Eur. J. Mineral.
2007, **19**, 51–63

Djerfisherite in the Udachnaya-East pipe kimberlites (Sakha-Yakutia, Russia): paragenesis, composition and origin

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Abstract: Djerfisherite, an unusual potassium- and chlorine-bearing sulphide $K_6Na(Fe,Ni,Cu)_{24}S_{26}Cl$, is found in remarkably fresh rocks of the Udachnaya-East kimberlite pipe, including several varieties of kimberlite and a kimberlite-hosted phlogopite-spinel lherzolite xenolith. In both kimberlite breccia and monticellite kimberlite djerfisherite is a common groundmass mineral. Djerfisherite is also present as a daughter phase in olivine-hosted inclusions of trapped carbonate-chloride melt and sulphide melt. The mineral is present as irregular or rounded grains (up to 80–100 μm) in association with magnetite and pyrrhotite in the kimberlite groundmass, and together with carbonates, Na-K-chlorides, silicates, magnetite, sulphates and Fe-Ni-sulphides in melt inclusions. Djerfisherite in the lherzolite xenolith is mainly interstitial (up to 100 μm) and commonly rims primary mantle sulphides that show clear signs of replacement. Broad compositional variations in Fe, Ni and Cu are common in djerfisherite from different occurrences of the Udachnaya-East pipe. Textural relations, heating stage experiments with melt inclusions and compositional data, suggest a late magmatic origin of djerfisherite in the Udachnaya-East kimberlite groundmass, at shallow depths and at $T \leq 800°C$. In contrast, djerfisherite in the lherzolite xenolith appears to be a product of direct precipitation from evolved kimberlite magma infiltrating into lithospheric xenoliths or reactions of evolved kimberlite fluids/melts with primary minerals in xenoliths.

Key-words: djerfisherite, kimberlite, carbonatite, magma, mantle xenolith.

Introduction

Djerfisherite, a rare potassium- and chlorine-bearing sulphide $K_6Na(Fe,Ni,Cu)_{24}S_{26}Cl$, was first discovered in enstatite chondrite meteorites (Funchs, 1966). This mineral is a member of the group of sulphides based upon Fe_8S_{14} clusters which includes pentlandite $(Fe,Ni)_9S_8$, argentopentlandite $Ag(Fe,Ni)_8S_8$, cobalt pentlandite 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 $(Ba,Pb)_6(Cu,Fe,Ni)_{25}S_{27}$. Following the first discovery, reports of djerfisherite were published for other meteorites, and for 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). The most recent comprehensive review of djerfisherite occurrences and possible origins was presented by Clarke *et al.* (1994), although since then the number of reports has almost doubled (Kogarko *et al.*, 1991; Dawson *et al.*, 1992; 1995; Konev *et al.*, 1996; Solovova *et al.*, 1996; Barkov *et al.*, 1997, and references therein; Jamtveit *et al.*, 1997; Korobeinikov *et al.*, 1998; Malich & Auge, 1998; Henderson *et al.*, 1999; Takechi *et al.*, 2000; Sukharzhevskaya & Artyukhova, 2000; Panina *et al.*, 2001; Pascal *et al.*, 2001; Lin & El Gosery, 2002; Lisitsin *et al.*, 2002; Pertsev *et al.*, 2003; Yakovenchuk *et al.*, 2003).

The specific interest of this study is the occurrence of djerfisherite in kimberlites and kimberlite-hosted peridotite xenoliths. Djerfisherite has been found as inclusions in diamonds and more commonly as overgrowths on primary Fe-Ni-Cu-sulphides in xenoliths from the Yakutian and South African kimberlites (Dobrovol'skaya *et al.*, 1975; Clarke *et al.*, 1977; Govorov *et al.*, 1984; Distler *et al.*, 1987; Spetsius *et al.*, 1987; Solov'yeva *et al.*, 1988; 1997; Bulanova *et al.*, 1990; Zedgenizov *et al.*, 1998; Misra *et al.*, 2004; Spetsius, 2004). However, the presence of djerfisherite in the groundmass of kimberlites is still poorly documented. There are rare records of djerfisherite in kimberlites from the Muza and Udachnaya pipes, Yakutia (Dobrovol'skaya *et al.*, 1975; Distler *et al.*, 1987; Golovin *et al.*, 2003; Sharygin *et al.*, 2003; Golovin, 2004; Kamenetsky *et al.*, 2004; Kamenetsky, 2005) and diatremes in the Northwest Territories, Canada (Clarke *et al.*, 1994; Chakhmouradian & Mitchell, 2001). The literature is very unspecific about the origin of djerfisherite in kimberlites and kimberlite-hosted rocks; some authors advocate direct crystallization from late-stage liquids (Clarke *et al.*, 1994; Golovin *et al.*, 2003; Sharygin *et al.*, 2003; Golovin, 2004; Kamenetsky *et*

0935-1221/07/0019-0051 $ 5.85

DOI: 10.1127/0935-1221/2007/0019-0051

al., 2004; Kamenetsky, 2005), whereas others invoke metasomatic reactions with a hypothetical K-Cl-S-rich fluid at different stages of kimberlite evolution (Dobrovol'skaya *et al.*, 1975; Clarke *et al.*, 1977; Dawson, 1980; Mitchell, 1986; Spetsius *et al.*, 1987; Solov'yeva *et al.*, 1988; Bulanova *et al.*, 1990; Misra *et al.*, 2004).

In this paper we characterise djerfisherite from a suite of uniquely fresh kimberlites of the Udachnaya-East pipe, Yakutia, and make inferences on the origin of this rare mineral. We also present the detailed comparison of djerfisherite found in the groundmass of the Yakutian kimberlites and mantle/crustal xenoliths.

Analytical techniques

Double-polished rock sections (~ 50–100 μm in thickness) were used for optical examination in transmitted and reflected light. Quantitative analyses of djerfisherite and other minerals were performed using a "CAMEBAX-micro" electron microprobe equipped with an EDS system at the Institute of Geology and Mineralogy (IGM), Novosibirsk, Russia. Operating conditions were accelerating voltage 20 kV, beam current 15–30 nA, beam diameter about 2 μm, counting time 30 s. Precision for major elements was better than 2 rel. %. Mineral standards and synthetic alloys were used during microprobe analysis of sulphides: chalcopyrite and pyrrhotite for Fe, Cu and S, synthetic Fe-Ni-Co alloy for Ni and Co, albite for Na, sanidine for Si, Al and K, chlorapatite for Cl. Microprobe analyses was performed on the grains larger than 10 μm. The EDS system was used for preliminary identification of minerals, neighbouring with sulphides. Back-scattered electron images (BSE) and elemental mapping were carried out with a LEO electron scanning microscope at IGM, Novosibirsk.

Udachnaya-East pipe kimberlite: geological background and petrography

The Middle Palaeozoic Udachnaya pipe (western and eastern bodies) belongs to the Daldyn field of the Yakutian Kimberlite Province, and is hosted within the Upper-Middle Cambrian and Lower Ordovician dolomites, dolomitic limestones, mudstones, sandstones, and calcareous conglomerates. The Udachnaya-East pipe consists of at least four phases of emplacement, including three facies of kimberlite breccias, and late stage kimberlite veins and dykes (Khar'kiv *et al.*, 1998). The studied rocks, collected at the 500 m depth in the open pit in the eastern part of the Udachnaya-East pipe, belong to the third and forth emplacement phases. The rocks are hypabyssal kimberlites and lack any sign of alteration (*e.g.*, serpentine and chlorite in the groundmass and around olivine crystals). Djerfisherite-bearing rock varieties are represented by kimberlite breccia, monticellite kimberlite, and phlogopite-spinel lherzolite xenolith.

Kimberlite breccias contain olivine and phlogopite mainly as macrocrysts and phenocrysts, and abundant mantle and crustal xenoliths and xenocrysts. The fine-grained groundmass consists of olivine, calcite, phlogopite, perovskite, zoned spinel (chromite-Ti-magnetite-magnetite), ilmenite, Fe-sulphides, Na-K-chlorides and Ca-Na-carbonates.

Monticellite kimberlites of the later intrusive phase form large injections (Kornilova *et al.*, 1998), or more rarely thin (up to 2 cm) veins in kimberlite breccias of the third stage of the Udachnaya-East pipe. These spongy black rocks are much poorer in xenogenic material (< 5 vol%) than the breccias. They contain olivine and rare phlogopite as macro- or phenocrysts in a fine-grained groundmass consisting of olivine, perovskite, phlogopite, monticellite, zoned spinel, sodalite, djerfisherite, Na-K-chlorides and rare calcite.

Table 1. Chemical composition (in wt.%) of minerals from phlogopite-spinel lherzolite xenolith, Udachnaya-East pipe.

	Primary association					Interstitial association					
Phase	Ol-1	Opx-1	Cpx-1	Sp-1	Phl-1	Ol-2	Cpx-2	Sp-2	Phl-2	Phl-2	Phl-2
n	6	6	7	4	27	9	7	3	1	1	2
SiO_2	41.52	56.75	54.27	0.00	37.68	41.55	54.68	0.00	42.08	39.33	38.93
TiO_2	0.00	0.05	0.09	0.04	4.09	0.00	0.24	0.06	0.09	1.70	4.28
Cr_2O_3	0.01	0.64	1.47	30.55	1.36	0.12	0.30	39.43	0.40	0.87	0.03
Al_2O_3	0.00	2.29	3.11	36.98	14.35	0.00	0.21	27.46	11.99	12.28	11.42
FeO	6.86	4.63	1.69	16.47	2.50	5.86	2.38	17.82	1.85	4.10	7.05
MnO	0.09	0.10	0.05	0.17		0.30		0.42	0.02	0.01	0.07
MgO	50.98	35.31	15.70	15.05	22.49	51.57	17.76	13.54	26.74	24.94	22.14
CaO	0.00	0.29	22.15	0.00	0.02	0.36	23.84	0.00	0.10	0.07	0.03
BaO	0.00		0.00	0.00	2.16	0.00	0.00	0.00		0.27	0.62
Na_2O	0.00	0.04	1.54	0.00	0.17	0.00	0.42	0.00	0.14	0.47	0.56
K_2O	0.00	0.00	0.00	0.00	9.34	0.00	0.00	0.00	10.50	9.90	9.13
NiO	0.47	0.10	0.04	0.12		0.31		0.10	0.28		
F										2.05	1.50
Cl										0.01	0.01
Total	99.92	100.20	100.12	99.37	94.15	100.08	99.84	98.84	94.20	96.00	95.76
Mg#	0.93	0.93	0.94	0.65	0.94	0.94	0.93	0.62	0.96	0.92	0.85

Note: Ol = olivine; Opx = orthopyroxene; Cpx = clinopyroxene; Sp = spinel; Phl = phlogopite. *n* – number of analyses. For silicates Mg# means $Mg/(Mg+Fe_{tot})$, for spinel – $Mg/(Mg+Fe^{2+})$.

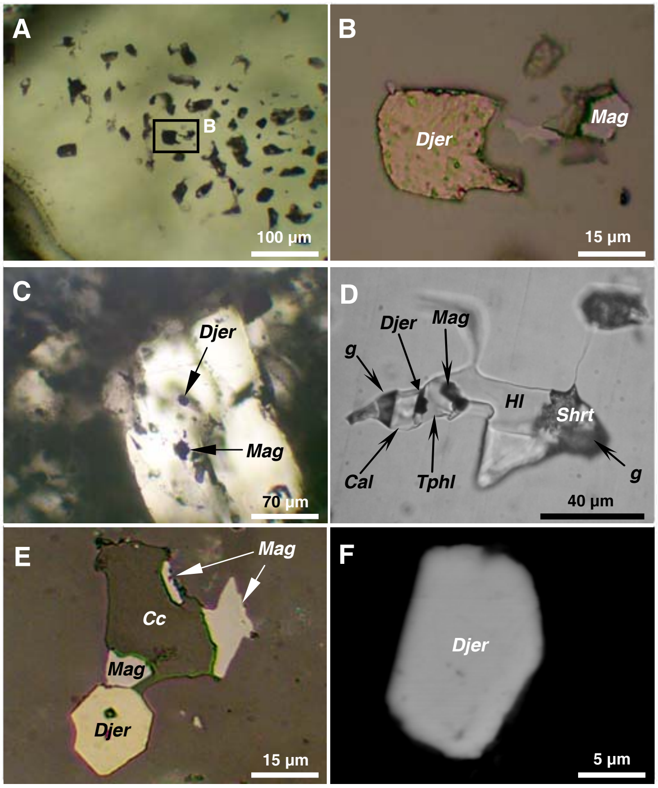

Fig. 1. Djerfisherite from secondary inclusions in olivine of kimberlite breccia, Udachnaya-East pipe.
A – general view of trail of secondary inclusions in macrocrystal olivine, ordinary light; B – djerfisherite in association with magnetite, reflected light; C – djerfisherite and magnetite from trail of secondary inclusions in groundmass olivine, ordinary light; D – secondary melt inclusion containing djerfisherite, calcite, halite, tetraferriphlogopite, shortite and magnetite, ordinary light; E – polycrystalline inclusion consisting of calcite, djerfisherite and magnetite, reflected light; F – individual djerfisherite bleb in olivine, BSE image.
Symbols: *Djer* – djerfisherite; *Mag* – magnetite; *Hl* – halite; *Tphl* – tetraferriphlogopite; *Cal* – calcite; *Shrt* – shortite; *g* – gas bubble.

In general, the unaltered kimberlites of the Udachnaya-East pipe are characteristically different to kimberlites world-wide in having H_2O-poor compositions (< 2 wt.%, Kornilova *et al.*, 1998; Kamenetsky *et al.*, 2004; Maas *et al.*, 2005) and enrichment in halides and sodalite.

The studied phlogopite-bearing spinel lherzolite xenolith is round, 20 cm in diameter, hosted by the third phase kimberlite breccia, and mantled by an autolithic kimberlite (see definition in Mitchell, 1986). The xenolith is strongly enriched in primary Fe-Ni-sulphides (monosulphide solid solution + pentlandite or pentlandite + pyrrhotite). Interstitial spaces between primary minerals are filled with fine-grained assemblage of olivine, clinopyroxene, Cr-spinel, phlogopite and djerfisherite + pyrrhotite. Such interstitial assemblages are common of the outer part of the xenolith and sometimes are spatially connected with the host kimberlite. Moreover, small cavities occur in the xenolith and contain halite, sylvite, Na-Ca-carbonates and sulphides. The chemical compositions of silicate and oxide minerals from primary and interstitial assemblages (Table 1) are significantly different.

Djerfisherite in the Udachnaya-East pipe

Djerfisherite was identified: (i) in melt inclusions in the kimberlitic olivine; (ii) in the kimberlite groundmass; (iii) in a contact zone between kimberlite and phlogopite-spinel lherzolite xenolith; and (iv) among interstitial minerals in this xenolith.

Melt inclusions in kimberlitic olivine

Djerfisherite occurs as individual blebs (up to 30 µm) and as a daughter phase in melt inclusions (5–80 µm, Fig. 1), trails of which are hosted by olivine macrocrysts and phenocrysts. Djerfisherite in melt inclusions is associated with carbonates (calcite, shortite, dolomite, magnesite-siderite, northupite), silicates (phlogopite-tetraferriphlogopite, olivine, humite-clinohumite, diopside, monticellite), magnetite, Na-K chlorides, sulphates, and rarely Mg-phosphate and Ni-rich pyrrhotite (or monosulphide solid solution, 4.4 wt. % Ni) (Golovin *et al.*, 2003). The size of djerfisherite grains in melt inclusions varies from 2 to 15 µm. Melt inclusions homogenise at 660–800°C, and the low density of the CO_2 bubbles into these inclusions suggest they were trapped at shallow depths (Golovin *et al.*, 2003; Kamenetsky *et al.*, 2004). During heating, djerfisherite grains dissolve near the homogenisation temperatures.

Kimberlite groundmass

Djerfisherite in the groundmass of the kimberlite breccia is the latest crystallised mineral. It either forms individual subhedral grains (up to 50–100 µm) in association with magnetite, and sometimes with pyrrhotite, or occupies the interstitial space between other groundmass minerals. Olivine, calcite and other groundmass minerals occur as crystal inclusions in the grains of djerfisherite (Fig. 2 A–D).

Djerfisherite in the monticellite kimberlite is also a late stage mineral. It forms rounded clots (up to 20 µm) in the groundmass, or individual blebs together with small grains of monticellite, perovskite, and magnetite in the oikilitic sodalite (Fig. 2 E–F). Crystal inclusions of monticellite are most common in the groundmass djerfisherite.

It should be noted that djerfisherite is the dominant and, sometimes, sole sulphide phase in the kimberlitic rocks of this study.

Phlogopite-bearing spinel lherzolite xenolith

Djerfisherite in the phlogopite-bearing spinel lherzolite xenolith occurs interstitially (Fig. 3 A), in the form of rims (up to 100 µm) around early sulphide masses (monosulphide solid solution + pentlandite or pentlandite + pyrrhotite, Fig. 3 B–E), and as individual anhedral grains or rims around pyrrhotite in the intergranular spaces of the xenolith (Fig. 3 F). Early sulphides associations (monosulphide solid solution + pentlandite) without djerfisherite rim are scarce (Fig. 3 G). In some cases, djerfisherite occurs in trails along mi-

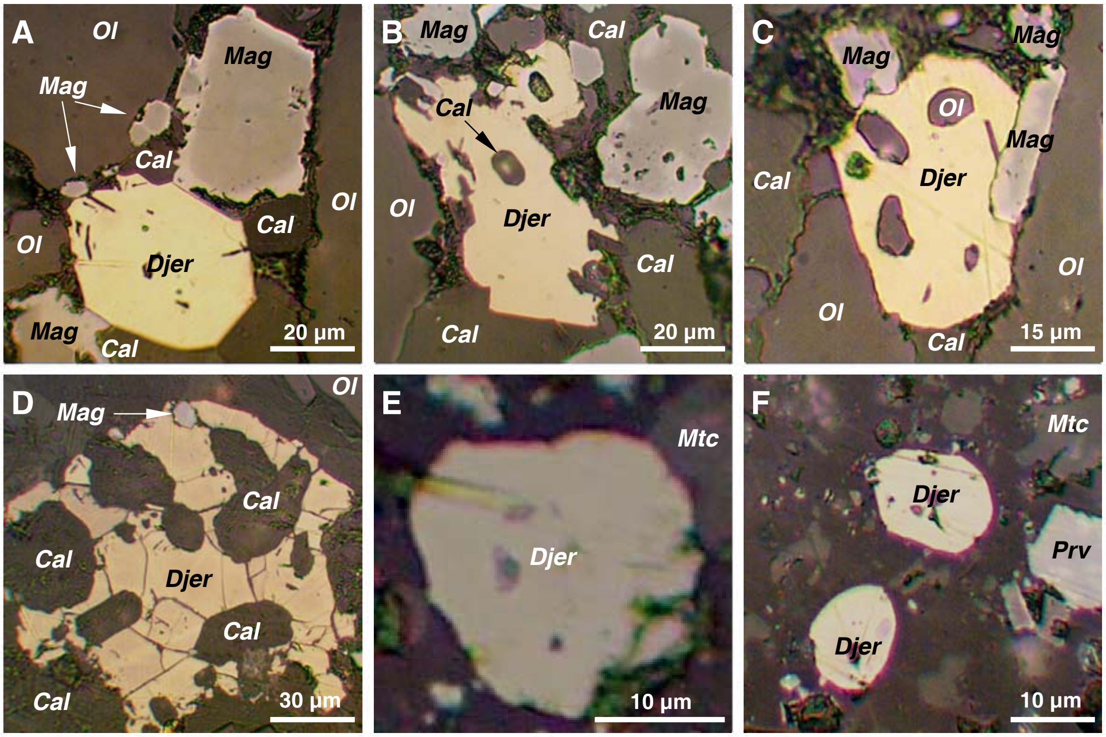

Fig. 2. Djerfisherite from kimberlite groundmass of the Udachnaya-East pipe (reflected light).
A–D – in kimberlite breccia: A – polygonal grain in groundmass in association with zoned spinel, olivine and calcite; B – xenomorphic isolation with calcite inclusion; C – grain with olivine inclusions; D – xenomorphic isolation with calcite inclusions; E, F – rounded blebs of djerfisherite in association with monticellite and perovskite in oikilitic sodalite from groundmass of monticellite kimberlite.
Symbols: *Mag* – zoned spinel (core – Cr-spinel, middle – Ti-magnetite, rim – magnetite); *Ol* – olivine; *Mtc* – monticellite; *Prv* – perovskite. Other symbols see Figure 1.

Table 2. Chemical composition of Fe-Ni-sulphides from phlogopite-spinel lherzolite nodule and from contact with kimberlite breccia, Udachnaya-East pipe.

	Sulphide association	Phase	n	Fe	Ni	Co	Cu	S	Total
1	Mss+Pn+Djer	Mss	5	55.04	8.47	0.23	0.01	36.35	100.10
		Pn in Mss	3	40.96	24.80	0.66	0.03	33.63	100.09
		Pn	4	35.60	29.70	1.50	0.03	33.36	100.19
2	Mss+Pn+Djer	Pn	1	36.04	29.33	0.84	0.02	33.78	100.00
3	Mss+Pn+Djer	Pn in Mss	1	33.44	32.45	0.73	0.07	33.40	100.09
		Pn	1	32.91	32.56	0.98	0.06	33.47	99.98
4	Pn+Po+Djer	Pn	1	40.03	25.19	1.77	0.02	33.16	100.17
		Po	2	62.67	0.27	0.00	0.01	36.64	99.58
5	Pn+Po+Djer	Pn	2	38.51	25.95	2.07	0.03	33.53	100.08
		Po	2	63.06	0.14	0.00	0.00	36.82	100.02
6	Pn+Po+Djer	Pn	1	35.82	29.64	0.48	0.06	33.55	99.54
7	Po+Djer	Po	1	62.85	0.17	0.00	0.00	36.78	99.80
8	Po+Djer	Po	2	62.77	0.17	0.00	0.00	36.81	99.75
9	Mss+Pn+Djer	Mss	1	54.82	8.80	0.26	0.03	36.08	99.99
		Pn	2	40.20	25.57	0.33	0.13	33.83	100.05
10	Mss+Pn+Djer	Pn	2	37.82	28.35	0.77	0.03	32.75	99.72
11	Mss+Pn+Djer	Mss	1	55.26	8.66	0.42	0.02	35.82	100.18
		Pn	1	37.22	28.84	1.09	0.02	32.89	100.06
12	Po+Djer	Po	2	63.24	0.03	0.00	0.00	36.52	99.79
13	Po+Djer	Po	2	63.25	0.06	0.01	0.00	36.66	99.97
14	Po+Djer	Po	2	63.12	0.05	0.00	0.04	36.61	99.82
15	Po+Djer	Po	1	63.20	0.03	0.00	0.02	36.61	99.86
16	Po+Djer	Po	1	63.14	0.08	0.01	0.00	36.76	99.99

Note: 1–8 – intraxenolith suphides; 9–11 – sulphides from cavities in the xenolith, in association with Na-Ca-carbonates and halite; 12–16 – sulphides on the xenolith-kimberlite breccia contact; Mss = monosulphide solid solution; Pn = pentlandite; Po = pyrrhotite; Djer – djerfisherite, *n* = number of analyses.

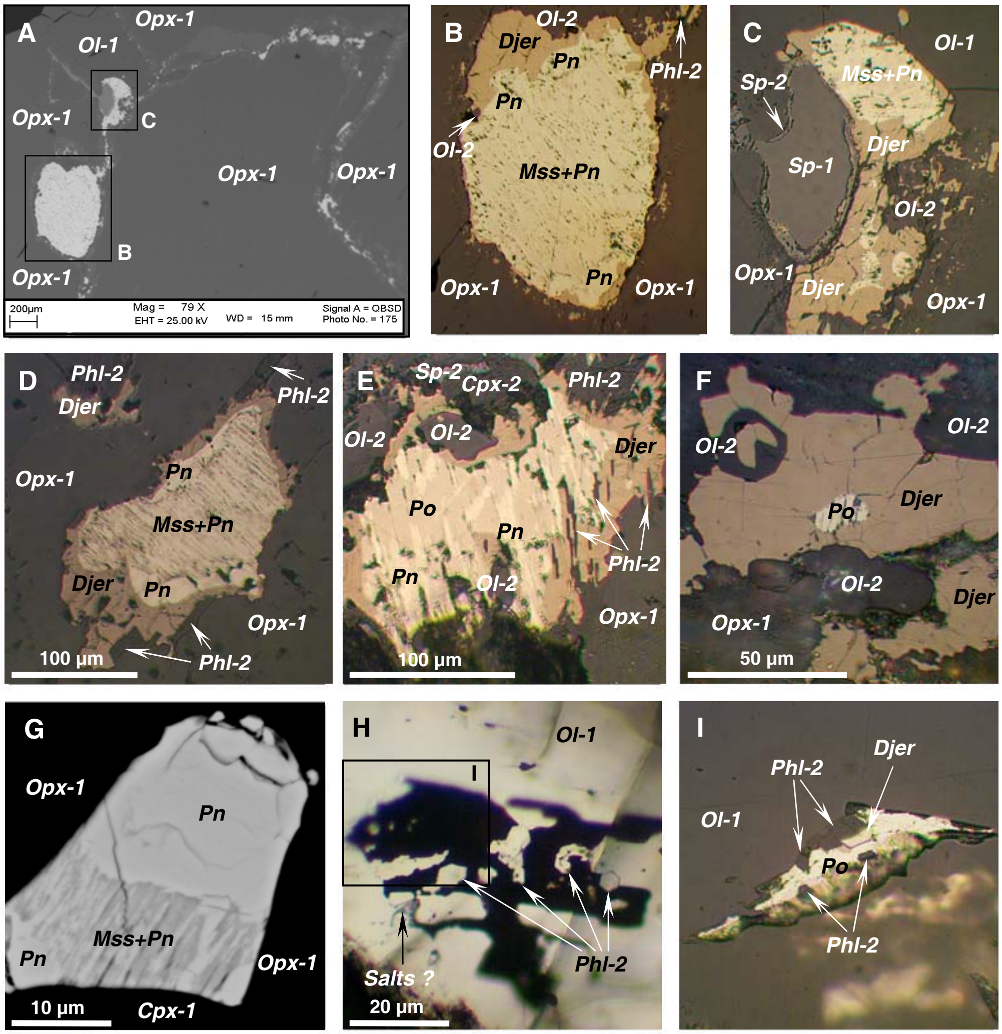

Fig. 3. Djerfisherite and Fe-Ni-sulphides in phlogopite-spinel lherzolite xenolth from the Udachnaya-East pipe.
A – distribution of sulphides in the xenolith; B-G – interstitial sulphide associations in the xenolith; H-I – trails of inclusions in the xenolith olivine-1. A, G – BSE images; B-F, I – reflected light; H – ordinary light.
Symbols: *Opx-1, Ol-1, Cpx-1, Sp-1* – primary orthopyroxene, olivine, clinopyroxenes and Cr-spinel of the xenolith; *Ol-2, Phl-2, Cpx-2, Sp-2* – olivine, phlogopite, clinopyroxene and Cr-spinel from interstices of the xenolith; *Mss* – monosulphide solid solution; *Pn* – pentlandite; *Po* -pyrrhotite; *Salts?* – chlorides + sulphates + carbonates. Other symbols see Figures 1–2.

crofractures in primary silicate minerals of the xenolith (Fig. 3 H–I). The observed textural relationships of the mineral grains clearly indicate that djerfisherite crystallised after silicates and pyrrhotite.

Contact zone between kimberlite and phlogopite-spinel lherzolite xenolith

Djerfisherite is also present in the autolithic kimberlite that rims surfaces of entrapped xenoliths (nodules). Morphologically it resembles interstitial djerfisherite in the xenolith (Fig. 4), and sometimes contains grains of Cu-rich sulphide (chalcopyrite ?) (Fig. 4 G). Mineral relationships indicate crystallisation of djerfisherite after pyrrhotite, and both sulphides after olivine, calcite and other groundmass phases. The compositions of Fe-Ni-sulphides in the xenolith and from a kimberlite-xenolith interface are given in Table 2.

Chemistry of djerfisherite

Djerfisherite appears to be compositionally homogeneous within single grains, but there are strong variations within and between different occurrences in the Udachnaya-East kimberlite (Table 3–5, Fig. 5–6).

Djerfisherite from the groundmass of the kimberlite breccia has the following compositional variations in transition elements (based on 57 analyses, in wt. %): Fe – 37.0–42.7; Ni – 2.0–6.3; Co – 0.2–0.4; Cu – 9.9–14.9. The mineral from the kimberlite breccia has two compositional clusters differing in the Fe, (Ni+Co) and Cu abundances (in apfu: first cluster – 18.7–19.5, 0.7–1.5, 4–5; second cluster – 16.7–18.5, 2–3, 4.5–6, respectively). The Fe-poorer cluster overlaps with the compositions of some djerfisherite grains from the olivine-hosted inclusions of these rocks.

Djerfisherite from the groundmass of monticellite kimberlite is characterized by lower Cu and higher Ni (based on

Table 3. Representative compositions of djerfisherite from olivine-hosted inclusions in kimberlite breccia and monticellite kimberlite, Udachnaya-East pipe.

	1	2	3	4		5	6	7		8		9		10	11	12
wt.%				c	r			c	r	c	r	c	r			
K	8.97	9.10	8.89	8.97	8.92	9.08	9.08	9.08	9.08	9.15	9.27	8.95	8.85	9.12	9.18	9.40
Na	0.06	0.10	0.05	0.08	0.06	0.03	0.06	0.04	0.04	0.00	0.00	0.69	0.44	0.00	0.53	0.35
Fe	35.32	34.31	34.78	36.00	36.03	36.41	35.98	35.40	35.17	37.08	37.06	34.78	34.94	49.03	41.64	40.23
Ni	20.34	20.28	17.54	15.98	15.94	12.17	11.59	10.26	10.52	5.30	5.28	5.33	5.37	5.97	6.99	7.99
Co	0.43	0.39	0.45	0.36	0.38	0.27	0.24	0.31	0.27	0.18	0.20	0.16	0.14	0.28	0.08	0.10
Cu	0.21	1.47	3.57	4.47	4.30	7.54	8.53	10.98	10.79	14.43	14.18	15.95	16.04	0.23	6.52	7.01
S	33.36	33.01	33.35	32.93	32.97	32.89	32.94	32.86	32.74	32.53	32.91	32.80	32.81	33.40	33.16	33.52
Cl	1.33	1.39	1.38	1.33	1.29	1.39	1.24	1.22	1.36	1.38	1.38	1.28	1.43	1.55	1.32	1.37
Total	100.02	100.05	100.01	100.12	99.89	99.78	99.66	100.15	99.97	100.05	100.28	99.94	100.02	99.58	99.41	99.97
Formula based on 26 sulphurs																
K	5.733	5.877	5.683	5.807	5.768	5.886	5.877	5.891	5.913	5.997	6.005	5.817	5.751	5.821	5.902	5.979
Na	0.065	0.110	0.054	0.088	0.066	0.033	0.066	0.044	0.044	0.000	0.000	0.763	0.486	0.000	0.574	0.380
Fe	15.803	15.514	15.566	16.317	16.311	16.523	16.303	16.080	16.034	17.013	16.808	15.827	15.895	21.911	18.743	17.914
Ni	8.658	8.724	7.468	6.891	6.865	5.254	4.996	4.434	4.563	2.314	2.278	2.308	2.324	2.538	2.993	3.385
Co	0.182	0.166	0.191	0.155	0.161	0.116	0.104	0.132	0.117	0.079	0.088	0.067	0.062	0.120	0.032	0.041
Cu	0.084	0.584	1.404	1.781	1.711	3.007	3.397	4.383	4.323	5.819	5.652	6.379	6.413	0.090	2.579	2.743
S	26.000	26.000	26.000	26.000	26.000	26.000	26.000	26.000	26.000	26.000	26.000	26.000	26.000	26.000	26.000	26.000
Cl	0.937	0.990	0.973	0.950	0.920	0.994	0.885	0.873	0.977	0.997	0.986	0.918	1.025	1.091	0.936	0.961

Note: Microprobe beam diameter was 2 μm. 1–9 – kimberlite breccia; 10–12 – monticellite kimberlite; c = core, r = rim of djerfisherite grains.

Table 4. Representative compositions of djerfisherite from groundmass of kimberlite breccia and monticellite kimberlite, Udachnaya-East pipe.

	1	2	3		4		5		6		7	8	9		10	11
wt.%			c	r	c	r	c	r	c	r			c	r		
K	9.07	9.36	9.15	9.14	9.07	9.10	9.21	9.12	9.07	9.02	9.21	9.17	9.25	9.28	9.11	9.18
Na	0.00	0.12	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe	41.72	42.35	38.86	38.80	38.86	39.08	37.91	37.79	37.14	37.03	42.01	42.43	42.13	42.13	40.90	38.63
Ni	2.26	2.24	4.79	4.75	4.79	4.59	4.34	4.33	4.72	4.60	7.17	6.90	6.32	6.33	6.91	7.48
Co	0.21	0.20	0.32	0.33	0.34	0.30	0.39	0.36	0.18	0.18	0.18	0.21	0.20	0.19	0.17	0.15
Cu	9.99	10.60	12.82	12.76	13.04	13.14	14.00	14.09	14.87	14.86	6.20	6.54	7.54	7.37	8.16	9.92
S	32.99	33.02	32.84	32.91	32.89	32.91	32.78	32.69	32.87	32.75	33.38	33.28	33.11	33.15	33.24	33.18
Cl	1.35	1.29	1.40	1.30	1.27	1.22	1.38	1.33	1.34	1.34	1.39	1.38	1.38	1.37	1.43	1.43
Total	97.59	99.18	100.18	99.99	100.26	100.34	100.01	99.71	100.19	99.78	99.54	99.91	99.93	99.82	99.92	99.97
Formula based on 26 sulphurs																
K	5.861	6.043	5.940	5.921	5.879	5.895	5.990	5.948	5.883	5.872	5.882	5.874	5.956	5.968	5.843	5.899
Na	0.000	0.133	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Fe	18.876	19.143	17.662	17.597	17.635	17.724	17.262	17.254	16.865	16.876	18.785	19.029	18.992	18.969	18.365	17.377
Ni	0.973	0.963	2.071	2.050	2.068	1.981	1.880	1.881	2.039	1.995	3.050	2.944	2.711	2.712	2.952	3.201
Co	0.089	0.086	0.140	0.144	0.148	0.127	0.169	0.155	0.076	0.077	0.078	0.089	0.085	0.083	0.071	0.062
Cu	3.972	4.211	5.121	5.086	5.201	5.237	5.602	5.654	5.934	5.952	2.436	2.578	2.987	2.916	3.220	3.922
S	26.000	26.000	26.000	26.000	26.000	26.000	26.000	26.000	26.000	26.000	26.000	26.000	26.000	26.000	26.000	26.000
Cl	0.962	0.919	1.002	0.929	0.908	0.872	0.990	0.957	0.958	0.962	0.979	0.975	0.980	0.972	1.011	1.013

Note: 1–6 – kimberlite breccia; 7–11 – monticellite kimberlite.

36 analyses, in wt. %): Fe – 38.1–43.5; Ni – 5.8–9.2; Co – 0.1–0.2; Cu – 6.1–10.

Broad variations in the contents of transition elements are characteristic of djerfisherite from inclusions in olivine from kimberlite breccias (based on 26 analyses, in wt. %): Fe – 32.6–38.8; Ni – 4.2–23.1; Co – 0.2–0.5; Cu – 0.1–17.6. In contrast, djerfisherite from olivine-hosted inclusions in monticellite kimberlite has Fe-rich compositions (based on 4 analyses, in wt. %): Fe – 40.2–49; Ni – 6–8; Co – 0.1–0.3; Cu – 0.2–7. They fall in the compositional field for the monticellite kimberlite groundmass (Fig. 5). Such broad variations for djerfisherite from inclusions may relate to the source of host olivine (*e.g.*, phenocrysts *vs.* xenocrysts).

In general, djerfisherite from the groundmass of the kimberlite breccia and monticellite kimberlite show negative correlations between Cu and Fe and no significant variation (or only a slight increase) in Ni+Co with increasing Fe. For a given Fe content, djerfisherites from the kimberlite brec-

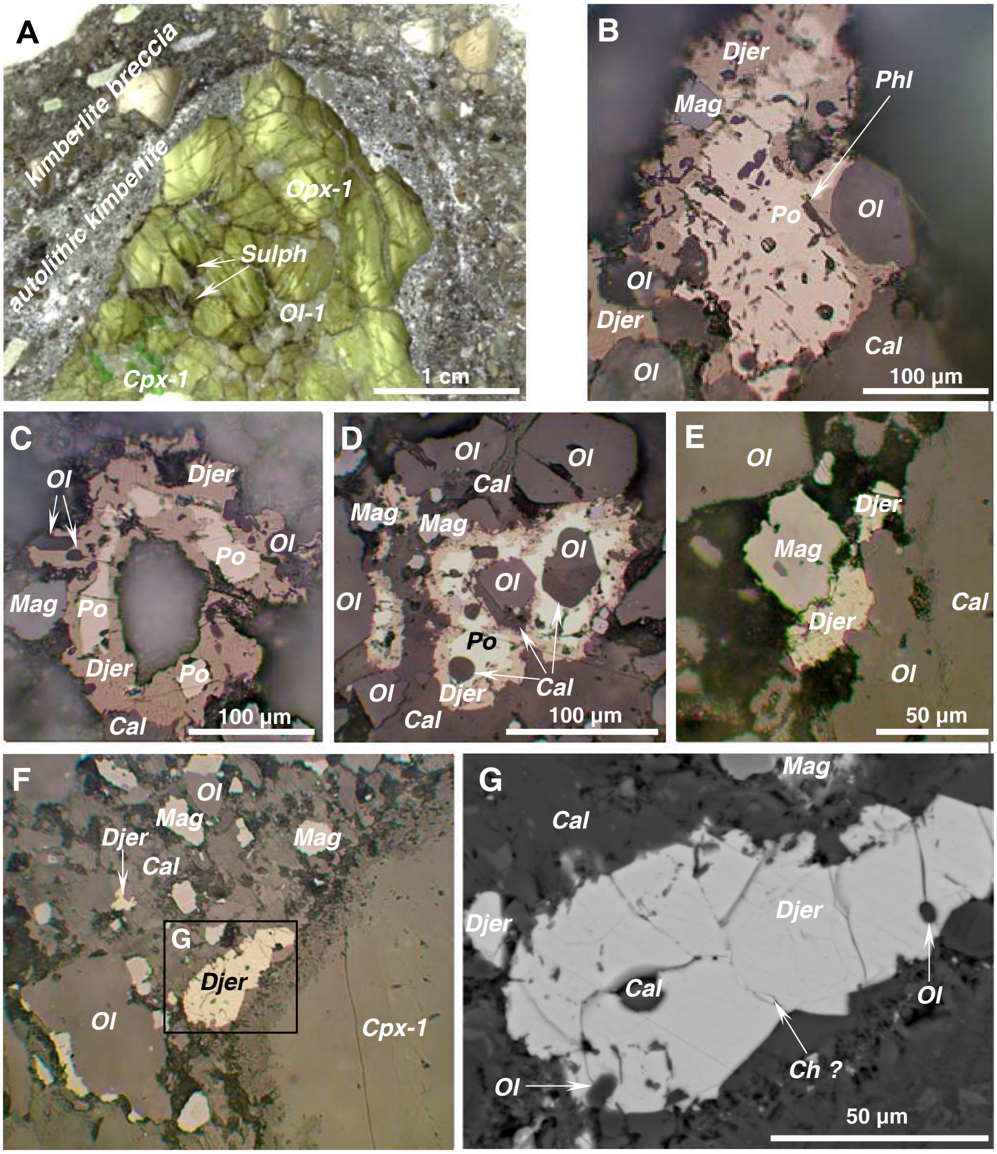

Fig. 4. Djerfisherite and pyrrhotite on the contact between kimberlite breccia and phlogopite-spinel lherzolite xenolith, Udachnaya-East pipe. A – light zone in kimberlite (autolithic kimberlite) on the contact with the xenolith; B-G – djerfisherite and other sulphides in autolithic kimberlite on the contact. A – ordinary light; B-F – reflected light; G – BSE image.
Sulph – polysulphide associations in the xenolith (Fig. 3 B–C); *Ch ?* – Cu-rich sulphide (chalcopyrite ?); other symbols see Figures 1–3.

cia groundmass are enriched in Cu. Djerfisherites from monticellite kimberlites (groundmass and inclusions in olivine) and Fe-rich djerfisherites from olivine-hosted inclusions in kimberlite breccias seem to follow distinct trends of increasing Cu with increasing Ni+Co. Inclusions in olivine from kimberlite breccias show broad compositional variations, no apparent correlation between Cu and Fe, and a strong negative correlation between Cu and Ni+Co. Some of the Ni-poor inclusions overlap with the Fe-poor groundmass djerfisherites in kimberlite breccias.

Djerfisherite in the phlogopite-spinel lherzolite xenolith is rich in Ni and poor in Cu (based on 40 analyses, in wt. %): Fe – 34.0–42.2; Ni – 12.5–19.6; Co – up to 0.2; Cu – 0.4–5.7. K-sulphides from small cavities in the xenolith have similar compositional variations. In contrast, djerfisherite from the contact zone between the xenolith and kimberlite is richer in Fe and poorer in Ni (based on 33 analyses, in wt. %): Fe – 41.1–49.8; Ni – 4.5–8.6; Co – 0.1–0.6; Cu – 0.5–8.3 (Table 5); and thus similar to that from the groundmass and olivine-hosted inclusions of monticellite kimberlite.

The majority of the Udachnaya-East djerfisherite (excluding xenolith) is within the compositional fields of this mineral from the Yakutian diamonds and xenoliths in the Yakutian and Frank Smith (South Africa) kimberlites (Fig. 5). Djerfisherite from the Udachnaya-East kimberlite groundmass is richer in Cu than K-sulphide from the Elwin Bay kimberlite (Clarke *et al.*, 1994). Unlike Udachnaya-East djerfisherite, the Canadian mineral has strong variations in Fe, Cu and Ni within a single grains, from Cu-rich core to Ni-rich rim (Clarke *et al.*, 1994).

Djerfisherite grains from the phlogopite-bearing spinel lherzolite, host kimberlite breccia and their contact are sig-

Table 5. Representative compositions (wt.%) of djerfisherite from phlogopite-spinel lherzolite xenolith and from the contact with kimberlite breccia, Udachnaya-East pipe.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Sulph. association	Mss+ Pn+ Djer	Mss+ Pn+ Djer	Pn+ Po+ Djer	Pn+ Po+ Djer	Po+ Djer	Po+ Djer	Djer	Djer	Mss+ Pn+ Djer	Mss+ Pn+ Djer	Po+ Djer	Po+ Djer	Djer	Djer	Djer	Djer
n	10	2	2	1	1	2	1	2	1	1	2	3	2	4	3	2
K	9.38	9.32	9.29	9.25	9.30	9.33	9.23	9.23	9.04	9.05	9.36	9.33	9.39	9.32	9.34	9.23
Na	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.05	0.05	0.00	0.00	0.00	0.00	0.00	0.00
Fe	35.61	36.34	38.65	34.54	37.11	35.56	33.99	34.64	41.51	35.78	48.39	47.87	49.53	45.21	41.85	41.05
Ni	18.71	16.00	16.64	19.00	18.17	17.82	19.61	15.86	12.77	15.47	6.04	5.48	4.54	7.79	6.74	6.64
Co	0.08	0.01	0.20	0.13	0.18	0.18	0.16	0.00	0.07	0.08	0.46	0.32	0.10	0.14	0.12	0.11
Cu	1.62	3.59	0.49	2.18	0.52	2.25	2.40	5.67	1.95	5.14	0.71	1.89	1.14	2.49	7.10	8.16
S	33.17	33.36	33.45	33.39	33.38	33.35	33.48	33.09	33.28	33.17	33.53	33.35	33.33	33.36	33.38	33.23
Cl	1.38	1.27	1.33	1.31	1.33	1.33	1.32	1.25	1.31	1.33	1.44	1.45	1.39	1.39	1.39	1.38
Total	99.94	99.87	100.05	99.80	99.98	99.81	100.19	99.74	99.98	100.07	99.91	99.69	99.41	99.69	99.93	99.79
Formula based on 26 sulphurs																
K	6.028	5.954	5.921	5.906	5.940	5.965	5.878	5.947	5.791	5.817	5.949	5.964	6.006	5.955	5.963	5.922
Na	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.054	0.057	0.000	0.000	0.000	0.000	0.000	0.000
Fe	16.025	16.262	17.246	15.440	16.594	15.917	15.153	15.625	18.617	16.100	21.544	21.424	22.180	20.230	18.715	18.438
Ni	8.012	6.810	7.064	8.080	7.730	7.587	8.317	6.806	5.449	6.623	2.558	2.333	1.932	3.314	2.869	2.838
Co	0.032	0.003	0.085	0.055	0.074	0.078	0.068	0.001	0.031	0.032	0.192	0.135	0.043	0.057	0.051	0.045
Cu	0.640	1.410	0.192	0.856	0.204	0.885	0.940	2.246	0.769	2.033	0.278	0.742	0.448	0.978	2.791	3.221
S	26.000	26.000	26.000	26.000	26.000	26.000	26.000	26.000	26.000	26.000	26.000	26.000	26.000	26.000	26.000	26.000
Cl	0.981	0.895	0.935	0.922	0.937	0.934	0.927	0.888	0.925	0.943	1.006	1.022	0.977	0.980	0.981	0.973

Note: 1–8 – interstitial in Phl-Sp lherzolite; 9–10 – from cavities in the xenolith, in association with Na-Ca-carbonates and halite; 11–16 – on the xenolith-kimberlite breccia contact. Symbols of sulphides as in Table 2.

nificantly different in composition (Fig. 6). In general, djerfisherite from the xenolith is rich in Ni and poor in Cu, and bears a resemblance to that from sulphide assemblages in diamonds and peridotite xenoliths of Yakutia. In contrast, djerfisherite in the kimberlite groundmass is rich in Cu and poor in Ni. Djerfisherite from the kimberlite-xenolith contact has an intermediate position in the Cu-Ni space (Fig. 6).

The overall compositional data for the Udachnaya pipe (Tables 3–5) show that Cl is an essential component of djerfisherite (1.2–1.6 wt.%) and Na is minor (usually up to 0.2 wt.%, except some grains from inclusions, up to 0.7 wt.%). The variations of S and K are also not significant (32.5–33.9 and 8.9–9.6 wt.%, respectively). Tl was not detected in all studied djerfisherites.

Discussion

Temperature estimates for djerfisherite from the Udachnaya pipe

The synthesis of K-Fe-Ni-sulphides (Clarke, 1979) indicated that djerfisherite may be formed at temperatures from 356°C to at least 950°C, i.e. at temperatures both above and below the solidus in the K-Fe-Ni-S-Cl sulphide system. The crystallisation of djerfisherite in skarns was estimated as 700–820°C (Konev & Samoilov, 1974; Al-Hermezi *et al.*, 1986; Orsoev *et al.*, 1993; Kislov *et al.*, 1994; Jamtveit *et al.*, 1997; Takechi *et al.*, 2000; Pascal *et al.*, 2001; Pertsev *et al.*, 2003). Petrographic relations in the groundmass of kimberlite breccia (Fig. 2) indicate that djerfisherite undoubtedly crystallised after the groundmass olivine and calcite. The homogenisation temperatures of secondary melt inclusions in kimberlite olivine of the Udachnaya-East pipe showed that djerfisherite crystallised at T≤660–800°C (Golovin *et al.*, 2003; Kamenetsky *et al.*, 2004), consistent with estimates of crystallisation temperature for the Udachnaya groundmass olivine (1000–850°C, Golovin, 2004).

It is not easy to evaluate the formation temperature of djerfisherite in the studied phlogopite-spinel lherzolite. Assuming a garnet lherzolite source rock, as suggested by the majority of lherzolites in the Udachnaya-East pipe, and using various geobarometers (Wells, 1977; Brey & Köhler, 1990; Taylor, 1998; Nimis & Taylor, 2000), the compositions of the primary minerals allow rough estimates of the PT-conditions for this xenolith as 700–800°C and 31–33 kbar. However, djerfisherite belongs to the interstitial association of the xenolith. Olivine-spinel thermometry (Fabries, 1979; Sack & Ghiorso, 1991) on the xenolith interstitial phases indicates a temperature range of 520–630°C. For comparison, the study of the Frank Smith xenolith suggested that K-sulphide formed under subsolidus conditions after pentlandite and pyrrhotite at T≤600°C (Clarke *et al.*, 1977; Clarke, 1979).

Djerfisherite in the kimberlite groundmass

The last two decades of intensive research on the petrography and mineralogy of mafic alkaline rocks and carbonatites, have seen increasing evidence that djerfisherite and other "unusual" K-bearing sulphide minerals appear to be more

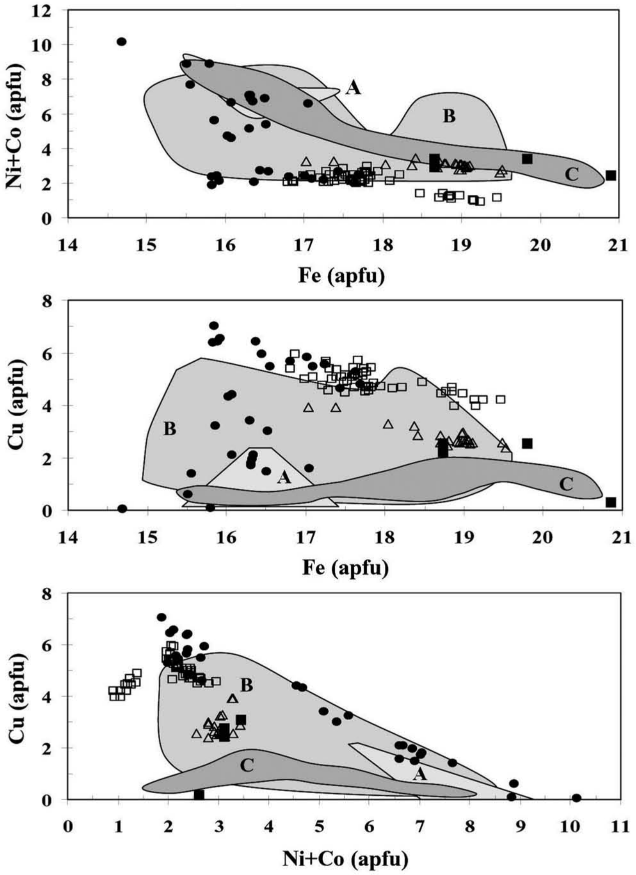

Fig. 5. Compositional variations of djerfisherite (in apfu) from kimberlites of the Udachnaya-East pipe.
Solid circles – from inclusions in olivine of kimberlite breccia; solid squares – from inclusions in olivine of monticellite kimberlite; open squares – from groundmass of kimberlite breccia; open triangles – from groundmass of monticellite kimberlite. Compositional fields of djerfisherite: A – from primary sulphide inclusions in diamonds of Yakutia (Bulanova *et al.*, 1990; Zedgenizov *et al.*, 1998); B – from sulphide associations in deep-seated xenoliths from the Yakutian and South Africa kimberlites (Dobrovol'skaya *et al.*, 1975; Dmitrieva, 1976; Clarke *et al.*, 1977; 1994; Spetsius *et al.*, 1987; Solov'yeva *et al.*, 1988; 1997; Bulanova *et al.*, 1990; Misra *et al.*, 2004; Spetsius, 2004); C – from groundmass of the Elwin Bay kimberlites (Clarke *et al.*, 1994).

common than previously thought (Yeremeer *et al.*, 1982; Dawson *et al.*, 1992; 1995; Kogarko *et al.*, 1991; Clarke *et al.*, 1994; Barkov *et al.*, 1997; Mitchell, 1997; Henderson *et al.*, 1999; Jago & Gittins, 1999; Panina *et al.*, 2001; Pekov *et al.*, 2003; Sharygin *et al.*, 2003). The main result of this study of the djerfisherite occurrence in the Udachnaya-East kimberlite is that this mineral, although accessory in amount, represents an important constituent of a late magmatic assemblage. Thus, associations and chemical composition of djerfisherite can be used in characterising those stages of kimberlite magma evolution that are typically obscured by post-emplacement modifications.

Djerfisherite and other potassium sulphides are common late-stage phases in volcanic and intrusive carbonatites and related alkaline silicate rocks (Ifantopulo *et al.*, 1978; Balabonin *et al.*, 1980; Czamanske *et al.*, 1979; 1981; Dawson *et al.*, 1992; 1995; Solovova *et al.*, 1996; Henderson *et al.*, 1999; Barkov *et al.*, 1997; Mitchell, 1997; Stoppa *et al.*, 1997; Jago & Gittins, 1999; Sukharzhevskaya & Artyukhova, 2000; Panina *et al.*, 2001; Yakovenchuk *et al.*, 2003). The occurrence of djerfisherite in diverse magmatic and metasomatic rocks implies widely variable conditions of its origin. However, the strict association of djerfisherite and other potassium sulphides with carbonates and graphite indicates that these minerals have strong affinities with carbon-rich systems.

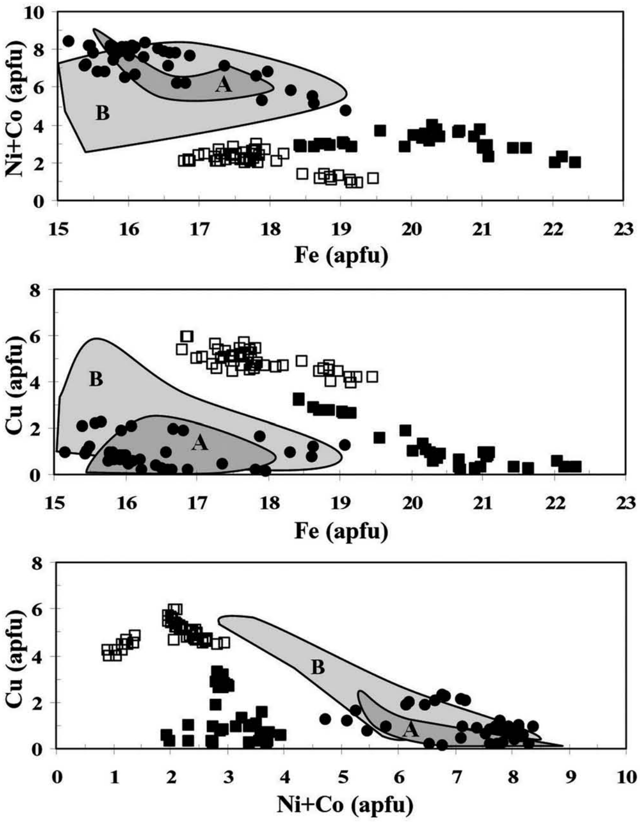

Fig. 6. Compositional variations of djerfisherite (in apfu) from phlogopite-spinel lherzolite xenolith and contact between kimberlite breccia and xenolith, Udachnaya-East pipe.
Solid circles – from phlogopite-spinel lherzolite; solid squares – on the contact between kimberlite breccia and xenolith; open squares – from groundmass of kimberlite breccia. Compositional fields of djerfisherite: A – from primary sulphide inclusions in diamonds of Yakutia (Bulanova *et al.*, 1990; Zedgenizov *et al.*, 1998); B – from sulphide associations of peridotite xenoliths in kimberlites of Yakutia (Bulanova *et al.*, 1990; Spetsius *et al.*, 1987; Spetsius, 2004).

Petrographic data show that djerfisherite in the unaltered kimberlites of the Udachnaya-East pipe is a primary magmatic mineral belonging to the stage of groundmass crystallisation. It has been suggested that the initial Udachnaya-East kimberlite melt evolved towards carbonate-rich residua enriched in Cl and S (Golovin *et al.*, 2003; Kamenetsky *et al.*, 2004) after extensive olivine and phlogopite fractionation. The remaining (residual) magma was parental to djerfisherite, which is, in essence, originated in a volatile-rich silicate-carbonate mush. Presumably, a large variety of late-stage magmatic liquids/fluids could be formed by variable

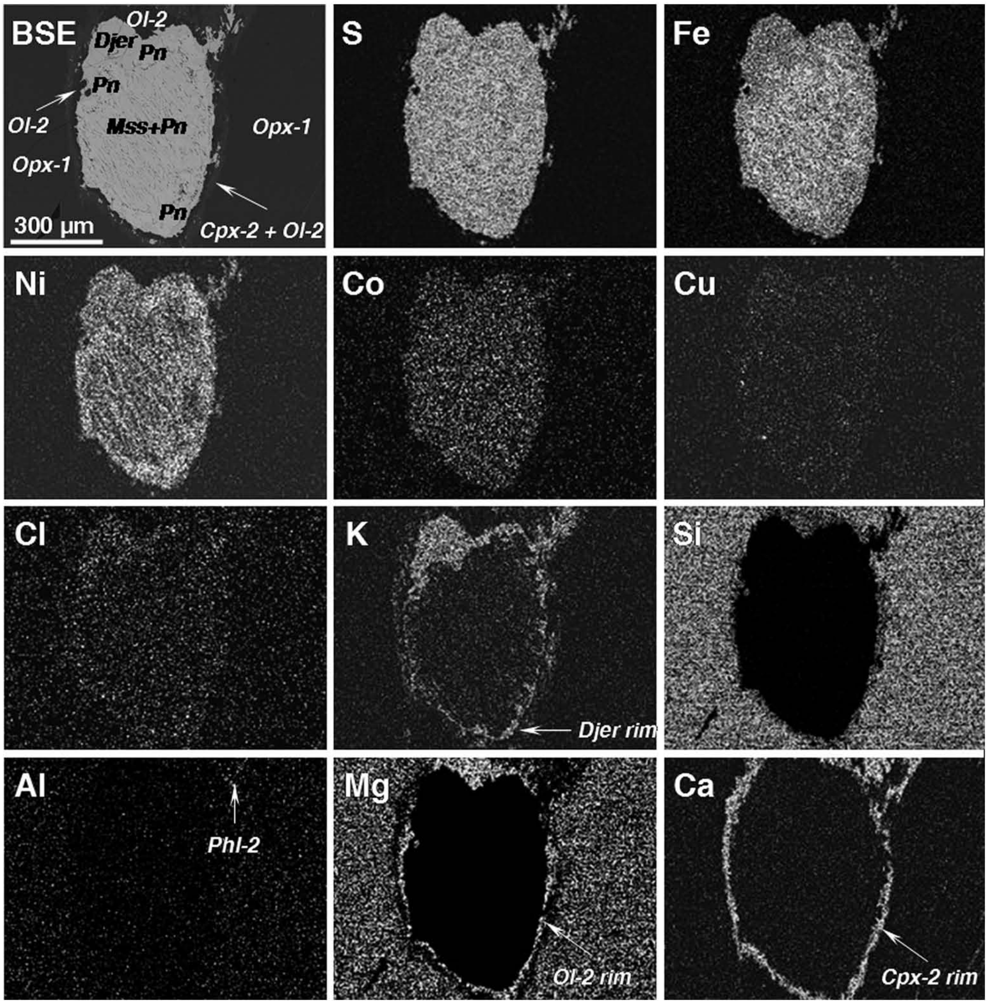

Fig. 7. BSE image and X-ray maps for an interstitial association in phlogopite-spinel lherzolite xenolith in kimberlite breccia, Udachnaya-East pipe. For details see Fig. 3 A–B.

degrees of closed system fractionation, giving rise to different assemblages and compositions of late magmatic minerals, including djerfisherite. For example, monticellite kimberlite is characteristically depleted in carbonate minerals, but enriched in monticellite and sodalite compared with the dominant kimberlite breccia. The differences in mineral compositions are clearly reflected in the whole-rock chemical compositions which were interpreted as crystallisation products of evolved kimberlite magmas with possible effects of contamination by platform evaporites (Kornilova *et al.*, 1998). However, in our opinion, the absence of halide-rich rocks in the sedimentary suite around the pipe (according to core drilling down to 1700 m) does not support such mechanism. Alternatively, monticellite kimberlite and kimberlite breccias may represent distinct differentiates of the parental kimberlite melt. In this case, the differences in composition of djerfisherites from particular kimberlite rock types of the Udachnaya-East pipe would reflect the different compositions of the parent melt.

The appearance of such K-Cl-bearing sulphides as djerfisherite $K_6NaFe_{24}S_{26}Cl$, bartonite $K_6Fe_{24}S_{26}(S,Cl)$ and chlorobartonite $K_6Fe_{24}S_{26}(Cl,S)$ in magmatic and metasomatic rocks, and even in carbonaceous chondrites also highlights the importance of chlorine in the system. Chlorine-rich solutions are common components in skarn-forming systems. Continuous build-up of the Cl abundances is typical of evolution of carbonatitic and peralkaline magmas in which Cl-rich silicates and chlorides are common late crystallisation products (Kostyleva-Labuntsova *et al.*, 1978; Dawson *et al.*, 1995; Henderson *et al.*, 1999; Mitchell, 1997; Stoppa *et al.*, 1997; Panina *et al.*, 2001; Pekov *et al.*, 2003). The Cl-enriched nature of Udachnaya-East kimberlites has been suggested in a number of studies, although the origin of the Cl enrichment is still under debate (Pavlov & Ilupin, 1973; Kornilova *et al.*, 1998; Golovin *et al.*, 2003; Kamenetsky *et al.*, 2004). In other djerfisherite-bearing kimberlites (*e.g.* Elwin Bay, Clarke *et al.*, 1994), the presence of this mineral may indicate high activity of Cl in the magma, even if Cl is depleted in the rocks. On the other hand, in the absence of comprehensive experimental data on the synthesis of djerfisherite, we are not in position to argue to what extent a high chlorine activity is essential for crystallisation of K-Cl-bearing sulphides. Chlorine-poor or even chlorine-free djerfisherite and bartonite may indeed occur in some magmatites and skarns

(Balabonin *et al.*, 1980; Barkov *et al.*, 1997; Czamanske *et al.*, 1981; Dobrovol'skaya *et al.*, 1975; Kislov *et al.*, 1994; Kostyleva-Labuntsova *et al.*, 1978; Stoppa *et al.*, 1997; Pekov *et al.*, 2003; Spetsius, 2004). Sometimes Cl-rich and Cl-poor varieties may coexist in the same rock (Czamanske *et al.*, 1981; Pekov *et al.*, 2005).

Djerfisherite in phlogopite-spinel lherzolite xenolith

The most pronounced feature of djerfisherite in the phlogopite-spinel lherzolite xenolith is that this mineral partially or completely replaced early Ni-Fe-rich and Cu-poor sulphide associations (monosulphide solid solution + pentlandite, pentlandite + pyrrhotite, Fig. 3). Djerfisherite from the xenolith-kimberlite contact replaced pyrrhotite only (Fig. 4).

The occurrence of djerfisherite in the lherzolite xenolith and on the contact with kimberlite possibly implies a metasomatic origin, *e.g.* due to infiltration of evolved kimberlitic fluid/melt into xenolith, or reaction between xenolith and kimberlite melt. The interstitial associations shown in Figures 3 and 7 indicate that not only djerfisherite, but also interstitial silicate and oxide phases (olivine, clinopyroxene and phologopite, Table 1) are the products of this event.

Previous studies on djerfisherite from mantle-derived xenoliths and xenocrysts (Dobrovol'skaya *et al.*, 1975; Clarke *et al.*, 1977; Govorov *et al.*, 1984; Spetsius *et al.*, 1987; Solov'yeva *et al.*, 1988; 1997; Bulanova *et al.*, 1990; Misra *et al.*, 2004; Spetsius, 2004) directly showed that this mineral typically forms after primary mantle sulphides, due to metasomatising fluids/melts, either prior to or after entrapment in the host kimberlite. However, in most cases the sources of metasomatising agents and P-T-conditions for the primary sulphide replacement remain unspecified. Based on our results on the phlogopite-spinel lherzolite xenolith from the Udachnaya pipe we can speculate that all djerfisherites in xenoliths from kimberlites may be products of reactions between evolved kimberlitic melt/ fluid and primary sulphides at shallow depths. In the case of djerfisherites rimming primary sulphide blebs in diamonds and in primary silicate and oxide minerals of mantle-derived xenoliths, penetration of this fluid/melt could be aided by microfracturing caused by crystallisation and transformation of sulphide melt (Bulanova *et al.*, 1990). For the primary sulphide associations occurring in intergranular space of mantle xenoliths direct crystallisation of djerfisherite from the infiltrating kimberlitic melt can not be excluded. If this is the case, primary sulphides, especially pentlandite, might act as seeds for djerfisherite, owing to similarities of their crystal structures (Evans & Clark, 1981).

Acknowledgments: The authors would like to thank Drs. L.N. Pospelova and A.T. Titov (IGM, Novosibirsk) for assistance during microprobe analysis and scanning microscopy, respectively. Reviews and comments by Prof. Angelo Peccerillo, Prof. Roger Mitchell, Dr. Frances Wall and anonymous reviewer significantly improved this manuscript. Dr. Paul Davidson is thanked for improving English. This work was supported by the Russian Foundation of Basic Research (grant no. 02-05-64620, 04-05-64886), Siberian Division of RAS (integration project no. 6.15) and the Australian Research Council's Fellowship and Discovery Grant to VSK.

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Received 29 June 2006
Modified version received 27 September 2006
Accepted 13 November 2006