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GEOCHEMISTRY

Djerfisherite in Unaltered Kimberlites of the Udachnaya-East Pipe, Yakutia

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Djerfisherite $K_6Na(Fe, Ni, Cu)_{24}S_{26}Cl$, first discovered in meteorites [1], was subsequently found in Cu–Ni ores, kimberlites, alkaline ultrabasic rocks and carbonatites, peralkaline rocks, and in skarns around alkaline rock massifs. Clarke *et al.* [2] presented a review on findings of djerfisherite and its genesis. New relevant information was discussed in [3–5]. Djerfisherite is rare in kimberlites. This mineral was first identified in diamonds and xenoliths from kimberlites of Yakutia and South Africa as a phase that rims the primary Fe–Ni–Cu sulfides [6–8]. Subsequently, djerfisherite was detected in the groundmass of Canadian kimberlites from the Northwest Territories as a primary phase crystallized at the late magmatic stage [2, 9].

In this communication, we report the results of a comprehensive examination of djerfisherite from the groundmass of unaltered kimberlite breccia and the monticellite kimberlite of the Udachnaya-East pipe. Previously we had only detected and analyzed djerfisherite from secondary melt inclusions in olivine of kimberlite breccia [10].

The studied kimberlite breccia is related to the third, major stage of the Udachnaya-East pipe emplacement. This rock occurs in the central part of the pipe at a depth greater than 350 m and contains many mantle-derived xenocrysts, xenoliths, and the crustal xenogenic material. Phenocrysts are composed of olivine and phlogopite. The groundmass consists of olivine, calcite, phlogopite, perovskite, zonal spinel (chromite–titanomagnetite–magnetite), ilmenite, djerfisherite, pyrrhotite, and, probably, Na–Ca-carbonates. Monticellite kimberlite is a younger intrusive phase with respect to kimberlite breccia and is occasionally observed as large blocks or injections [11]. We studied the thin (up to 2–3 cm) black-colored veinlets of the monticellite rock. The amount of xenogenic material in the monticellite kimberlite is less than 5 vol %. Phenocrysts are composed of olivine and less abundant phlogopite. The groundmass contains olivine, perovskite, phlogopite monticellite, sodalite, and djerfisherite. The studied kimberlite samples are nearly devoid of signs indicating secondary alteration. It should also be noted that djerfisherite is a prevalent sulfide phase in all the kimberlitic rocks studied.

Djerfisherite is the latest phase in the groundmass of kimberlite breccia and occurs either as separate grains (up to 50–100 μm in size) in close association with magnetite and sporadic pyrrhotite, or as a filling of the interstitial space between other minerals. Olivine, calcite, and other groundmass minerals are observed as inclusions in djerfisherite (Figs. 1a–1d).

Djerfisherite also occurs in secondary inclusions grouped as chains within olivine phenocrysts. Olivine-hosted djerfisherite is found as isolated sulfide globules (up to 30 μm in diameter) or individual phases in the polymineral and secondary melt inclusions (5–80 μm). This mineral is associated in melt inclusions with carbonates, silicates, magnetite, chlorides, sulfates, and Ni-pyrrhotite containing 4.4 wt % Ni [10]. The size of djerfisherite grains varies from 2 to 15 μm. The melt inclusions, which homogenize at 700–800°C, were captured under shallow conditions [10]. The polymineral inclusions are composed of calcite, magnetite, and djerfisherite (Fig. 1e).

Djerfisherite contained in the monticellite kimberlite, together with monticellite, perovskite, and magnetite, makes up rounded segregations (up to 20 μm in diameter) in the groundmass and poikilitic sodalite (Fig. 1f).

The chemical composition of djerfisherite was determined with a CAMEBAX microprobe at the United Institute of Geology, Geophysics, and Mineralogy, Novosibirsk. Grains larger than 10 μm in diameter were selected for microprobe analysis (beam, 2 μm). Djerfisherite from olivine-hosted inclusions in the kimberlite breccia is characterized by the maximal compositional variation (wt %): Fe 32.6–38.8, Ni 4.2–23.1, Co 0.2–0.5, Cu 0.1–17.56, K 8.9–9.3, Na 0.04–0.70, S 32.5–33.4, and Cl 1.2–1.4. However, the variation from the core to margin within a single grain is insignificant. Djerfisherite from the groundmass of kimberlite breccia and monticellite kimberlite is characterized by narrower ranges of Fe, Ni, and Cu contents and minimal compositional variation within a grain (table). For

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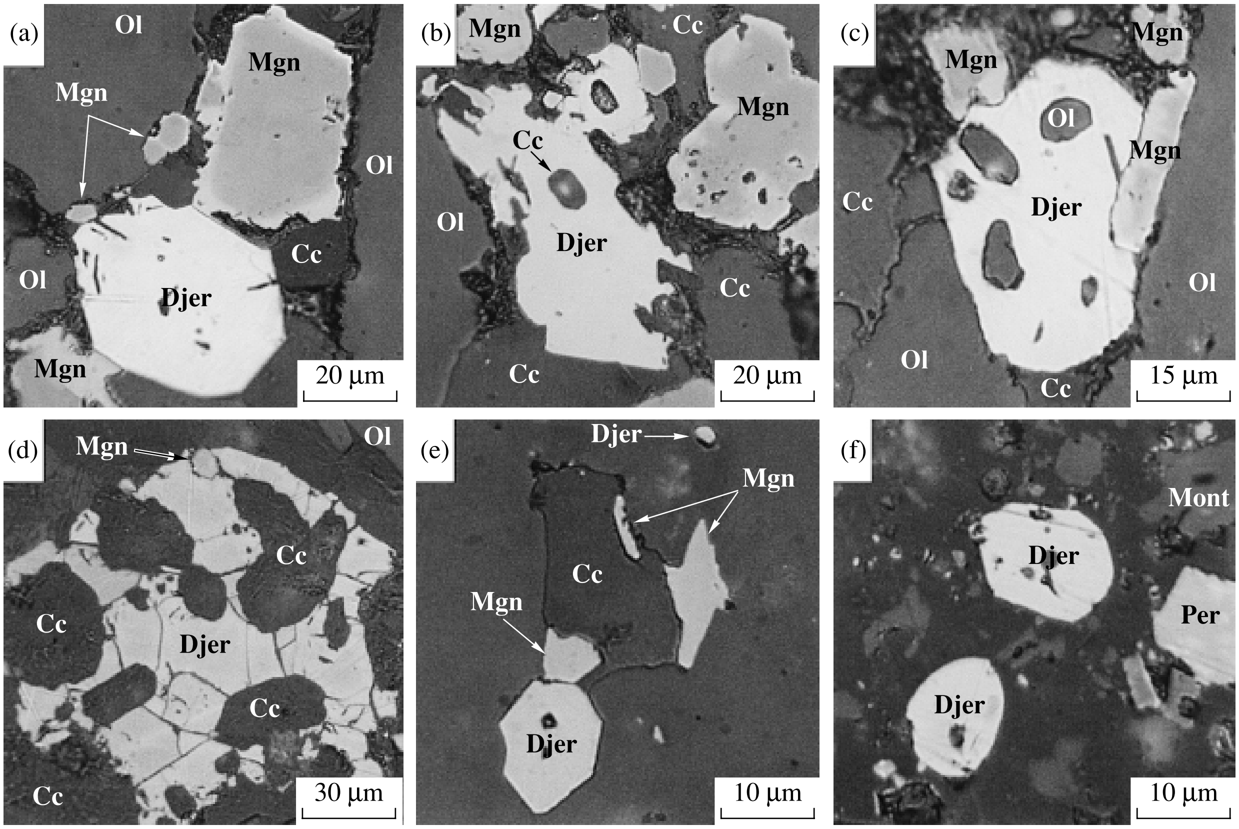

Fig. 1. Djerfisherite from kimberlites of the Udachnaya-East pipe (reflected light). Kimberlite breccia: (a) polygonal grain in the groundmass associated with a zonal spinel (Cr-spinel in the center, Ti-magnesioferrite in the middle zone, and magnesioferrite in the rim), olivine, and calcite; (b) xenomorphic grain with calcite inclusion; (c) grain with olivine inclusion; (d) secondary polymineral inclusion (calcite + magnetite + djerfisherite) in the marginal zone of olivine xenocryst; (e) djerfisherite globules in association with monticellite and perovskite within sodalite oikocryst in the monticellite kimberlite. (Djer) djerfisherite, (Mgn) zonal spinel, (Ol) olivine, (Cc) calcite, (Mont) monticellite, (Per) perovskite.

example, djerfisherite from the kimberlite breccia groundmass has the following composition (wt %): Fe 37.0–42.7, Ni 2.0–6.3, Co 0.2–0.4, Cu 9.9–14.9, K 8.8–9.4, Na 0–0.2, S 32.6–33.3, and Cl 1.2–1.5. The K-sulfide from the monticellite kimberlite groundmass is characterized by lower Cu and higher Ni contents (wt %): Fe 38.1–43.5, Ni 5.8–7.9, Co 0.15–0.22, Cu 6.1–10.0, K 9.1–9.4, S 33.1–33.4, and Cl 1.3–1.5 (table).

The difference between djerfisherite from the inclusions in olivine, on the one hand, and groundmass of kimberlite breccia and monticellite kimberlite, on the other hand, is clearly seen in the variation diagram (Fig. 2). The djerfisherite from the kimberlite breccia groundmass is subdivided into two groups by Cu content and one of them overlaps part of the K-sulfide domain of olivine-hosted inclusions. This indicates that part of the djerfisherite in olivine is probably a result of injection of the residual kimberlitic melt [10], whereas the remaining djerfisherite in olivine xenocrysts was likely formed as a result of primary sulfide replacement. In general, djerfisherite from the groundmass of kimberlite breccia and monticellite kimberlite reveals a negative correlation between Fe and Cu, and this likely suggests isomorphism of these elements in djerfisherite structure. At the same time, there is no correlation between Cu and (Ni + Co). In contrast to the groundmass, djerfisherite in olivine-hosted inclusions shows a negative correlation between Cu and (Ni + Co).

We compared djerfisherite composition in kimberlite of the Udachnaya-East pipe with the literature data on djerfisherite from sulfide assemblages in diamond and xenoliths of Yakutian kimberlites and from the groundmass of Canadian kimberlites [2, 6–8]. The majority of djerfisherite compositions from the Udachnaya-East pipe fall into the domain of this mineral from Yakutian diamonds and xenoliths (Fig. 2). However, djerfisherite from the kimberlite groundmass of this pipe is enriched in Cu relative to the counterpart from the Elwin Bay kimberlite, Canada [2].

The data obtained indicate that djerfisherite from the Udachnaya-East kimberlite is probably a product of the late magmatic crystallization when the residual melt was close to carbonatitic liquid in composition [10]. It should be noted that djerfisherite and other potassium sulfides are rather common late phases in volcanic and intrusive carbonatites and genetically related alkaline

Representative compositions of djerfisherite from kimberlites of the Udachnaya-East pipe, wt %

Element	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
K	8.94	8.95	9.05	9.00	9.01	9.30	9.04	9.38	9.02	9.10	9.27	9.25	9.23	9.14	9.41
Na	0.08	0.69	<0.05	0.05	0.07	0.09	<0.05	0.19	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Fe	34.82	34.78	38.83	35.96	32.56	42.79	42.23	42.73	37.03	38.99	43.49	42.13	43.40	38.07	40.85
Ni	4.20	5.33	5.45	15.54	23.09	1.97	1.98	2.50	4.60	6.30	5.84	6.32	6.35	7.55	7.85
Co	0.17	0.16	0.26	0.34	0.50	0.19	0.20	0.19	0.18	0.49	0.19	0.20	0.18	0.17	0.15
Cu	17.56	15.95	12.01	4.88	0.06	10.66	9.93	10.47	14.86	11.33	6.53	7.54	6.05	10.00	7.23
S	32.81	32.80	32.74	32.88	33.09	33.18	32.90	32.77	32.75	32.68	33.31	33.11	33.18	33.37	33.10
Cl	1.35	1.28	1.35	1.32	1.29	1.33	1.33	1.40	1.34	1.29	1.41	1.38	1.40	1.45	1.42
Total	99.93	99.94	99.69	99.97	99.67	99.51	97.61	99.63	99.78	100.18	100.04	99.93	99.80	99.75	100.01
K	5.81	5.82	5.89	5.84	5.81	5.98	5.86	6.10	5.87	5.94	5.93	5.96	5.93	5.84	6.06
Na	0.09	0.76	0.00	0.06	0.08	0.10	0.00	0.21	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe	15.84	15.83	17.70	16.32	14.69	19.25	19.16	19.46	16.88	17.81	19.49	18.99	19.52	17.03	18.42
Ni	1.82	2.31	2.36	6.71	9.91	0.84	0.86	1.08	2.00	2.74	2.49	2.71	2.72	3.21	3.37
Co	0.07	0.07	0.11	0.14	0.21	0.08	0.09	0.08	0.08	0.21	0.08	0.09	0.08	0.07	0.07
Cu	7.02	6.38	4.81	1.95	0.02	4.21	3.96	4.19	5.95	4.55	2.57	2.99	2.40	3.93	2.87
S	26.00	26.00	26.00	26.00	26.00	26.00	26.00	26.00	26.00	26.00	26.00	26.00	26.00	26.00	26.00
Cl	0.97	0.92	0.97	0.94	0.92	0.94	0.95	1.00	0.96	0.93	1.00	0.98	0.99	1.02	1.01

Note: (1–5) inclusions in olivine xenocrysts from kimberlite breccia; (6–10) groundmass of the kimberlite breccia; (11–15) groundmass of monticellite kimberlite. The formula was calculated for 26 sulfur atoms.

rocks [3–5]. The phenocryst crystallization gradually shifts the composition of kimberlitic melt toward carbonatite. The carbonate crystallization from the silicate–carbonate melt likely enhanced the stability of djerfisherite. Monticellite kimberlite principally differs in mineral composition of groundmass from the kimberlite breccia, particularly, by the absence (or minor presence) of carbonate and presence of monticellite and sodalite [11]. This shows that the kimberlitic melt had somewhat different composition at the late stage. The composition and character of kimberlitic melt evolution at various stages of the Udachnayay-East pipe formation likely determined the specific composition of djerfisherite.

The comparison of chemical composition of djerfisherite from kimberlites and xenoliths therein allows us to draw some inferences concerning the genesis of this sulfide in xenoliths and xenocrysts. Results of previous investigations [6–8] show that djerfisherite in diamond and xenoliths is a secondary mineral formed after primary mantle sulfides under the influence of metasomatizing fluid (or melt) enriched in K, Cl, S and other components. At present, the source of the metasomizing agent and *PT* parameters of fluid impact on the primary sulfides remain debatable issues. The metasomatism of primary mantle sulfides by the fluid or melt is supposed to take place at the following alternative stages: (1) before their entrapment by the kimberlitic melt; (2) during xenolith transport to the surface; or (3) at the late magmatic (or postmagmatic) stage of kimberlite formation [2, 6–8].

At the present time, some strong arguments favor the mantle origin of djerfisherite. In particular, the presence of primary phlogopite and biotite inclusions with diamond faceting (occasionally, as intergrowths with garnet and omphacite) and primary inclusions of complex K-titanates in diamonds from different regions of the world convincingly indicate the possible existence of K- and Cl-bearing fluids or melts in the mantle within the diamond stability field [12–14].

At the same time, it cannot be ruled out that djerfisherite in diamonds and xenoliths from kimberlites is a reaction product of a residual kimberlitic melt (or related fluid) with primary mantle sulfides in the shallow environment. In other words, the kimberlitic melt and related fluids could serve as a metasomatizing agent. When djerfisherite makes up an outer rim of the primary sulfide inclusions in diamonds and minerals of the mantle-derived xenoliths, it can be suggested that the fluid or melt penetrated along the fractures that are commonly formed around inclusions during the crystallization or transformation of the sulfide melt [8]. As concerns the mantle sulfide assemblages in the interstitial space of xenoliths, djerfisherite could be formed as a result of both reaction processes and melt crystallization. In this case, the primary sulfides, first of all, structurally close pentlandite [15], could serve as seeds for the djerfisherite crystallization from a residual kimberlitic melt injected into xenolith through the intergranular space.

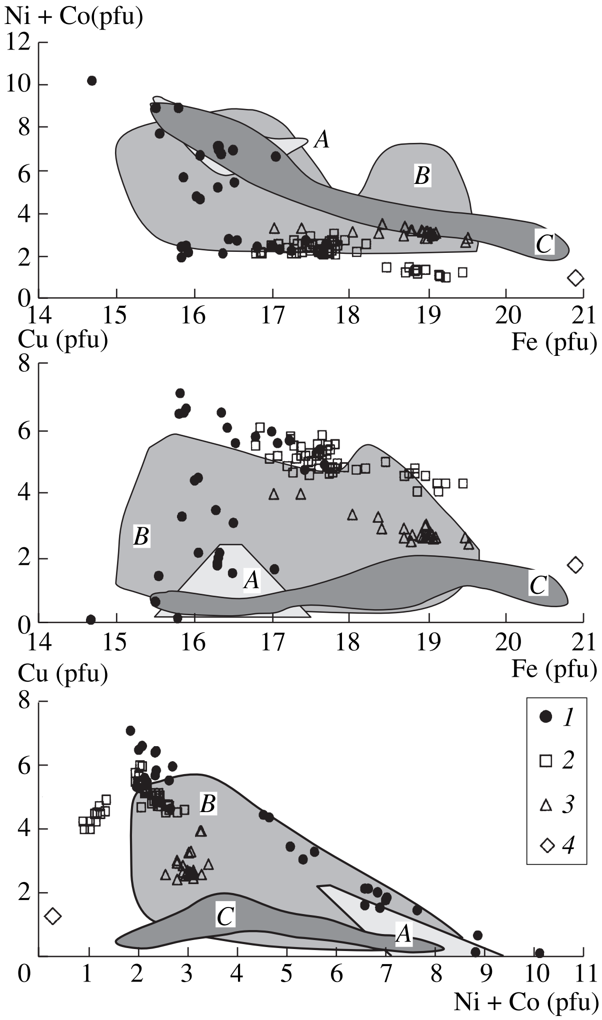

Fig. 2. Variation of djerfisherite composition (pfu). Djerfisherite from the Udachnaya-East pipe: (*1*) inclusions in olivine from kimberlite breccia, (*2*) groundmass of the kimberlite breccia, (*3*) groundmass of monticellite kimberlite; (*4*) djerfisherite from meteorites [1]. Fields of djerfisherite compositions: (*A*) primary sulfide inclusions in diamonds from Yakutian kimberlites [8], (*B*) sulfide assemblages in mantle-derived xenoliths from Yakutian kimberlites [6–8], (*C*) groundmass of the Elwin Bay kimberlite, Canada [2].

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