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SHORT COMMUNICATIONS

Genetic Linkage of Corundum Plagioclasites–Kyshtymites and Miaskites of the Ilmenogorsky–Vishnevogorsky Complex, South Urals, Russia: New Rb–Sr and Sm–Nd Isotopic, Geochemical and Mineralogical Data

M. I. Filina[a], *, E. S. Sorokina[a], M. A. Rassomakhin[b], N. N. Kononkova[a], Yu. A. Kostitsyn[a], and A. V. Somsikova[a]

[a]*Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences (GEOKHI RAS), Moscow, Russia*
[b]*Ilmen State Reserve, Chelyabinsk oblast, Miass, Russia*
**e-mail: makimm@mail.ru*

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Abstract—New geochemical, mineralogical, and Rb–Sr and Sm–Nd isotopic data have been obtained on corundum plagioclasites–kyshtymites from the 5th Versta deposit (South Urals, Russia). The genetic link of miaskites and kyshtymites is shown. The formation of the kyshtymites is associated with the redistribution and accumulation of aluminum, calcium, HFSE, and LIL-elements at the stage of tectonic-metamorphic deformations of the Ilmenogorsky–Vishnevogorsky alkaline complex.

Keywords: corundum plagioclasites, kyshtymites, miaskites, corundum geochemistry, Ilmenogorsky–Vishnevogorsky alkaline complex

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INTRODUCTION

Corundum α–Al_2O_3 is a typical mineral of many magmatic and metamorphic rocks. However, its blue variety, sapphire, colored by Fe^{3+} and/or Fe^{2+}/Ti^{4+}–ions, occurs only in Al-rich Si-poor rocks (Giuliani et al., 2014). Gem-quality sapphires are mainly mined from placer deposits, the genesis of which remains controversial. Therefore, the study of the genetic nature of the mineral found in situ in bearing rocks could provide insight into the fundamental problem of genesis of blue sapphire in the secondary placers.

The studied abrasive corundum from 5th Versta deposit at the South Urals was discovered by A.P. Karpinsky in 1883 (Kler, 1918). In 1910, it was described by A.V. Nikolaev, who found three kyshtymite bodies during prospecting. Kyshtymite, the corundum-bearing plagioclasite, is the plutonic mafic rock (containing up to 95% plagioclase) classified as gabbro of normal series. The deposit has been exploited up to 1930. Much earlier, in 1823, similar kyshtymite veins were found and described by K.F. Fuks, the professor of the Kazan University, during examination of gold mine wastes at the Borzovka River. Later, this abrasive corundum deposit was named as Borzovskoe (Koptev-Dvornikov et al., 1931; Kolesnik et al., 1974; Kolesnik, 1976).

Corundum plagioclasites were described in the large Sittampundi layered complex (India), where they are represented by Archean metamorphosed rocks (Karmakar et al., 2017). They were also found in the Black Giants complex, New Zealand. This complex is the part of the Tuhuan orogenic belt and was subjected to the multiphase amphibolite-facies metamorphism in the Devonian and Carboniferous (Gibson et al., 1979). One more occurrence of corundum plagioclases was described in the Alpine-type Chunky Gal-Mountain Belt (North Karolina, USA) in association with amphibolites and peridotites (Pratt, 1906; McElhaney, McSween, 1983).

In spite of the fact that large corundum plagioclase–kyshtymite massifs have been found at the South Urals two centuries ago, their mineralogy and geochemistry remain poorly studied, while their genetic nature is hotly debatable yet.

GEOLOGY

The plagioclasite veins of the 5th Versta deposit are located northeast of the Borzovskoe deposit and are practically in contact with the eastern flank of the Vishnevogorsky massif. In this area, meta-ultramafic bodies with lenses of corundum plagioclasites are exposed among quartzite schists of the metaterrigenous Saitov Group. The latter is the lithotectonic unit of the Ilmenogorsky–Vishnevogorsky polymetamorphic zone, which is the deep fragment of the regional postcolli-

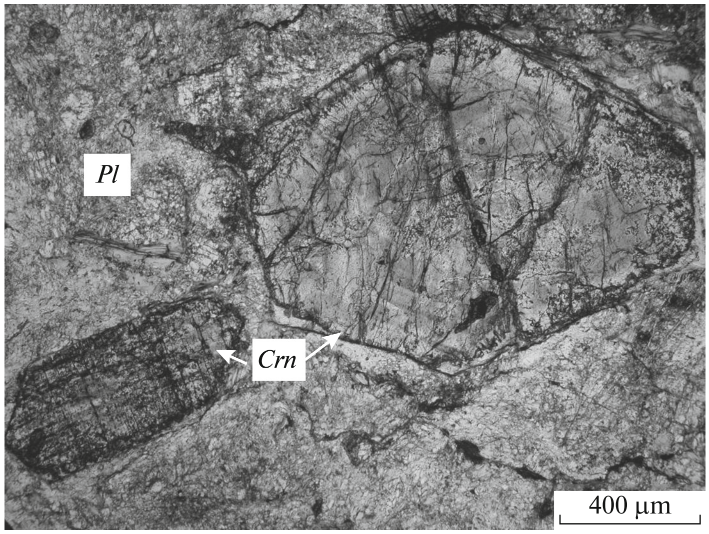

Fig. 1. Bipyramidal–prismatic corundum crystals (Crn) in a fine-grained plagioclase (Pl) matrix.

sional shear (Rusin et al., 2006). SHRIMP U–Pb zircon geochronology of the meta-ultramafites reflects a complex evolution of the rocks: the stage of ~1.3 Ga likely reflects the age of mantle protolith; ~460–420 Ma marks the stages of metamorphic evolution related to the emplacement of main intrusive bodies of carbonatites and miaskites (leucocratic variety of nepheline syenites recently found in the vicinity of the town of Miass) of the Ilmenogrsky–Vishnevogorsky Complex, the age of ~320–280 Ma yeilded the collisional processes (Krasnobaev et al., 2008).

The studied kyshtymite vein is a 3-m thick lenticular body recovered by an open pit. The host rocks are meta-ultramafites consisting mainly of enstatite. The contact of the host rocks and the kyshtymites is marked by the reaction rim (10–25 cm) made up of chrysotile–asbebstos.

The miaskites of the Vishnevogorsky massif in contact with the 5th Versta kyshtymites consist of K-feldspar (20–60 vol %), nepheline (20–30 vol %), lepidomelane (5–20 vol %), amphibole (up to 20 vol %), and sodic plagioclase (up to 20 vol %). Accessory minerals are calcite (up to 3 vol %), cancrinite and sodalite (Arslanov et al., 1978).

MINERALOGY, GEOCHEMISTRY, AND Rb–Sr AND Sm–Nd ISOTOPE DATA

Minerals of the rocks were identified by the Raman spectroscopy on a Renishaw inVia spectrometer. Chemical compositions of the minerals were determined by the electron-microprobe analysis on a Cameca SX100 equipped with four wavelength energy dispersive spectrometers, at an accelerating voltage of 15 kV and beam current of 30 nA. Kyshtymite is mainly composed of euhedral grains of corundum (up to 50 vol %), plagioclase (40–50 vol %); muscovite, clinochlore, and clinozoisite of up to 10 vol %. Accessory minerals are zircon, churchite-(Y), and apatite-group minerals. The rock has a porphyritic texture: large corundum crystals are embedded in a fine-grained matrix of other minerals (Fig. 1).

Corundum 1–7 mm in size forms bipyramidal–prismatic crystals extended along c axis (Fig. 1). The best shaped faces of the crystals are hexagonal prism $(11\bar{2}0)$, pinacoid (0001), and hexagonal dipyramid $(22\bar{4}3)$. The mineral has a typical magmatic oscillatory zoning expressed in alternating the colorless and bright blue (transparent) zones. The blue color of the mineral is related to Fe^{3+} ions substituting Al^{3+} in octahedral sites of the mineral structure and/or to the presence of the exchange ion pairs $Fe^{2+} + Ti^{4+} \leftrightarrow Al^{3+}$. Plagioclase forms a fine-grained mass common distributed over the entire rock volume and varies from labradorite to anorthite An_{61-93}. The musvovite forms fine flakes 0.1–0.2 mm in size and occurs in association with clinochlore and clinozoisite. Measured contents of Mg in muscovite (up to 1.71 wt %) and K in clinochlore (up to 7.11 wt %) are related to the muscovite replacement by clinochlore. The clinozoisite was found as small rounded grains up to 0.1 mm in size replacing plagioclase. It contains up to 2.07 wt% of Fe admixture. The churchite-(Y) forms small xenomorphic crystals up to 30–70 μm in size, which usually occur as microinclusions in corundum. In addition, churchite-(Y) was found in intergrowths with Ce, La, Nd-phosphate, and apatite.

Based on the petrographic study, the following sequence of mineral crystallization was determined in kyshtymites: corundum → plagioclase → muscovite + clinozoisite→ clinochlore. In particular, corundum as the highest temperature mineral was first to crystallize at the magmatic stage, while plagioclase crystallized

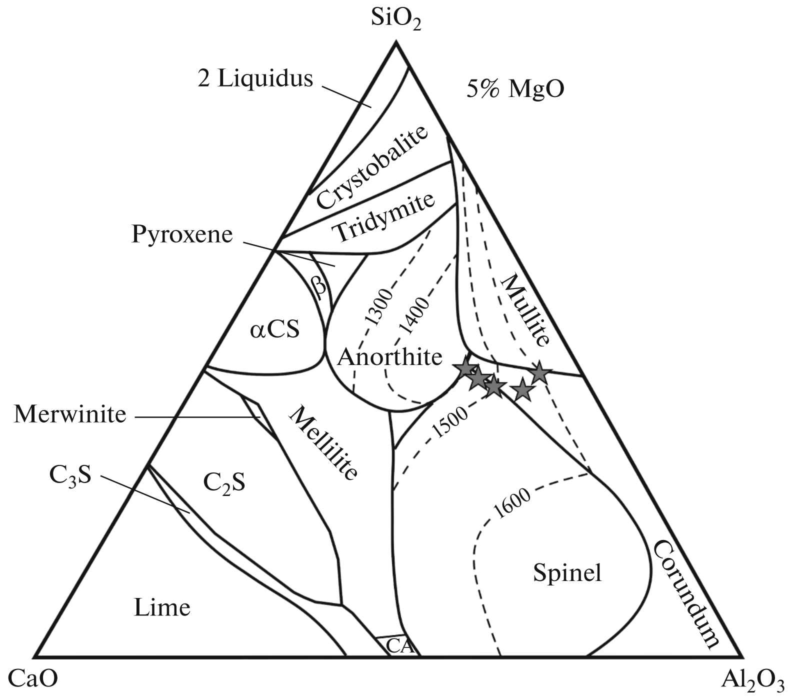

Fig. 2. Phase diagram $CaO–SiO_2–Al_2O_3–MgO$ according to Tang et al. (2015), asterisks show the bulk compositions of kyshtymites.

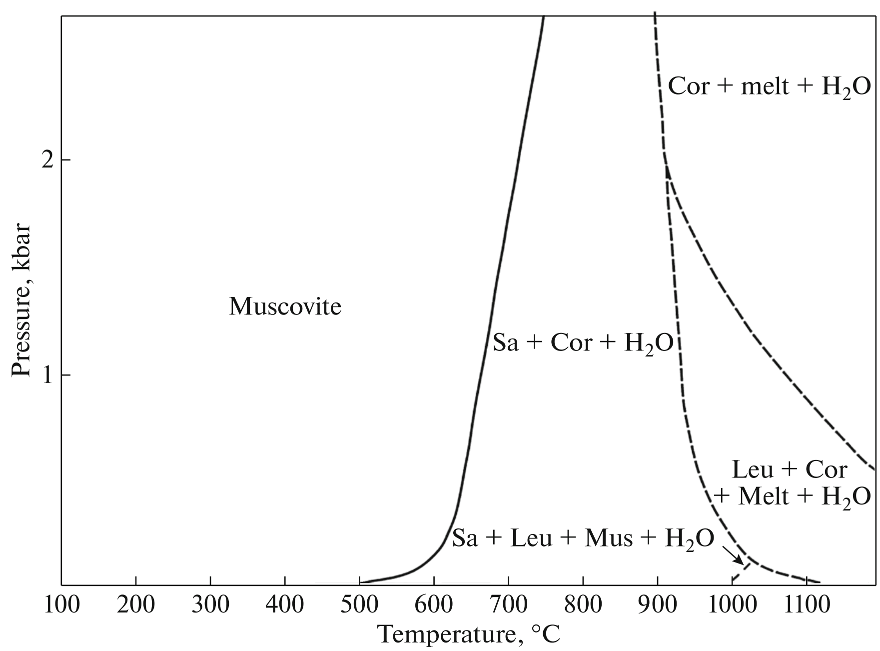

Fig. 3. Equilibrium curve (solid line) for reaction Mus (muscovite) ↔ Sa (sanidine) + Cor (corundum) + H_2O, as well as estimated equilibrium curve for melting of sanidine and leucite (dashed lines) in association with muscovite and one possible ratio in assemblages Sa + Cor + H_2O and Sa + Leu (leucite) + Mus + H_2O (Yoder and Eugster, 1955).

with further decreasing of temperature. This crystallization sequence is consistent with petrological modeling of phases in the $CaO–SiO_2–Al_2O_3–MgO$ system (Fig. 2, Tang et al., 2015). At the metasomatic stage, the further decrease of temperature and/or pressure and potassium influx led to the formation of muscovite, which is the lower temperature phase as compared to corundum and feldspar (Fig. 3), as well as clinozoisite partially replacing plagioclase. Clinochlore crystallized at the final metasomatic stage due to the

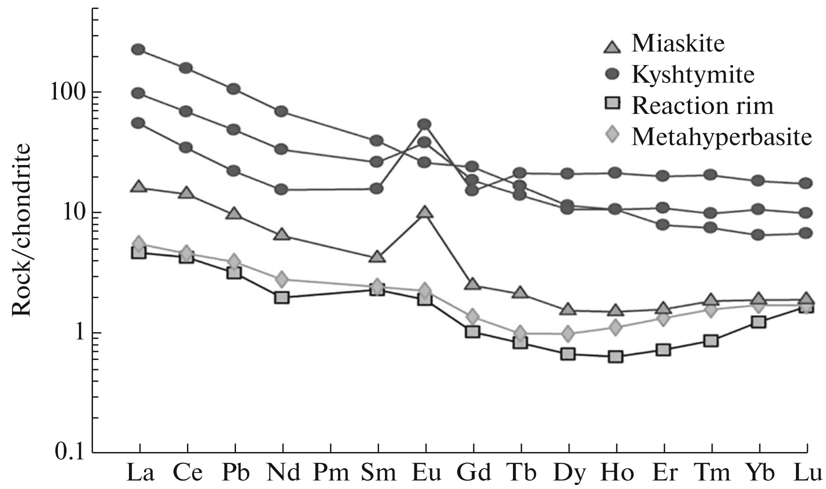

Fig. 4. Chondrite-normalized (Sun and McDonough, 1989) REE and trace-element distribution patterns in kyshtymite, host metahyperbasites, reaction rim between metahyperbasite and kyshtymite, as well as in the miaskite of the Ilmenogorsky–Vishnevogorsky Complex (Ishkul area).

replacement of muscovite and Mg influx in the system from host meta-ultramafites during their metasomatic reworking.

Table 1 presents EDXRF data (AXIOS Advanced spectrometer, PAN alytical B.V.). The SiO_2 content in the kyshtymite varies from 40.84 to 42.72 wt %, Al_2O_3 is from 34.76 to 42.94 wt %, CaO is from 5.89 to 15.79 wt %, total alkalis (Na_2O + K_2O) are from 1.58 to 5.03 wt %, and MgO are from 0.60 to 2.86 wt %. In the classification diagram for magmatic rocks after (Cox et al., 1979), the chemical compositions of kyshtymite fall in the fields of ijolites and alkali gabbros. The rocks have extremely high aluminum saturation index ASI (Al_2O_3/(CaO + Na_2O + K_2O) mol) = 1.12–2.32.

Figures 4, 5 show the REE distribution patterns. The REE contents were measured using inductively coupled plasma mass-spectrometry on an Agilent 7500. The chondrite-normalized REE distribution pattern of kyshtymites demonstrates the LREE enrichment relative to HREE. The pattern is similar to that of miaskites, but is more enriched in REE. Some samples

Table 1. Chemical compositions of kyshtymites of the "5th versta" and miaskites of the Ilmenogorsky–Vishnevogorsky Complex (wt %)

Component	Kyshtymite					Miaskite*	
	6-k	8-k	12-k	16KC4	13-k	miask-1	miask-2
SiO_2	42.37	42.72	40.84	41.56	41.24	58.67	60.34
TiO_2	0.04	0.10	0.07	0.08	0.13	0.85	0.25
Al_2O_3	34.76	36.77	42.94	35.33	42.77	22.76	22.49
FeO_{tot}	0.35	1.20	0.11	0.56	0.46	2.05	1.38
MnO	0.01	0.01	–	–	0.01	0.06	0.04
MgO	1.61	2.52	0.60	2.86	1.11	0.33	0.20
CaO	15.79	11.23	7.46	13.82	5.89	0.58	0.52
Na_2O	1.08	2.17	4.01	0.82	3.98	8.95	8.86
K_2O	0.50	0.99	0.98	1.29	1.05	4.38	4.42
P_2O_5	0.06	0.07	0.04	0.04	0.04	0.03	0.04
S	0.03	0.02	0.02	0.02	0.02	0.30	0.28
L.O.I.	2.51	1.44	2.42	2.96	2.71	0.57	0.69
Total	99.11	99.24	99.49	99.34	99.41	99.53	99.51

(–) Below detection limite. * Miaskite from the Ishkul area, Ilmenogorsky–Vishnevogorsky Complex.

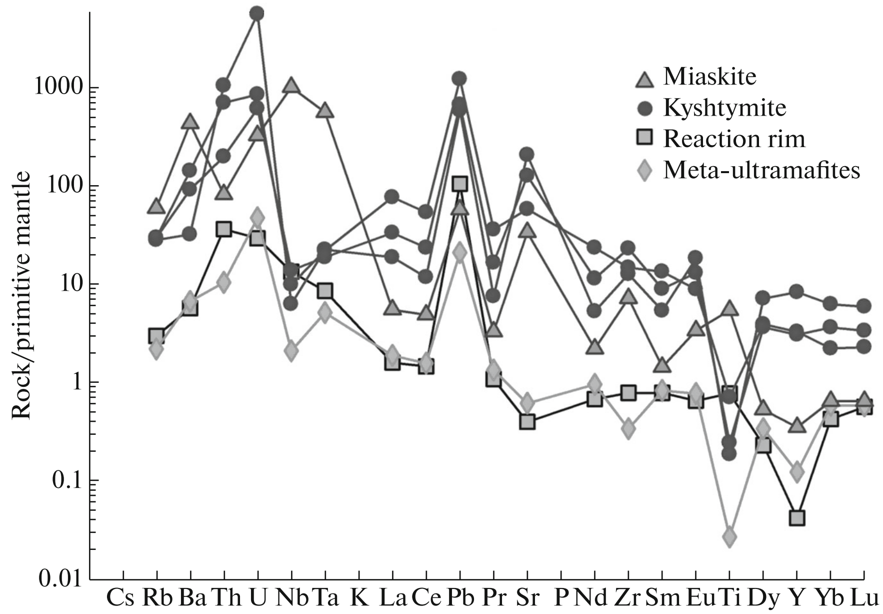

Fig. 5. Primitive mantle-normalized (Sun and McDonough, 1989) trace-element distribution patterns for kyshtymites, host meta-ultramafites, reaction rim between the meta-ultramafite and kyshtymite, as well as miaskite of the Ilmenogorsky–Vishnevogrsky Complex (Ishkul area).

of the kyshtymites and miaskites have a distinct positive Eu anomaly (Fig. 4). Primitive mantle-normalized patterns are shown in Fig. 5. The kyshtymites have clearly expressed U, Th, Nb, Pb, Sr, and Ti anomalies (Fig. 5). The Eu and Sr anomalies are explained by the accumulation of these elements in plagioclase, while U and Th anomalies are related to the presence of these trace elements in zircon; and the negative Nb anomaly marks the absence of Nb-bearing phases in the rock. Host meta-ultramafites as compared to the miaskites and kyshtymites are depleted in REE and have a pattern with less expressed LREE enrichment.

The kyshtymites display moderate to high REE fractionation ($(La/Yb)_N$ = 4.20–48.12), with insignificant positive Eu anomaly (Eu/Eu* = 1.02–1.32).

It is seen in the Y–Nb diagram that the data points of the kyshtymites and miaskites of the Vishnevogorsky massif fall in the field of syn-collisional rocks (Eby et al., 1998; Fig. 6). Miaskite samples fall on or close to the boundary with within-plate rocks (removal of some Y from miaskites is likely related to the further evolution of the alkaline complex and its modification by tectonothermal processes).

Table 2 shows Rb–Sr and Sm–Nd isotope data on the kyshtymites using a Finnigan Triton (ThermoFisher Scientific) thermal ionization multicollector mass spectrometer. The Sr content in the kyshtymite is 1272–3799 ppmw. The Rb content is about 19–31 ppmw. Initial $^{87}Sr/^{86}Sr$ isotope ratio for the studied kyshtymites calculated for an age of 280 Ma (age of the final stage

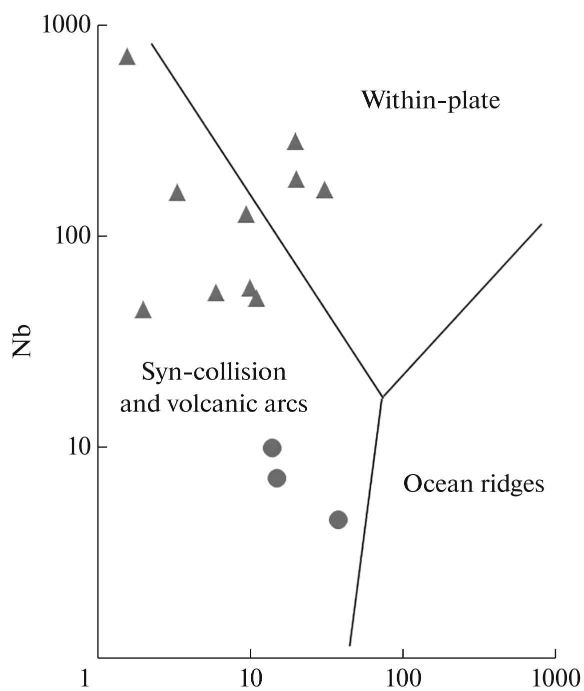

Fig. 6. Diagram Y–Nb according to Pearce et al. (1984) and Eby et al. (1998) showing the compositions of the kyshtymites (circles) and miaskites of the Vishnevogorsky Complex (triangles). The chemical compositions of miaskites according to (Nedosekova et al., 2009) and unpublished data by E.V. Medvedeva. (Syncol) are the rocks formed during syncollisional processes; (Volc) rocks formed in volcanic arcs.

Table 2. Rb–Sr and Sm–Nd isotope data on the kyshtymites of the Ilmenogorsky–Vishnevogorsky massif

Value	Sample				
	3-k*	6-k	8-k	12-k	13-k
Rb, ppm	21.5	19.4	28.8	30.2	31.9
Sr, ppm	1272	3799	2699	2830	2661
$^{87}Rb/^{86}Sr$**	0.0488	0.0147	0.0309	0.0309	0.0347
$^{87}Sr/^{86}Sr$	0.706566	0.706665	0.706665	0.707024	0.707074
$\pm 2\sigma$	0.000007	0.000012	0.000010	0.000008	0.000020
$(^{87}Sr/^{86}Sr)_{280}$	0.706371	0.706607	0.706721	0.706901	0.706936
ε^{Sr}, T	26.6	29.9	31.5	34.1	34.6
Sm, ppm	8.01	4.28	63.34	–	8.89
Nd, ppm	48.27	12.93	324.35	–	33.99
$^{147}Sm/^{144}Nd$	0.1004	0.2002	0.1181	–	0.1582
$\pm 2\sigma$	0.000007	0.000009	0.000008	–	0.000007
$(^{143}Nd/^{144}Nd)_{280}$	1.5122	0.5120	0.5119	–	0.5119
ε^{Nd}, T	–1.9	–5.9	–7.9	–	–6.9

* 3-k, 6-k, 8-k, 12-k, 13-kyshtymite; ** measurement error 2σ $^{87}Rb/^{86}Sr$ = 1%, measurement error 2σ $^{147}Sm/^{144}Nd$ = 0.1%.

of collisional process) is 0.706371–0.706936. The initial isotope ratios of $^{143}Nd/^{144}Nd$, recalculated for 280 Ma, are 0.5119–0.5122, ε^{Nd} (T) varies from –1.9 to –7.9. Similar ratios of $^{87}Sr/^{86}Sr$ and low ε^{Nd} are characteristic of the crustal conditions of formation of the Kyshmymite samples studied. On the ε^{Nd} (T) to ε^{Sr} (T) diagram for the Ilmeno-Vishnevogorsky-complex rocks (Fig. 7), the values obtained for the Kyshmymites also indicate the crustal origin (3 points beyond the mantle reservoirs), 1 point located in the mantle reservoir area EM2, possibly indicative of the processing of primary plagioclacites with the removal of radioactive strontium, for more accurate conclusions, additional isotopic studies are required.

DISCUSSION AND CONCLUSIONS

The genesis of kyshtymites of the South Urals has been studied since 20th century (Fersman, 1940; Korzhinskii, 1953, and others) and described in more detail in (Kolesnik et al., 1974; Kolesnik, 1976) by the example of the Borzovskoe deposit. The last author suggested that kyshtymites are formed during metasomatic processes accompanying the emplacement of granitoid dikes in ultrabasic rocks. In particular, the development of corundum anorthosite in the selvage of the aplitic granite dike with pegmatoid zones were observed in one of well bottoms (Koptev-Dvornikov et al., 1931). However, the source of aluminum and calcium required to form the corundum plagioclasite–kyshtymites massifs remains controversial.

The Rb–Sr and Sm–Nd isotope data obtained for the first time for these rocks in combination with new mineralogical and geochemical data show that the formation of high-Al assemblages within the Ilmenogorsky–Vishnevogorsky polymetamorphic complex is related to the accumulation of aluminum, calcium, HFSE and LIL-elements during formation of nepheline–syenite (miaskite) alkaline massif at stage of 440–420 Ma (magmatic age according to Krasnobaev et al., 2008). The subsequent stage of tectono-metamorphic transformations at 280–320 Ma (age of regional metamorphism according to (Krasnobaev et al., 2008) was responsible for the formation of a magma in the Earth crust that is genetically related to miaskites and enriched in aluminum, calcium, and alkalis. This magma provided the remobilization and redistribution of aluminum, calcium, HFSE and LIL-elements.

According to the previously obtained data, the high-Al rocks genetically related to the miaskite massifs and formed during collisional stage are corundum syenite pegmatites of the Ilmenogorsky alkaline massif (veins 298, 299, 311, and 349; Sorokina et al., 2017) and corundum-bearing metasomatites in host metaultramafites of the Saitov Group of the Ilmenogorsky metamorphic complex (vein 418, Sorokina et al., 2019). The genetic link between the kyshtymites and miaskites is supported by the find of solid microinclusions of churchite-(Y) in association with apatite and REE-phosphate previously identified in the miaskites of the Vishnevogorsky massif (Eskova et al., 1964) in the kyshtymites, the extremely high Al_2O_3 contents in the kyshtymites (up to 42.94 wt %) and miaskites of the Ilmenogosky–Vishnevogorsky Complex (up to 22.76 wt %), similar REE distribution (LREE enrichment relative to HREE, positive Eu anomaly (Fig. 4), anomalies of U, Nb, Pb, Sr, and Ti

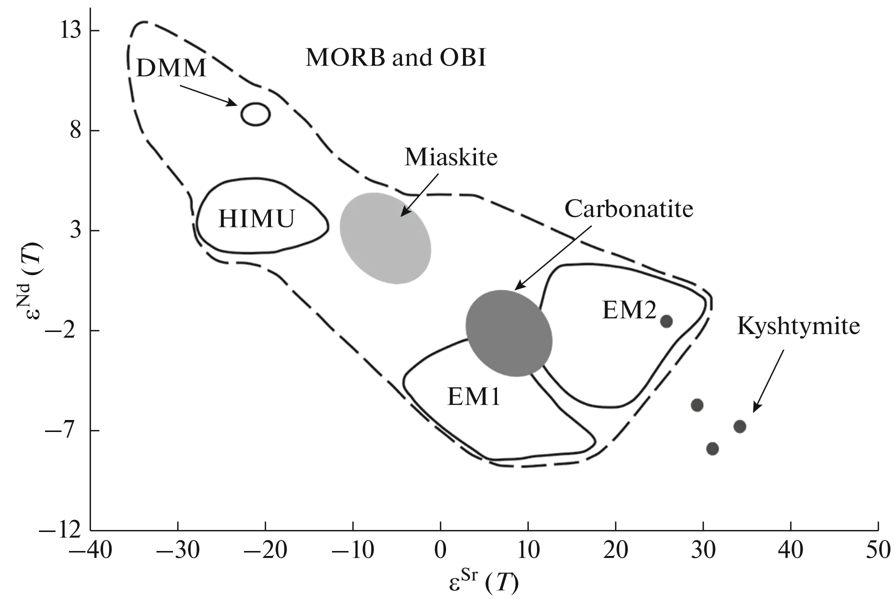

Fig. 7. Diagram ε^{Sr} (T)–ε^{Nd} (T) for kyshtymites and miaskites of the Ilmenogorsky–Vishnevogorsky Complex (Nedosekova et al., 2009); the diagram shows mantle reservoirs DMM, HIMU, EM1, EM2, MORB, and OBI according to (Hofmann, 1997).

(Fig. 5)). In particular, the comagmatic genesis of plagioclasites and syenites was previously determined in the Adirondak (US): Rb-Sr isotope compositions of syenite and plagioclasite define a common isochron with an age of 1 Ga (Health, 1967).

In the kyshtymites of the Ilmenogorsky–Vishnevogorsky Complex, corundum as the highest temperature mineral of the system was formed immediately from Al-oversaturated magma (Morozewicz, 1898). According to Morozewicz (1898), crystallization of corundum from aluminosilicate melt is possible at $nSiO_2 < 6$ for compositions with general formula (Ca, K_2, Na_2)O · Al_2O_3 · $nSiO_2$; in the studied kyshtymites, *n* varied from ~1 to 2.5 (aluminosilicates are formed at $nSiO_2 > 6$). The further decrease of temperature led to the crystallization of anorthite from kyshtymite magma. The lower temperature minerals of the kyshtymites (muscovite, clinozoisite, and clinochlore) were formed at the metasomatic stage.

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