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DJERFISHERITE IN THE GULI DUNITE COMPLEX, POLAR SIBERIA: A PRIMARY OR METASOMATIC PHASE?

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Abstract

The uncommon sulfide djerfisherite, ideally $K_6(Fe,Cu,Ni)_{25}S_{26}Cl$, occurs in the dunite portion of the Guli complex, located in Polar Siberia, Russia. Distinctive features of the Guli complex are its considerable size, ~2000 km^2, making it the largest dunite–clinopyroxenite massif in the world, and its complicated geology. The exposed part is composed predominantly (60%) of variably serpentinized dunite. Melanocratic alkaline rocks cover about 30%, and other rock types, including melilitolite, ijolite, alkaline syenite and carbonatite, occupy less than 10% of the area. The sample with the most abundant djerfisherite is a coarse-grained phlogopite–magnetite-rich clinopyroxenite. Djerfisherite most commonly occurs in irregular patches of sulfide composed mainly of pyrrhotite accompanied by minor chalcopyrite and rare galena, in a matrix of Ti-bearing andradite, clinopyroxene, phlogopite, plagioclase, apatite and rare zircon, titanite and pyrophanite. It forms crystals generally less than 100 μm in size and occurs as irregular single-phase grains or it fills fissures of the silicate matrix and infiltrates phlogopite along its cleavage planes. We provide new data on the physical and crystallographic properties of djerfisherite. Its composition is characterized by an extensive substitution among Fe, Cu and Ni; their reciprocal substitutions are mainly controlled by the nature of the host rock. The djerfisherite from the Guli complex is Cu-rich and resembles that reported from alkaline rocks. This feature is consistent with the proposal that djerfisherite in the Guli complex crystallized as a primary mineral, during the late-stage fractionation of a highly alkaline melt portion, derived from successive fractional melting of an ascending mantle plume under metasomatic conditions.

Keywords: djerfisherite, Raman spectroscopy, crystal-structure analysis, Guli dunite complex, mantle, Siberia, Russia.

Sommaire

La djerfisherite, de formule idéale $K_6(Fe,Cu,Ni)_{25}S_{26}Cl$, sulfure assez inhabituel, a été trouvée dans la dunite du complexe de Guli, située en Sibérie polaire, en Russie. Le complexe de Guli se distingue par sa dimension, environ 2000 km^2, ce qui en fait le massif de dunite–clinopyroxénite le plus grand au monde, et par la complexité des relations géologiques. Les affleurements consistent surtout (60%) de dunite variablement serpentinisée. Les roches alcalines mélanocratiques couvrent environ 30%, et les autres variétés de roches, y inclus mélilitolite, ijolite, syénite alcaline et carbonatite, occupent moins de 10% de la superficie. L'échantillon contenant la plus grande proportion de djerfisherite est une clinopyroxénite à phlogopite–magnétite à gros grains. La djerfisherite se présente surtout en amas irréguliers de sulfures faits de pyrrhotite avec chalcopyrite accessoire et galène plus rare, dans une matrice d'andradite titanifère, clinopyroxène, phlogopite, plagioclase, apatite, et zircon, titanite et pyrophanite plus rares. Elle se présente en monocristaux irréguliers, généralement de moins de 100 μm, ou bien elle remplit les fissures dans la matrice silicatée et s'infiltre dans la phlogopite le long de clivages. Nous avons effectué de nouvelles mesures des propriétés

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physiques et cristallographiques de la djerfisherite. Elle montre un taux de substitution étendu impliquant Fe, Cu et Ni; les substitutions réciproques sont surtout régies par la nature des roches hôtes. La djerfisherite du complexe de Guli est riche en Cu, et ressemble à celle des roches alcalines. Cette caractéristique concorde avec l'hypothèse voulant que la djerfisherite du complexe de Guli aurait cristallisé comme minéral primaire à un stade tardif du fractionnement d'un magma fortement alcalin, dérivé par fusion partielle successive d'un panache mantellique montant, activement impliqué dans une métasomatose.

(Traduit par la Rédaction)

Mots-clés: djerfisherite, spectroscopie de Raman, analyse de la structure cristalline, complexe dunitique du massif de Guli, manteau, Sibérie, Russie.

INTRODUCTION

In 1966, Fuchs described djerfisherite, a new species in an enstatite chondrite, and proposed the formula $K_3(Na,Cu)(Fe,Ni)_{12}S_{14}$ for this uncommon sulfide. The formula $K_6Na(Fe,Cu,Ni)_{24}S_{26}Cl$ was proposed by Dmitrieva (1976), Dmitrieva *et al.* (1978) and Czamanske *et al.* (1979) on the basis of crystal chemistry and findings about its structure. However, the composition of terrestrial djerfisherite deviates from this formula, as the Na site is fully occupied by transition elements, generally Cu. As a result, the formula $K_6(Fe,Cu,Ni)_{25}S_{26}Cl$ proposed by Henderson *et al.* (1999) is considered the most appropriate for terrestrial djerfisherite. This mineral can be grouped among the various sulfides approaching the ideal formula Fe_8S_{14}, such as pentlandite, $(Fe,Ni)_9S_8$, argentopentlandite, $Ag(Fe,Ni)_8S_8$, 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, $(Ba,Pb)_6(Cu,Fe,Ni)_{25}S_{27}$ (Sharygin *et al.* 2007). Djerfisherite has been found in various meteorites (El Goresy *et al.* 1971, Kimura & El Goresy 1988, Ntaflos *et al.* 1988, Lin & El Goresy 2002, Muenow *et al.* 1992), and it has been reported from a variety of terrestrial magmatic occurrences in silica-undersaturated rocks, including kimberlites, mafic xenoliths in kimberlite, peralkaline ultramafic, mafic and syenite rocks, carbonatite, metamorphosed calcareous rocks and several types of sulfide deposits (Henderson *et al.* 1999, and references therein). Despite the reports of djerfisherite from various localities, few authors provided a detailed description of its chemical composition and physical properties. Furthermore, the crystal structure obtained on djerfisherite from terrestrial occurrences has been documented in few papers (Dmitrieva & Ilyukhin 1975, Clarke *et al.* 1977, Czamanske *et al.* 1979, Evans & Clarke 1981). In the Guli complex, located in the Taymir Province, northern Siberia, Russia, djerfisherite was previously found associated with carbonatite (Kogarko *et al.* 1991).

In this paper, we describe djerfisherite, found for the first time in the dunite complex at Guli. The composition of djerfisherite is compared with chemical data available in the literature from other terrestrial localities and meteorites. The results are used to discuss the chemical substitutions that occur in djerfisherite as well as to better understand its genesis. The discovery of djerfisherite in the Guli dunite complex provides new insights into the origin of this uncommon mineral, associated with mantle-derived rocks.

GEOLOGY, PETROLOGY AND SAMPLING OF THE GULI COMPLEX

Distinctive features of the Guli complex, located in the Taymir Province of northern Siberia, are its considerable size and its complicated geology (Fig. 1). Including the part buried by Quaternary sediments of the Khatanga trough, the complex covers an area of about 2000 km^2, and thus represents the largest dunite–clinopyroxenite massif in the world (Kogarko & Zartman 2007). The exposed part is composed predominantly (about 60%) of variably serpentinized dunite. Melanocratic alkaline rocks cover about 30%, and other rock types, including melilitolite, ijolite, alkaline syenite and carbonatite occupy less than 10% of the area (Fedorenko & Czamanske 1997, Malitch & Thalhammer 2002, Kogarko & Zartman 2007). Wehrlite and magnetite-rich clinopyroxenite form dykes, stockwork and lenticular bodies within the dunite; highly disseminated to schlieren-type chromitites occur in the southern peripheral parts of the complex (Thalhammer & Meisel 2005). According to Kogarko & Zartman (2007), the Guli complex is a composite multistage pluton; six principal intrusive stages have been recognized. Dunites are the oldest rocks of the complex, and they were cut by a number of small bodies mainly composed of pyroxene and titanian magnetite (stage 1). According to McKelson *et al.* (2005) and Loidl & Thalhammer (2005), the Guli dunite complex represents a giant portion of mantle restite strongly metasomatized, with an age of 329 ± 57 Ma. During a second stage, melilitic rocks intruded the dunites. Stage 3 corresponds to the intrusion of a series of alkaline mafic and ultramafic rocks. The most abundant rocks produced during stage 3 are jacupirangite and melteigites; these were cut by dykes of ijolite and ijolite pegmatites (stage 4). Several bodies composed of peralkaline syenite, syenite, quartz-rich syenite and granites are widespread in the central part of the massif, and they correspond to stage 5. Finally, rocks of stage 6 are carbonatites and phoscorite. On the basis of a Pb isotope investigation, Kogarko &

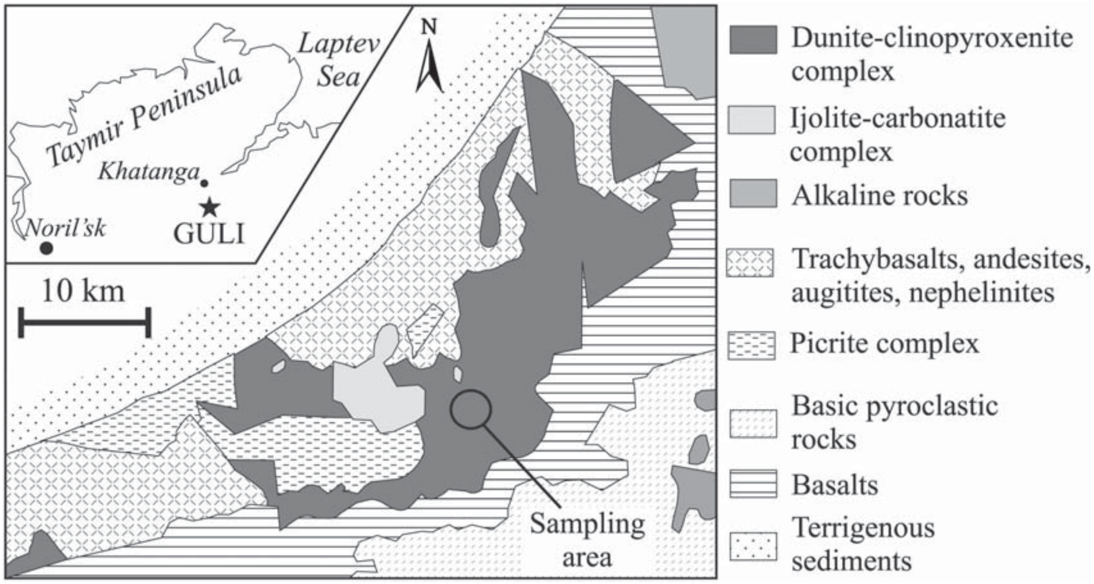

FIG. 1. Geological sketch-map of the Guli complex, modified after Malitch & Thalhammer (2002).

Zartman (2007) recognized that a metasomatic process related to the invasion of the Siberian superplume occurred shortly before 251 Ma, and was responsible for the extreme enrichment in rare elements and related elements found in some rocks of the Guli complex.

The Guli complex has been extensively drilled, with more than 26 km of core taken from throughout the complex. The samples of this investigation were collected by one of us (O.A.R.T.) during field work in August 2003. They were obtained from drill core (G–28), which is 506 meters long and is located at the edge of the dunite core complex in the vicinity of the northern carbonatite intrusion (GPS data are not available). The drill core (G–28) samples a single clinopyroxenite stock within the dunite and, thus, consists predominantly of phlogopite– and magnetite-rich clinopyroxenites with abundant veins and dykes of carbonatite, up to 1.5 meters in thickness. The sample with the greatest abundance of djerfisherite is a coarse-grained, phlogopite- and magnetite-rich clinopyroxenite with Ti-bearing andradite, a perovskite-group mineral, minor apatite, calcite, titanite, rare plagioclase, zircon, pyrophanite and disseminated sulfides.

The grains of djerfisherite most commonly occur in irregular patches of sulfide (Fig. 2) composed of pyrrhotite accompanied by minor chalcopyrite and rare galena. In these blebs of sulfide, djerfisherite may be the most abundant sulfide or, in some cases, it may constitute only a small portion of the total volume of the bleb. Djerfisherite is generally less than 100 μm in size, although crystals up to 500 μm have been found. It displays a variable shape: it forms irregular single crystals or it fills fissures of the silicate matrix and infiltrates phlogopite along its cleavage planes (Fig. 2). The textural relationships among djerfisherite, pyrrhotite and chalcopyrite suggest that these sulfides crystallized contemporaneously. Galena is less than 50 μm in size and occurs included in djerfisherite or pyrrhotite.

PHYSICAL AND OPTICAL PROPERTIES

The Knoop microhardness was determined using a Leitz miniload 2. Ten indentations were made on three selected grains of djerfisherite about 300 μm in size, applying a load of 98.1 mN, with a time of lowering plus dwelling of 15 seconds. The microhardness values are listed in Table 1.

Raman spectra were obtained using a Jobin–Yvon Labram instrument with a He–Ne laser, excitation wavelength 632.81 nm. Spectra obtained on three different crystals of djerfisherite show a peak at 300 cm^{-1} (Fig. 3).

In plane-polarized reflected light, djerfisherite is pale brown in color, with no internal reflections and no discernible anisotropism. Reflectance measurements were made using a Zeiss microspectrophotometer [relative to a WTiC reflectance standard (Zeiss 314)]; the procedures and equipment were as described by Criddle *et al.* (1983). The data obtained are listed in Table 2.

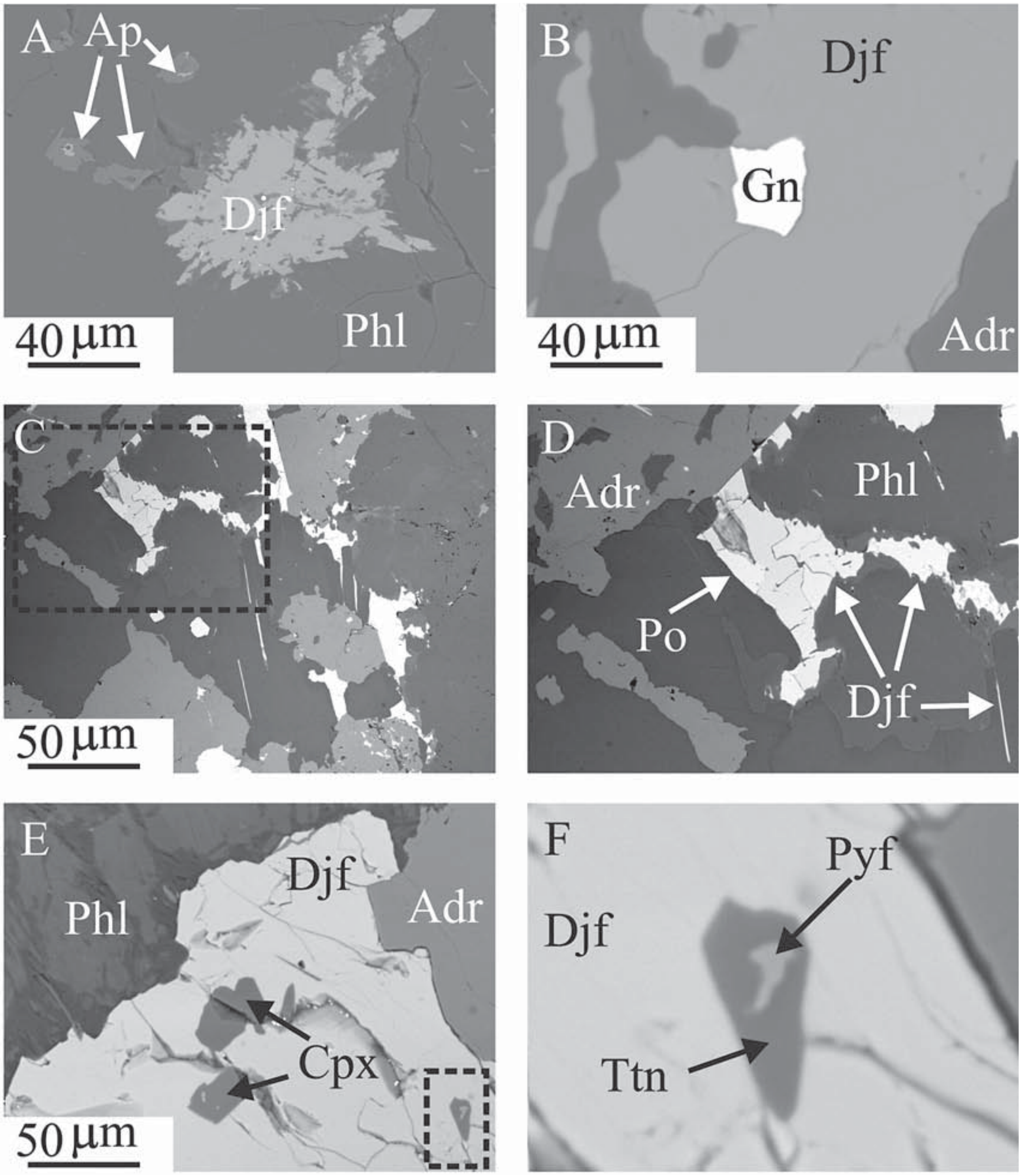

FIG. 2. BSE images of djerfisherite. A. Irregular single-phase djerfisherite in contact with phlogopite and apatite. B. Galena included in djerfisherite in contact with Ti-rich andradite. C. Texture of djerfisherite and pyrrhotite in the silicate matrix. D. Enlargement of C. E. Djerfisherite in contact with phlogopite and Ti-rich andradite, with small inclusions of clinopyroxene and titanite + pyrophanite. F. Enlargement of the inclusion titanite + pyrophanite. Abbreviations: Djf: djerfisherite, Ap: apatite, Phl: phlogopite, Gn: galena, Adr: Ti-rich andradite, Po: pyrrhotite, Cpx: clinopyroxene, Ttn: titanite, Pyf: pyrophanite.

CHEMICAL COMPOSITION

Quantitative analyses of djerfisherite and associated pyrrhotite were carried out using an ARL–SEMQ electron microprobe, operated in wavelength-dispersion mode at 15 kV accelerating voltage and 15 nA beam current with a beam diameter of about 1 μm, using counting times of 20 and 5 seconds for peak and backgrounds, respectively. The following reference materials were used: pyrite, tugtupite, microcline, albite, chalcopyrite, nickeline. X-ray *K*α lines were used for all the elements sought. On-line reduction of data and calculation of detection limits were performed with PRSUPR v. 3.63 (Donovan & Rivers 1990). Tables 3 and 4 present representative results of analyses of djerfisherite and pyrrhotite. In djerfisherite, the amount of Fe is relatively constant between 36.66 and 37.88 wt%, whereas the Cu content is more variable, ranging from 15.84 to 19.54 wt%. Nickel may reach 2.45 wt%, although in some grains, its content is below the detection limits. Potassium shows a narrow range of variation between 9.23 and 10.53 wt%. Chlorine varies from 1.07 to 1.45 wt%; contents of Na above the detection limit were detected in one grain only. Our data indicate that djerfisherite, calculated on the basis of 58 atoms according to the formula shown by Mandarino & Back (2004), approximates to: $K_{6.31}(Fe_{17.29}Cu_{7.49}Ni_{0.34})_{\Sigma 25.12}S_{25.52}Cl_{1.05}$. It is evident that the Guli djerfisherite deviates from the theoretical composition $K_6(Fe,Cu,Ni)_{24}S_{26}Cl$ owing to its enrichment in K and Fe–Cu–Ni and slight deficiency in S. Our data show that Cl is an essential component in the analyzed djerfisherite at the level of 1 atom per formula unit (*apfu*), whereas Na is below detection. Small compositional variations exist from grain to grain, whereas variations within a single crystal were not observed, suggesting that the analyzed grains are compositionally homogeneous.

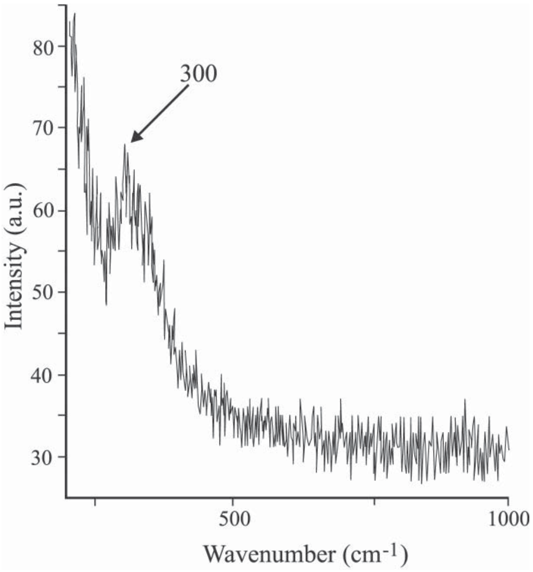

FIG. 3. Raman spectrum of djerfisherite.

TABLE 1. KNOOP MICROHARDNESS OF DJERFISHERITE FROM THE GULI COMPLEX

(10)	minimum	maximum	average*
DJ1	148	169	154
DJ2	127	139	132
DJ3	139	148	144

Units: kg/mm². * Average of ten measurements.

On the basis of its chemical composition, pyrrhotite associated with djerfisherite has been classified as intermediate, *i.e.*, characterized by a composition between Fe_9S_{10} and $Fe_{11}S_{12}$ (Morimoto *et al.* 1975).

CRYSTAL STRUCTURE

Data collection

Djerfisherite crystallizes in the isometric hexaoctahedral class $4/m\,\bar{3}\,2/m$, space group $Pm\bar{3}m$; its structure was first studied by Dmitrieva & Ilyukhin (1975) and Dmitrieva *et al.* (1978), who reported a cell edge of about 10.465(1) Å. With respect to the crystal studied here, the sample reported by Dmitrieva *et al.* (1978) is relatively depleted in K, Cu, Ni and Cl, and enriched in Na, Fe and S.

The intensity data were collected for a single crystal of about 0.06 × 0.06 × 0.01 mm on a Nonius Kappa CCD area-detector diffractometer at the window of a

TABLE 2. THE REFLECTANCE OF DJERFISHERITE FROM THE GULI COMPLEX

λ	R% in air	R% in oil	λ	R% in air	R% in oil
400	15.8	7.0	560	24.2	12.6
420	17.1	7.9	580	24.9	13.0
440	18.4	8.8	**589**	**25.3**	**13.2**
460	19.6	9.6	600	25.5	13.4
470	**20.2**	**10.1**	620	26.0	13.7
480	20.8	10.4	640	26.3	13.9
500	21.8	11.1	**650**	**26.2**	**14.0**
520	22.8	11.6	660	26.7	14.1
540	23.6	12.2	680	27.0	14.3
546	**23.8**	**12.3**	700	27.1	14.5

Wavelength λ in nm. In bold, standard wavelengths specified by the IMA Commission on Ore Mineralogy.

copper rotating anode FR591 generator equipped with a graphite monochromator at the Centre of Excellence in Biocrystallography (University of Trieste). Data were integrated with DENZO and scaled with WINGX; we used SORTAV for empirical absorption-corrections. The structure was refined with SHELXL97, and the isotropic least-squares refinement gave a final R value of 0.07 for 220 independent data.

Refinement of the structure

Our crystal of djerfisherite has a cell edge equal to 10.385(5) Å, close to that reported by Dmitrieva *et al.* (1978). The refined atomic parameters are listed in Table 5. A table of observed and calculated structure-factors is available from the Depository of Unpublished Data on the MAC web site [document Djerfisherite CM45_xxx].

TABLE 3. SELECTED RESULTS OF ELECTRON-MICROPROBE ANALYSES OF DJERFISHERITE FROM THE GULI COMPLEX

	S	Fe	Cu	Ni	K	Cl	Total
d.l.	0.02	0.07	0.12	0.09	0.02	0.03	
DJ1 2 wt%	32.05	37.71	16.92	2.16	10.29	1.33	100.46
DJ1 3	31.70	37.88	17.21	1.92	9.65	1.30	99.65
DJ1 4	31.81	37.38	16.97	1.99	10.17	1.34	99.67
DJ1 5	31.46	37.47	17.03	2.18	10.02	1.39	99.56
DJ1 7	32.08	37.46	17.40	2.30	9.70	1.25	100.19
DJ2 9	31.66	37.43	17.98	0.88	9.99	1.36	99.29
DJ2 10	31.97	37.42	18.24	0.71	10.09	1.41	99.84
DJ2 11	31.73	37.57	18.32	0.78	9.92	1.30	99.62
DJ2 13	31.86	37.60	18.55	0.78	9.61	1.45	99.84
DJ3 15	31.49	37.78	18.73	b.d.l.	10.11	1.40	99.57
DJ3 16	31.74	37.51	19.05	b.d.l.	10.01	1.38	99.75
DJ3 17	31.51	37.38	18.78	b.d.l.	9.62	1.39	98.69
DJ3 18	31.34	37.57	19.07	0.16	10.00	1.39	99.54
DJ3 19	32.04	37.44	19.21	b.d.l.	9.71	1.33	99.79
DJ3 20	32.05	37.18	19.39	b.d.l.	10.03	1.35	100.04
DJ1 2 atom %	43.87	29.63	11.69	1.61	11.55	1.65	
DJ1 3	43.87	30.09	12.02	1.45	10.95	1.62	
DJ1 4	43.89	29.61	11.81	1.50	11.51	1.68	
DJ1 5	43.56	29.78	11.90	1.65	11.37	1.73	
DJ1 7	44.12	29.58	12.08	1.72	10.94	1.56	
DJ2 9	43.90	29.80	12.58	0.67	11.36	1.70	
DJ2 10	44.04	29.59	12.68	0.53	11.40	1.76	
DJ2 11	43.90	29.84	12.79	0.59	11.26	1.63	
DJ2 13	43.99	29.81	12.92	0.59	10.88	1.82	
DJ3 15	43.60	30.03	13.08	b.d.l.	11.48	1.75	
DJ3 16	43.86	29.76	13.28	b.d.l.	11.34	1.73	
DJ3 17	44.00	29.97	13.24	b.d.l.	11.02	1.76	
DJ3 18	43.48	29.92	13.35	0.12	11.37	1.75	
DJ3 19	44.24	29.68	13.38	b.d.l.	10.99	1.66	
DJ3 20	44.11	29.38	13.47	b.d.l.	11.32	1.68	
DJ1 2 *apfu*	25.44	17.19	6.78	0.94	6.70	0.96	
DJ1 3	25.45	17.45	6.97	0.84	6.35	0.94	
DJ1 4	25.46	17.17	6.85	0.87	6.68	0.97	
DJ1 5	25.26	17.28	6.90	0.96	6.60	1.01	
DJ1 7	25.59	17.16	7.00	1.00	6.34	0.90	
DJ2 9	25.46	17.28	7.30	0.39	6.59	0.99	
DJ2 10	25.54	17.16	7.35	0.31	6.61	1.02	
DJ2 11	25.46	17.31	7.42	0.34	6.53	0.94	
DJ2 13	25.52	17.29	7.49	0.34	6.31	1.05	
DJ3 15	25.29	17.42	7.59	b.d.l.	6.66	1.02	
DJ3 16	25.44	17.26	7.70	b.d.l.	6.58	1.00	
DJ3 17	25.52	17.38	7.68	b.d.l.	6.39	1.02	
DJ3 18	25.22	17.36	7.74	0.07	6.60	1.01	
DJ3 19	25.66	17.21	7.76	b.d.l.	6.38	0.96	
DJ3 20	25.59	17.04	7.81	b.d.l.	6.57	0.98	

d.l.: detection limit, b.d.l.: below detection limit. The formula in atoms per formula unit (apfu) is calculated on the basis of 58 atoms.

There are four S sites: S1 at the origin [0, 0, 0], S2 at [*x*, ½, 0], S3 at [½,½, *z*], and S4 at [*x, x, x*]. The (Cu, Fe, Ni) atom is found at the [½,½, ½] position and at [*x, x, y*], whereas the K atom is found at [0, 0, *z*]. With S1 at the origin and K along each axis, there is a fourfold axis through these two atoms. There are four S2 atoms at 3.320(5) Å and four S4 atoms at 3.428(4) Å arranged in a somewhat distorted square antiprism. Atom is S1 is at 3.099(5) Å. A tridecahedron with nine vertices is thus formed around K. Copper is at the center of the unit cell, and is surrounded by six S3 atoms (at ½, ½, *z*) at a distance of 2.502(6) Å in perfect octahedral coordination. The Fe atom is in a somewhat distorted tetrahedral coordination, with two S2 at 2.325(3) Å, S3 at 2.335(4) Å, and S4 at 2.260(3) Å. The coordination of the S atoms is as follows: S1, at the origin, is in perfect octahedral coordination, linked to K atoms at 3.099(5) Å. Atom S2 is bonded to two K atoms and four Fe atoms in a distorted triangular prism. Atom S3 is bonded to four Fe atoms [2.335(4) Å] at the base of a square pyramid, with Cu [2.502(6) Å] at the apex. Atom S4 has three Fe atoms [2.260(3) Å] adjacent to

TABLE 4. SELECTED RESULTS OF ELECTRON-MICROPROBE ANALYSES OF PYRRHOTITE ASSOCIATED WITH DJERFISHERITE FROM THE GULI COMPLEX

	Fe	Ni	Co	Cu	S	Total
DJ1 po 1 wt%	59.68	0.19	0.17	0.07	39.05	99.27
DJ1 po 2	60.02	0.29	0.07	0.00	38.96	99.34
DJ1 po 3	60.45	0.19	0.23	0.06	37.88	98.92
DJ1 po 4	58.67	0.30	0.11	0.00	39.72	98.79
DJ1 po 5	59.31	0.04	0.13	0.02	39.22	98.77
DJ1 po 1 atom %	46.56	0.14	0.13	0.05	53.07	
DJ1 po 2	46.81	0.21	0.05	0.00	52.92	
DJ1 po 3	47.61	0.14	0.17	0.04	51.97	
DJ1 po 4	45.75	0.22	0.08	0.00	53.95	
DJ1 po 5	46.39	0.03	0.10	0.01	53.44	

TABLE 5. ATOM PARAMETERS FOR DJERFISHERITE FROM THE GULI MASSIF

atom	site	*x*	*y*	*z*	U_{eq}
S1	1*a*	0	0	0	0.026(3)
S2	12*h*	0.24813(44)	0.5	0	0.029(1)
S3	6*f*	0.5	0.5	0.25909(55)	0.025(1)
S4	8*g*	0.22800(29)	0.22800(29)	0.22800(29)	0.030(1)
K	6*e*	0	0	0.29846(50)	0.034(1)
Cu	1*b*	0.5	0.5	0.5	0.045(3)
Fe	24*m*	0.13537(17)	0.36721(13)	0.36721(13)	0.030(1)

each other and three K atoms [3.428(4) Å] adjacent to each other. Fourier analyses of differences do not show evidence of residual peaks.

DISCUSSION

Comparison of djerfisherite occurrences

Djerfisherite was described in several kimberlites from Russia, Canada and South Africa (Dobrovol'skaya *et al.* 1975, Clarke *et al.* 1977, 1994, Bulanova *et al.* 1980, Distler *et al.* 1987, Spetsius *et al.* 1987, Solov'yeva *et al.* 1988, Sobolev *et al.* 1999, Chakhmouradian & Mitchell 2001, Sharygin *et al.* 2003, 2007, Misra *et al.* 2004) and in alkaline ultramafic–mafic complexes located in Italy, USA, Greenland and Russia (Bianconi *et al.* 1978, Czamanske *et al.* 1979, Eremeev *et al.* 1982, Morgan *et al.* 1985, Harnois & Mineau 1991, Petersen & Secher 1993, Barkov *et al.* 1997, Hogarth 1997, Korobeinikov *et al.* 1998, Henderson *et al.* 1999, Sokolov *et al.* 2007). Djerfisherite rarely occurs in alkaline felsic rocks (Sokolova *et al.* 1971, Ifantopulo *et al.* 1978) as well as in carbonatite from Russia (Balabonin *et al.* 1980, Panina *et al.* 2001, Kogarko *et al.* 1991). In a single case, djerfisherite was described from strongly metamorphosed calcareous rocks situated in southern Norway (Jamtveit *et al.* 1997). A number of sulfide deposits worldwide contain djerfisherite (Genkin *et al.* 1970, Konev *et al.* 1972, Dobrovol'skaya *et al.* 1980, Zang & Chen 1985, Barkov *et al.* 1997, Korobeinikov *et al.* 1998, Takechi *et al.* 2000, Lisitsin *et al.* 2002).

Henderson *et al.* (1999) observed that the composition of djerfisherite, in terms of Fe–Cu–Ni substitutions, is related to the nature of its host rocks. In order to compare the compositions of djerfisherite (in at. %) of the Guli complex with that from different locations and rock associations from the literature, we have plotted our composition in the system Fe–Cu–Ni (Fig. 4). Djerfisherite from kimberlites is characterized by variable substitutions among Fe, Cu and Ni, whereas djerfisherite occurring in alkaline mafic–ultramafic and alkaline felsic rocks tends to be richer in Cu and poorer in Ni. In the latter, thus, the dominant substitution takes place between Fe and Cu. Djerfisherite associated with melt inclusions in melilitolite from the Kugda massif (Henderson *et al.* 1999) plots in the field of kimberlite. The three published compositions of djerfisherite from Kovdor (Kola Peninsula), from Guli (Siberia) and Ile Cadieux, Monteregian Hills (Canada) show that djerfisherite found in carbonatitic rocks displays a great variability in composition (Kogarko *et al.* 1991, Harnois & Mineau 1991). Note that djerfisherite found in carbonatite from the Guli complex is Ni- and Cu-free, and its composition plots at the Fe apex of the

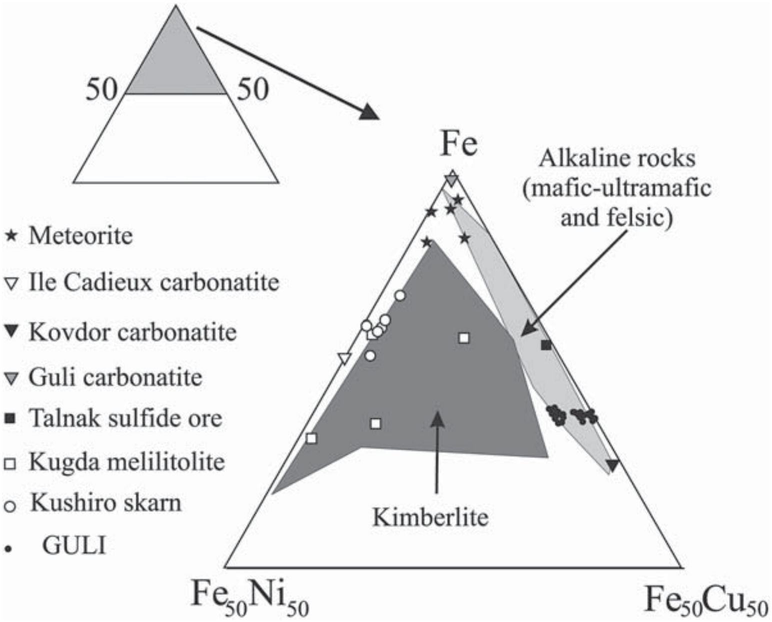

FIG. 4. Triangular Fe–Cu–Ni diagram (at. %) of djerfisherite from the Guli dunite complex compared with compositional fields of djerfisherite from alkaline rocks (mafic–ultramafic and felsic) and kimberlite. Individual symbols: occurrences with fewer than six compositions. See text for the sources of data.

Fe–Cu–Ni triangular diagram, whereas djerfisherite from Kovdor (Balabonin *et al.* 1980) and from Ile Cadieux (Harnois & Mineau 1991) is Cu-rich, Ni-poor and Ni-rich, Cu-poor, respectively. Djerfisherite from meteorites is particularly Fe-rich and Cu- and Ni-poor. The djerfisherite from Guli described here is rich in Cu and poor in Ni, similarly to those reported from mafic–ultramafic and alkaline felsic rocks.

The correlations of Fe, Cu and Ni (in wt%) in djerfisherite from kimberlite, alkaline rocks and the Guli complex are shown in Figure 5. Copper and Fe (Fig. 5A) show a clear negative correlation in the djerfisherite from alkaline rocks, whereas no correlation between Ni and Cu is detectable in djerfisherite from kimberlite. In contrast, the correlations between the pairs Ni–Cu and Ni–Fe (Figs. 5B, C) are negative in djerfisherite from kimberlite and well observed in djerfisherite from alkaline rocks. The Ni, Fe and Cu covariations in djerfisherite from the Guli dunite match those reported from alkaline rocks.

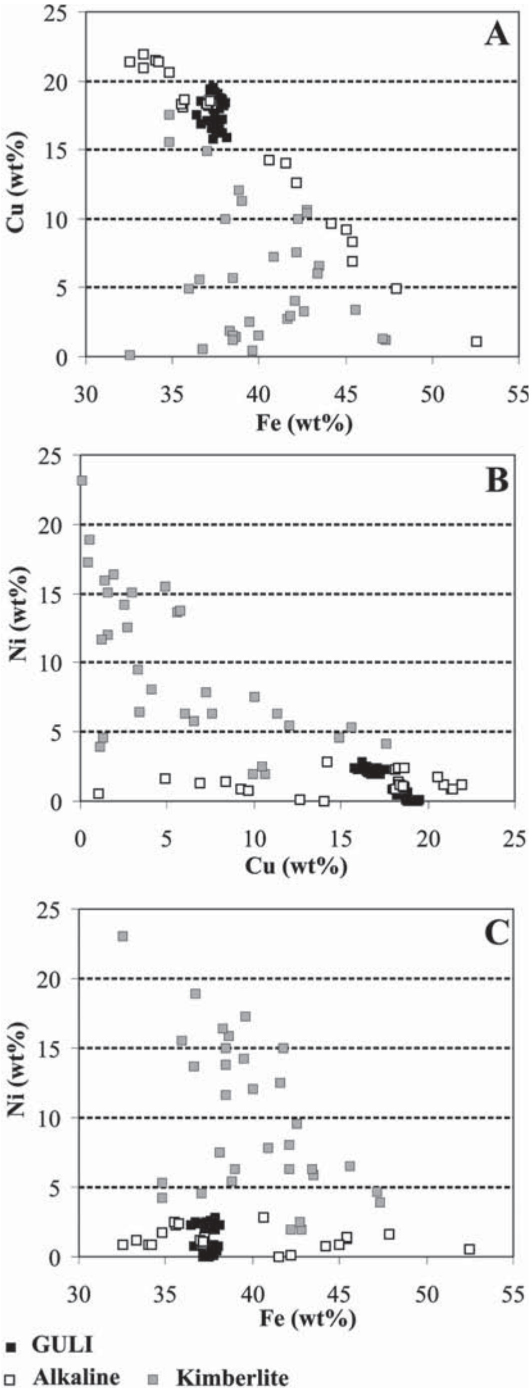

FIG. 5. Reciprocal variations among Cu–Fe–Ni in djerfisherite from Guli dunite complex, alkaline rocks (mafic–ultramafic and felsic) and kimberlite. A. Cu–Fe negative correlation in djerfisherite from the Guli dunite complex and alkaline rocks. B. Ni–Cu negative correlation in djerfisherite from kimberlite. C. Ni–Fe negative correlation in djerfisherite from kimberlite.

Origin of djerfisherite

There is a general consensus that most occurrences of djerfisherite are the product of metasomatic alteration of pre-existing alkali-free magmatic sulfides by introduction of K- and Cl-bearing fluids (Clarke *et al.* 1977, Korobeinikov *et al.* 1998). The origin of these fluids as well as the locus where the metasomatic event took place, *i.e.*, mantle or crust, still remains unsolved, although Barkov *et al.* (1997) and Korobeinikov *et al.* (1998) suggested that K was first released from mica and then incorporated into the djerfisherite. In some cases, djerfisherite is believed to have formed during the latest magmatic stage (Henderson *et al.* 1999, Sharygin *et al.* 2003). Evidence that djerfisherite crystallized as a primary mineral during an early magmatic stage was never established.

In the Kugda alkaline complex of Siberia, djerfisherite is the product of a fractional crystallization sequence, in a closed system, from an evolved melilitic magma through to a residual alkali carbonatite melt (Henderson *et al.* 1999). This fractionation process started at a temperature above 1000°C and was supplemented by processes of deuteric alteration at temperatures below 500°C (Henderson *et al.* 1999). In the Elwin Bay kimberlite (Canada), djerfisherite was considered to be a primary magmatic mineral formed during the late stages of kimberlite crystallization. On the basis of chemical zonation, Clarke *et al.* (1994) established the presence of disequilibrium conditions during crystallization of djerfisherite in the Elwin Bay kimberlite, but the relationship of djerfisherite and primary pyrrhotite and pentlandite was not identified. In the Udachnaya-East kimberlite, two different types of djerfisherite have been recognized. One, related to the kimberlite, represents a product that crystallized late during the magma's evolution (Sharygin *et al*. 2007, Golovin *et al*. 2007). The other type occurs in a kimberlite-hosted phlogopite–spinel lherzolite xenolith. In this case, djerfisherite possibly formed during a reaction between the evolved kimberlite fluid or melt with primary minerals in xenoliths (Sharygin *et al*. 2007). In the Finero mafic–ultramafic complex, affected by alkaline–carbonatite metasomatism, djerfisherite was considered to be a secondary mineral formed at the expense of magmatic pentlandite during serpentinization, reduction and sulfidization of peridotite (Bianconi *et al*. 1978). Djerfisherite associated with calcareous rocks from the Oslo Rift (Norway) seems to have formed at the expense of primary pyrrhotite because of the infiltration of C-poor fluids during a contact metamorphism near 700°C (Jamtveit *et al*. 1997).

In the Guli complex, djerfisherite occurs within a phlogopite–magnetite-rich clinopyroxenite stock emplaced along the edge of the dunite core complex. The giant dunite complex of Guli is suggested to be the result of successive fractional melting of an ascending mantle plume under metasomatic (*i.e*. "wet") conditions (Loidl 2005). The clinopyroxenite stocks and dykes are suggested to have been derived from a fractional melt portion of the ascending mantle plume, that had intruded at the periphery of the dunite complex.

CONCLUDING REMARKS

In this paper, we have reported finding the uncommon mineral djerfisherite in the Guli complex of Siberia; we provide data on its chemical composition, physical and crystallographic properties.

We have clearly shown, on the basis of worldwide occurrences, that djerfisherite is characterized by an extensive substitution among the transition elements Fe, Cu and Ni. The reciprocal substitutions of these three elements are mainly controlled by the composition of the host rock.

The textural relationships of djerfisherite, pyrrhotite, chalcopyrite and galena in the Guli complex strongly suggest that these sulfides crystallized during the same event. Furthermore, there is no evidence that at Guli, djerfisherite formed at the expense of primary pyrrhotite, as reported in calcareous rocks (Jamtveit *et al*. 1997), or that it represents a product of alteration after magmatic pentlandite, as reported at the Finero complex (Bianconi *et al*. 1978). Chemical zonation, as reported in djerfisherite from the Elwin Bay kimberlite (Clarke *et al*. 1994) is absent in the Guli djerfisherite, indicating equilibrium conditions during its crystallization. Its Cu-rich composition resembles that reported in djerfisherite from alkaline rocks.

We conclude that djerfisherite and the associated sulfides are part of the accessory assemblage (phlogopite, perovskite-group mineral, apatite, calcite, titanite, plagioclase, zircon, and pyrophanite) formed as a result of the metasomatic event that affected the Guli dunite. The compositional similarity of the Guli material with djerfisherite from alkaline rocks support our contention that the metasomatic fluids had an alkaline signature.

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