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GEOCHEMISTRY

Rasvumite from the Udachnaya-East Pipe: The First Finding in Kimberlites

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Rasvumite, KFe_2S_3, a very rare potassium sulfide, has been identified in peralkaline rocks of large plutons (Khibiny and Lovozero, Kola Peninsula; Mont Saint-Hilaire, Canada [1–4]), alkaline volcanics (Coyote Peak, California and Point-of-Rocks, New Mexico [5, 6]), carbonatites of the Oldoinyo Lengai Volcano (Tanzania) [7, 8], and high-temperature skarns from Norway [9]. This mineral is commonly associated with djerfisherite, $K_6(Fe,Ni,Cu)_{24}S_{26}Cl$ and less frequently with other potassium sulfides. In this communication, we report on the first finding of rasvumite in kimberlite, more precisely in extremely fresh kimberlitic breccia from the Udachnaya-East pipe. This mineral has been identified in three different associations: in the groundmass of fresh kimberlite, as well as in "nyerereite"–chloride and substantially carbonate nodules from kimberlites.

The studied kimberlitic breccias are related to the third, main phase of emplacement of the Udachnaya-East Pipe. This rock occupies the central part of the pipe at a depth of 350–500 m and contains numerous mantle-derived xenocrysts and xenoliths, as well as the crustal xenogenic material. Phenocryts of olivine and phlogopite are incorporated into the groundmass consisting of olivine, calcite, phlogopite, perovskite, zonal spinel (chromite–titanomagnetite–magnetite), djerfisherite, pyrrhotite, Na–Ca carbonates, halite, and sylvite.

In addition to alkali carbonates and chlorides in the groundmass, these kimberlites contain abundant rounded and angular segregations and nodules of carbonate–chloride composition. The brief mineralogical and petrographic description of some carbonate–chloride segregations and nodules and discussion on their possible origin are given in [10, 11]. The size of segregations and nodules commonly ranges from 0.5 to 30 cm, and their mineral composition is widely variable. The chloride nodules (NaCl + KCl >90–95%) are most abundant. Carbonate–chloride (approximately 1 : 1), and carbonate nodules with a small percentage of chlorides occur rarely. In addition to chloride and carbonate components, these nodules also contain a fine crystalline aggregate (commonly 1–5%, occasionally up to 10–15%) of silicates, carbonates, and sulfates (±sulfides).

Rasvumite is rare in the groundmass of kimberlite and occurs as small grains (10–15 μm) in close association with djerfisherite and pyrrhotite. Thereby, djerfisherite makes up a rim around rasvumite grains, while pyrrhotite is retained as xenomorphic relicts in potassium sulfides (Fig. 1a).

Carbonate nodules with a small amount of chlorides are rather rare in kimberlites. This fine-grained rock consists of calcite (50–70 vol %), Na–Ca carbonates, chlorides, and phlogopite–tetraferriphlogopite. Olivine, pyrrhotite, and potassium sulfides occur in subordinate amounts. Rasvumite (10–20 μm) together with djerfisherite surrounds pyrrhotite as reaction rims (Fig. 1b). The sulfide assemblage is commonly located near the contact (1–2 cm) with kimberlite.

Carbonate–chloride nodules found in kimberlites of the Udachnaya-East Pipe may be divided into two groups with different mineral compositions of carbonates: (1) "nyerereite" and (2) shortite–calcite–northupite [11]. So far, rasvumite has been revealed only in "nyerereite"–chloride nodules. Halite, sylvite, zonal "nyerereite" (Na–K–Ca–S carbonate), aphthitalite, and rasvumite are the major minerals of these nodules. Apatite, phlogopite–tetraferriphlogopite, djerfisherite, olivine, humite–clinohumite, Fe–Ti oxides, and perovskite occur in insignificant amounts. The zoning of "nyerereite" crystals (up to 5 cm in size) is emphasized by a constant presence of the rim that consists of the fine-grained sponge aggregate of shortite, calcite, and aphthitalite [11]. The core of the crystals is composed of K–Ca–S carbonate close in composition to nyerereite from Oldoinyo Lengai carbonatite (Tanzania) and zemkorite from Udachnaya-East kimberlite and southern India but distinct in the X-ray pattern. Rasvumite in

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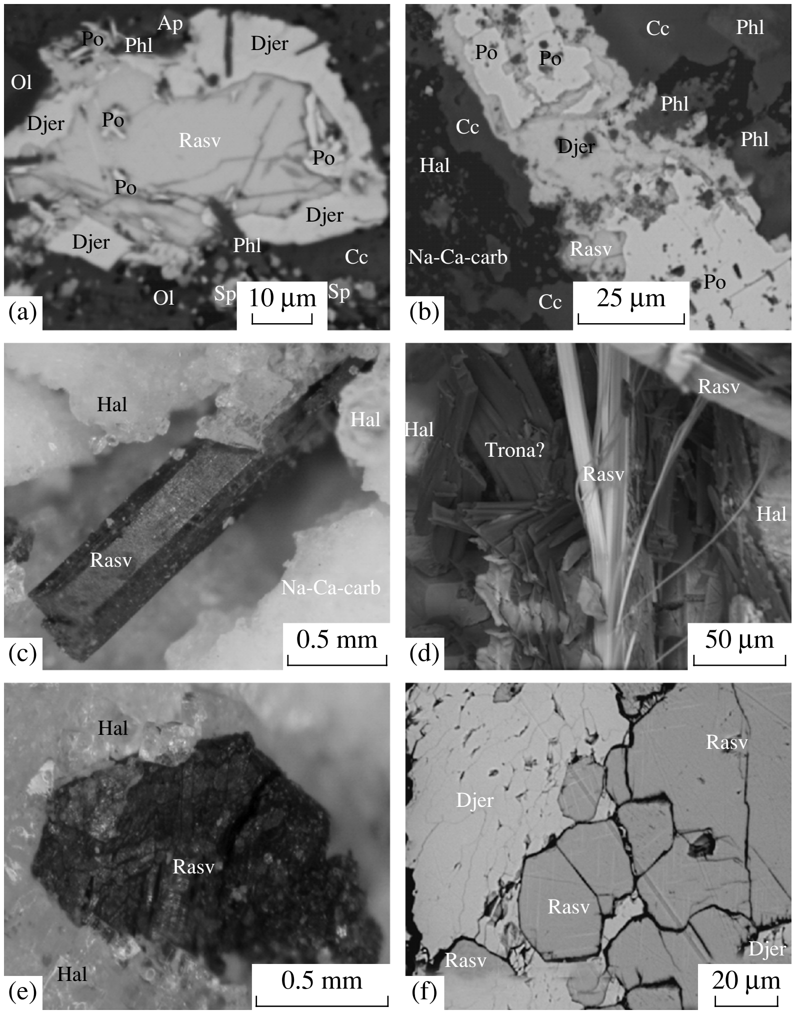

Fig. 1. Rasvumite from the Udachnaya-East Pipe. (a) From groundmass of kimberlite in association with djerfisherite and pyrrhotite; (b) from the carbonate nodule in kimberlite in association with djerfisherite and pyrrhotite; (c–f) from "nyerereite"–chloride nodules in kimberlite: (c, d) crystals from leaching vugs, sample Uv-5c-03; (e, f) sample Uv-1-03: (e) partly oxidized crystal in the chloride mass, (f) from fine-grained silicate–chloride–carbonate–sulfate aggregate in association with djerfisherite. Rasvumite contains oriented inclusions of copper sulfide. (a, b, d, f) SEM images; (c, e) photomicrographs in common light. (Rsv) rasvumite, (Po) pyrrhotite, (Djer) djerfisherite, (Cc) calcite, (Hal) halite, (Na–Ca-carb) Na–Ca carbonates, (Ol) olivine, (Phl) phlogopite–tetraferriphlogopite, (Sp) spinel (magnetite–titanomagnetite), (Ap) apatite.

"nyerereite"–chloride nodules occasionally occurs as acicular crystals (up to 10 μm) in the central and marginal zones of Na–Ca carbonate and mostly as elongated, in some cases, split crystals up to 5 mm in length in the chloride mass, at the contact with "nyerereite" (Fig. 1c). Rasvumite crystals are commonly coated with an ocherous film, especially as concerns the crystals in leaching vugs formed as a result of dissolution in thawed snow or rainwater (Figs. 1c–1e). In some cases, rasvumite is found as euhedral crystals (up to 50–100 μm in size) together with djerfisherite in the fine-grained silicate–chloride–carbonate–sulfate aggregate between "nyerereite" crystals (Fig. 1e, samples Uv-1-03 and Uv-5a-03). Some rasvumite grains contain oriented submicrometric inclusions of copper sulfide (Fig. 1f). The relationships between rasvumite and djerfisherite indicate that rasvumite is an earlier phase.

Rasvumite from "nyerereite"–chloride nodules in the Udachnaya Pipe (samples Uv-1-03, Uv-5c-03) has been identified from the X-ray pattern taken from the Gandolfi camera at the Institute of Geology and Mineralogy in Novosibirsk. Parameters of the rasvumite unit cell were determined with a STADI-4 (Stoe) monocrystal X-ray diffractometer at Novosibirsk State University. The values obtained (a = 9.0346(16), b = 11.025(3), c = 5.435 (3) Å; V = 541.3(3) Å^3) are consistent with the data for rasvumite from other occurrences [1, 3, 5, 12].

The chemical composition of rasvumite from the Udachnaya Pipe was determined on a Camebax microprobe at the Institute of Geology and Mineralogy, Novosibirsk (analytical conditions: beam diameter 2 μm, 15 nA, 20 kV). The grains more than 20 μm in size were selected for the analysis. Rasvumite from peralkaline rocks of the Khibiny and Lovozero plutons were analyzed simultaneously with this mineral from the Udachnaya Pipe for comparative purpose. The material from these occurrences has been described in [1, 2, 4].In addition to the major components, some trace elements (Na, Rb, Cs, Ni, and Co) were determined with the microprobe. The complete set of trace elements was determined only for the largest and unaltered grains (>50 μm) with LA-ICP-MS using a NWR UP213 Nd-YAG laser connected with an HP 4500 quadrupole mass spectrometer at the University of Tasmania. The diameter of the laser beam was 25–50 μm. The discrepancy in Na, Co, Ni, and Cs concentrations determined with the microprobe and LA-ICP-MS was 15–20%. The LA-ICP-MS systematically overestimated the Rb contents by 17–63% relative to microprobe.

Rasvumite is the most abundant natural compound of the group of rare iron sulfides with orthorhombic cell *Cmmc* in the KFe_2S_3–$RbFe_2S_3$–$CsFe_2S_3$–Tl Fe_2S_3 system that implies possible isomorphism of K, Rb, Cs, and Tl. The complete isomorphism of K, Rb, and Cs has been shown in experiments with synthetic analogues [13]. At present, picotpaulite $TlFe_2S_3$ and pautovite $CsFe_2S_3$ have been found in nature in addition to rasvumite [14]. Phase $RbFeS_2S_3$ is known thus far only as an artificial compound [13]. The study of rasvumite from ultraperalkaline rocks in the Mont Saint-Hilaire pluton, Canada, has shown that this mineral may be enriched in Rb and Cs simultaneously [3]. Thus, it may be suggested that low totals (95–98%) in some of the published rasvumite analyses may be resulted from undetermined Rb, Cs, and Tl.

In general, the chemical composition of rasvumite from the Udachnaya Pipe is close to the theoretical KFe_2S_3 composition. The Rb, Cs, and Na contents are <0.9, <0.2, and <0.15 wt %, respectively. Such concentrations do not exert a substantial influence on the crystallochemical characteristics of rasvumite. The variations in these elements from the core to the margin of a grain are also insignificant (table). However, the compositions of rasvumites from various mineral assemblages in the Udachnaya Pipe appreciably differ in Rb. The mineral from the groundmass of kimberlites and carbonate nodules contains 0.2–0.3 wt % Rb, whereas rasvumite from "nyerereite"–chloride nodules contains 0.55–0.85 wt % Rb (Fig. 2). The LA-ICP-MS data confirmed relatively high Rb, Cs, and Na contents and revealed significant concentrations of other trace elements (ppm): Tl (95–480), Ba (110–215), Pb (25–190), Te (up to 60), Se (20–135), and Co (25–100) (table). Furthermore, laser ablation revealed geochemical differences between unaltered rasvumite and its oxidized rim as is exemplified in the largest crystal (table, Fig. 3). In comparison with unaltered rasvumite, the oxidized rim contains anomalously high (by an order of magnitude and higher) Na, Mg, V, Mn, Ni, As, Sr, Sb, and W concentrations. The Rb, Te, Cs, Ba, Tl, and Pb contents increase by 1.5–2.0 times.

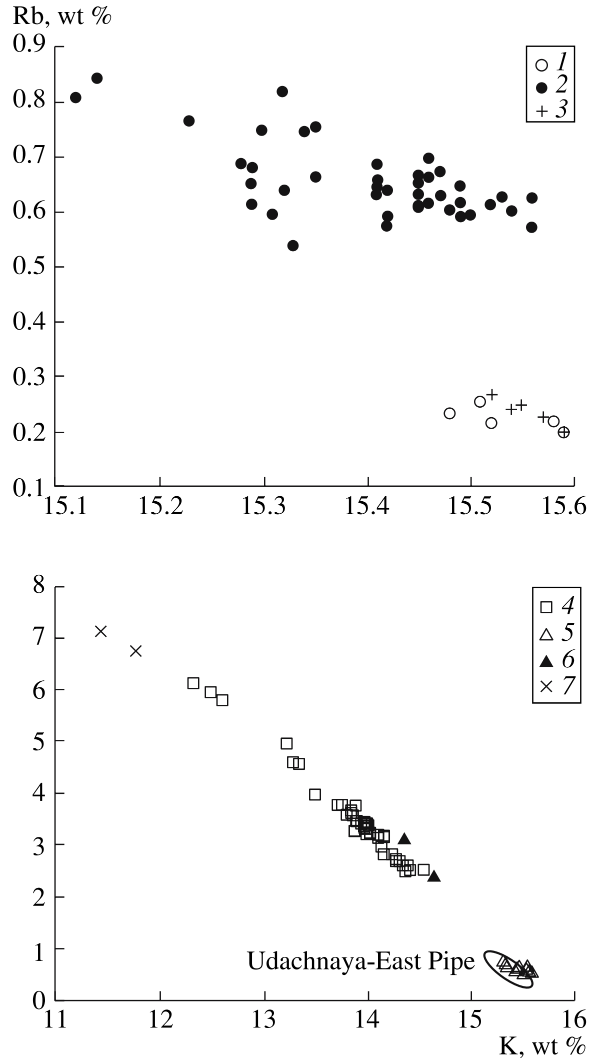

Fig. 2. Variations of K and Rb contents in rasvumite from kimberlites of the Udachnaya-East Pipe in comparison with rasvumite from alkaline plutons. (*1–3*) Udachnaya-East Pipe: (*1*) groundmass of kimberlite, (*2*) "nyerereite"–chloride nodules, (*3*) carbonate nodules with a small percentage of chlorides; (*4*) ussingite veinlet in peralkaline nepheline syenite, Lovozero pluton (sample FM79858, Fersman Mineralogical Museum); (*5*) ultraperalkaline pegmatite, Mt. Koashva, Khibiny pluton; (*6, 7*) Mont Saint-Hilaire pluton, Canada [3]. (*6*) Marble xenolith in the nepheline syenite (0.4–0.5 wt % Cs); (*7*) inclusion in sodalite from sodalitolite xenolith in nepheline syenite (2.3–2.6 wt % Cs).

The comparison of the available data on rasvumite from worldwide occurrences shows that the mineral from the Udachnaya Pipe differs from rasvumites contained in peralkaline rocks and carbonatites both in major and trace elements. For example, rasvumite from ultraperalkaline pegmatite in the Khibiny pluton is close to this mineral from the Udachnaya Pipe in Rb content, but is depleted (ppm) in Na (30–75), Cs (95–

Representative analyses of rasvumite from kimberlites of the Udachnaya-East Pipe and peralkaline pegmatites of the Lovozero and Khibiny plutons, wt %

Component	1	2	3	4	5	6	7a	7b·	8	9	10	11	12	13
K	15.58	15.42	15.14	15.45	15.56	15.45	15.52	15.52	15.52	15.59	13.78	12.31	15.44	15.30
Na	0.12	0.04	0.16	0.04	0.01	0.03	0.03		0.07	0.05	0.07	0.04	0.00	0.03
Rb	0.22	0.59	0.84	0.65	0.63	0.67	0.61		0.27	0.20	3.59	6.13	0.64	0.75
Cs	0.05	0.06	0.11	0.03	0.15	0.09	0.07		0.04	0.06	0.01	0.11	0.02	0.08
Fe	45.00	45.06	45.08	45.06	45.12	45.07	45.02	45.12	44.99	45.01	44.19	43.61	45.06	45.07
Ni	0.02	0.00	0.06	0.05	0.00	0.00	0.00		0.02	0.03	0.00	0.00	0.00	0.00
Co	0.02	0.02	0.02	0.03	0.00	0.00	0.00		0.05	0.00	0.00	0.00	0.00	0.00
S	38.75	38.81	38.86	38.81	38.85	38.82	38.76		38.79	38.75	38.26	37.59	38.85	38.82
Total	99.76	100.01	100.27	100.12	100.32	100.13	100.01		99.75	99.69	99.90	99.80	100.01	100.05
Formula units based on 3S														
K	0.989	0.977	0.958	0.979	0.985	0.979	0.985		0.984	0.990	0.886	0.806	0.978	0.970
Na	0.013	0.005	0.017	0.004	0.001	0.003	0.004		0.008	0.005	0.008	0.005	0.000	0.003
Rb	0.006	0.017	0.024	0.019	0.018	0.019	0.018		0.008	0.006	0.106	0.184	0.018	0.022
Cs	0.001	0.001	0.002	0.001	0.003	0.002	0.001		0.001	0.001	0.000	0.002	0.000	0.001
Fe	2.000	2.000	1.998	2.000	2.000	1.999	2.000		1.997	2.000	1.989	1.998	1.997	1.999
S	3.000	3.000	3.000	3.000	3.000	3.000	3.000		3.000	3.000	3.000	3.000	3.000	3.000
ppm (LA-ICP-MS)														
Na	1292	380			103	187	151	31280			742		31	75
Mg	52	0.00			18	0.41	0.17	5275			1.2		0.00	0.43
Ti	26	5.5			11	5.9	9.1	11			4.6		1.1	4.0
V	5.1	0.00			12	0.13	0.00	2890			0.00		0.08	0.00
Mn	3.2	0.09			2.9	3.0	1.6	51.9			6.7		0.00	2.3
Co	102	93			34	25	32	37			0.04		0.32	2.0
Ni	194	0.00			4.6	2.7	3.2	46			0.01		0.16	0.00
Cu	23	2.2			13	4.3	0.00	95			0.19		5.6	1.5
Zn	9.0	1.9			1.5	2.3	2.4	3.7			2.3		0.39	0.00
As	30	0.76			5.7	0.71	3.5	555			0.38		0.00	0.65
Se	21	51			109	135	103	64			12		83	59
Rb	3595	9386			7586	8028	8100	10914			44199		7297	8882
Sr	5.1	0.10			3	0.00	0.00	115			2.6		0.07	0.08
Ag	0.75	3.0			3.0	0.00	0.00	2.0			0.03		0.00	0.03
Sb	0.83	0.80			0.71	0.16	0.1	6.1			0.31		0.00	0.00
Te	0.00	45			39	62	56	86			1.22		0.09	0.00
Cs	654	1009			1906	692	714	1064			665		96	135
Ba	174	215			167	113	107	219			380		0.3	0.1
W	0.07	0.00			0.10	0.10	0.08	28			0.05		0.08	0.00
Tl	95	414			475	429	398	689			170		9.9	7.2
Pb	26	13			15	188	136	262			0.12		0.15	0.02

Note: (1–9) Udachnaya-East Pipe: (1) from the groundmass of kimberlite breccia in association with djerfisherite and pyrrhotite (Fig. 1a); (2–7) from “nyererite”–chloride nodules, including (2, 3) the core and margin of the crystal, sample Uv-1-03; (4) from fine-crystalline tetraferriphlogopite–carbonate aggregate in association with djerfisherite, sample Uv-1-03 (Fig. 1f); (5) crystal core, sample Uv-5a-03; (6, 7) core and margin, respectively, of the large crystal: (7a) unaltered part, (7b) oxidized outer rim, sample Uv-5c-03, Fig. 3; (8, 9) from the carbonate-rich nodule in association with djerfisherite and pyrrhotite (Fig. 1b); (10, 11) from the ussingite veinlet in peralkaline nepheline syenite, Lovozero pluton, sample FM79858, Fersman Mineralogical Museum; (12, 13) from ultraperalkaline pegmatite, Mt. Koashva, Khibiny pluton. Cl, Cu, and Mn concentrations are below the detection limit of the microprobe. The uncertainty of the microprobe and LA-ICP-MS determinations of elements is <5%.

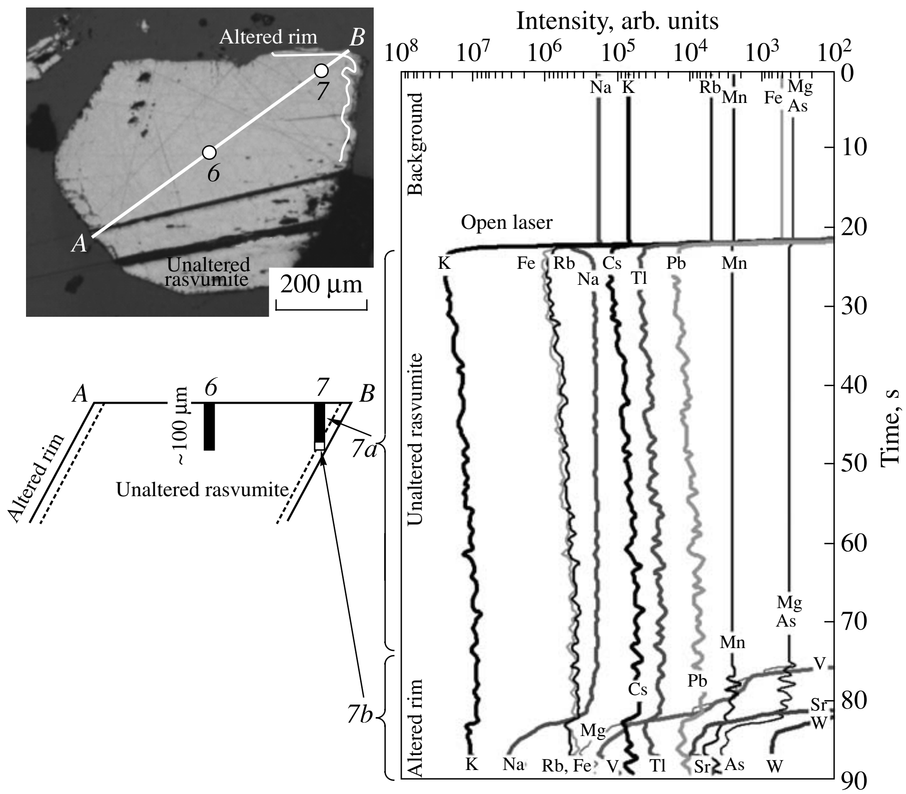

Fig. 3. LA-ICP-MS spectrum of rasvumite crystal from "nyerereite"–chloride nodule (sample Uv-5c-03) in unaltered kimberlite, Udachnaya-East Pipe. Numbers *6, 7a*, and *7b* are as in the table.

135), Tl (<10), Ba (<0.3), Pb (<0.1), and other elements (table, Fig. 2). Rasvumite from Lovozero, in contrast, is highly enriched in Rb (2.5–6.1 wt %) and Ba (380 ppm) at approximately equal Cs contents, but the Tl, Pb, and Te contents (170, 0.1, and 1.0 ppm, respectively) are low (table, Fig. 2). Some rasvumites from the Mont Saint-Hilaire pluton are characterized by high Rb (up to 7.2 wt %) and Cs (up to 2.6 wt %) contents [3]. Potassium sulfide from carbonatite and silicate lava of Oldoinyo Lengai Volcano is distinguished by high contents of Mn (up to 3 wt %), Na (up to 0.6 wt %), Cl (up to 0.7 wt %), and in some cases F (up to 1.9 wt %) [7, 8].

The relationships of sulfides in the groundmass of kimberlites and in carbonate–chloride nodules indicate the following sequence of crystallization: pyrrhotite–rasvumite–djerfisherite. Similar relationships have been described for rasvumite-bearing assemblages in the Khibiny and Lovozero plutons and in skarns from Norway [1, 2, 9]. As has been shown for the Udachnaya-East Pipe previously, djerfisherite as a late magmatic mineral crystallized from the residual kimberlitic melt of substantially carbonate–chloride composition [10, 15]. Thus, rasvumite in the groundmass of kimberlites also may be regarded as a late magmatic mineral. In contrast to djerfisherite, rasvumite is much less abundant in kimberlites. The situation in carbonate–chloride and chloride nodules is quite different. In "nyerereite"–chloride rocks, rasvumite prevails over djerfisherite. In shortite–calcite–northupite–chloride and chloride nodules, only djerfisherite is present, whereas rasvumite has not been detected [11]. Such behavior of potassium sulfides may be explained only by earlier crystallization of rasvumite relative to djerfisherite. With increasing concentration of chlorine, rasvumite ceases to crystallize and is overgrown and even replaced with Cl-bearing djerfisherite. Inclusions of rasvumite in "nyerereite" indicate that this mineral is the earliest phase in "nyerereite"–chloride nodules as well and gives way to djerfisherite at the late stage of crystallization (Fig. 1f).

The origin of carbonate–chloride and chloride nodules in kimberlites of the Udachnaya-East Pipe cannot be treated unequivocally. Carbonate–chloride segregations and nodules are commonly considered to be products of the late evolution of the kimberlitic melt [10, 11]. Unfortunately, no direct evidence of chloride rocks in the sedimentary cover is known around the Udachnaya Pipe. Nevertheless, in the opinion of Sharygin, it cannot be ruled out that carbonate–chloride and chloride nodules are fragments of evaporites that underwent thermometamorphism induced by the kimberlitic melt. In any case, these nodules are high-temperature products and carbonate–chloride nodules are rather close in mineral composition to natrocarbonatites from the Oldoinyo Lengai Volcano [11]. Rasvumite is an ordinary accessory mineral of this carbonatite [7, 8].

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