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POTASSIUM SULFIDES IN KIMBERLITE-HOSTED CHLORIDE–“NYEREREITE” AND CHLORIDE CLASTS OF UDACHNAYA-EAST PIPE, YAKUTIA, RUSSIA

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ABSTRACT

Chloride-bearing clasts from the Udachnaya-East pipe kimberlites, Yakutia, Russia, contain abundant to accessory rasvumite, KFe_2S_3, and djerfisherite, $K_6Na_{0-1}(Fe,Ni,Cu)_{24}S_{26}Cl$, which have been previously described in the groundmass of the host kimberlite. Rasvumite occurs in chloride–“nyerereite” and carbonate clasts, where it forms prismatic crystals (up to 5 mm) or is associated with djerfisherite in a rim around pyrrhotite. Djerfisherite is the omnipresent sulfide in all types of chloride-containing clasts, in which it rims pyrrhotite and forms individual xenomorphic to subhedral grains and, more rarely, octahedral crystals at the contact with host kimberlite. In chloride clasts and the host kimberlites, the following sequence of crystallization was found: pyrrhotite → rasvumite → djerfisherite, reflecting an increase in the activity of Cl in the evolved melt. The composition of rasvumite from the Udachnaya-East pipe is close to ideal KFe_2S_3, with low abundances of Rb, Cs and Na (<0.9, <0.2 and <0.15 wt.%, respectively). Analyses of the rasvumite by the LA–ICP–MS technique indicates the presence of Tl (95–480), Ba (110–215), Pb (25–190), Te (up to 60), Se (20–135) and Co (25–100 ppm). These data also indicate compositional differences between unaltered rasvumite and its oxidized rim; the levels of Na, Mg, V, Mn, Ni, As, Sr, Sb and W increase by an order of magnitude. Unlike djerfisherite in the kimberlite groundmass, that in the chloride clasts is generally characterized by higher amounts of Fe and lower amounts of Cu, with low contents of Rb (<2000 ppm), Cs (<100 ppm), and Tl (<330 ppm). Sulfides of potassium in chloride-bearing clasts are considered to be primary phases crystallized from an evolved kimberlitic melt.

Keywords: rasvumite, djerfisherite, chloride clasts, carbonatite, kimberlite, rubidium, cesium, Udachnaya pipe, Yakutia, Russia.

SOMMAIRE

Les clastes contenant des chlorures trouvés dans les kimberlites de la cheminée Udachnaya-Est, en Yakoutie, Russie, contiennent en abondance ou en quantité accessoire la rasvumite, KFe_2S_3, et la djerfisherite, $K_6Na_{0-1}(Fe,Ni,Cu)_{24}S_{26}Cl$, minéraux décrits précédemment dans la pâte de la kimberlite hôte. La rasvumite est présente dans ces clastes à chlorure–“nyéréréite” et à carbonate, où elle forme des cristaux prismatiques atteignant 5 mm, ou elle est associée à la djerfisherite dans un liseré autour de la pyrrhotite. La djerfisherite est le sulfure omniprésent dans tous les types de clastes contenant des chlorures; elle entoure la pyrrhotite et forme des grains individuels xénomorphes à sub-idiomorphes et, plus rarement, des cristaux octaédriques en contact avec la kimberlite hôte. Dans les clastes à chlorures et les kimberlites hôtes, la séquence de cristallisation semble être: pyrrhotite → rasvumite → djerfisherite; elle témoigne d’une activité de Cl en augmentation dans le magma évolué. La composition de la rasvumite de la cheminée Udachnaya-Est est voisine de la stoechiométrie idéale, KFe_2S_3, avec de faibles teneurs en Rb, Cs et Na (<0.9, <0.2 et <0.15% en poids, respectivement). Nos analyses de la rasvumite par la technique LA–ICP–MS indiquent la présence de Tl (95–480), Ba (110–215), Pb (25–190), Te (jusqu’à 60), Se (20–135) et Co (25–100 ppm). Ces données démontrent aussi les différences en composition entre la rasvumite saine et sa bordure altérée; les niveaux de Na, Mg, V, Mn, Ni, As, Sr, Sb et W y augmentent selon un ordre de grandeur. Contrairement au cas de la djerfisherite de la pâte de la kimberlite, celle des clastes à chlorures contient généralement des teneurs plus élevées en Fe et plus faibles en Cu, avec de faibles teneurs en Rb (<2000

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ppm), Cs (<100 ppm), et Tl (<330 ppm). Les sulfures de potassium des clastes à chlorures sont jugés être des phases primaires cristallisées à partir d'un magma kimberlitique évolué.

(Traduit par la Rédaction)

Mots-clés: rasvumite, djerfisherite, clastes de chlorures, carbonatite, kimberlite, rubidium, césium, cheminée Udachnaya, Yakoutie, Russie.

INTRODUCTION

Chloride-containing clasts have been recently found in the diamondiferous Udachnaya-East pipe in Yakutia (Kamenetsky *et al.* 2006, 2007a). They occur in the deep levels of the pipe (>350 m) in exceptionally fresh kimberlites (Marshintsev *et al.* 1976). The lack of secondary, alteration-related minerals in these Udachnaya-East kimberlites (UEK) is associated with an essentially carbonate–chloride groundmass and the presence of chloride-bearing clasts (Kamenetsky *et al.* 2004, 2006, 2007a).

Chloride minerals (principally halite and sylvite) are unusual for magmatic rocks in general. Until recently, the only rocks known to host an abundant magmatic chloride (Na-bearing sylvite) are the natrocarbonatites of Oldoinyo Lengai (Keller & Kraft 1990, Mitchell 1997, 2006a, b). The origin of chloride-bearing clasts in the UEK and salts in other Siberian kimberlites is still debated (Pavlov & Ilupin 1973, Egorov *et al.* 1988, Kornilova *et al.* 1998, Golovin *et al.* 2007, Kamenetsky *et al.* 2004, 2007b). However, most recent petrological, geochemical and melt-inclusion studies provide strong evidence for high-temperature crystallization of chlorides in the UEK (Golovin *et al.* 2003, 2007, Kamenetsky *et al.* 2004, Maas *et al.* 2005) and demonstrate a mineralogical similarity to the groundmass of the natrocarbonatite lavas of Oldoinyo Lengai volcano (Kamenetsky *et al.* 2006, 2007a, b, Sharygin *et al.* 2007b). The mineral assemblage of the chloride-bearing clasts in the UEK is exceptionally diverse, compared to the host kimberlites, and resembles the mineralogy of some evolved peralkaline and carbonatite magmas (Dawson *et al.* 1992, 1995a, Mitchell 1997, 2006a, Stoppa *et al.* 1997, Lisitsin *et al.* 2002). One of the striking similarities between the UEK chloride-bearing assemblages and alkaline silicate – carbonatite magmatic associations is the occurrence of the potassium sulfides rasvumite and djerfisherite.

In this study, we describe a new occurrence of rasvumite and djerfisherite in the UEK chloride-bearing clasts and consider their origin on the basis of textural and chemical data.

BACKGROUND INFORMATION

Rasvumite, KFe_2S_3, has been previously described in agpaitic rocks from Khibina and Lovozero, Kola Peninsula, and Mont Saint-Hilaire, Quebec (Sokolova *et al.* 1970, Czamanske *et al.* 1979, Ifantopulo *et al.* 1983, Gebhard & Schlüter 1994, Chakhmouradian *et al.* 2001, 2007, Lisitsin *et al.* 2002, Yakovenchuk *et al.* 2003), alkali-rich volcanic rocks at Coyote Peak, California, and Point of Rocks, New Mexico (Czamanske *et al.* 1979, 1981, DeMark 1984), natrocarbonatites of the Oldoinyo Lengai volcano, Tanzania (Jago & Gittins 1999, Mitchell 2006a), and high-temperature skarns in Norway (Jamtveit *et al.* 1997).

Djerfisherite, $K_6Na_{0-1}(Fe,Ni,Cu)_{24}S_{26}Cl$, appears to be more common than rasvumite. It occurs in meteorites and terrestrial rocks such as mafic alkaline rocks (*e.g.,* kimberlites), agpaitic rocks and related carbonatites, and also specific types of ore deposits associated with alkaline mafic and more siliceous magmas (Cu–Ni ores and skarns) (Clarke *et al.* 1994, Barkov *et al.* 1997, Sharygin *et al.* 2007a, and references therein, Zaccarini *et al.* 2007).

CHLORIDE-CONTAINING CLASTS AND THE HOST KIMBERLITE

Unaltered kimberlites, which host chloride-bearing clasts, are found in the central part of the Udachnaya-East pipe at a depth of 350–500 m. These rocks also contain xenocrysts and xenoliths of mantle and crustal origin. Phenocrysts of olivine and rare phlogopite are set in the fine-grained groundmass composed of olivine, calcite, phlogopite, perovskite, zoned spinel [from core to rim: $(Mg,Fe)(Cr,Al,Fe)_2O_4$ – $(Mg,Fe)(Fe,Ti,Al)_2O_4$ – $(Mg,Fe)Fe_2O_4$], ilmenite, Na–Ca and Na–K–Ca carbonates, halite and sylvite. The most common accessory minerals are pyrrhotite, djerfisherite, rasvumite, apatite and sphalerite.

The kimberlites contain abundant segregations and clasts consisting of chlorides (Kamenetsky *et al.* 2004, 2006, 2007a). Their shapes and sizes are variable, from spherical and round to angular and from 0.5 to 30 cm in diameter, rarely up to 1 m. The contacts of the clasts with the host kimberlite are sharp (<1 mm), without evidence of thermal metamorphic effects. In some cases, the contact zone is composed of a breccia-like aggregate of olivine, calcite, Na–Ca carbonates, sodalite, phlogopite–tetraferriphlogopite, humite–clinohumite, perovskite, apatite, Fe–Ti oxides, djerfisherite and alkali sulfates set in a matrix of chlorides (Kamenetsky *et al.* 2006, 2007a).

The mineral assemblage of the clasts is dominated by chlorides, and the chloride-rich (>90–95% NaCl +

KCl) varieties are most common. Chloride–carbonate (~50% NaCl + KCl), chloride – carbonate – silicate (50–70% NaCl + KCl), and carbonate-rich clasts (<10% NaCl + KCl) are less common. The chloride–carbonate clasts are represented by nyerereite-like sulfate-bearing Na–K–Ca carbonate and shortite – northupite – calcite assemblages (Kamenetsky *et al.* 2006, 2007a). In addition to chloride and carbonate components, the presence of fine-grained aggregate of chlorides, silicates, carbonates and sulfates ± sulfides (1–5 vol.%, rarely up to 30 vol.% in chloride – carbonate – silicate species) is typical of the clasts. In individual samples of essentially chloride clasts, such aggregates vary from chloride – sulfate – silicate to chloride – carbonate – silicate in composition, and are commonly found among chloride grains or near a contact with the host kimberlite. Textural and mineralogical features and occurrences of potassium sulfides in all types of chloride-bearing clasts are compared with the UEK groundmass in Table 1.

The minerals of the clasts are prone to alteration, with complete degradation observed under surface conditions. The water-soluble chlorides and alkali sulfates are dissolved, whereas alkali carbonates are replaced by pirssonite, $Na_2Ca(CO_3)_2{\bullet}2H_2O$, and other H_2O-bearing carbonates, and a Fe-rich oxidized coating is developed on the surface of the sulfides of potassium. Similar alteration has been described as typical of the Oldoinyo Lengai natrocarbonatites (Keller & Kraft 1990, Genge *et al.* 2001, Mitchell 2006b).

ANALYTICAL TECHNIQUES

Doubly-polished rock sections (~50–100 μm in thickness) and individual grains of K sulfides mounted in epoxy were used for optical examination in transmitted and reflected light. Quantitative analyses of rasvumite and djerfisherite were performed using a CAMEBAX-micro electron microprobe at the Institute of Geology and Mineralogy (IGM), Novosibirsk, Russia, using an accelerating voltage of 20 kV and a beam current of 15–25 nA, a beam diameter of about 2 μm, and a counting time of 40 s. Precision for major elements was better than 2% relative. We used the following mineral standards and synthetic compounds for the analysis of sulfides: chalcopyrite and pyrrhotite (Fe, Cu and S), synthetic Fe–Ni–Co alloy (Ni, Co), albite (Na), sanidine (Si, Al and K), apatite-(CaCl) (Cl), synthetic $RbNd(WO_4)_2$ and $CsNd(MoO_4)_2$ (Rb and Cs, respectively). The electron-microprobe analyses were undertaken on grains larger than 10 μm. Backscattered electron images (BSE) were obtained with a JEOL 6380LA scanning electron microscope at IGM, Novosibirsk, and a FEI Quanta-600 scanning electron microscope at the University of Tasmania, Hobart.

Trace-element concentrations in the largest unaltered grains of sulfides were established by laser-ablation – inductively coupled plasma – mass spectrometry (LA–ICP–MS) at the University of Tasmania. This instrumentation consists of a New Wave Research UP213 Nd–YAG (213 nm) laser coupled to an Agilent 4500 quadrupole mass-spectrometer. For this study, analyses were performed in a He atmosphere by ablating spots of 25–50 μm in diameter at a rate of 5–10 pulses/s using a laser power of ~10 J/cm^2. Data reduction was undertaken according to standard methods using the NIST612 and STDGL2b–2 glasses. Discrepancies in the concentrations of Na, Co, Ni and Cs determined by the electron microprobe and by LA–ICP–MS were ±15–20% relative, whereas Rb was higher by 17–63% relative in the LA–ICP–MS analyses. For comparison with UEK minerals, we analyzed by microprobe and LA–ICP–MS the K sulfides from agpaitic rocks of the Khibina and Lovozero intrusive complexes, and from kimberlite of the Internatsional'naya pipe (Yakutia), previously described by Sokolova *et al.* (1970), Ifantopulo *et al.* (1983), Lisitsin et *al.* (2002) and Sharygin (2006).

POTASSIUM SULFIDES IN KIMBERLITES AND CHLORIDE-CONTAINING CLASTS

Djerfisherite is a common accessory groundmass mineral in the unaltered UEK, forming individual grains and an overgrowth around pyrrhotite. It also occurs as a daughter mineral in the olivine-hosted melt inclusions (Sharygin *et al.* 2003, 2007a). Rasvumite is exceptionally rare in the UEK groundmass, and was first reported by Sharygin *et al.* (2007b). It is present as small (<10–20 μm) anhedral grains in association with djerfisherite; both minerals form a rim around pyrrhotite relics (Figs. 1a, b). The same relationships between the sulfides was found in small (<1–2 cm) carbonate-rich clasts occurring in UEK (Figs. 1c, d).

Chloride–carbonate clasts are characterized by greater amounts of both djerfisherite and rasvumite than the UEK groundmass. The sulfide assemblage is mainly restricted to the contacts (within 1–2 cm) with the host kimberlite.

Rasvumite in the chloride–"nyerereite" clasts (samples Uv–1–03, Uv–5a–03, and Uv–5c–03) forms prismatic, commonly split crystals, up to 5 mm long, in a chloride matrix at the contact with "nyerereite" (Fig. 2). Usually, the crystals are coated with a film of oxidation products. In some cases, tiny needles of rasvumite (up to 10 μm) are present within "nyerereite". Rarely, it forms euhedral grains (up to 50–100 μm) intergrown with djerfisherite in the fine-grained silicate – chloride – carbonate – sulfate aggregate, interstitial to the "nyerereite" crystals (Fig. 3). Some rasvumite grains contain submicrometric inclusions of Cu sulfide (Fig. 3b).

Djerfisherite in a chloride – shortite – northupite – calcite clast (Uv–2–03) is the only sulfide of potassium, occurring as subhedral grains in the chloride mass and euhedral inclusions in shortite (Fig. 4a). We also found octahedral crystals of djerfisherite close to the contact

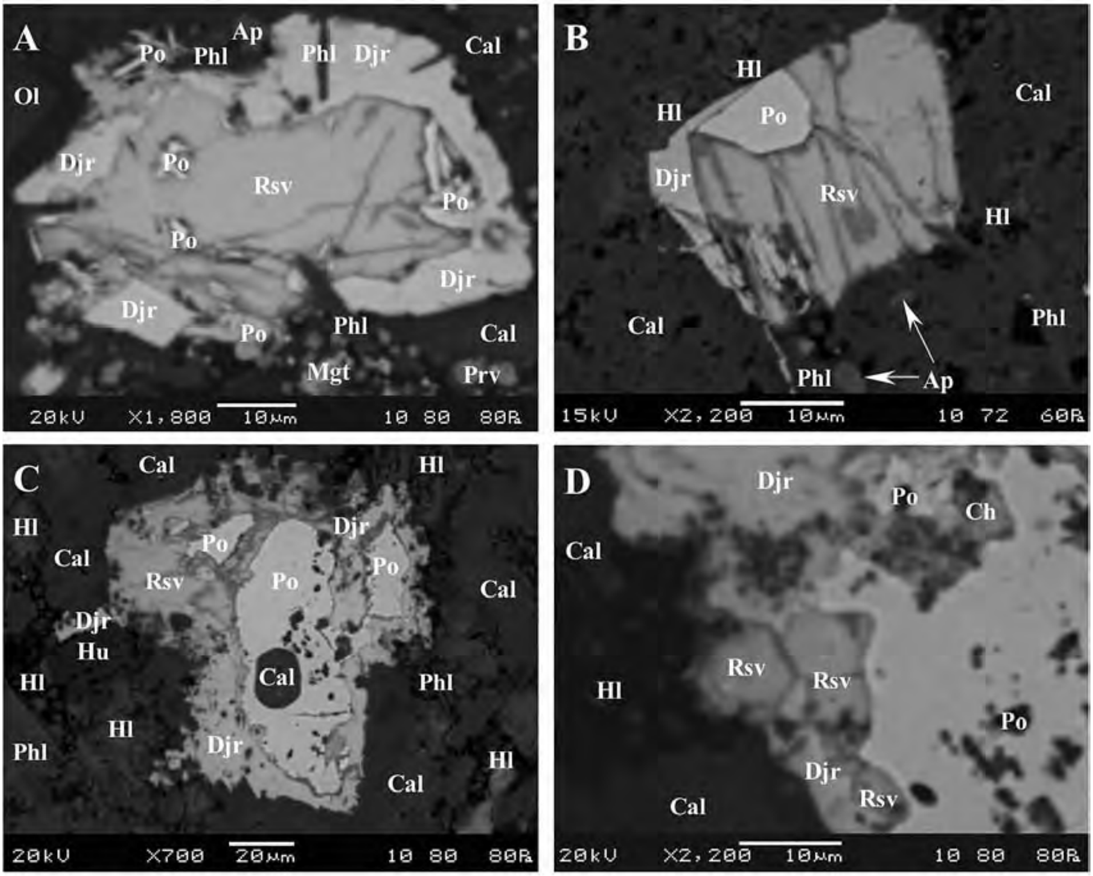

FIG. 1. Associated rasvumite, djerfisherite and pyrrhotite in the UEK groundmass and essentially carbonate clasts (BSE images, sample YBK–0). A–B: kimberlite groundmass, C–D: essentially carbonate clasts. Hl: halite; for other symbols, see Table 1.

with the host kimberlite (Figs. 4b, c). In essentially chloride clasts, only djerfisherite was found. It rims pyrrhotite in a fine-grained aggregate between chloride grains or individual subhedral grains near the contact with kimberlite (Fig. 4d).

RELATIONSHIPS AMONG SULFIDES

Rasvumite is the earlier-formed mineral where it coexists with djerfisherite in the UEK groundmass and chloride-containing clasts (Figs. 1, 3). Where pyrrhotite is present together with K-bearing sulfides, the following sequence was found: pyrrhotite → rasvumite → djerfisherite (Fig. 1). A similar sequence was described for the rasvumite-bearing assemblages of the Khibina and Lovozero intrusions, and the skarns of Norway (Sokolova *et al.* 1970, Ifantopulo *et al.* 1983, Jamtveit *et al.* 1997). In the Oldoinyo Lengai natrocarbonatites, rasvumite and ternary KFe_2S_3–KFe_3S_4–$K_2Fe_3S_4$ sulfides form individual crystals or an overgrowth around alabandite (Dawson *et al.* 1995a, 1996, Mitchell 1997, 2006a, Jago & Gittins 1999). Djerfisherite has not been reported in natrocarbonatites, but is quite common in some of the silicate rocks of Oldoinyo Lengai (Dawson *et al.* 1992, 1995b).

CHEMICAL COMPOSITION OF POTASSIUM SULFIDES

Rasvumite

Previously, unit-cell dimensions were obtained for rasvumite from the chloride–"nyerereite" clasts (samples Uv–1–03, Uv–5c–03) of the UEK (Sharygin *et al.* 2007b). They are: $a = 9.0346(16)$, $b = 11.025(3)$, $c = 5.435(3)$ Å, $V = 541.3(3)$ Å^3, and thus consistent with data for rasvumite from other localities (Sokolova

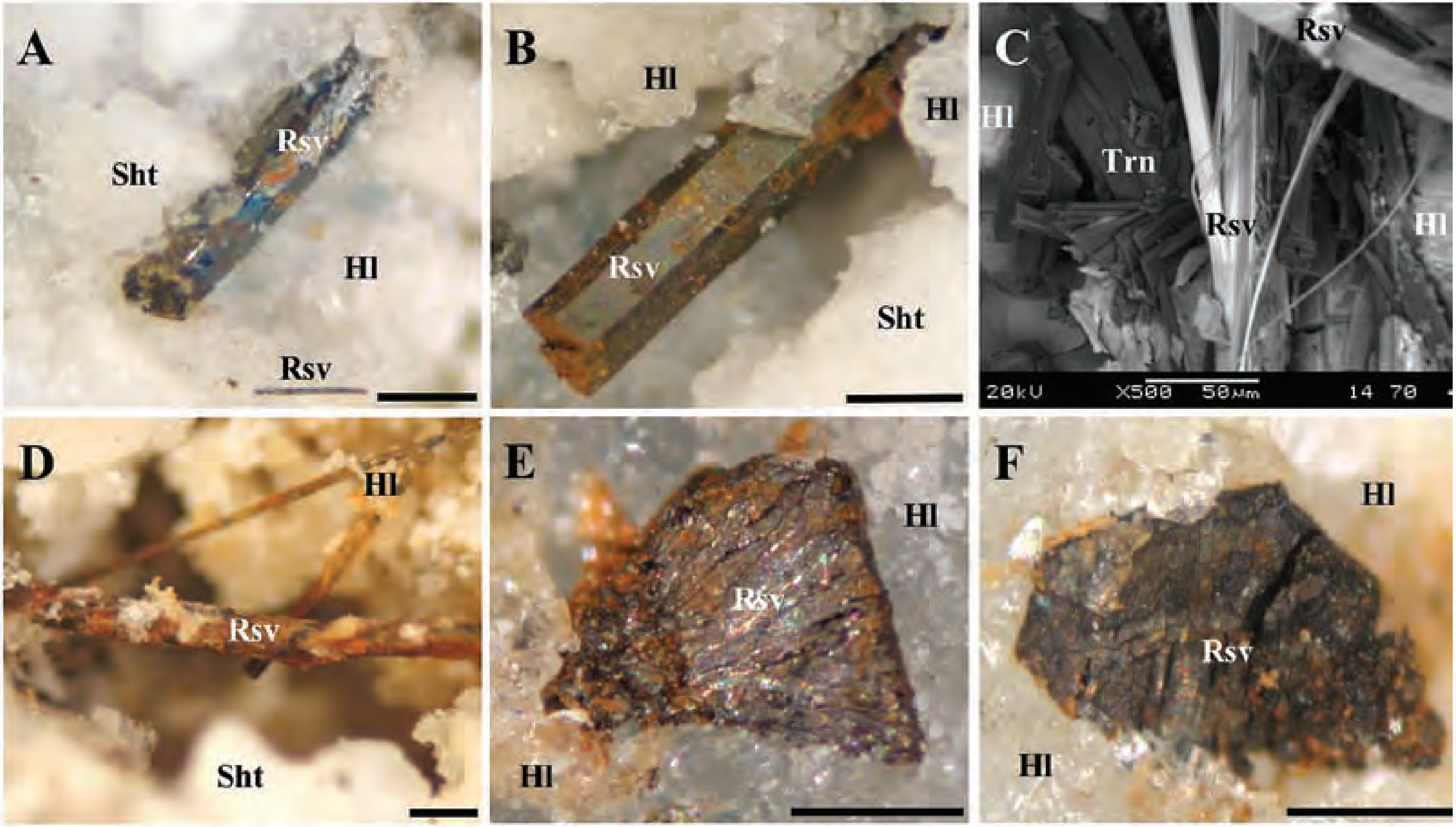

FIG. 2. Morphology of rasvumite crystals in chloride–”nyerereite” clasts, Udachnaya-East pipe. Scale bar is 0.5 mm for A–B, D–F images (ordinary light). C: BSE image. A–D: sample Uv–5a–03; E–F: sample Uv–1–03. For symbols, see Table 1.

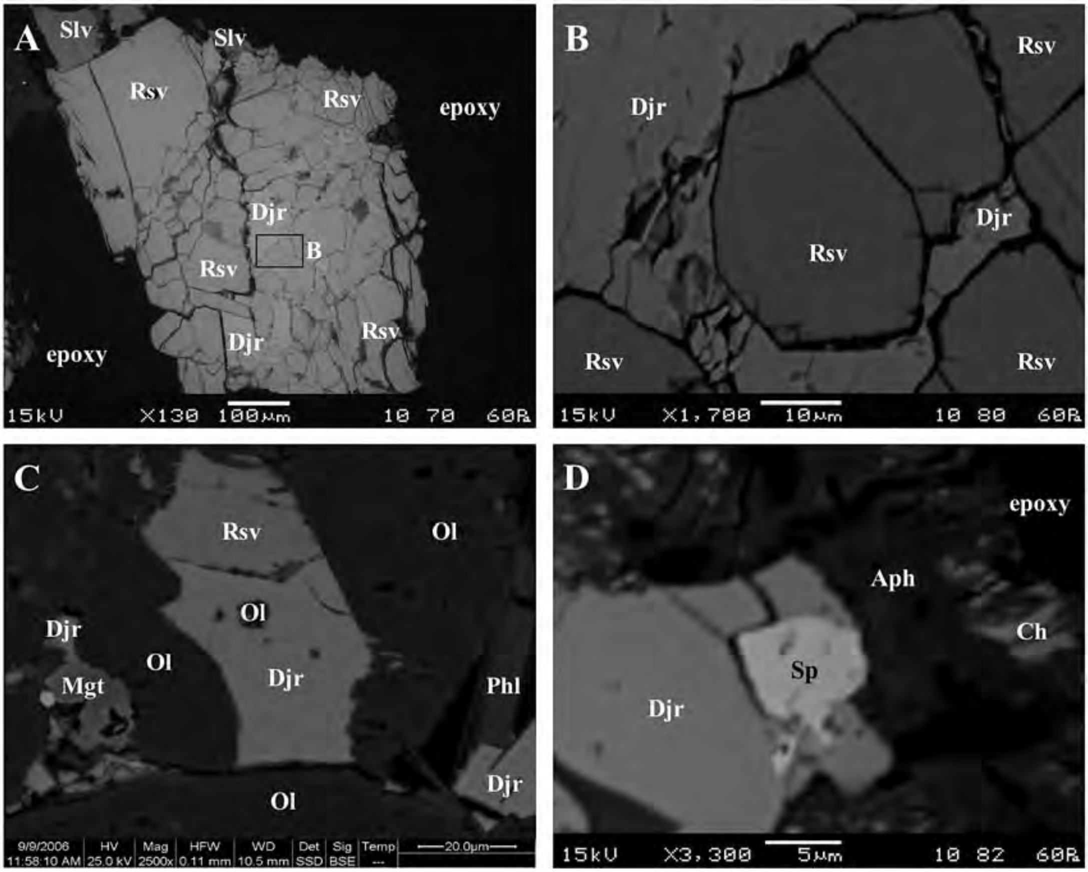

FIG. 3. Associated K sulfides and ferroan sphalerite in fine-grained aggregate of chloride–"nyerereite" clasts (BSE images). A–C: sample Uv–1–03; D: sample Uv–5a–03. Slv: sylvite; for other symbols, see Table 1.

et al. 1970, Czamanske *et al.* 1979, Clark & Brown 1980, Chakhmouradian *et al.* 2007).

Rasvumite, KFe_2S_3, is the most widespread of the natural sulfides of Fe with orthorhombic *Cmmc* symmetry in the system KFe_2S_3 – $RbFe_2S_3$ – $CsFe_2S_3$ – $TlFe_2S_3$. Complete miscibility among the synthetic K, Rb and Cs end-members has been demonstrated by Mitchell *et al.* (2004). The natural sulfides belonging to this system are rasvumite, picotpaulite, $TlFe_2S_3$, and pautovite, $CsFe_2S_3$ (Johan *et al.* 1970, Pekov *et al.* 2005). The $RbFe_2S_3$ phase is so far known only as an artificial compound (Mitchell *et al.* 2004). Rasvumite from hyperalkaline rocks of the Mont Saint-Hilaire intrusive complex, in Quebec, Canada, has significant enrichment of Rb and Cs (Chakhmouradian *et al.* 2007).

In general, the composition of rasvumite from the Udachnaya-East pipe is close to ideal KFe_2S_3. The abundances of Rb, Cs and Na are low (<0.9, <0.2 and <0.15 wt.%, respectively), and the variations of these elements within a single grain (core to rim) are insignificant (Table 2). In contrast, rasvumite from different lithologies of this pipe is notably variable in Rb content. Rasvumite from the UEK groundmass and essentially carbonate clasts contains 0.2–0.3 wt.% Rb, whereas rasvumite from the chloride–"nyerereite" clasts is more enriched (0.55–0.85 wt.% Rb, Fig. 5). Analysis of the UEK rasvumite by LA–ICP–MS determined the presence of other trace elements (*i.e.*, in ppm, Table 3): Tl (95–480), Ba (110–215), Pb (25–190), Te (up to 60), Se (20–135), and Co (25–100). Compositional differences exist between unaltered rasvumite and its oxidized rim (Table 2, Fig. 6). In the rim, the abundances of Na, Mg, V, Mn, Ni, As, Sr, Sb and W increase by an order of magnitude, whereas Rb, Te, Cs, Ba, Tl are Pb are higher by a factor of 1.5–2.

The composition of rasvumite from the Udachnaya-East pipe is somewhat different from the composition of rasvumite from peralkaline rocks and carbonatites (Tables 2, 3, Figs. 5, 7). For example, rasvumite from the Khibina hyperalkaline pegmatites is similar to the UEK rasvumite in terms of Rb content, but has lower abundances of Na (30–75 ppm), Cs (95–135 ppm), Tl (<10 ppm), Ba (<0.3 ppm) and other elements. Rasvumite from Lovozero has a similar Cs contents, but significantly higher Rb (2.5–6.1 wt.%) and Ba (380 ppm), and lower Tl (170 ppm) and Te (1 ppm). Some compositions of rasvumite from Mont Saint-Hilaire are characteristically Rb- and Cs-enriched (up to 7.2 wt.% and 2.6 wt.%, respectively, Chakhmouradian *et al.* 2001, 2007). Rasvumite found in the 1988 flows of the Oldoinyo Lengai natrocarbonatite volcano (Jago & Gittins 1999) is unusually Mn-rich (up to 3 wt.%), and contains elevated Na (up to 0.6 wt.%), Cl (up to 0.7 wt.%) and F (up to 1.9 wt.%). Rasvumite from the natrocarbonatite lavas erupted on July, 2000 is close to ideal stoichiometry, KFe_2S_3, and has low Mn, Na and Cl contents (Mitchell 2006a) in contrast to the ternary potassic Fe sulfides found in other lavas. These are enriched in Mn (0.4–1.7 wt.%) and Na (0.1–4.1 wt.%) and in the KFe_3S_4 and $K_2Fe_3S_4$ components (Dawson *et al.* 1995a, 1996, Mitchell 1997). Rasvumite from the alkali-rich ultramafic rocks of Coyote Peak and the skarns of Norway is nearly stoichiometric KFe_2S_3 (Czamanske *et al.* 1979, 1981, Jamtveit *et al.* 1997).

Djerfisherite

Djerfisherite, a cubic K–Cl-bearing sulfide, $K_6Na_{0-1}(Fe,Ni,Cu)_{24}S_{26}Cl$, is a member of the group of sulfides based upon Fe_8S_{14} clusters which includes pentlandite, $(Fe,Ni)_9S_8$, argentopentlandite, $Ag(Fe,Ni)_8S_8$, cobaltpentlandite, Co_9S_8, bartonite, $K_6Fe_{24}S_{26}(S,Cl)$, chlorbartonite, $K_6Fe_{24}S_{26}(Cl,S)$, thalfenisite, $Tl_6(Fe,Ni,Cu)_{25}S_{26}Cl$, and owensite, $(Ba,Pb)_6(Cu,Fe,Ni)_{25}S_{27}$ (Rudashevsky *et al.* 1979, Czamanske *et al.* 1981,

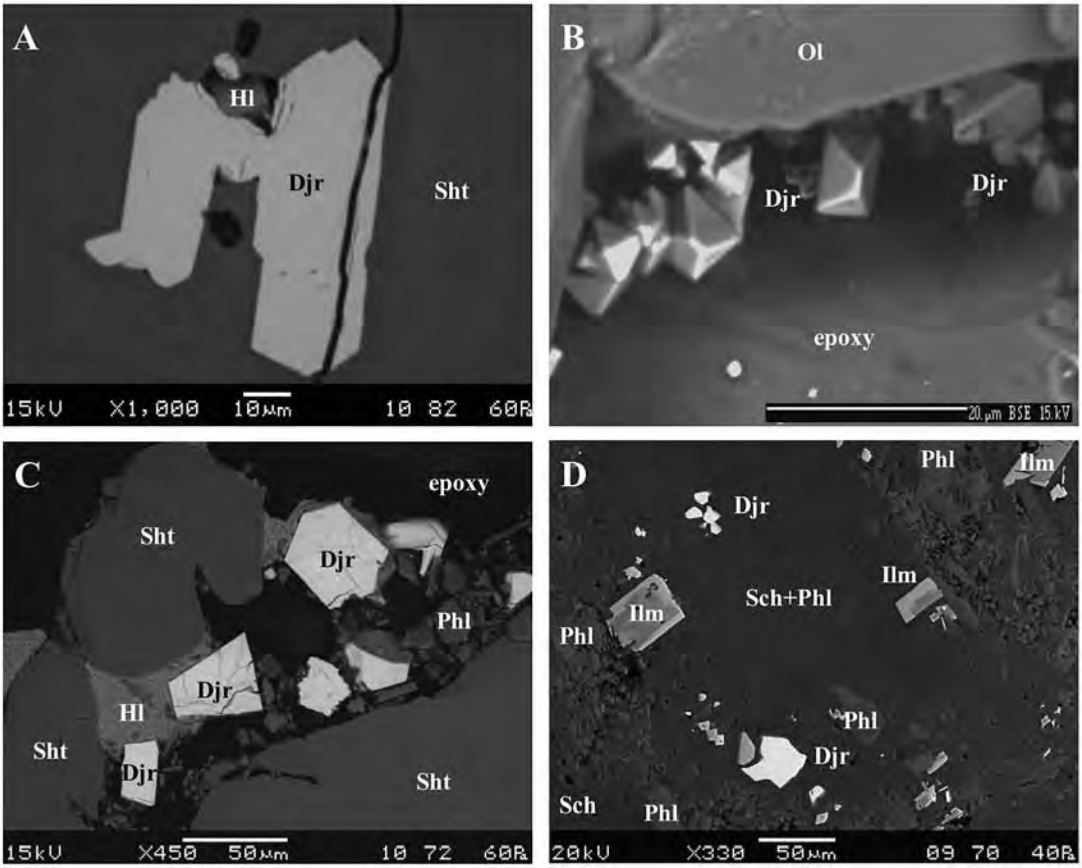

FIG. 4. Djerfisherite in chloride – shortite – northupite – calcite (Uv–2–03) and chloride (Uv–25–05) clasts (BSE images). A–C: sample Uv–2–03, D: sample Uv–25–05. Ilm: zoned ilmenite (core: ilmenite, rim: pyrophanite), Sch: schairerite; for other symbols, see Table 1.

TABLE 1. SUMMARY OF OCCURRENCES OF POTASSIUM SULFIDES IN CHLORIDE-CONTAINING CLASTS AND KIMBERLITE GROUNDMASS, UDACHNAYA-EAST PIPE

Association	Texture // Main assemblage	NaCl + KCl vol.%	Carbonates, vol.%	Rasvumite	Djerfisherite	Other phases
Kimberlite groundmass	fine-grained // Ol + Phl + zoned Spl + Prv + Cal	<10	20-40 mainly Cal, minor Sht, Zem, Nye	Djr-Rsv reaction rims on Po	anhedral to subhedral grains, Djr ± Rsv reaction rims on Po	Ap, Tfp, Ilm, Sp, Aph, Rt, Cp
Chloride clasts	middle to coarse-grained, in some cases banded // chlorides	>90-95	<5 mainly Cal, minor Als	not found	reaction rims on Po, anhedral grains, octahedral crystals near kimberlite contact	Mtc, Di, Cus, Wo, Adr, Phl, Tfp, Kfs, Sdl, Ne, Aph, Rt, Anh, Ilm-Pyf, Mgt, Brt, Prv, Ap, Brc, Sch, K-Ca sulfate
Chloride – "nyerereite" clasts	coarse-grained // chlorides + carbonates + Rsv	50-60	40-50, mainly Nye, minor Sht, Prs, Cal, Gls, Trn	prismatic or split crystals up to 5 mm, Rsv–Djr intergrowth, needles in Nye	rare anhedral grains, Rsv–Djr inter-growths	Aph, Hu, Phl, Tfp, Mgt, Ol, Prv, Ap, Sp, Cp
Chloride – shortite – northupite – calcite clasts	coarse-grained // chlorides + carbonates	≈50	≈50 mainly Sht, Nrt, Cal, minor Als, Olm	not found	subhedral grains, euhedral inclusions in Sht, octahedral crystals near kimberlite contact	Ap, Aph, Phl, Tfp, Mgt, Gn, Prv, Brt, Cls, Bra, Sch, Cp, Kgr, Brc
Chloride – carbonate – silicate clasts	coarse-grained chloride and fine-grained silicate - carbonate parts // chlorides + carbonates + silicates	50-70	10-30 Cal, Nye, Sht, Gls	not found	reaction rims on Po	Mtc, Di, Phl, Tfp, Mgt, Ap, Prv, Aph, Sp, Tch
Carbonate clasts	fine-grained // Cal + Phl	5-10	80-90 Cal, Sht	Djr–Rsv reaction rims on Po	Djr ± Rsv reaction rims on Po	Hu, Aph, Ap, Cp, Tch

Mineral symbols: Adr: Ti-rich andradite, Anh: anhydrite, Als: alstonite-paralstonite, Ap: apatite, Aph: aphthitalite, Brc: brucite (?), Bra: bradleyite, Brt: barite, Cal: calcite, Cls: Celestine, Cp: Cu-sulfide (chalcopyrite ?), Cus: cuspidine, Di: diopside, Djr: djerfisherite, Gls: gaylussite, Gn: galena, Hu: humite-clinohumite, Ilm-Pyf: ilmenite-pyrophanite, Kfs: K-feldspar, Kgr: kogarkoite (?), Mgt: Ti-rich magnetite, Mtc: monticellite, Nrt: northupite, Nye: nyerereite-like Na-Ca-K-S carbonate, Ol: olivine, Olm: olekminskite, Phl: phlogopite, Po: pyrrhotite, Prs: pirssonite, Prv: perovskite, Rsv: rasvumite, Rt: rutile, Sch: schairerite, Ne: Na-foid mineral (nepheline ?), Sdl: sodalite, Sht: shortite, Sp: sphalerite, Spl: spinel, Tch: tochilinite, Tfp: tetraferriphlogopite, Trn: trona, Wo: wollastonite, Zem: zemkorite.

Evans & Clark 1981, Szymański 1995, Pekov *et al.* 2003, Yakovenchuk *et al.* 2003). Bartonite and chlorbartonite are the tetragonal analogs of djerfisherite. Chlorbartonite, djerfisherite and rasvumite coexist in the alkaline ultramafic rocks of Coyote Peak, California, and the hyperagpaitic rocks of Mt. Koashva, Khibina intrusion (Czamanske *et al.* 1981, Evans & Clark 1981, Yakovenchuk *et al.* 2003). Potassium–Fe sulfide (bartonite–chlorbartonite ?) with variable abundances of Cl is reported in melilitolites of the Pian di Celle volcano, Italy (Stoppa *et al.* 1997). The existing data argue for the natural appearance of both Cl-bearing and Cl-free varieties of bartonite and djerfisherite, even within a single specimen; thus isomorphic substitution between Cl and S is a possibility (Czamanske *et al.* 1981). Regarding anhedral grains of K–Cl sulfides, the electron-microprobe data (Czamanske *et al.* 1981, Barkov *et al.* 1997, Stoppa *et al.* 1997, Sharygin 2006) are insufficient to classify correctly these mineral species.

The octahedral habit and the composition of crystals of the K–Cl sulfide from the UEK samples leave no doubt that they are djerfisherite. The mineral from the chloride-containing clasts, as well as the UEK groundmass (Sharygin *et al.* 2007a), exhibits significant variations in composition (Tables 4, 5). However, djerfisherite appears to be compositionally homogeneous within individual grains. The abundances of Fe, Cu, Ni and Co are used to discriminate between djerfisherite from different lithologies in the chloride rocks studied (Fig. 8). The first compositional group of djerfisherite with the following abundances (in wt.%) of Fe (41.1–50.1), Ni (3.8–12), Co (0.1–0.9), and Cu (0.15–7.3) is found mainly in the chloride–"nyerereite", essentially chloride and carbonate clasts. Djerfisherite from the second group is richer in Fe (53.4–55.6 wt.%), but poorer in other elements [in wt.%, Ni (0–1.1), Co (<0.15), Cu (<0.5)], and occurs in a chloride – shortite – northupite – calcite clast. Some crystals entrapped in shortite belong to the first compositional group (Table 4). Djerfisherite coexisting with rasvumite in the chloride–"nyerereite" clasts has the following composition (in wt.%): Fe (41.1–45.7), Ni (7.3–11.9), Co (0.5–0.9), and Cu (0.2–1.8), whereas djerfisherite in the same association in the UEK groundmass is compositionally different (in wt.%): Fe (48.3–48.9), Ni (5.5–6.2), Co (0.4–0.5), and Cu (0.2–0.3). Such Fe-rich and Cu-free species are not typical of djerfisherite from the UEK groundmass (Sharygin *et al.* 2007a).

Djerfisherite from the chloride-containing clasts shows no significant variations in potassium (8.8–9.6 wt.%), and those with lower K have elevated Na (up to 0.7 wt.%) compared to what is typical, <0.3 wt.% Na. In most cases, Rb and Cs are less than 0.05 wt.%, although djerfisherite from the chloride –"nyerereite" clasts can be slightly enriched in Rb (up to 0.15 wt.%). The variations of S and Cl are also not significant (33.5–34.3 and 1.2–1.5 wt.%, respectively).

The LA–ICP–MS analysis of djerfisherite from the UEK and kimberlite-hosted chloride–carbonate clasts

TABLE 2. REPRESENTATIVE COMPOSITIONS OF RASVUMITE FROM THE UEK CHLORIDE-CONTAINING CLASTS, IN COMPARISON WITH RASVUMITE FROM LOVOZERO AND KHIBINA

wt.%	1	2	3	4	5	6	7	8	9	10	11	12	13
K	15.55	15.59	15.29	15.29	15.12	15.48	15.46	15.49	14.35	13.49	12.31	15.49	15.36
Na	0.05	0.05	0.11	0.10	0.13	0.01	0.00	0.02	0.11	0.00	0.04	0.03	0.03
Rb	0.25	0.20	0.61	0.68	0.81	0.60	0.70	0.59	2.49	4.00	6.13	0.53	0.72
Cs	0.06	0.06	0.08	0.08	0.24	0.17	0.07	0.02	0.06	0.10	0.11	0.00	0.05
Fe	45.06	45.01	45.08	45.13	44.98	45.10	45.07	45.08	44.49	44.09	43.61	45.09	45.04
Ni	0.02	0.03	0.03	0.00	0.04	0.01	0.00	0.00	0.02	0.01	0.00	0.00	0.00
Co	0.03	0.00	0.00	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.01	0.00
Cu	0.00	0.04	0.02	0.00	0.05	0.04	0.00	0.01	0.02	0.03	0.01	0.00	0.03
S	38.79	38.75	38.83	38.82	38.79	38.79	38.79	38.80	38.36	38.12	37.59	38.78	38.79
Total	99.81	99.73	100.04	100.12	100.16	100.21	100.09	100.01	99.90	99.84	99.80	99.94	100.02
K	0.986	0.990	0.969	0.969	0.959	0.982	0.980	0.982	0.920	0.871	0.806	0.983	0.974
Na	0.005	0.005	0.011	0.011	0.014	0.001	0.000	0.002	0.012	0.000	0.005	0.003	0.004
Rb	0.007	0.006	0.018	0.020	0.023	0.017	0.020	0.017	0.073	0.118	0.184	0.015	0.021
Cs	0.001	0.001	0.002	0.002	0.004	0.003	0.001	0.000	0.001	0.002	0.002	0.000	0.001
Fe	2.001	2.000	1.999	2.002	1.997	2.002	2.001	2.001	1.997	1.992	1.998	2.002	2.000
Ni	0.001	0.001	0.001	0.000	0.002	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.000
Co	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000
Cu	0.000	0.002	0.001	0.000	0.002	0.002	0.000	0.000	0.001	0.001	0.000	0.000	0.001
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

The formulae are calculated on the basis of three aroms of sulfur per formula unit. The level of Cl is below the detection limit. 1–2: Rasvumite in association with pyrrhotite and djerfisherite, essentially carbonate clasts (sample YBK–0, Figs. 1C, D); 3–8: chloride – "nyerereite" clasts: 3–5: sample Uv–1–03: 3–4: core and rim of crystal; 5: in association with djerfisherite (Fig. 3C); 6: from fine-grained aggregate, sample Uv–5a–03; 7–8: core and rim of crystal, sample Uv–5c–03; 9–11: ussingite vein in peralkaline nepheline syenite, Lovozero alkaline complex, Russia (sample FM79858, Fersman Mineralogical Museum, RAS, Moscow); 12–13: hyperperalkaline pegmatite, Mt. Koashva, Khibina alkaline complex, Russia.

TABLE 3. MAJOR- (EMPA) AND TRACE-ELEMENT (LA–ICP–MS) COMPOSITIONS OF SELECTED SAMPLES OF RASVUMITE FROM THE UEK GROUNDMASS AND CHLORIDE–CARBONATE CLASTS, IN COMPARISON WITH RASVUMITE FROM LOVOZERO AND KHIBINA

	1	2	3	4	5	6	7	8a	8b	9	10	11	12
K	15.56	15.32	15.52	15.63	15.57	15.50	15.45	15.52	15.52	14.02	13.92	15.60	15.46
Na	0.06	0.10	0.05	0.10	0.01	0.02	0.07	0.03		0.01	0.03	0.03	0.03
Rb	0.22	0.64	0.58	0.54	0.61	0.61	0.76	0.61		3.26	3.45	0.59	0.72
Cs	0.06	0.05	0.08	0.08	0.16	0.07	0.10	0.07		0.08	0.07	0.02	0.05
Fe	45.10	45.13	45.13	45.10	45.11	45.16	45.16	45.12	45.12	44.31	44.35	45.10	45.04
Ni	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00		0.00	0.00	0.00	0.00
Co	0.05	0.03	0.00	0.00	0.00	0.00	0.00	0.00		0.00	0.00	0.00	0.00
Cu	0.00	0.00	0.00	0.00	0.03	0.00	0.00	0.00		0.00	0.00	0.00	0.00
S	38.79	38.86	38.80	38.83	38.82	38.82	38.78	38.74		38.25	38.40	38.84	38.79
Total	99.87	100.13	100.16	100.28	100.35	100.19	100.31	100.10		99.93	100.22	100.17	100.09
Na	1142	50	432	267	130	235	131	190	39482	609	42	41	97
Mg	51.8	0.42	10	28	18	0.41	0.54	0.17	5275	0.10	0.05	0.00	0.43
Ti	26	4.1	3.0	3.6	11	5.9	7.4	9.1	11	3.3	4.3	1.1	4.0
V	49	0.00	22	1.9	12	0.13	0.00	0.00	2890	0.00	0.00	0.08	0.00
Mn	3.2	0.33	4.1	2.2	2.9	3.0	0.84	1.6	52	0.28	0.47	0.00	2.3
Co	102	70	44	35	34	25	35	32	37	0.03	0.00	0.32	2.0
Ni	168	0.69	6.8	2.1	4.1	2.4	1.4	2.8	41	0.07	0.04	0.15	0.00
Cu	203	5.6	13	16	1205	3.9	2.5	0.52	85	0.31	0.53	5.1	1.4
Zn	9.0	0.64	1.6	0.17	1.5	2.3	0.06	2.4	3.7	0.65	0.86	0.39	0.38
As	30	4.5	6.6	2.6	5.7	0.71	2.2	3.5	555	0.26	0.46	0.00	0.65
Se	21	84	73	74	109	135	57	103	64	22	15	83	59
Rb	2848	7869	8129	7984	7586	8028	6978	8100	10914	35306	40393	7297	8882
Sr	5.1	0.02	6.2	0.40	3.1	0.00	0.06	0.00	115	0.91	0.00	0.07	0.08
Ag	8.8	1.9	2.9	6.7	3.0	0.00	0.51	0.00	2.0	0.03	0.00	0.00	0.03
Sb	1.8	0.28	0.39	0.41	0.71	0.16	0.26	0.14	6.1	0.07	0.07	0.36	0.00
Te	2.4	38	38	32	39	62	33	56	86	1.1	0.89	0.09	1.1
Cs	654	696	733	678	1906	692	932	714	1064	495	558	96	135
Ba	174	93	114	109	167	113	155	107	219	290	148	0.33	0.13
W	0.76	0.09	0.86	2.2	0.10	0.10	0.01	0.08	28	0.02	0.00	0.08	0.04
Tl	95	476	439	399	475	429	373	398	689	941	226	9.9	7.2
Pb	26	17	45	58	15	188	42	136	262	0.10	0.06	0.15	0.02

Compositions are expressed in wt.% (major elements) and in ppm (trace elements). The level of Cl is below detection limit. 1: Rasvumite from the UEK groundmass, in association with pyrrhotite and djerfisherite (sample YBK–0, Fig. 1A); 2–8: chloride – "nyerereite" clasts: 2–4: single crystals, sample Uv–1–03; 5: from fine-grained aggregate, sample Uv–5a–03; 6–8: core (6) and rim (7, 8) of large (>1 mm) crystal, sample Uv–5c–03: 8a–8b: fresh sample and oxidized rim, respectively; 9–10: ussingite vein in peralkaline nepheline syenite, Lovozero alkaline complex, Russia (sample FM79858, Fersman Mineralogical Museum, RAS, Moscow); 11–12: hyperperalkaline pegmatite, Mt. Koashva, Khibina alkaline complex, Russia.

confirmed relatively low abundances of Rb (<2000 ppm), Cs (<100 ppm), Tl (<330 ppm), and other trace elements that can substitute for K, Fe and S (<50–100 ppm; Table 4). Djerfisherite from the Udachnaya-East pipe is compositionally similar to djerfisherite (chlorbartonite ?) from the groundmass of the dolomite kimberlite of the Internatsional'naya pipe, Yakutia (Table 4), which also has low Tl (20–40 ppm) and Rb (490–830 ppm).

DISCUSSION

Partitioning of Rb, Cs, Tl and Ba between rasvumite and djerfisherite

The discovery of Rb–Cs-rich rasvumite (Chakhmouradian *et al.* 2001, 2007) and pautovite (Pekov *et al.* 2005) shows new aspects of the behavior of Rb and Cs during the late evolution of agpaitic magmas (Lovozero, Mont Saint-Hilaire). Among all K-bearing sulfides, the rasvumite-type structure is the most suitable for large ions such as Rb and Cs (Pekov *et al.* 2005). This is because of the greater interatomic distance <K–S> in the structure of rasvumite [3.41–3.70 (mean 3.52) Å (Clark & Brown 1980)] compared to other sulfides: bartonite [3.12–3.47 (mean 3.37) Å (Evans & Clark 1981)], chlorbartonite [3.27–3.44 (mean 3.35) Å (Yakovenchuk *et al.* 2003)] and djerfisherite [3.13–3.46 (mean 3.36) Å (Dmitrieva & Ilyukhin 1975, Zaccarini *et al.* 2007)].

The compositions of associated rasvumite and djerfisherite in the UEK groundmass and related chloride-containing clasts show strong partitioning of Rb and Cs into rasvumite (Tables 3, 5). In the UEK groundmass, the contents of Rb and Cs in rasvumite are 3590 and 650 ppm, whereas in djerfisherite they are 920 and 100 ppm, respectively. This distinction is more pronounced in chloride–“nyerereite” clasts: 7600–9400 ppm Rb and 700–1900 ppm Cs in rasvumite, 1980 ppm Rb and 80 ppm Cs in djerfisherite.

Rasvumite shows a less pronounced preference for Tl and Ba (Tables 2, 4). In the UEK groundmass, rasvumite contains 95 ppm Tl and 170 ppm Ba, whereas djerfisherite has 90 ppm Tl and 10 ppm Ba. In chloride–“nyerereite” clasts, rasvumite contains 400–480 ppm Tl and 100–210 ppm Ba, whereas djerfisherite has 170 and 30 ppm, respectively.

Origin of chloride-containing clasts

Chloride minerals and chloride-bearing clasts in the UEK groundmass represent a petrological oddity, the origin of which may well be important in understanding petrogenesis and emplacement of kimberlitic magmas. In the first paper describing chlorides in the Siberian kimberlites, their origin was *a priori* ascribed to post-magmatic crystallization from platform brines (Pavlov & Ilupin 1973). The weakness of such idea is that platform brines cause a strong alteration in kimberlites, whereas the UEK samples studied have no serpentine of other low-temperature hydrous silicates. In contrast, the UEK chloride and chloride–carbonate clasts are essentially water-free, and their mineral assemblage (*e.g.,* presence of “nyerereite”, phlogopite, olivine, Ca silicates and K sulfides; see Table 1) strongly supports high-temperature crystallization (Kamenetsky *et al.* 2004, 2006, 2007a, b, Golovin *et al.* 2007). Another model considered contamination of the kimberlitic magma by platform brines during emplacement (Egorov *et al.* 1988, Kornilova *et al.* 1998). However, such process should inevitably result in the formation of abundant H_2O-rich minerals and further autometasomatic reactions. The UEK and chloride-containing clasts contain one potentially H_2O-bearing mineral, phlogopite, but its abundance is low (<5 vol.%).

Two other scenarios can be responsible for the high-temperature origin of chlorides in the UEK. The chloride-bearing clasts may represent fragments of evaporites entrapped by and reacted with the kimberlitic magma. Such a mechanism is possible for some kimberlite pipes from the southern Siberian craton (*e.g.*, Mir and Internatsional’naya pipes), where evaporites (halite and dolomite lithologies) are present among the country rocks. This is not the case for the sedimentary sequence around the Udachnaya pipe (Zinchuk 2000), even at significant depths (up to 2000 m). Small lenses of halite (5–10 cm) were recorded in large carbonate blocks within the UEK (N.P. Pokhilenko, pers. commun.), but these cannot be taken as ample evidence of wider occurrence of chlorides in local sediments. Moreover, our samples lack borate minerals and bitumen (or products of their pyrolysis) that are typical of Siberian evaporites.

In our preferred model, we propose the formation of chloride-bearing assemblages at the latest evolutionary stages of the kimberlitic magma (Golovin *et al.* 2003, 2007, Kamenetsky *et al.* 2004, 2006, 2007a, b) and a mantle origin of chlorine in the UEK (Maas *et al.* 2005). An earlier crystallization of olivine drives the residual melt toward essentially “dry” and non-silicate

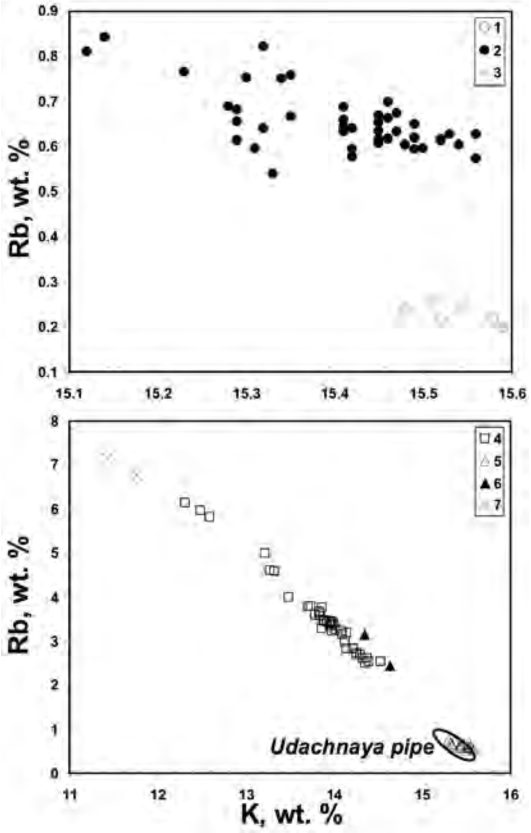

FIG. 5. Compositional variations in K and Rb (wt.%) for rasvumite from the UEK groundmass and chloride-bearing nodules in comparison with rasvumite from alkaline massifs. 1–3: Udachnaya-East pipe. 1: Kimberlite groundmass, 2: chloride–“nyerereite” clasts, 3: essentially carbonate clasts; 4: ussingite vein in peralkaline nepheline syenite, Lovozero alkaline complex, Russia (sample FM79858, Fersman Mineralogical Museum, RAS, Moscow), 5: hyperperalkaline pegmatite, Mt. Koashva, Khibina alkaline complex, Russia, 6–7: Mont Saint-Hilaire alkaline complex, Quebec, Canada (Chakhmouradian *et al.* 2007), 6: marble xenoliths in nepheline syenite (0.4–0.5 wt.% Cs_2O), 7: inclusions in sodalite tawite “xenolith” in nepheline syenite (2.3–2.6 wt.% Cs_2O).

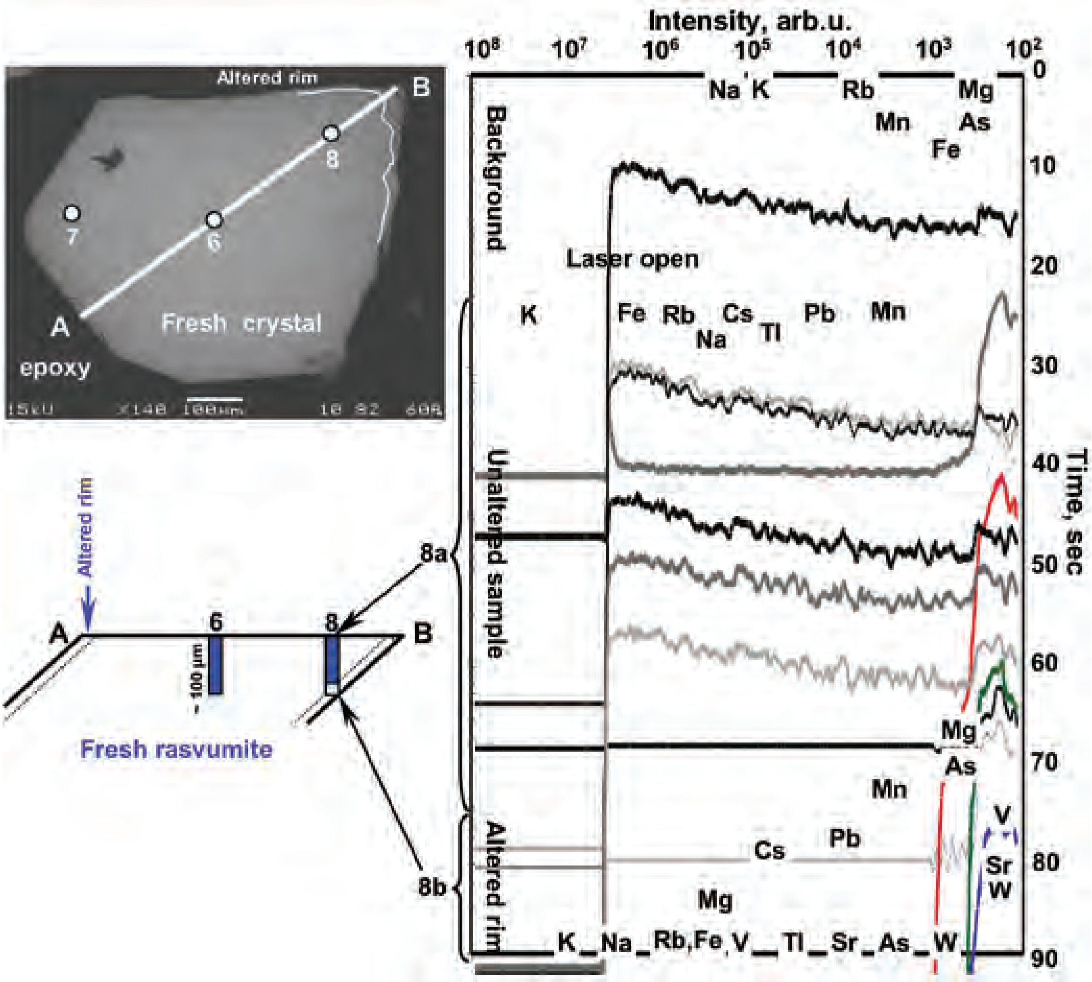

FIG. 6. LA–ICP–MS spectrum for rasvumite crystal from chloride–"nyerereite" clast, sample Uv–5c–03, Udachnaya-East pipe. Numbers 6, 7, 8a, 8b correspond to compositions in Table 3.

compositions, as recorded by melt inclusions in the UEK olivine (Golovin *et al.* 2003, 2007, Kamenetsky *et al.* 2004, 2006, 2007a), which crystallize calcite, alkali carbonates, chlorides, sulfates and potassium sulfides at temperatures below 800°C. A late magmatic crystallization of potassium sulfides is also suggested for the Elwin Bay kimberlite and the Coyote Peak diatreme (Czamanske *et al.* 1981, Clarke *et al.* 1994).

Genetic aspects of crystallization of potassium sulfides

The petrographic relationships among different sulfides in the samples of the UEK groundmass and chloride-containing clasts that we have studied suggest that pyrrhotite was the earliest, and djerfisherite was the latest in the crystallization sequence. Djerfisherite is considered to be a late-magmatic mineral in the UEK, where it formed in the residual, essentially carbonate–chloride melt (Golovin *et al.* 2003, 2007, Sharygin *et al.* 2003, 2007a). This conclusion can also be applied to the Udachnaya-East rasvumite, which precedes djerfisherite (Fig. 3). The latter only forms as chlorine becomes concentrated.

The solid-state synthesis of K–Fe–Ni sulfides (Clarke 1979) indicates that djerfisherite can form at temperatures from 356°C to at least 950°C. The crystallization of djerfisherite in the UEK groundmass was estimated to occur at 660–800°C (Golovin *et al.* 2003, 2007, Sharygin *et al.* 2007a). Thus, we envisage even

TABLE 4. REPRESENTATIVE COMPOSITIONS OF DJERFISHERITE FROM THE UEK GROUNDMASS AND CHLORIDE-CONTAINING CLASTS

wt.%	1	2	3	4	5	6	7	8	9	10	11	12	13
K	9.23	9.38	9.55	9.25	9.12	9.09	9.05	9.02	9.10	9.07	9.61	9.21	9.27
Na	0.04	0.07	0.03	0.06	0.02	0.01	0.20	0.22	0.17	0.17	0.11	0.16	0.04
Rb	0.00	0.00	0.00	0.00	0.11	0.11	0.09	0.08	0.13	0.12		0.00	0.00
Cs	0.00	0.04	0.00	0.01	0.05	0.00	0.02	0.06	0.00	0.02		0.01	0.00
Fe	48.30	47.55	49.00	47.40	42.97	44.37	46.22	47.75	41.50	45.74	53.65	54.56	55.37
Ni	6.16	5.90	4.67	5.65	11.95	9.90	7.41	5.36	11.50	7.27	1.10	0.00	0.00
Co	0.63	0.36	0.60	0.13	0.37	0.58	0.38	0.32	0.84	0.51	0.09	0.05	0.07
Cu	0.22	0.82	0.49	2.05	0.18	0.29	1.25	1.93	1.11	1.77	0.23	0.52	0.10
S	33.84	34.14	33.98	33.99	33.97	34.29	33.84	33.84	33.86	33.87	33.89	34.07	33.82
Cl	1.33	1.37	1.39	1.43	1.31	1.27	1.22	1.30	1.27	1.22	1.48	1.28	1.32
Total	99.76	99.62	99.71	99.98	100.05	99.92	99.68	99.88	99.48	99.75	100.16	99.87	100.00
K	5.815	5.858	5.992	5.802	5.724	5.652	5.702	5.683	5.724	5.709	6.046	5.763	5.844
Na	0.046	0.071	0.032	0.066	0.025	0.007	0.216	0.239	0.090	0.177	0.120	0.170	0.045
Rb	0.000	0.000	0.000	0.000	0.032	0.032	0.026	0.023	0.029	0.034		0.000	0.000
Cs	0.000	0.007	0.000	0.002	0.008	0.000	0.003	0.011	0.009	0.004		0.002	0.000
Fe	21.304	20.789	21.523	20.814	18.880	19.313	20.386	21.061	20.302	20.157	23.628	23.902	24.436
Ni	2.585	2.454	1.952	2.360	4.995	4.100	3.109	2.249	3.418	3.048	0.461	0.000	0.000
Co	0.265	0.147	0.250	0.055	0.152	0.240	0.158	0.133	0.161	0.211	0.037	0.022	0.031
Cu	0.086	0.316	0.189	0.791	0.070	0.112	0.485	0.748	0.302	0.685	0.090	0.201	0.040
S	26	26	26	26	26	26	26	26	26	26	26	26	26
Cl	0.924	0.943	0.962	0.989	0.907	0.871	0.848	0.903	0.906	0.847	1.027	0.883	0.918

The formulae are calculated on the basis of 26 atoms of sulfur per formula unit. Columns: 1: rim on rasvumite and pyrrhotite, UEK groundmass (sample YBK–0, Fig. 1); 2–3: in association with pyrrhotite and rasvumite, in carbonate clast near contact with kimberlite (sample YBK–0, Figs. 1c, d); 4: unzoned subhedral grain in chloride clast near contact with kimberlite (sample Uv–25–5, Fig. 4d); 5–10: from fine-grained silicate – carbonate – sulfate – chloride aggregate of chloride–"nyerereite" clasts: 5–8: sample Uv–5a–03; 9–10: in association with rasvumite, (sample Uv–1–03); 11–13: chloride – shortite – northupite – calcite clast (sample Uv–2–03): 11: in halite; 12–13: unzoned octahedral crystals near contact with kimberlite (Fig. 4).

higher temperatures of crystallization for the earlier rasvumite in the UEK groundmass. However, these estimates of temperature of crystallization for potassium sulfides in the chloride-containing clasts are imprecisely known. The presence of rasvumite included in "nyerereite" can be considered as indicating simultaneous crystallization of these minerals. The liquidus temperature of nyerereite in the system Na_2CO_3–K_2CO_3–$CaCO_3$ (Cooper *et al.* 1975), 810°C, provides the estimate of the maximum temperature for crystallization of rasvumite in the chloride–"nyerereite" clasts. As noted above, djerfisherite crystallized later, presumably at decreasing temperature, but above 415°C. The latter is deduced from the presence of djerfisherite inclusions in shortite, the homogenization temperature of salt inclusions in shortite (Kamenetsky *et al.* 2007a), and phase relationships in the system Na_2CO_3–K_2CO_3–$CaCO_3$ (Cooper *et al.* 1975). Replacement of pyrrhotite by the rasvumite–djerfisherite association in the skarns of Norway was estimated to occur at ~700°C (Jamtveit *et al.* 1997).

FINAL REMARKS

During the last decade of intensive research of alkaline rocks, carbonatites and skarns, "specific" K-bearing sulfides appear to be more common accessories than previously considered (Clarke *et al.* 1994, Barkov *et al.* 1997, Jamtveit *et al.* 1997, Mitchell 1997, 2006a, Stoppa *et al.* 1997, Jago & Gittins 1999, Chakhmouradian *et al.* 2001, 2007, Lisitsin *et al.* 2002, Yakovenchuk *et al.* 2003, Pekov *et al.* 2003, Sharygin *et al.* 2007a, b, Zaccarini *et al.* 2007). The occurrence of rasvumite and djerfisherite in diverse magmatic and metasomatic rocks implies widely variable conditions of their origin. However, high-alkaline chlorine- and carbon-rich systems, such as the residual kimberlitic magma of the Udachnaya-East pipe and natrocarbonatite lavas of the Oldoinyo Lengai volcano, are then most favorable environment of formation of potassium sulfides.

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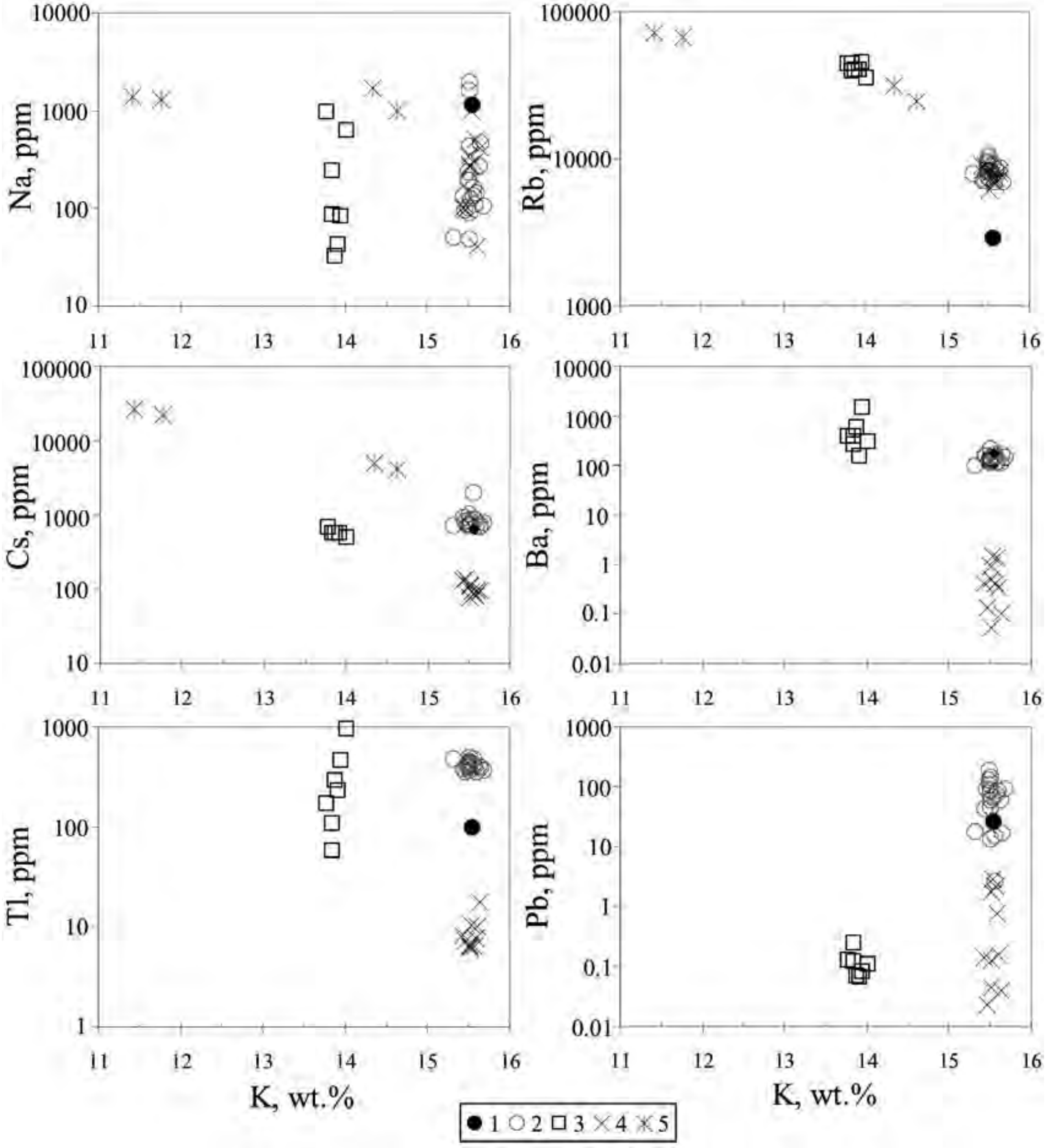

FIG. 7. Composition of rasvumite plotted in terms of K (in wt.%, EMPA) *versus* trace elements substituting for K (in ppm, LA–ICP–MS). 1–2: Udachnaya-East pipe. 1: kimberlite groundmass, 2: chloride–"nyerereite" clasts, 3: Lovozero, 4: Khibina, 5: Mont Saint-Hilaire, data recalculated in ppm after Chakhmouradian *et al.* (2007).

K sulfides from the Khibina and Lovozero intrusions and the Internatsional'naya pipe used in this study. The paper benefitted from thorough reviews and comments from R.H. Mitchell, R.F. Martin, D.B. Clarke and B.C. Jago. This work was supported by RFBR (grant 07–05–00072) and SB RAS (integration project 6.15) and funding from the Australian Research Council to VSK and CODES (Centre of Excellence in Ore Deposits).

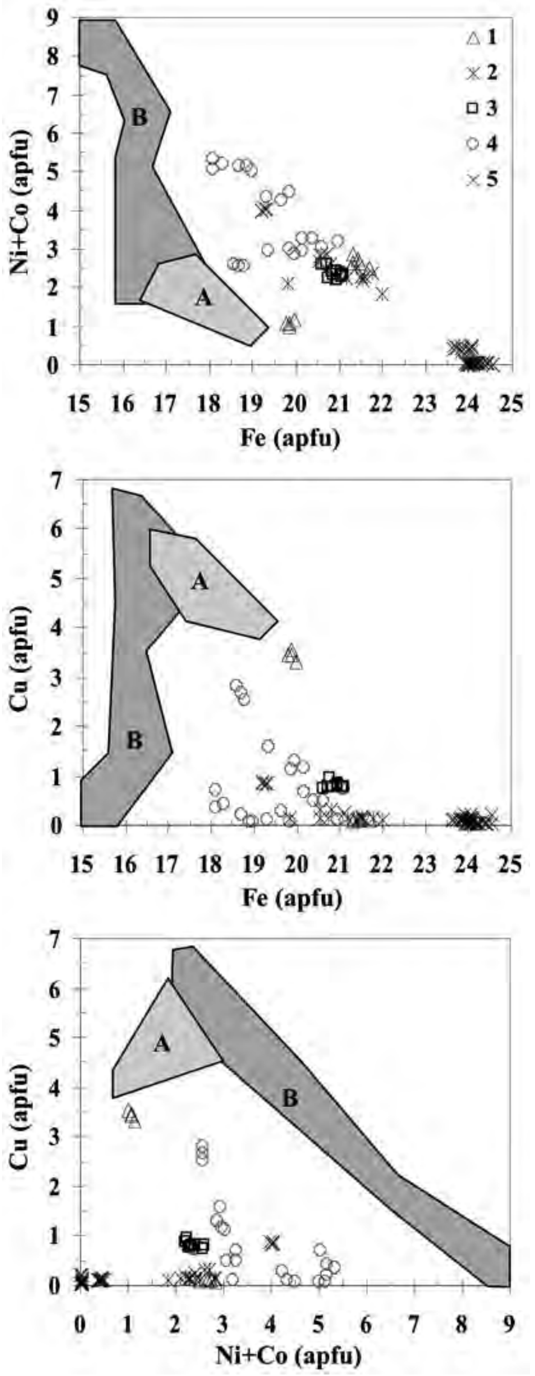

FIG. 8. Compositional variations (in *apfu*) of djerfisherite from chloride-containing clasts of the Udachnaya-East pipe. 1: Djerfisherite from kimberlite groundmass (new data), 2: from essentially carbonate clasts, 3: from chloride clasts, 4: from chloride–”nyerereite” clasts and chloride–carbonate in isolation in kimberlite (Kamenetsky *et al.* 2004), 5: from chloride – shortite – northupite – calcite clast. Compositional fields of the UEK djerfisherite (Sharygin *et al.* 2007a). A: from groundmass, B: from melt inclusions in olivine.

REFERENCES

BARKOV, A.Y., LAAJOKI, K.V.O., GEHÖR, S.A., YAKOVLEV, YU.N. & TAIKINA-AHO, O. (1997): Chlorine-poor analogues of djerfisherite – thalfenisite from Noril'sk, Siberia and Salmagorsky, Kola Peninsula, Russia. *Can. Mineral.* **35**, 1421-1430.

CHAKHMOURADIAN, A.R., HALDEN N.M., MITCHELL, R.H. & HORVÁTH, L. (2007): Rb–Cs-rich rasvumite and sector-zoned "loparite-(Ce)" from Mont Saint-Hilaire (Québec, Canada) and their petrologic significance. *Eur. J. Mineral.* **19**, 533-546.

CHAKHMOURADIAN, A.R., MITCHELL, R.H. & HORVÁTH, L. (2001): Rb–Cs-enriched rasvumite and sectorial loparite–lueshite intergrowths from the Mont Saint-Hilaire alkaline complex, Québec, Canada. *Geol. Assoc. Can. – Mineral. Assoc. Can., Program Abstr.* **26**, 24.

TABLE 5. MAJOR- AND TRACE-ELEMENT COMPOSITIONS OF DJERFISHERITE FROM THE UEK GROUNDMASS AND CHLORIDE–CARBONATE CLASTS, IN COMPARISON WITH K-BEARING SULFIDE FROM THE INTERNATSIONAL'NAYA PIPE

	1	2	3	4	5	6	7
K wt.%	9.21	9.07	9.54	9.25	9.19	9.70	10.13
Na	0.26	0.02	0.02	0.15	0.03	0.02	0.00
Rb	0.01	0.11	0.03	0.02	0.03		
Cs	0.00	0.02		0.01	0.00		
Fe	44.40	42.56	43.48	54.94	54.93	51.83	49.77
Ni	2.35	5.72	8.55	0.00	0.04	0.75	1.31
Co	0.16	0.43	0.98	0.06	0.06	0.03	0.02
Cu	8.73	6.91	2.20	0.38	0.13	0.88	0.80
S	33.35	33.99	33.72	34.03	33.91	35.58	36.28
Cl	1.38	1.26	1.34	1.35	1.30	1.46	1.44
Total	99.77	100.08	99.82	100.19	99.62	100.24	99.75
Na ppm	4141	202	297	1592	1535	270	144
Mg	26	0.21	6.6	66	22	4.0	27
Ti	4.9	2.3	1.9	2.6	9.6	6.9	14
V	2.9	0.05	0.13	0.51	13	0.52	0.59
Mn	8.6	2.1	26	1.1	26	3.8	2.9
Co	1639	4643	9908	87	43	122	93
Ni	23098	59474	81833	2.7	8.5	7399	10772
Cu	87386	71199	20790	462	42	10610	9797
Zn	2.0	1.1	2.6	1.3	3.1	1.4	2.5
As	42	1.4	27	3.2	12	21.9	5.5
Se	48	39	87	69	100	19	0.20
Rb	917	1984	375	254	431	489	834
Sr	4.5	0.03	0.98	1.2	2.4	0.12	0.18
Ag	4.7	9.7	13	12	3.3	6.1	0.60
Sb	1.7	0.65	0.3	0.72	2.0	0.23	0.21
Te	4.0	40	4.7	17	5.3	11	0.78
Cs	102	76	8.6	11	13	5.1	8.4
Ba	11	31	33	0.21	23	1.7	0.30
W	1.1	0.10	2.4	2.2	6.3	0.03	0.25
Tl	88	168	61	227	336	38	23
Pb	3.3	11	5.2	1.5	4.7	4.7	1.8

Samples 1–5: Udachnaya-East pipe; 1: kimberlite groundmass (sample YBK–0); 2: chloride–"nyerereite" clast (sample Uv–5a–03); 3–5: chloride – shortite – northupite – calcite clast (sample Uv–2–03), 3: inclusion in shortite (Fig. 4a); 4–5: octahedral crystals on the contact with kimberlite (Fig. 4b); 6–7: K-bearing sulfide (chlorbartonite?) from fresh kimberlite groundmass, Internatsional'naya pipe, Yakutia, Russia.

CLARK, J.R. & BROWN, G.E., JR. (1980): Crystal structure of rasvumite, KFe_2S_3. *Am. Mineral.* **65**, 477-482.

CLARKE, D.B. (1979): Synthesis of nickeloan djerfisherites and the origin of potassic sulphides at the Frank Smith mine. *In* The Mantle Sample: Inclusions in Kimberlites and Other Volcanics. *Proc. Second Int. Kimberlite Conf.* **2**, 300-307.

CLARKE, D.B., CHAPMAN, C.A.T., MACKAY, R.M. & MITCHELL, R.H. (1994): Occurrence and origin of djerfisherite from the Elwin Bay kimberlite, Somerset Island, Northwest Territories. *Can. Mineral.* **32**, 815-823.

COOPER, A.F., GITTINS, J. & TUTTLE, O.F. (1975): The system Na_2CO_3–K_2CO_3–$CaCO_3$ at 1 kilobar and its significance in carbonatite petrogenesis. *Am. J. Sci.* **275**, 534-560.

CZAMANSKE, G.K., ERD, R.C., LEONARD, B.F. & CLARK, J.R. (1981): Bartonite, a new potassium iron sulfide mineral. *Am. Mineral.* **66**, 369-375.

CZAMANSKE, G.K., ERD, R.C., SOKOLOVA, M.N., DOBROVOL'SKAYA, M.G. & DMITRIEVA, M.T. (1979): New data on rasvumite and djerfisherite. *Am. Mineral.* **64**, 776-778.

DAWSON, J.B., PINKERTON, H., NORTON, G.E., PYLE, D.M., BROWNING, P., JACKSON, D. & FALLICK, A.E. (1995a): Petrology and geochemistry of Oldoinyo Lengai lavas extruded in November 1988: magma source, ascent and crystallization. *In* Carbonatite Volcanism: Oldoinyo Lengai – Petrogenesis of Natrocarbonatite (K. Bell & J. Keller, eds.). Springer-Verlag, Berlin, Germany (47-69).

DAWSON, J.B., PYLE, D.M. & PINKERTON, H. (1996): Evolution of natrocarbonatite from a wollastonite nephelinite parent: evidence from the June 1993 eruption of Oldoinyo Lengai, Tanzania. *J. Geol.* **104**, 41-54.

DAWSON, J.B., SMITH, J.V. & STEELE, I.M. (1992): 1966 ash eruption of Oldoinyo Lengai: mineralogy of lapilli, and mixing of silicate and carbonate magmas. *Mineral. Mag.* **56**, 1-16.

DAWSON, J.B., SMITH, J.V. & STEELE, I.M. (1995b): Petrology and mineral chemistry of plutonic igneous xenoliths from the carbonatite volcano, Oldoinyo Lengai, Tanzania. *J. Petrol.* **36**, 797-826.

DEMARK, R.S. (1984): Minerals of Point of Rocks, New Mexico. *Mineral. Rec.* **15**, 149-156.

DMITRIEVA, M.T. & ILYUKHIN, V.V. (1975): Crystal structure of djerfisherite. *Dokl. Akad. Nauk SSSR* **223**, 343-346 (in Russ.).

EGOROV, K.N., USHCHAPOVSKAYA, Z.F., KASHAEV, A.A., BOGDANOV, G.V. & SIZYKH, I.I. (1988): Zemkorite – a new carbonate from Yakutian kimberlites. *Dokl. Akad. Nauk SSSR* **301**, 188-192 (in Russ.).

EVANS, H.T., JR. & CLARK, J.R. (1981): The crystal structure of bartonite, a potassium iron sulfide, and its relationship to pentlandite and djerfisherite. *Am. Mineral.* **66**, 376-384.

GEBHARD, G. & SCHLÜTER, J. (1994): Rasvumit vom Mont St. Hilaire, Kanada: die ersten Kristalle! *Lapis* **19**(10), 34-35.

GENGE, M.J., BALME, M. & JONES, A.P. (2001): Salt-bearing fumarole deposits in the summit crater of Oldoinyo Lengai, northern Tanzania: interactions between natrocarbonatite lava and meteoric water. *J. Volcanol. Geotherm. Res.* **106**, 111-122.

GOLOVIN, A.V., SHARYGIN, V.V. & POKHILENKO, N.P. (2007): Melt inclusions in olivine phenocrysts in unaltered kimberlites from the Udachnaya-East pipe, Yakutia: some aspects of kimberlite magma evolution during late crystallization stages. *Petrology* **15**, 168-183.

GOLOVIN, A.V., SHARYGIN, V.V., POKHILENKO, N.P., MAL'KOVETS, V.G., KOLESOV, B.A. & SOBOLEV, N.V. (2003): Secondary melt inclusions in olivine from unaltered kimberlites of the Udachnaya-Eastern pipe, Yakutia. *Dokl. Earth Sci.* **388**, 93-96.

IFANTOPULO, T.N., YUSHKO-ZAKHAROVA, O.Y., DUBAKINA, L.S. & SHCHERBACHEV, D.K. (1983): Rasvumite from the Lovozero massif. *Dokl. Akad. Nauk SSSR* **269**, 195-197 (in Russ.).

JAGO, B.C. & GITTINS, J. (1999): Mn- and F-bearing rasvumite in natrocarbonatite at Oldoinyo Lengai volcano, Tanzania. *Mineral. Mag.* **63**, 53-55.

JAMTVEIT, B., DAHLGREN, S. & AUSTRHEIM, H. (1997): High-grade contact metamorphism of calcareous rocks from the Oslo Rift, southern Norway. *Am. Mineral.* **82**, 1241-1254.

JOHAN, Z., PIERROT, R., SCHUBNEL, H.-J. & PERMINGEAT, F. (1970): La picotpaulite, $TlFe_2S_3$, une nouvelle espèce minérale. *Bul. Soc. Fr. Minéral. Cristallogr.* **93**, 545-549.

KAMENETSKY, M.B., SOBOLEV, A.V., KAMENETSKY, V.S., MAAS, R., DANYUSHEVSKY, L.V., THOMAS, R., POKHILENKO, N.P. & SOBOLEV, N.V. (2004): Kimberlite melts rich in alkali chlorides and carbonates: a potent metasomatic agent in the mantle. *Geology* **32**, 845-848.

KAMENETSKY, V.S., KAMENETSKY, M.B., SHARYGIN, V.V., FAURE, K. & GOLOVIN, A.V. (2007a): Chloride and carbonate immiscible liquids at the closure of the kimberlite magma evolution (Udachnaya-East kimberlite, Siberia). *Chem. Geol.* **237**, 384-400.

KAMENETSKY, V.S., KAMENETSKY, M.B., SHARYGIN, V.V. & GOLOVIN, A.V. (2007b): Carbonate–chloride enrichment in fresh kimberlites of the Udachnaya-East kimberlite, Siberia: a clue to physical properties of kimberlite magmas? *Geophys. Res. Lett.* **34**, L09316, doi: 10:1029/2007GL029389.

KAMENETSKY, V.S., SHARYGIN, V.V., KAMENETSKY, M.B. & GOLOVIN, A.V. (2006): Chloride–carbonate nodules in kimberlites from the Udachnaya pipe: alternative approach to the evolution of kimberlite magmas. *Geochem. Int.* **44**, 935-940.

KELLER, J. & KRAFT, M. (1990): Effusive natrocarbonatite activity of Oldoinyo Lengai, June 1988. *Bull. Volcanol.* **52**, 629-645.

KORNILOVA, V.P., EGOROV, K.N., SAFRONOV, A.F., FILIPPOV, N.D. & ZAITSEV, A.I. (1998): Monticellite kimberlite from the Udachnaya-East pipe and some aspects of the evolution of kimberlite melts. *Otech. Geol.* (**1**), 48-51 (in Russ.).

LISITSIN, D.V., DOBROVOL'SKAYA, M.G., TSEPIN, A.I., SHCHERBACHEV, D.K., TRUBKIN, N.V. & KONONKOVA, N.N. (2002): Sulfide mineralization in high-alkaline pegmatites of the Koashva deposit (Khibiny massif, Kola Peninsula). *Geol. Ore Deposits* **44**(5), 385-395.

MAAS, R., KAMENETSKY, M.B., SOBOLEV, A.V., KAMENETSKY, V.S. & SOBOLEV, N.V. (2005): Sr, Nd, and Pb isotope evidence for a mantle origin of alkali chlorides and carbonates in the Udachnaya kimberlite, Siberia. *Geology* **33**, 549-552.

MARSHINTSEV, V.K., MIGALKIN, K.N., NIKOLAEV, N.C. & BARASHKOV, Y.P. (1976): Unaltered kimberlite of the Udachnaya-East pipe. *Dokl. Akad. Nauk SSSR* **231**, 961-964 (in Russ.).

MITCHELL, R.H. (1997): Carbonate–carbonate immiscibility, neighborite and potassium iron sulphide in Oldoinyo Lengai natrocarbonatite. *Mineral. Mag.* **61**, 779-789.

MITCHELL, R.H. (2006a): Sylvite and fluorite microcrysts, and fluorite–nyerereite intergrowths from natrocarbonatite, Oldoinyo Lengai, Tanzania. *Mineral. Mag.* **70**, 103-114.

MITCHELL, R.H. (2006b): Mineralogy of stalactites formed by subaerial weathering of natrocarbonatite hornitos at Oldoinyo Lengai, Tanzania. *Mineral. Mag.* **70**, 437-444.

MITCHELL, R.H., ROSS, K.C. & POTTER, E.G. (2004): Crystal structures of $CsFe_2S_3$ and $RbFe_2S_3$: synthetic analogs of rasvumite KFe_2S_3. *J. Solid State Chem.* **177**, 1867-1872.

PAVLOV, D.I. & ILUPIN, I.P. (1973): Halite in the Yakutian kimberlites: its relationships with serpentine and question about source of solutions precipitated it. *Dokl. Akad. Nauk SSSR* **213**, 1406-1409 (in Russ.).

PEKOV, I.V., AGAKHANOV, A.A., BOLDYREVA, M.M. & GRISHIN, V.G. (2005): Pautovite, $CsFe_2S_3$, a new mineral species from the Lovozero alkaline complex, Kola Peninsula, Russia. *Can. Mineral.* **43**, 965-972.

PEKOV, I.V., SHCHERBACHEV, K.D. & KONONKOVA, N.N. (2003): Bartonite from the Lovozero massif (Kola Peninsula). *Zap. Vser. Mineral. Obshchest.* **132**(3), 97-101 (in Russ.).

RUDASHEVSKY, N.S., KARPENKOV, A.M., SHIPOVA, G.S., SHISHKIN, N.N. & RYABKIN, V.A. (1979): Thalfenisite – thallium analogue of djerfisherite. *Zap. Vses. Mineral. Obshchest.* **99**, 712-720 (in Russ.).

SHARYGIN, V.V. (2006): Potassium sulfide from kimberlites of the Internatsional'naya pipe (Yakutia). *In* Geochemistry, Petrology, Mineralogy and Genesis of Alkaline Rocks (V.N. Anfilogov, ed.). IMin UB RAS, Miass, Russia (304-307; in Russ.).

SHARYGIN, V.V., GOLOVIN, A.V., POKHILENKO, N.P. & KAMENETSKY, V.S. (2007a): Djerfisherite in the Udachnaya-East pipe kimberlites (Sakha–Yakutia, Russia): paragenesis, composition and origin. *Eur. J. Mineral.* **19**, 51-63.

SHARYGIN, V.V., GOLOVIN, A.V., POKHILENKO, N.P. & SOBOLEV, N.V. (2003): Djerfisherite in unaltered kimberlites of the Udachnaya-Eastern pipe, Yakutia. *Dokl. Earth Sci.* **390**, 554-557.

SHARYGIN, V.V., KAMENETSKY, V.S., KAMENETSKAYA, M.B., SERETKIN, YU.V. & POKHILENKO, N.P. (2007b): Rasvumite from the Udachnaya-East pipe, Yakutia: the first finding in kimberlites. *Dokl. Earth Sci.* **415A**, 929-934.

SOKOLOVA, M.N., DOBROVOL'SKAYA, M.G., ORGANOVA, N.I., KAZAKOVA, M.E. & DMITRIK, A.L. (1970): A sulphide of iron and potassium – the new mineral rasvumite. *Zap. Vses. Mineral. Obshchest.* **99**, 712-720 (in Russ.).

STOPPA, F., SHARYGIN, V.V. & CUNDARI, A. (1997): New mineral data from the kamafugite–carbonatite association: the melilitolite of Pian di Celle, Italy. *Mineral. Petrol.* **61**, 27-45.

SZYMAŃSKI, J.T. (1995): The crystal structure of owensite, $(Ba,Pb)_6(Cu,Fe,Ni)_{25}S_{27}$, a new member of the djerfisherite group. *Can. Mineral.* **33**, 671-677.

YAKOVENCHUK, V.N., PAKHOMOVSKY, Y.A., MEN'SHIKOV, Y.P., IVANYUK, G.Y., KRIVOVICHEV, S.V. & BURNS, P.C. (2003): Chlorbartonite, $K_6Fe_{24}S_{26}(Cl,S)$, a new mineral species from a hydrothermal vein in the Khibina massif, Kola Peninsula, Russia: description and crystal structure. *Can. Mineral.* **41**, 503-511.

ZACCARINI, F., THALHAMMER, O.A.R., PRINCIVALLE, F., LENAZ, D., STANLEY, C.J. & GARUTI, G. (2007): Djerfisherite in the Guli dunite complex, Polar Siberia: a primary or metasomatic phase? *Can. Mineral.* **45**, 1201-1211.

ZINCHUK, N.N. (2000): *Postmagmatic Minerals of Kimberlites*. Nedra, Moscow, Russia (in Russ.).

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