24.58	24.08	25.10	24.03	25.14	25.13	20.93	23.01	22.29
Na ₂ O	0.25	0.38	0.17	0.43	0.15	0.10	0.07	0.42	0.17	0.21
K ₂ O	0.00	0.15	0.01	0.00	0.00	0.00	0.07	0.01	0.09	0.11
Cr ₂ O ₃	0.00	0.00	0.07	0.00	0.13	0.07	0.11	0.12	0.18	0.30
Total	99.22	99.15	99.73	100.80	99.19	99.59	100.61	99.33	98.61	99.32
Number of ions per six O atoms										
Si	1.978	1.978	1.981	1.971	1.978	1.996	1.985	1.772	1.893	1.904
Al ^{IV}	0.003	0.006	0.004	0.000	0.019	0.004	0.005	0.228	0.107	0.096
Fe ³⁺	0.019	0.017	0.015	0.029	0.003	0.000	0.010	0.000	0.000	0.000
Al ^{VI}	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.046	0.014	0.015
Ti	0.000	0.000	0.010	0.040	0.003	0.002	0.000	0.029	0.011	0.010
Cr	0.000	0.000	0.002	0.000	0.004	0.002	0.003	0.004	0.005	0.009
Fe ³⁺	0.040	0.057	0.029	0.051	0.022	0.005	0.020	0.151	0.081	0.072
Fe ²⁺	0.204	0.090	0.207	0.093	0.202	0.105	0.206	0.126	0.249	0.124
Mn	0.045	0.041	0.033	0.010	0.009	0.008	0.017	0.003	0.022	0.002
Mg	0.692	0.796	0.749	0.829	0.768	0.878	0.746	0.775	0.658	0.865
Ca	1.000	0.892	0.967	0.983	0.967	0.991	0.999	0.835	0.942	0.884
Na	0.018	0.027	0.120	0.030	0.110	0.007	0.005	0.300	0.013	0.015
K	0.000	0.007	0.000	0.000	0.000	0.000	0.003	0.000	0.004	0.005
fm	0.22	0.10	0.21	0.010	0.21	0.11	0.21	0.14	0.25	0.13
Wo	49.99	49.53	48.36	49.27	48.72	49.86	50.02	44.16	48.27	45.43
En	34.58	40.15	37.47	41.57	38.71	44.18	37.33	41.01	33.71	44.43
Fs	15.43	10.31	14.18	9.15	12.57	5.97	12.66	14.84	18.02	10.15

* Rodingites from Mt. Savulch: 1-3, 5, 6, 9 - Sample S-18/81; 4, 7, 10 - Sample S-20/81; 8 - Sample S-16/81.

** All iron is given as FeO; Fe³⁺ was calculated stoichiometrically on the basis of fm = Fe²⁺/(Fe²⁺ + Mg+Mn).

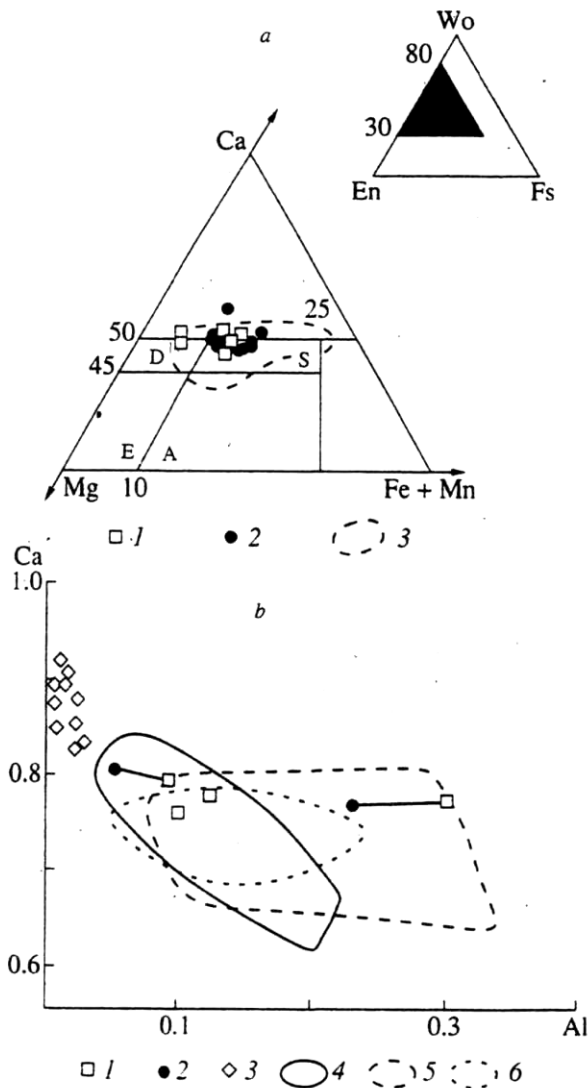


Figure 2 Ternary composition diagram Wo-En-Fs (mol.%) (a) for different clinopyroxene generations from the alkaline-ultramafic volcanic rodingites of the Valaginsky Range (Eastern Kamchatka). Clinopyroxene composition data points and fields: 1 - relict cores, 2 - regeneration rims, 3 - newly formed clinopyroxenes in amygdules and pseudomorphs. Pyroxene fields: D - diopside, S - salite, E - endiopside, A - augite. Minerals: Wo - wollastonite, En - enstatite, Fs - ferrosilite. b - Ca-Al diagram (form, units) for the compositions of clinopyroxenes from the volcanic rodingites of the Valaginsky Range: 1-3 - the compositions of the coexisting core and rim pairs are connected by lines like in Fig. 2, a. Fields of clinopyroxenes from ultramafics (4), meymechites (5), and Cretaceous basalts.

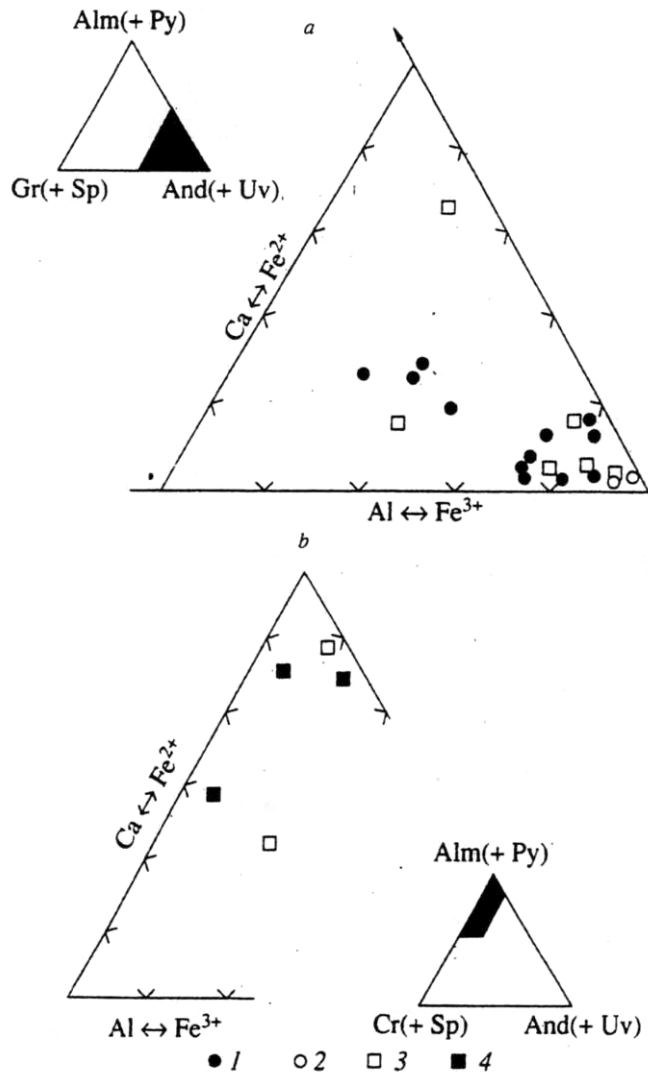


Figure 3 Ternary composition diagrams Alm(Py)-Gr(Sp)-And(Uv) for the compositions of newly formed (a) and accessory magmatic (b) garnets from the alkaline ultramafic volcanic rocks of the Valaginsky Range. Composition data points for garnets from rodingites in the Uzkii Creek area (1) and in Mt. Savulch area (2); 3, 4 - data from [3] and [19], respectively. Minerals: Alm - almandine, And - andradite, Gr - grossular, Py - pyrope, Sp - spessartine, Uv - uvarovite.

amygdules are filled only with garnet grains, brownish in the cores and transparent in the rims. The chemical composition of the garnet (Table 2) shows that the analyzed minerals are high-Ca andradites (Ti-andradite in some samples), containing as much as 35% of

Table 2 Representative chemical compositions of garnets from rodingites in the Valaginsky alkaline ultramafic volcanics. wt. %.

Oxide	1*	2	3	4	5	6	7	8	9
SiO ₂	36.02	35.77	35.51	34.69	34.58	35.96	36.08	35.55	35.00
TiO ₂	0.78	1.06	2.49	0.67	2.65	6.47	6.31	1.03	0.63
Al ₂ O ₃	0.81	0.56	0.34	3.14	0.38	1.19	0.89	0.74	2.84
Cr ₂ O ₃	0.02	0.08	0.07	0.47	0.15	0.07	0.86	0.03	1.10
Fe ₂ O ₃ **	28.11	28.22	28.71	26.76	29.38	24.68	23.38	29.55	25.88
FeO	0.00	0.00	1.44	1.08	1.27	0.44	1.33	0.00	1.30
MnO	0.14	0.05	0.04	0.04	0.00	0.05	0.05	0.04	0.00
MgO	0.15	0.20	0.03	0.05	0.13	0.03	0.07	0.10	0.23
CaO	33.89	34.01	32.09	32.32	32.01	32.97	32.51	33.25	31.80
Na ₂ O	0.09	0.26	0.04	0.07	0.00	0.00	0.00	0.03	0.06
Total	99.91	100.20	100.76	99.29	100.55	101.88	101.48	100.32	98.94
	Number of ions per 12 O atoms								
Si	2.948	2.930	2.987	2.920	2.918	2.977	2.999	2.985	2.958
Al ^{IV}	0.052	0.054	0.013	0.080	0.038	0.023	0.001	0.015	0.042
Al ^{VI}	0.027	0.000	0.021	0.231	0.000	0.093	0.086	0.059	0.240
Ti	0.048	0.065	0.158	0.042	0.168	0.403	0.395	0.065	0.040
Cr	0.001	0.005	0.005	0.031	0.010	0.005	0.056	0.002	0.073
Fe ³⁺	1.924	1.933	1.673	1.732	1.779	1.119	1.068	1.824	1.647
Fe ²⁺	0.000	0.000	0.246	0.040	0.176	0.499	0.487	0.044	0.091
Mn	0.010	0.003	0.003	0.003	0.000	0.004	0.004	0.003	0.000
Mg	0.018	0.024	0.004	0.006	0.016	0.004	0.009	0.013	0.029
Ca	2.972	2.985	2.892	2.915	2.894	2.924	2.895	2.992	2.879
Na	0.014	0.041	0.006	0.012	0.000	0.000	0.000	0.004	0.010
Alm	0.00	0.00	7.82	1.33	5.70	13.27	14.33	1.43	3.02
Andr	96.19	96.48	90.15	85.03	90.90	69.10	66.54	93.56	83.31
Gross	2.82	2.33	1.57	11.80	2.36	17.13	15.25	4.41	10.03
Pyr	0.61	0.81	0.12	0.21	0.53	0.11	0.26	0.41	0.97
Spess	0.32	0.12	0.09	0.10	0.00	0.10	0.10	0.09	0.00
Vv	0.07	0.26	0.25	1.53	0.51	0.28	3.52	0.10	3.67

*1, 2 - Mt. Savulch rodingites, Sample 18/81; 3-9 - rodingite xenoliths in meymechite tuff in the Uzkiek Creek area; 3-7 - Sample 149-10; 8, 0 - Sample 128-12.

** Calculated stoichiometrically.

other molecules (Fig. 3, *a*). These garnets are high in Fe and Ti and extremely low in Al, the features that distinguish them from the garnets of the rodingites from the ophiolite complexes of Kamchatka [13]. The composition of the secondary metasomatic garnets is also different notably from the compositions of the primary magmatic accessory garnets of the Kamchatkan ultrabasic volcanics [3], [19], which are generally higher in Al and Cr (Fig. 3, *b*) than the garnets of the apomeymechite rodingites, the latter being higher in Ca and Ti.

In many samples the interstices between the pyroxene needles and garnet grains in the amygdules are filled with minerals of the serpentine-chlorite group, carbonate, and barite. Where garnetization is widely developed, small hexahedral or isometric crystals of this mineral appear first in the uncrystallized portions of the groundmass and then inside the clinopyroxene microlites. These relations can be taken as the evidence of a later garnet origin.

The subsequent transformations of the early rodingite associations consisted in their replacement by hydroxyl-bearing minerals. The process of hydration was most complete in fault zones where the clinopyroxenes of the rodingite groundmass were replaced by aggregates of magnesian chlorite and amphibole of the tremolite-actinolite type (Table 3), while an association of chlorite, prehnite, amphibole, and hydrogarnet (?) developed in the garnet-filled amygdules and pseudomorphs after olivine.

Characteristic of the rodingites are carbonates, phosphates, and sulfates, which, being the minerals of the final (hydrothermal) stage of rodingitization, fill (wholly or partially) cracks and voids in the amygdules or in the pseudomorphs after olivine. The chemical analyses of the carbonates show that they are represented mainly by calcite with minor Mg, Fe, and Sr contents. Less common are barite, strontium-calcite, strontianite, and witherite. The examined phosphates were found to be fluorapatites.

The ore minerals are represented by two main types: magnetite and sulfides, the magnetite being obviously predominant, occasionally making up as much as 20-30% of the rock volume. The sulfides are represented by millerite, pentlandite, chalcopyrite, and galena.

PETROCHEMISTRY AND GEOCHEMISTRY

The chemical composition of the rodingites from the alkaline ultramafic rock association of the Valaginsky Range (Table 4) produces on an ACF diagram a compact composition field shifted toward the CF axis relative to the composition of the rodingites from the ophiolite complexes of Eastern Kamchatka, primarily, because of the higher Al content of the latter (Fig. 4, *a*). On a CaO-SiO₂-Al₂O₃ diagram (Fig. 4, *b*), the compositions of the Valaginsky rodingites are grouped near the theoretical composition of diopside, which agrees with the modal mineralogy of the rocks. The analysis of the variation diagrams

Table 3 Chemical compositions of amphiboles and chlorites from the Valaginsky rodingites, wt. %.

Oxide	1*	2	3	4	5	6	7	8
SiO ₂	53.64	52.17	51.25	50.74	35.83	30.40	35.94	32.13
TiO ₂	0.25	0.11	0.05	0.04	0.00	0.00	0.00	0.00
Al ₂ O ₃	2.42	4.53	5.11	3.02	10.25	14.54	10.29	15.54
FeO**	12.77	11.43	10.94	11.95	8.85	11.99	5.51	6.86
MnO	1.07	0.13	0.31	0.31	0.14	0.26	0.31	1.70
MgO	15.26	17.01	18.97	16.39	29.45	25.00	31.96	27.79
CaO	12.70	13.73	11.93	11.45	0.30	0.60	0.03	0.31
Na ₂ O	0.00	0.32	0.00	0.09	0.00	0.00	0.00	0.00
K ₂ O	0.00	0.01	0.00	0.00	0.54	0.07	0.03	0.02
Total	98.11	98.44	97.56	97.39	85.36	82.86	84.75	84.35
			23(O, OH)***				36(O, OH, F)***	
Si	7.662	7.261	7.076	7.104	7.071	6.319	7.014	6.395
Al ^{IV}	0.338	0.739	0.924	0.896	0.929	1.681	0.986	1.605
Al ^{VI}	0.069	0.018	0.003	0.097	1.453	1.878	1.379	2.037
Ti	0.027	0.012	0.015	0.046	0.000	0.000	0.000	0.000
Fe ³⁺	0.328	0.433	0.000	0.152	0.000	0.000	0.000	0.000
Fe ²⁺	1.197	0.924	1.054	1.247	1.461	2.084	0.899	1.142
Mn	0.129	0.016	0.036	0.037	0.023	0.046	0.051	0.287
Mg	3.249	3.598	3.904	3.421	8.665	7.746	9.299	8.245
Ca	1.944	2.166	2.087	1.765	0.063	0.134	0.006	0.066
Na	0.000	0.088	0.000	0.024	0.000	0.000	0.000	0.000
K	0.000	0.002	0.000	0.000	0.136	0.019	0.002	0.005
al	-	-	-	-	0.22	0.26	0.19	0.27
fm	0.26	0.20	0.21	0.27	0.14	0.21	0.09	0.12

*Mt. Savulch area, Sample S-18: 1-4 - amphiboles; 5-8 - chlorites.

** AH iron is given as FeO; al = Al/(Al + Fe²⁺ + Mg + Mn); fm = Fe²⁺/(Fe²⁺ + Mg+Mn).

*** Number of ions per 23 atoms (O, OH) and per 36 atoms (O, OH, F), respectively.

Table 4

Oxide	1	2	3	4	5	6	7	8	9	10	11	12	13
SiO ₂	48.70	37.90	43.12	46.96	46.44	48.50	41.22	43.96	46.98	46.66	46.26	46.14	47.20
TiO ₂	0.40	1.02	0.60	0.66	0.66	1.00	1.00	0.65	0T80	0.62	0.60	0.52	0.95
Al ₂ O ₃	1.91	1.75	2.42	0.60	1.81	0.29	0.68	1.02	2.98	3.99	1.30	0.80	1.43
Fe ₂ O ₃	4.40	12.26	10.51	6.58	7.13	11.07	5.57	8.15	6.40	7.80	5.99	4.59	6.87
FeO	3.28	2.21	3.73	6.92	6.91	3.36	6.33	2.96	5.99	4.85	6.36	6.72	5.12
MnO	0.16	0.20	0.16	0.31	0.22	0.27	0.29	0.19	0.20	0.18	0.21	0.23	0.25
MgO	13.97	6.24	9.39	10.80	13.34	13.18	12.01	9.80	10.00	7.45	12.72	13.48	10.68
CaO	22.55	28.28	28.46	22.18	20.69	20.46	24.23	27.18	20.73	21.00	22.58	22.80	25.00
Na ₂ O	0.23	0.16	0.09	0.18	0.22	0.20	0.22	0.10	0.15	0.10	0.15	0.20	0.17
K ₂ O	0.09	0.12	0.07	0.20	0.20	0.20	0.20	0.40	0.20	2.90	0.20	0.20	0.20
P ₂ O ₅	0.29	1.06	-	0.98	1.34	0.36	0.64	1.06	0.87	0.56	0.77	0.23	1.02
H ₂ O ⁺	2.40	0.39	1.41	1.50	0.80	0.90	2.40	0.80	3.40	2.40	1.00	1.60	0.70
H ₂ O ⁻	0.70	0.37	0.14	0.59	0.46	0.54	0.40	0.46	0.74	0.65	0.51	0.33	0.44
CO ₂	-	4.61	-	0.24	0.18	0.13	4.55	3.13	0.18	0.23	1.23	1.63	0.24
SrO	0.03	2.80	-	-	-	-	-	-	-	-	-	-	-
BaO	0.76	0.57	-	-	-	-	-	-	-	-	-	-	-
Total	99.87	99.94	100.10	98.70	100.40	100.46	99.74	99.86	99.62	99.39	99.91	99.47	100.2

Note. 1-4 - Uzkii Creek area: 1 - Sample PL 2-4, 2 - PL 5-8, 3 - K616-14, 4 - 158-10; 5-13 - Mt. Savulch area: 5 - Sample S-11, 6 - S-13, 7 - S-14, 8 - S-18, 9 - S-20, 10 - S-21, 11 - S-22, 12 - S-12, 13 - S-15.

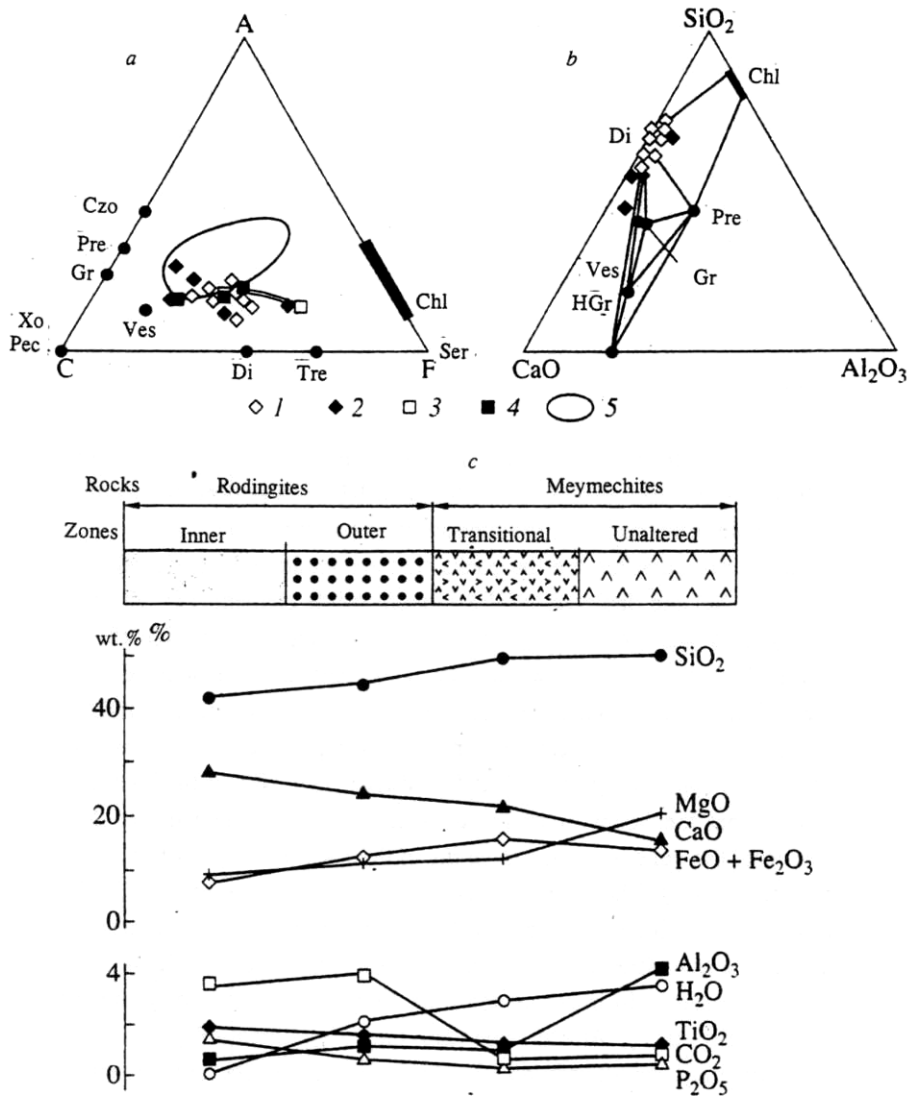


Figure 4 ACF (a) and CaO-SiO₂-Al₂O₃ (wt.%) (b) diagrams for the Valaginsky volcanic rodingites: 1, 2 - rodingites from Mt. Savulch and Uzkii Creek, respectively; 3 - parent meymechite; 4 - rocks from different zones of the metasomatic column of apomeymechite rodingites; 5 - composition field of rodingites from the ophiolite complexes of Kamchatka [13]. The arrow in the ACF diagram shows the variation trend of the chemical compositions of rocks during the meymechite rodingitization. Code: Ves - vesuvian, HGr - hydrogarnet, Gr - grossular, Di - diopside, Xo - xonotlite, Czo - zoisite, Pec - pectolite, Pre - prehnite, Ser - serpentine, Tre - tremolite, Chi - chlorite, c - chemical variation of rocks in different zones of the volcanic rodingite metasomatic column in the Mt. Savulch area, Valaginsky Range.

demonstrating the variation of the chemical composition of the rocks along the zones of the metasomatic column of the apomeymechite rodingites (Fig. 4, *c*) shows that the inner zones of the rodingite xenoliths are enriched in CaO, TiO₂, P₂O₅ and CO₂. Compared with the inner zones, the outer zones and the adjacent portions of the enclosing meymechite tuff are distinguished by their markedly higher MgO and Al₂O₃ contents. The total iron content decreases, but the oxidation ratio Fe₂O₃/FeO increases. The contents of SiO₂ and alkalis increase gradually from the most altered zones in the xenoliths to the unaltered volcanics.

The behavior of chemical elements in the Valaginsky rodingites (Table 5; Fig. 5, *a*) shows that in the course of the protolith rodingitization, the resulting metasomatic rocks grow highly enriched in Sr and Ba to the extent of the formation of independent mineral phases (barite, strontianite, and the like). The enrichment in V, Y, and Nb in the direction from the host meymechites toward the centers of the rodingitized xenoliths is not that high, though shows a steady trend. Compared with the host rocks, the rodingites are much lower in Cr and to a lesser extent in Zn, Co, and Rb. The concentration of Zr remains virtually invariable in all zones of the metasomatic column.

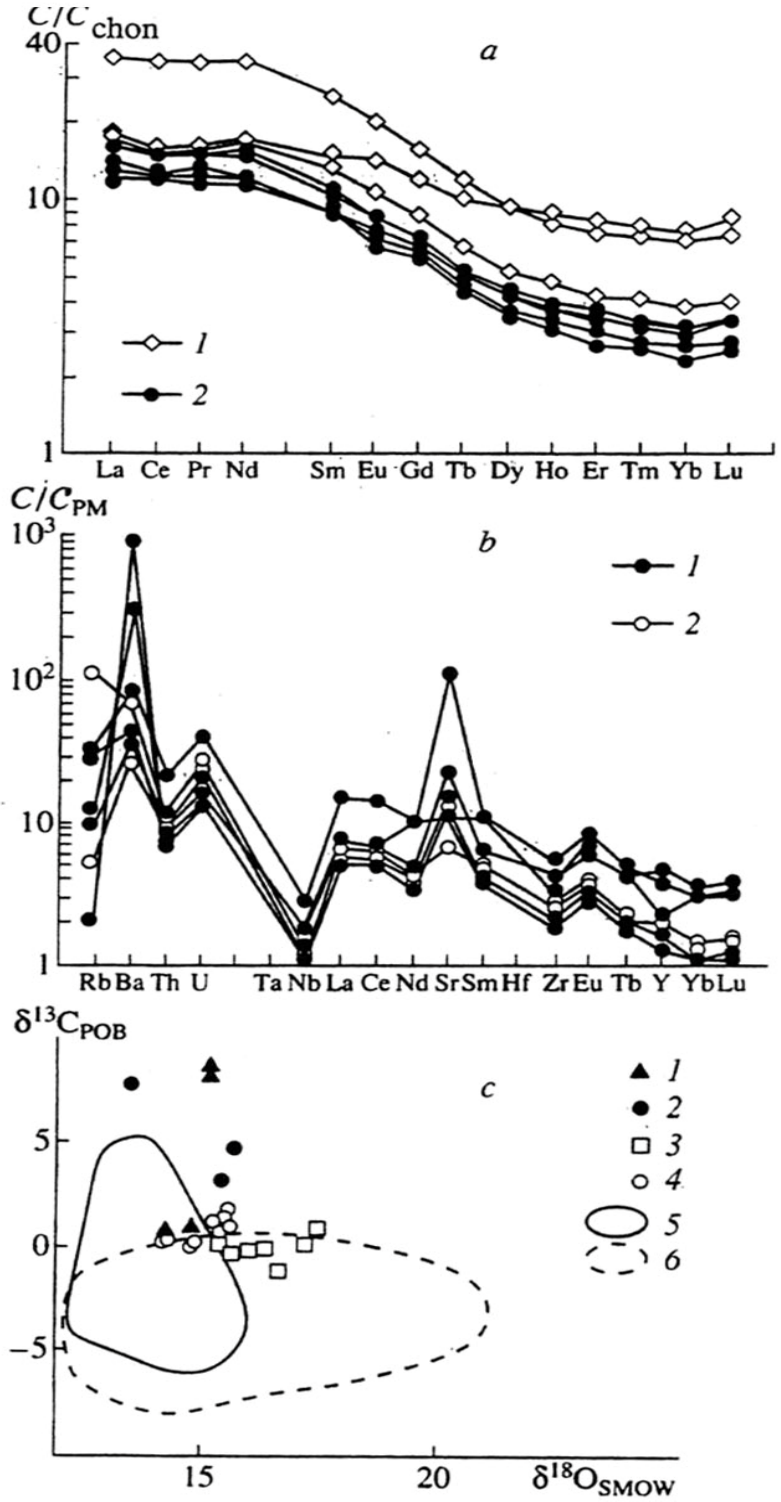
The studied metasomatites are the rocks that are moderately enriched in compatible elements (Cr, Ni, Sc) and depleted in HFSE incompatible elements (Ti, Zr, Y, Hf) (Table 5). The rodingites of the alkaline ultramafic rock association are considerably enriched in large-ion lithophile elements (LILE: Rb, Sr, Ba). Another geochemical feature of the Valaginsky rodingites is a high REE fractionation (high enrichment in light lanthanides relative to the heavy ones), this feature being clearly expressed in the characteristic bends of the curves. The spider diagrams of REE and trace elements in the rodingites (Fig. 5, *a* and *b*) show that the behavior of the different groups of elements in the rodingites generally reflects the general trends inherent in their supposed protoliths (meymechites, lamproites, and the like). The main differences concern the behavior of LIL elements, the petrologic sources of which are discussed below in the Section "Discussion of Results".

The studied metasomatites showed high $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values (Table 6), notably higher than the values measured in minerals and bulk samples from the rodingites of ophiolite complexes [40] (Fig. 5, *c*). At the same time they are comparable with the $\delta^{18}\text{O}$ value found for carbonated apoultramafics [2]. The proximity to the latter is emphasized by a wide development of carbonates in the rocks of the alkaline ultramafic rock association and by the high weight contents of CO₂ in them indicated by the results of chemical analysis (an. 2, 7, 8 in Table 4). At the same time the isotopic characteristics of carbon in the studied rodingites are comparable with the $\delta^{13}\text{C}$ values of sedimentary carbonates and seem to be the consequence of carbon isotope fractionation resulting from the thermal decomposition of carbonate matter during the pyromorphism of the parent rocks in a meymechite melt.

Table 5 Trace element and REE concentrations in the Valaginsky rodingites, ppm.

Element	1	2	3	4	Oxide	1	2	3	4
Be	3.85	1.95	2.06	1.51	Ta	0.03	0.05	0.05	0.05
Sc	19.18	30.03	27.26	32.79	Pb	5.41	19.12	7.63	6.52
V	250.72	402.70	218.69	373.44	Th	0.75	1.43	0.52	1.01
Cr	8.56	1.31	5.16	1.36	U	0.40	0.77	0.30	0.53
Ni	354.37	91.51	269.68	140.51	La	4.13	8.56	4.12	7.59
Cu	18.18	17.66	33.80	20.58	Ce	9.80	21.11	9.70	17.75
Zn	106.04	65.26	121.17	194.74	Pr	1.55	3.25	1.50	2.64
Rb	7.12	19.19	1.20	1.85	Nd	8.02	16.41	7.82	12.37
Sr	1045.9	1162.9	408.7	2058.6	Sm	2.05	3.87	2.29	2.99
Y	7.90	13.76	15.34	13.75	Eu	0.63	1.13	0.84	1.01
Zr	27.77	45.24	35.50	39.54	Gd	1.77	3.22	2.45	2.81
Nb	0.82	1.62	1.08	1.21	Tb	0.24	0.43	0.38	0.39
Mo	0.05	0.13	1.85	0.07	Dy	1.34	2.37	2.36	2.15
Sn	1.35	0.83	0.57	1.16	Ho	0.27	0.47	0.49	0.42
Cs	0.05	0.11	0.06	0.04	Er	0.68	1.25	1.37	1.06
Ba	1601.4	440.04	7088.5	1327.6	Tm	0.10	0.18	0.20	0.15
Hf	0.82	1.36	0.98	1.10	Yb	0.64	1.15	1.27	0.99
					Lu	0.10	0.19	0.21	0.16

Note. Sample numbers: 1 - K607-1, 2 - K606-34, 3 - K416-13, 4 - SI-3.



DISCUSSION OF RESULTS

The discovery of high-temperature rodingites in the alkaline ultramafic volcanics of the Valaginsky Range called for refining the volume and contents of the term "rodingite". The recognition of the fact that the studied rocks are typical rodingites, - and their formal attributes (CaO content, spatial and genetic relations with ultramafics, and the dominant role of Ca silicates and aluminosilicates) prove this to be the case, — brings up the question: Do "rodingites and rodingites" exist (by analogy with the eclogite problem), or the thermodynamic range of the rodingitization process, derived from the study of rodingites in ophiolite complexes, should be expanded substantially? The solution of this problem calls for the discussion of some petrologic aspects which seem to be the key items for the understanding of the rodingitization process as a whole.

Source of calcium and the mechanism of protolith saturation with it during rodingitization. In the modern petrologic classification, rodingites are defined as metasomatic polymineral calc-silicate rocks with a CaO content above 20 wt. %, produced as a result of the reworking of gabbro and other rocks in ultramafics [5], [6], [9], [16], [26], [29], [37]. Consequently, the key problem in rodingite genesis is the problem of the mechanism and conditions of protolith saturation with lime. Analysis of mineral assemblages in the rodingites of this type revealed that the compositional evolution of these calc-silicate metasomatites consisted of two successive stages, pyromorphism and hydration [18], [21], each of them consisting of several phases. We found that the chemical composition of rodingites had been formed during the early (pyromorphic) stage under high-temperature conditions sufficient for protolith melting, and that the hydration of the rocks had basically been a metamorphic and isochemical process which had not had any substantial impact on the final chemical composition of the rocks, except for the addition of hydroxyl-ion.

The initial phase of meymechite pyroxenization consisted in the solid phase high-temperature reactions of the solid-melt type and in the metasomatic (pneumatolytic?) addition of calcium ion into the xenoliths from the surrounding ultramafic magma at temperatures that did not exceed the temperature of the complete or partial meymechite melting in the range of 600-900 °C [23]. In this case the metasomatic process acted as an

Figure 5 REE distribution pattern (*a*) and geochemistry of rodingites (*1*) and meymechites (*2*). The contents of elements are normalized to the composition of carbonaceous chondrite C1 [30] (*a*) and to primitive mantle composition [31], [38] (*b*). *c* - Oxygen and carbon isotope relationships in the alkaline ultramafic rocks of the Valaginsky Range: *1* - apomeymechite rodingites, *2* - meymechite tuff, *3* - alkaline nepheline basalt, *4* - carbonatite inclusions in meymechites, *5, 6* - fields of the isotopic compositions of carbonates from ophiolitic rodingites [40] and of carbonate-bearing apoultramafic metasomatites, respectively.

agency for the transfer of Ca, Mg, and Fe from the ultramafic magma to a xenolith, the elements required for building the crystal lattice of clinopyroxene. As a result, the CaO content in the protolith increased but was not higher than 14-16 wt. %.

Table 6 Isotopic compositions of oxygen and carbon in rodingites and associated alkaline ultramafic volcanics from the Valaginsky Range.

Rock	$\delta^{18}\text{O}$, ‰ (SMOW)	$\delta^{13}\text{C}$, ‰ (PDB)
Apomechite rodingites	14.2-15.2	+0.8...+ 8.8
Meymechite tuff	13.5-15.9	+3.1...+7.8
Nepheline trachybasalts	15.5-17.5	-1.2...+0.2
Carbonatite fragments	14.2-16.0	+0.2... + 1.6

Note. Determined by B. G. Pokrovsky (Geological Institute, Russian Academy of Sciences, Moscow).

In the dominant volcanic-type rodingites, composed of a regularly repeated glass±clinopyroxene assemblage, the groundmass has an amygdaloidal or vesicular structure and a glassy or microlitic texture, the microlites being represented by acicular, radiated, star diopside. These features are treated as the evidence of the complete or partial protolith melting. Because the newly formed palingenetic melt was highly saturated with gas, it swelled up intensively during the eruption and an abrupt pressure drop to produce an amygdaloidal structure. The chemical composition of the newly formed magma approximated that of the typical rodingite, and its further crystallization, even the most complete, did not influence much the relations of the rock-forming oxides. This served as a basis for our model of the palingenetic-metasomatic genesis of rodingites originating as a result of the metasomatic reworking and exchange reactions of the apoprotolith melt with the surrounding magma.

In the framework of our model we assume that the reaction of the melt-melt type was the most efficient formation mechanism of rodingites, calc-silicate rocks with the CaO contents above 20-25 wt%. Concerning the essence of these reactions, it should be noted that in accordance with the strict definition of this term proposed by D. S. Korzhinsky [7], they are not metasomatic. Nevertheless, his indication that bases and acids may interact in melts as a result of their ionization in the similar way as they do in aqueous solutions permits us to neglect the above mentioned constraint and use the term "palingenetic-metasomatic" for this stage.

In the case of partial melting the saturation of the protolith melt with lime occurs mainly by way of the removal of Si, Al, Mg, Fe, and alkalis, Fe being the least active element. As a result, the fairly mobile components dissipate in the dynamically active host melt. Also there occurs a counter migration of Ca from the host melt, though the amount of the added Ca in the final rodingite composition cannot be estimated thus far. To sum

up, the final product of interaction between xenoliths and the host magma (complete assimilation of the former by way of magmatic digestion) undergoes an obligatory intermediate stage of palingenesis and metasomatism, during which petrographically varying protoliths melt and undergo a kind of conditioning which results in the averaging of compositionally different xenoliths to the composition of diopside. In this context the observed growth of the MgO content in the inner contact zones of rodingites can be treated as a precursor of xenolith assimilation.

The results of experimental studies can be used to estimate the conditions of xenolith melting in ultramafic magma and of exchange reactions during the rodingitization process. A. V. Sobolev *et al.* [23] found that the temperature of the host meymechite magma, from which the East-Kamchatkan volcanic rocks had been derived, had been in the range of 1610-1030°C, which is sufficient for the melting of not only mafic but also ultramafic xenoliths. The temperature of basalt lavas was measured instrumentally *in situ* to average 1100°C [25]. The temperature of alkaline, e.g. nephelinic, magmas is even lower, 980°C [24]. The high gas and water saturation of meymechite lavas and of their protoliths suggests that the melting of the latter began at 900-1000°C. The resulting liquid did not mix with the meymechite melt but interacted with it actively, as manifested by the migration of the above mentioned elements from the xenolith to the surrounding material. The high speed of the reactions leading to Ca accumulation in the protolith was stipulated by the high temperatures and dynamic activity of the melts during the volcanic process, responsible for their active mixing.

D. S. Korzhinsky [7] mentioned a skarnoid stage in the compositional evolution of metamorphic and metasomatic rocks produced without a significant addition of Ca and Si at the expense of the calc-silicate parental rocks. This stage is not always observed and is generally absent in the compositional evolution of volcanic rodingites. The secondary genesis of garnet in the rocks of the skarnoid stage is unambiguously determined by its reaction relations with the earlier products, glass and diopside. It should be emphasized that the formation of garnet is accompanied by changes in the chemical compositions of the rocks: the greater the granitization degree, the higher the Ca concentration in metasomatites. For instance, the formation of garnet in the amount of 30% of the rock volume increases the CaO content by ca. 5 wt%.

The final process of hydration occurred in the rodingites at the high oxygen, sulfur, and carbon dioxide activity under the conditions of the high alkalinity of the surrounding medium. This stage began with the deposition of iron and copper sulfides on the walls of the amygdules and in the cracks. The mineral sequence is then followed by calcite, strontium-calcite, strontianite, and witherite. Later, as a result of pressure decline or the effects of some other factors, the released oxygen oxidized the sulfur of the sulfides to a sulfate-ion with the formation of magnetite, on the one hand, and of barite and celestine, on the other. We believe that these processes were responsible for the formation of high background Sr and Ba concentrations in the rodingites and for the high REE concentrations in them compared to the enclosing rocks. 19

Genetic similarity of rodingitization in volcanic and plutonic mafic-ultramafic rocks. Without going into the detailed description of the geologic setting and chemical composition of rodingites from the ophiolite complexes of Eastern Kamchatka, discussed in our previous works [13], [17], [21], we will summarize the main conclusions of our studies.

1. The rodingites of the volcanic and plutonic rock associations show a significant similarity of their compositions and also an identity in the sequence of mineral transformations in both types of the metasomatites. This suggests that the clinopyroxene±glass assemblage, found in the plutonic rodingites [17], was also formed as a result of the palingenesis and high-temperature melting of the protolith and its saturation with lime. The minor differences are that the plutonic rodingites do not have vesicular or amygdaloidal structures, which seems to indicate that they crystallized at higher pressures.

2. The rodingites from tectonic zones in peridotites show the same structural-mineralogic features as do the rodingites from meymechites. This provided a basis for assuming their palingenetic-metasomatic genesis. However, whereas the melting of xenoliths in the meymechite magma looked natural and logical, the melting of mafic rocks entrapped during the intrusion of crystallized and obviously cold ultramafic bodies was hard to explain. The key to the solution of this problem was the structural setting of the most abundant type of plutonic rodingites: their exclusive restriction to zones of variously oriented faults. It seems highly realistic that the main transformation mechanism of mafic xenoliths in this geologic environment was the process of frictional melting as a result of tectonic movements in fault zones. If this assumption is correct, the formation mechanism of plutonic rodingites (at least most of them) was similar to those offered to interpret the genesis of pseudotachylites, basic glassy veins containing microlites of minerals and clasts of the enclosing rocks and localized in fault zones [35], [39]. Pseudotachylites bear a considerable resemblance to the rodingites of the early anhydrous association on a micro- and a macrostructural level. Both groups of rocks show indications of the complete or partial melting of the parent rocks. These indications are the presence of glass, the aphanitic and hyaline texture of the groundmass, the dendritic habitus of the newly formed microlites, droplike sulfide grains, etc. The structural setting of both rock types is virtually identical, the main differences being associated with the compositions of parent and enclosing rocks.

3. The calc-silicate composition the rodingites from ophiolite complexes was produced by the removal from the palingenic apogabbro melts of Si, Al, Mg, Fe, and alkalis, that is, the same elements that participate in the formation of volcanic rodingites. However, whereas the traces of the removed components seem to be lost in the volcanic rodingites, the migration directions of their various groups are easily traceable in the plutonic rodingites. For instance, the migration paths of Al_2O_3 and alkalis, especially of Na_2O , follow the thermal gradient toward the outer contact, where they are fixed in the pargasite and albite of amphibolites and stipulate the formation of chlorite-serpentine-chlorite

fringes. The temperature regime of these metasomatic reactions was controlled by the melting temperature of basic igneous rocks, 900-1100°C [10], [25] and, consequently, was not different from the temperature regime of the palingenetic-metasomatic transformations of volcanic rodingites.

Factors responsible for the universal character of rodingitization in volcanic and plutonic rodingites. The most probable cause of the universal rodingitization pattern in the rodingites of different rock associations and different geologic settings was the existence of a genetic succession between the magmatic and metasomatic stages of ultramafics evolution. This succession is especially clearly manifested in the palingenetic-metasomatic reworking of solid-phase enclosures in ultramafic rocks (molten or crystallized), which resulted in the peculiar conditioning of the newly formed rocks to the composition of rodingites. This suggests the conclusion that rodingites could be formed only in the ultramafic, high-Mg environment, the chemical processes in which were controlled by the temperature and pressure of the system, and also by the acid-alkali interaction of the components that participated in the bimetasomatic reactions [7], [8].

Magnesium and calcium behave in a contrasting manner at all stages of the formation of the chemical and mineral compositions of rodingites. It is conceivable that this behavior of these elements in nature is controlled by their fundamental properties which were formulated by D. S. Korzhinsky [7], [8] after his study of the principles of acid-alkali interaction. The substantially magnesium and substantially calcium minerals of magnesium skarn are known to concentrate in separate zones [14]. The antagonism of these elements was proved in experiments simulating the contact-reaction interaction of mafic and ultramafic rocks [15]. At the same time the metastability of a system under high-temperature conditions starts the magmatic replacement of a calc-silicate melt by an ultramafic, low-Ca one, the fact proved by the higher Mg content in the inner contact zones of the xenoliths.

The main element-indicator of palingenetic-metasomatic processes in ultramafic rocks is calcium. At the same time the results of this study suggest that the role of another rock-forming oxide, alumina, increases from volcanic to plutonic rodingites. For instance, the content of Al_2O_3 in the diopside of the rodingites derived from meymechites does not exceed a few tenths of a percent, whereas the concentration of this oxide is considerably higher (0.3-4.7 wt%) in the clinopyroxene of plutonic rodingites. The same trend is proved by garnets. Proceeding from differences in the structures of these rocks, there is good reason to believe that variations in the Al_2O_3 contents were controlled by pressure.

It is likely that the palingenetic-metasomatic transformation of the parent rocks, which produced calc-silicate metasomatites, took place during the early alkaline stage of the metasomatic process. Transition to the acid stage occurred as temperature continued to decline at the beginning of hydrothermal activity in rodingites, the process that operated under the conditions of high sulfur and carbon dioxide activity and facilitated the formation and precipitation (as the solutions continued to cool off) of heavy metal sulfides and later of carbonates and sulfates.

The regressive hydration of calc-silicate rocks in mafic-ultramafic complexes is usually associated with the mass serpentinization of peridotites. A wide development of hydration in the rodingites of ophiolite complexes is facilitated by the unstable dynamic situation which accompanies the intrusion of the disintegrated fragments of the ophiolite sequence into the upper crust. As a result of the alternating rises and drops of pressure, the early anhydrous mineral assemblages in rodingites become unstable, and the general temperature decline and the growing permeability of fault zones lead to the successive replacement of glass by an aggregate of hydroxyl-containing silicates and aluminosilicates. This process is accompanied by the redistribution of components within a volume limited by the size of a metasomatic body without the addition of any components from outside. This stage is poorly productive in terms of metasomatic transformations: its final result is the addition of hydroxyl-ion into the rock, this justifying the interpretation of hydration as an isochemically metamorphic process. It should be mentioned that the volcanic rodingites do not contain mineral assemblages of the hydration stage.

CONCLUSION

It can be recognized with certainty that there are several types of rodingites that developed in ultramafic volcanic and plutonic rocks in fold areas. The observed differences between the individual types of rodingites are associated with the age and lithology of the surrounding rocks, with the character of relations among the individual components of the sequence, with later magmatic and metamorphic processes, and with some other factors. All of these factors affect the character of calcic metasomatism in ultramafic rocks and stipulate the development of the individual features of the final products. At the same time it is clear that the universal character of the rodingitization of volcanic and plutonic mafic and ultramafic rocks cannot be explained by any particular factors.

Evaluating the geologic and petrologic significance of rodingites, it should be emphasized that they belong to a particular class of paligenetic-metasomatic rocks that develop only in a highly magnesian environment as they interact with the surrounding rocks during the pyromorphic stage. The chemical transformation of the parent rocks, consisting in their saturation with CaO, is merely part of this interaction, the final result of which is the complete assimilation of the xenolith by way of its magmatic replacement during the diffusion saturation of its inner contact zone with magnesium.

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