

CHLORINE-POOR ANALOGUES OF DJERFISHERITE – THALFENISITE FROM NORIL'SK, SIBERIA AND SALMAGORSKY, KOLA PENINSULA, RUSSIA

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ABSTRACT

Chlorine-poor (0–0.2 wt.% Cl) potassium–thallium–lead sulfides (analogues of djerfisherite–thalfenisite, *ADT*) occur as minute (5 – 30 µm) subhedral inclusions in chalcopyrite, in a galena-rich massive sulfide ore from the Oktyabrsky deposit, Noril'sk, Siberia. The ore contains froodite, Ag- and Pb-tellurides, Fe-rich argentopentlandite and cassiterite. There is an extensive solid-solution series between the K-rich [(K,Tl,Pb)₆(Fe,Ni,Cu)₂₅S₂₇] and Tl-rich [(Tl,K,Pb)₆(Fe,Ni,Cu)₂₅S₂₇] end-members. Two principal substitutions are suggested: (1) K⁺ → Tl⁺, and (2) Pb²⁺ + S²⁻ → K⁺(Tl⁺) + Cl⁻. Another occurrence of the Cl-poor analogue of djerfisherite, *AD* (0.03 – 0.72 wt.% Cl), is from the Salmagorsky alkaline ultramafic complex, in northwestern Russia, where it is associated with base-metal sulfides, *BMS*, and a Cu-rich djerfisherite (up to 21.9 wt.% Cu). Unlike the latter, the *AD* shows an essential decrease in K and an increase in Ni, the total of transition elements and S; the empirical values S (S + Cl) are ~27 atoms per formula unit, *apfu*. The compositions imply that the incorporation of S instead of Cl may have involved the incorporation of Ni in the K site, according to the coupled substitution: Ni²⁺ + S²⁻ → K⁺ + Cl⁻. The data suggest that (1) Cl-free analogues of djerfisherite and thalfenisite exist; there are (2) unlimited Tl-for-K substitution and (3) full Cl site occupancy by S in the members of the djerfisherite group, and (4) to maintain charge balance, the incorporation of S instead of Cl requires the substitution of a divalent cation (*e.g.*, Pb and Ni) for a monovalent cation (K and Tl).

Keywords: potassium sulfide, thallium sulfide, lead-bearing sulfide, base-metal sulfide, djerfisherite group, argentopentlandite, Cu–Ni ore, alkaline ultramafic complex, Oktyabrsky, Noril'sk, Salmagorsky, Kola Peninsula, Russia.

SOMMAIRE

Nous avons découvert des sulfures de potassium – thallium – plomb à faible teneur en chlore (0–0.2% en poids), phases analogues à la série djerfisherite–thalfenisite, en grains infimes (5–30 µm) sub-idiomorphes inclus dans la chalcopyrite, dans un minerai riche en galène provenant du gisement de Oktyabrsky, à Noril'sk, en Sibérie. Le minerai contient la froodite, des tellurures de Ag et Pb, l'argentopentlandite riche en fer, et la cassitérite. Il y a une étendue importante de solution solide entre les pôles riches en K [(K,Tl,Pb)₆(Fe,Ni,Cu)₂₅S₂₇] et en Tl [(Tl,K,Pb)₆(Fe,Ni,Cu)₂₅S₂₇]. Deux principaux schémas de substitution semblent importants: (1) K⁺ → Tl⁺, et (2) Pb²⁺ + S²⁻ → K⁺(Tl⁺) + Cl⁻. Un autre découverte, d'un analogue de la djerfisherite à faible teneur en Cl (0.03 – 0.72% Cl, en poids), provient du complexe alcalin ultramafique de Salmagorsky, dans le secteur nord-ouest de la Russie. Ce minéral, qui est associé à des sulfures de métaux de base et une djerfisherite cuprifère (jusqu'à 21.9% Cu, par poids), montre une diminution en K et une augmentation en teneurs de Ni, éléments de transition et S. Les teneurs observées en S + Cl sont d'environ 27 atomes par unité formulaire. Les compositions indiquent que l'incorporation du S à la place du Cl pourrait être liée à l'incorporation de Ni dans le site K, selon le schéma de substitution couplée: Ni²⁺ + S²⁻ → K⁺ + Cl⁻. Les données font penser que (1) des analogues sans chlore de la djerfisherite et de la thalfenisite existent, (2) il y a possibilité de solution solide complète entre les pôles Tl et K, (3) il est possible de trouver un taux d'occupation complet du site Cl par le S dans les membres du groupe de la djerfisherite, et (4) il est nécessaire, pour maintenir l'électronéutralité, d'impliquer, avec le S dans le site Cl, des ions bivalents (*e.g.*, Pb et Ni) à la place des cations monovalents (K et Tl).

(Traduit par la Rédaction)

Mots-clés: sulfure de potassium, sulfure de thallium, sulfure de plomb, sulfure de métaux de base, groupe de la djerfisherite, argentopentlandite, minerai de Cu–Ni, complexe alcalin ultramafique, Oktyabrsky, Noril'sk, Salmagorsky, péninsule de Kola, Russie.

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INTRODUCTION

Djerfisherite, a complex cubic potassium sulfide [ideally $K_6(Fe,Cu,Ni)_{25}S_{26}Cl$], was first discovered by Fuchs (1966) in meteorites (enstatite chondrites). The first terrestrial occurrence of djerfisherite was described by Genkin *et al.* (1969) from a Cu–Ni sulfide ore, Talnakh deposit, Noril'sk (Siberia, northern Russia). Since then, it has been reported from a number of various occurrences (Clarke *et al.* 1994, and references therein). Features of the djerfisherite structure were characterized by Dmitrieva & Ilyukhin (1975) and Dmitrieva (1976). The crystal structure of an electrochemically prepared djerfisherite-like inorganic compound, $K_6LiFe_{24}S_{26}Cl$, was characterized by Tani (1977). The thallium analogue of djerfisherite, *thalfenisite* [ideally $Tl_6(Fe,Ni,Cu)_{25}S_{26}Cl$], was discovered by Rudashevsky *et al.* (1979) in the Oktyabrsky deposit, Noril'sk. The Noril'sk complex appears to host the only occurrence of thalfenisite known to date. Recently, a new member of the djerfisherite group, *owensite* [ideally $(Ba,Pb)_6(Cu,Fe,Ni)_{25}S_{27}$], has been discovered in the Wellgreen Cu–Ni–Pt–Pd deposit, Yukon Territory (Laflamme *et al.* 1995). Its crystal structure was determined by Szymański (1995). In contrast to djerfisherite and thalfenisite, which are known to contain ~1 Cl atoms per formula unit (*apfu*), *owensite* is totally devoid of Cl, and yet it is structurally analogous to djerfisherite. The discovery of the Cl-free member of the djerfisherite group suggests that other Cl-free members may also occur in nature.

In 1995, during an examination of sulfide ores from Noril'sk, we found a number of small ($\leq 30 \mu m$ across) subhedral crystals of K–Tl–Pb-bearing Fe–Ni–Cu sulfides, which strongly resemble intermediate members of the djerfisherite–thalfenisite series, but chlorine was not detected in the minerals. In the same year, we discovered a new occurrence of a djerfisherite-like, Cl-deficient sulfide in the Salmagorsky alkaline ultramafic complex, in northwestern Russia, northeastern Fennoscandian Shield, where it occurs in intimate association with the normal, Cl-bearing djerfisherite. Owing to the small grain-size, no X-ray studies could be carried out on this material. However, these occurrences provide an excellent opportunity to characterize the chemistry and substitutions in the Cl-deficient phases, which appear to be Cl-poor analogues of djerfisherite (*AD*) and djerfisherite–thalfenisite (*ADT*) and, therefore, probable new mineral species. In this paper, we report the data obtained.

OCCURRENCES AND ASSOCIATED MINERALS

Noril'sk

The *ADT* occur in massive galena-rich sulfide ore from the Oktyabrsky deposit, which forms part of the Noril'sk complex. Galena-rich copper sulfide ores at

TABLE 1. MINERALS IN POTASSIUM-THALLIUM-(LEAD) SULFIDE-BEARING ORES FROM NORIL'SK, SIBERIA

Mineral	This study*	Rudashevsky <i>et al.</i> (1979)**
chalcopyrite	x (~ 80 - 85 vol.%)	x (60 - 65 vol.%)
galena	x ($\leq 10 \%$)	x (25 %)
pentlandite	x ($\leq 1 \%$)	x (5 - 7 %)
pyrrhotite	x ($\leq 3 \%$)	x (2 - 3 %)
cubanite	x	n.r.
magnetite	x	x
argentopentlandite	x	x
Ag–Au alloys	x	x
hessite	x	x
altaite	x	x
paolovite	n.f.	x
kotulskite	n.f.	x
moncheite	n.f.	x
froodite	x	n.r.
cassiterite	x	n.r.
mackinawite	x	n.r.
gangue	x ($\leq 1 \%$)	x (3 - 5 %)

Note: x = present; n.f. = not found; n.r. = not reported.

* Ore containing Cl-poor analogues of djerfisherite–thalfenisite from Oktyabrsky.

** Thalfenisite-bearing ore from Oktyabrsky.

Noril'sk generally are located at contacts of sulfide orebodies and veins. Such ores typically host large aggregates of platinum-group minerals and various tellurides (Rudashevsky *et al.* 1979, Genkin *et al.* 1981). In terms of modal composition (Table 1), the ore examined in this study clearly resembles that from Oktyabrsky, in which thalfenisite was discovered by Rudashevsky *et al.* (1979). The ore containing the *ADT* is principally composed of chalcopyrite and galena. Pentlandite and pyrrhotite are present in subordinate amounts. The other minerals, listed in Table 1, are accessories. Froodite and Ag- and Pb-tellurides (hessite and altaite, respectively) form large (up to ~1 mm), elongate, composite intergrowths with galena, Ag–Au alloy ($Ag_{63.6-64.2}Au_{35.8-36.4}$) and, more rarely, argentopentlandite. The latter mineral also occurs as (1) individual irregular grains, commonly up to ~0.1 mm across, (2) a thin (~10 μm) rim around the *ADT* (Fig. 1a) and, occasionally, (3) small, nearly triangular (in cross section) grains, which may represent a pseudomorph after the *ADT*. The argentopentlandite rims are of particular interest, since similar relationships were not previously reported for members of the djerfisherite group from other localities, although Genkin *et al.* (1981) described rims of sphalerite and some platinum-group minerals around djerfisherite from Talnakh. Cassiterite (identified by electron-microprobe analysis) is a trace constituent of the ore. It occurs as small (~5 μm to <0.1 mm) subhedral to anhedral grains, located mostly at the border between chalcopyrite and galena, and as minute crystals associated with the *ADT* (Fig. 1a). This seems to be the first

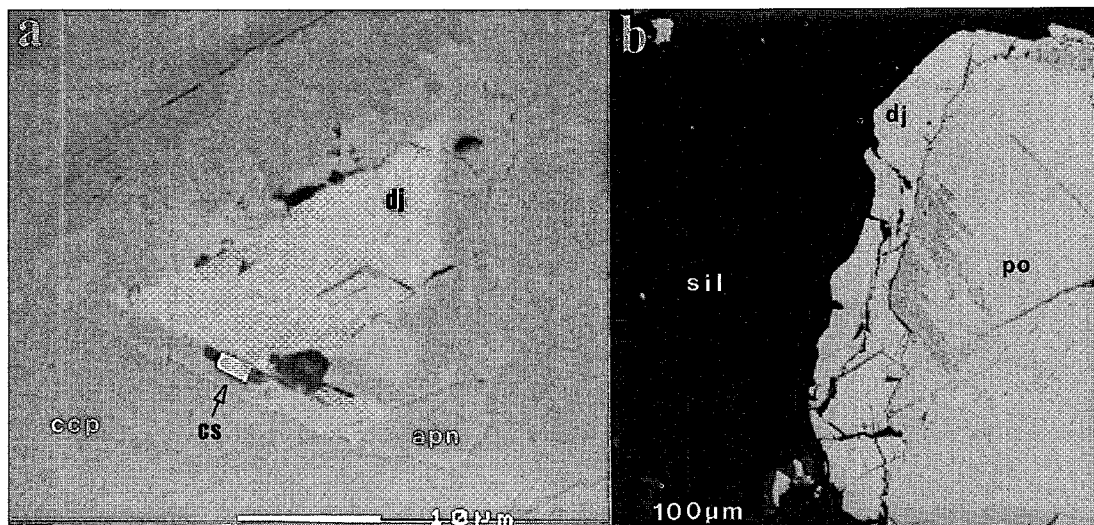


FIG. 1. (a) Chlorine-poor djerfisherite–(thalfeisite)-related sulfide (dj), mantled by argentopentlandite (apn); ccp: host chalcopyrite, cs: cassiterite; Oktyabrsky deposit, Noril'sk. (b) Djerfisherite rim (dj) around pyrrhotite (po) in the Salmagorsky complex. Sil: silicate. Back-scattered electron images. Scale bar is equivalent to 10 μm in a, 100 μm in b.

record of cassiterite *in situ* in the Noril'sk ores. Previously, Batyreva (1972) noted the presence of trace amounts of cassiterite and moissanite in "samples from the Noril'sk area" (no exact locality was reported), which were identified by X-ray diffraction and a laser (spectrum) micro-analysis.

In addition to chalcopyrite, there are various chalcopyrite-like minerals at Noril'sk: talnakhite $\text{Cu}_{18}(\text{Fe},\text{Ni})_{16}\text{S}_{32}$, haycockite $\text{Cu}_8\text{Fe}_{10}\text{S}_{16}$, mooihoekite $\text{Cu}_9\text{Fe}_9\text{S}_{16}$ and putranite $\text{Cu}_{16-18}(\text{Fe},\text{Ni})_{18-19}\text{S}_{32}$ (Cabri 1967, Cabri & Harris 1971, Filimonova *et al.* 1980, Genkin *et al.* 1981). The base-metal sulfide (BMS), containing inclusions of the ADT at Oktyabrsky, has the composition (basis: S = 16) $\text{Cu}_{7.5}\text{Fe}_{8.1}\text{S}_{16}$, ideally $\text{Cu}_8\text{Fe}_8\text{S}_{16}$ or CuFeS_2 , strongly suggesting that it is chalcopyrite.

The ADT appear as small (5–30 μm), subhedral to euhedral grains, typically triangular in cross-section, enclosed within chalcopyrite (Figs. 2a,c). This crystal habit is similar to that reported by Genkin *et al.* (1981) for djerfisherite from Talnakh, where regularly oriented, triangular grains of djerfisherite are observed as inclusions in talnakhite. Djerfisherite from the Elwin Bay kimberlite also occurs as subhedral grains (Clarke *et al.* 1994), whereas both thalfeisite from Oktyabrsky and owensite from Wellgreen are anhedral (Rudashevsky *et al.* 1979, Laflamme *et al.* 1995).

It should be noted that the ADT with a rim of argentopentlandite (Fig. 1a) typically show strong intergranular compositional variations, whereas the single grains (predominantly 5–8 μm across) without a

rim of argentopentlandite (Fig. 2) are homogeneous. For this reason, results of electron-microprobe analyses of the latter only are reported. In addition, crystals of a lead-rich mineral (probably galena), which are submicrometric in size, may occur in abundance at the border between the ADT and the host chalcopyrite (Figs. 2a, b).

Salmagorsky

The Salmagorsky (Salmagorskii or Salmagora) alkaline ultramafic complex forms part of the Khabozero group of intrusions (Kukharenko *et al.* 1965, Kogarko *et al.* 1995), Kola Peninsula, northwestern Russia. The estimated U–Pb age (schorlomite) of 375 Ma (cited in Kogarko *et al.* 1995) for the complex is in good agreement with Rb–Sr ages of 380–360 Ma for all alkaline magmatism in the Kola–Finnish province (Kramm *et al.* 1993). The complex represents a nearly circular, zoned intrusion (~20 km²), emplaced in Archean gneisses. A recent re-examination of the complex (Murmansk Geological Survey and GEOLKOM; unpublished data) significantly extended our knowledge of its geological structure and ore potential. At the contact with wallrocks, fenites and fenitized rocks are developed. The outermost, obviously discontinuous zone comprises olivine-bearing clinopyroxenites. The next concentric zone (toward the center) is predominantly composed of dunite; this zone was not previously recognized (*cf.* Kogarko *et al.* 1995). A discontinuous zone of melilitic rocks is

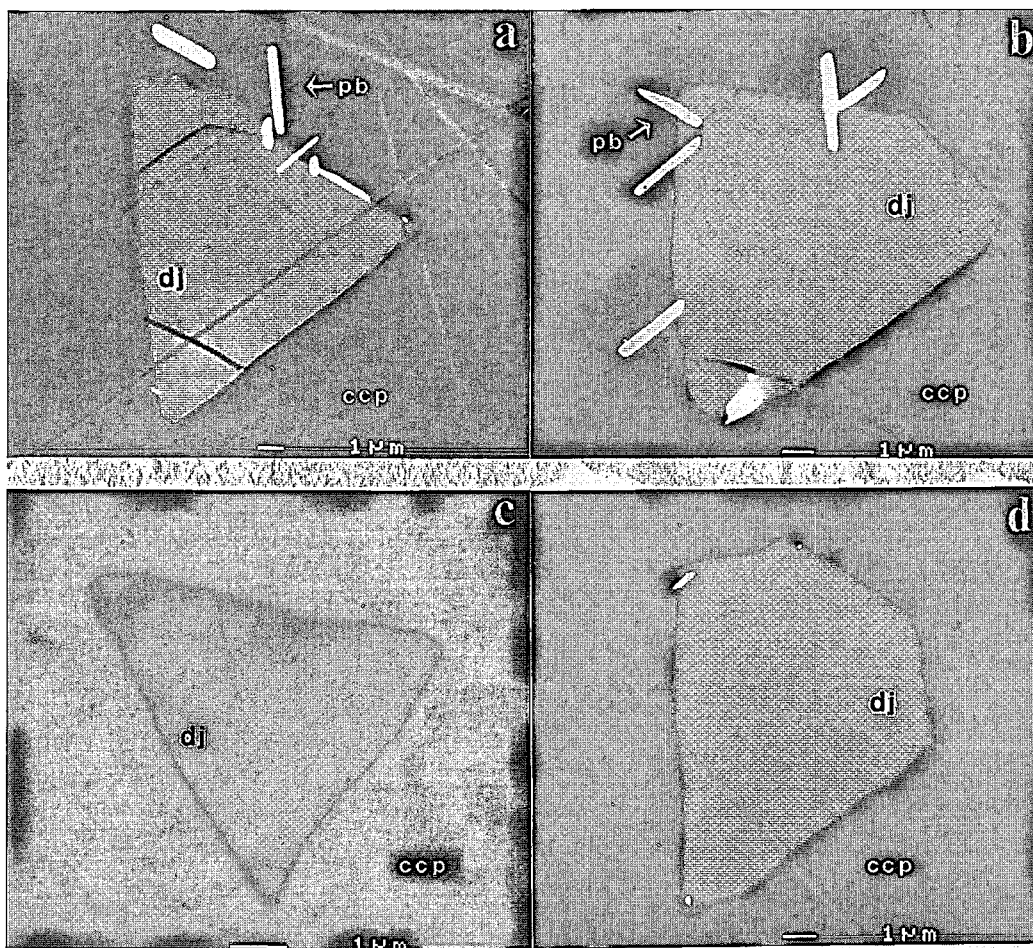


FIG. 2. (a) and (b) Subhedral crystals of Cl-poor djerfisherite-(thalfeisite)-related sulfides (dj), associated with a lead-rich mineral, probably galena (Pb). Note that the latter is located at the border with the host chalcopyrite (ccp). (c) A typical triangular crystal of the Cl-poor djerfisherite-thalfeisite analogue (dj) enclosed within chalcopyrite (ccp). (d) Subhedral inclusion of the djerfisherite-thalfeisite analogue (dj) within chalcopyrite (ccp). Oktyabrsky deposit. Back-scattered electron images. Scale bar is equal to 1 μm in each case.

observed closer to the center. The core of the complex is predominantly formed by melteigite and ijolite. An irregular body of carbonatite and a *BMS*-apatite orebody are situated at the center. The *BMS* are pyrrhotite, cubanite or isocubanite (or both), chalcocopyrite, pyrite, cobalt pentlandite and galena (Barkov *et al.*, unpubl. data). In places, djerfisherite represents an essential ore mineral.

The *AD* was identified in a *BMS*-bearing (6–8 modal %) melteigite that consists of ~75–80% clinopyroxene ($\text{Wo}_{44.1-45.7}\text{En}_{29.1-32.5}\text{Fs}_{21.7-26.0}$), <10% nepheline, and phlogopite as an abundant accessory mineral. Pyrrhotite is the major sulfide; djerfisherite, cubanite or isocubanite (or both), chalcocopyrite and pyrite are subordinate. The *AD* occurs as areas 10–20 μm

across within djerfisherite. The latter typically occurs as a rim around pyrrhotite (Fig. 1b). Veinlets of secondary magnetite and manganian ilmenite (up to 3.6 wt.% MnO) locally cut grains of djerfisherite. Minute grains of barite (10–20 μm) are encountered in a close spatial association with the djerfisherite-bearing mineralization.

COMPOSITIONS

Analytical methods

Both wavelength-dispersion (WDS) and energy-dispersion (EDS) methods of analysis were used at the Institute of Electron Optics, University of Oulu,

TABLE 2. CHEMICAL COMPOSITION* OF CHLORINE-POOR ANALOGUES OF DJERFISHERITE-THALFENISITE FROM NORIL'SK, SIBERIA

	Weight %									
	1	2	3	4	5	6	7	8	9	10
K	5.79	5.83	5.63	5.60	4.71	3.52	3.32	3.32	2.2	0.03
Tl	5.78	6.62	8.38	9.21	13.17	14.98	16.71	16.90	23.8	33.4
Pb	9.57	8.51	7.26	6.13	4.20	6.30	5.74	5.66	4.6	-
Fe	35.93	35.49	35.38	35.19	35.53	32.37	32.18	32.16	30.5	29.4
Ni	9.90	8.49	8.36	9.29	9.93	9.25	9.46	9.45	8.8	10.3
Cu	4.64	6.06	6.32	5.05	4.17	4.35	4.35	4.35	4.1	1.74
S	30.50	30.56	30.04	30.12	29.44	27.35	27.11	27.08	25.9	24.80
Cl	n.d.	0.16	n.d.	n.d.	n.d.	n.d.	0.13	0.15	n.d.	0.84
SUM	102.11	101.72	101.37	100.59	101.15	98.12	99.02	99.07	99.9	100.51

Atomic proportions (Σ atoms = 58)

K	4.17	4.21	4.11	4.10	3.50	2.82	2.66	2.66	1.85	0.03
Tl	0.80	0.91	1.17	1.29	1.87	2.29	2.56	2.59	3.83	5.61
Pb	1.30	1.16	1.00	0.85	0.59	0.98	0.87	0.86	0.73	-
Σ	6.27	6.28	6.28	6.24	5.96	6.06	6.09	6.11	6.41	5.64
Fe	18.12	17.93	18.08	18.05	18.50	18.19	18.07	18.06	17.96	18.06
Ni	4.75	4.08	4.07	4.53	4.92	4.93	5.05	5.05	4.93	6.02
Cu	2.06	2.69	2.84	2.28	1.91	2.14	2.15	2.15	2.12	0.94
Σ	24.93	24.70	24.99	24.86	25.33	25.22	25.27	25.26	25.01	25.02
S	26.80	26.89	26.74	26.90	26.70	26.71	26.51	26.49	26.57	26.33
Cl	-	0.13	-	-	-	-	0.13	0.13	-	0.81
Σ	26.80	27.02	26.74	26.90	26.70	26.71	26.64	26.62	26.57	27.34

* EDS electron-microprobe analyses; see text for analytical conditions. Analyses are listed in order of increasing thallium content. n.d. = not detected. Anal. # 1 - 9; this study; anal. # 10: thalferisite (Rudashevsky et al. 1979).

Finland, to obtain the compositional data. Owing to the small grain-size of the ADT, EDS was used to avoid (or, at least, to minimize) interference from the host chalcopyrite. For comparison, EDS also was used to analyze djerfisherite from Salmagorsky. The quantitative EDS analyses (Tables 2, 3 and 5) were carried out at 15 kV and 1.2 nA, using a JEOL JSM-6400 scanning-electron microscope equipped with a LINK eXL energy-dispersion spectrometer. Pure elements, orthoclase, pyrite, synthetic PbTe and NaCl were used

TABLE 3. CHEMICAL COMPOSITION* OF DJERFISHERITE FROM THE SALMAGORSKY COMPLEX, KOLA PENINSULA

	Weight %						
	1	2	3	4	5	6	7
K	9.18	9.17	9.21	9.15	9.09	9.27	9.30
Fe	37.25	37.06	37.07	36.98	37.15	37.18	37.16
Cu	18.32	18.16	18.63	18.35	18.52	18.67	18.57
Ni	1.39	0.92	1.07	1.15	0.82	0.95	1.11
S	33.00	32.66	32.71	32.78	32.76	32.89	32.94
Cl	1.34	1.42	1.38	1.41	1.38	1.37	1.38
SUM	100.48	99.39	100.07	99.82	99.72	100.33	100.46

Atomic proportions (Σ atoms = 58)

K	5.97	6.02	6.02	5.99	5.96	6.04	6.05
Fe	16.96	17.04	16.96	16.94	17.04	16.96	16.92
Cu	7.33	7.34	7.49	7.39	7.47	7.48	7.43
Ni	0.60	0.40	0.47	0.50	0.36	0.41	0.48
ΣMet.	24.89	24.78	24.92	24.83	24.87	24.85	24.83
S	26.17	26.16	26.07	26.16	26.18	26.13	26.13
Cl	0.96	1.03	0.99	1.02	1.00	0.98	0.99

*EDS electron-microprobe analyses; every analysis is an average of two individual analyses. The analyses in this Table and Table 4 refer to djerfisherite from different mineralized occurrences at Salmagorsky.

as standards. Counting periods were 100 s. The most finely focused beam was applied. The spectra were processed by Link ISIS (version 3.00) or ZAF-4 on-line programs. The estimated errors in the EDS analyses for Cl are <0.1 wt. %.

The WDS analyses (Table 4) were carried out using an automated JEOL 733 Superprobe, operated at 15 kV and 15 nA. Pure metals, orthoclase, pyrite and synthetic KCl were used as standards. The results were processed by an on-line (Link) ZAF program. Standard deviations in the WDS analyses for Cl (as found in the AD and djerfisherite) are 0.01-0.04% (minimum detection-level is ≤0.05 wt. % Cl).

TABLE 4. CHEMICAL COMPOSITION* OF DJERFISHERITE AND RELATED CHLORINE-POOR PHASES FROM THE SALMAGORSKY COMPLEX

	Weight %								
	1	2	3	4	5	6	7	8	9**
K	9.00	9.04	9.06	8.80	8.99	8.17	7.67	7.70	7.70
Fe	34.00	33.31	34.21	33.30	32.56	34.83	35.60	35.49	35.71
Ni	0.91	1.21	0.89	1.20	0.86	1.78	2.33	2.45	2.37
Cu	21.45	21.93	21.37	20.89	21.43	20.60	18.13	18.31	18.63
S	32.07	32.50	32.54	31.22	32.26	33.25	32.72	32.64	33.60
Cl	1.30	1.25	1.32	1.26	1.24	0.72	0.16	0.06	0.03
SUM	98.73	99.24	99.39	96.67	97.34	99.35	96.61	96.65	98.04

Atomic proportions (Σ atoms = 58)

K	5.99	5.98	5.98	5.99	6.04	5.40	5.21	5.23	5.15
Fe	15.84	15.43	15.81	15.87	15.33	16.12	16.93	16.89	16.72
Ni	0.40	0.53	0.39	0.54	0.39	0.78	1.05	1.11	1.06
Cu	8.78	8.93	8.68	8.75	8.87	8.38	7.58	7.66	7.67
ΣMet.	25.02	24.89	24.88	25.16	24.59	25.28	25.56	25.66	25.45
S	26.02	26.22	26.18	25.91	26.45	26.80	27.10	27.06	27.39
Cl	0.96	0.91	0.96	0.94	0.92	0.52	0.12	0.05	0.02
S + Cl	26.98	27.13	27.14	26.85	27.37	27.32	27.22	27.11	27.41

*WDS electron-microprobe analyses: JEOL-733 electron microprobe; see text for analytical conditions.

**Average of two analyses.

Cl-poor analogues of djerfisherite-thalferisite from Noril'sk

Initial (WDS: JEOL 733 microprobe) analyses of the ADT gave concentrations of chlorine and cobalt below the detection limits; Cl also was sought, but not detected, with a Cameca electron microprobe (Ya. Pakhomovskii, pers. commun.). Typically, chlorine does not occur in the phases (Table 2), and only a few of more than twenty ADT crystals analyzed with EDS imply the possible presence of minor chlorine (<0.2 wt. % Cl). This material contrasts with djerfisherite and thalferisite, which both invariably contain essential Cl (Clarke et al. 1994, Rudashevsky et al. 1979). As a test, the same EDS procedure was applied (almost simultaneously) to the Salmagorsky djerfisherite, which gave the normal level of Cl. The copper concentrations in the ADT are uniform (4.1-6.3 wt. % Cu), nickel is higher (8.4-9.9 wt. % Ni), and all the grains contain lead (4.2 to 9.6 wt. % Pb; 0.6-1.3 apfu). The empirical formulae, calculated on the basis of Σ atoms = 58 (Table 2),

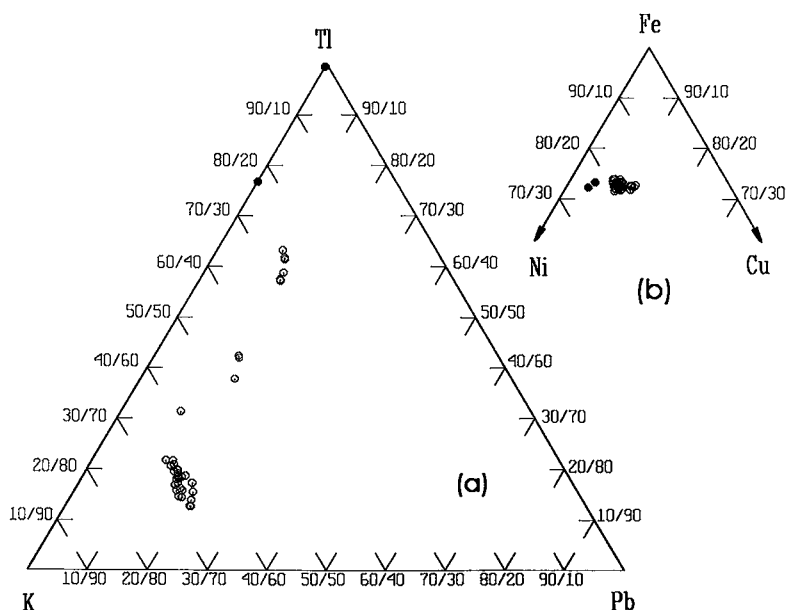


FIG. 3. Diagrams illustrating ranges in compositions of Cl-poor djerfisherite-thalfeisite analogues from Oktyabrsky (open symbol; this study), compared with thalfeisite (solid symbol; Rudashevsky *et al.* 1979): (a) K-Tl-Pb and (b) Ni-Fe-Cu (atom. %).

TABLE 5. REPRESENTATIVE COMPOSITIONS* OF ARGENTOPENTLANDITE FROM OKTYABRSKY

	Weight %				
	1	2	3	4	5
Fe	39.55	39.75	39.56	40.32	40.45
Ni	15.84	15.73	15.75	15.64	15.65
Ag	13.95	14.01	14.01	13.60	12.63
S	31.50	31.47	31.59	31.24	31.93
SUM	100.84	100.96	100.91	100.80	100.66
Atomic proportions (Σ atoms = 17)					
Fe	5.76	5.79	5.76	5.88	5.85
Ni	2.20	2.18	2.18	2.17	2.15
Σ	7.96	7.97	7.94	8.05	8.00
Ag	1.05	1.06	1.06	1.03	0.95
S	7.99	7.98	8.01	7.93	8.05

* EDS electron-microprobe analyses. # 1-3: irregular individual grains; # 4: nearly triangular grain (pseudomorph after Cl-poor analogue of djerfisherite-thalfeisite (?); # 5: rim around Cl-poor analogue of djerfisherite-thalfeisite.

correspond to the stoichiometry of owensite; the latter also contains lead (up to 5.2 wt.% Pb; Laflamme *et al.* 1995). An extensive solid-solution series between the K- and Tl-rich end members, $(K,Tl,Pb)_6(Fe,Ni,Cu)_{25}S_{27}$ and $(Tl,K,Pb)_6(Fe,Ni,Cu)_{25}S_{27}$, respectively, is evident

from data in this study (Fig. 3a). A very strong negative correlation ($R = -0.98$) between K and Tl in the compositions indicates that K is replaced by Tl in the structure.

Variations in concentrations of the transition elements in the ADT are rather restricted. In terms of the Fe-Ni-Cu content, the ADT are comparable with thalfeisite (Fig. 3b) and are distinct from owensite, which is Cu-rich.

The composition of the argentopentlandite that rims the ADT is close to that of the individual grains (Table 5). The compositions are in good agreement with the ideal formula, $(Fe,Ni)_8AgS_8$. Compared with most examples of argentopentlandite from the literature (Morales-Ruano & Fenoll Hach-Alf 1996, and references therein), the compositions in this study are noteworthy in being iron-rich: 5.8–5.9 *apfu* Fe (Table 5).

Djerfisherite from Salmagorsky

Djerfisherite may be nonstoichiometric with respect to transition elements: from 23 to 24 (Fe, Ni, Cu, Co) *apfu* are reported in the literature (Clarke *et al.* 1994, and references therein). In contrast, the Salmagorsky djerfisherite is remarkably stoichiometric, as revealed by both EDS and WDS analyses (Tables 3, 4), and closely corresponds to the formula $K_6(Fe,Cu,Ni)_{25}S_{26}Cl$. A narrow range of Cl content (1.24–1.42 wt.%; 0.91–1.03 *apfu* Cl) is characteristic of this djerfisherite.

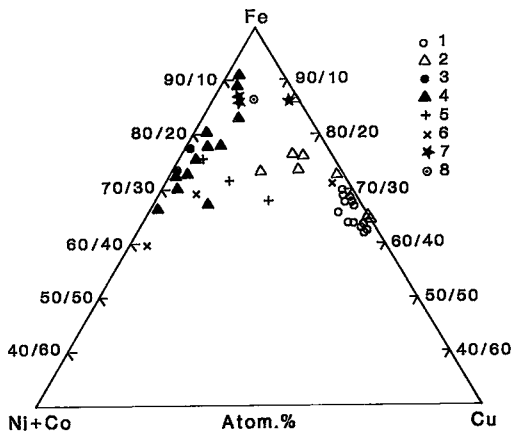


FIG. 4. Ni (+Co) – Fe – Cu plot of djerfisherite compositions from various terrestrial occurrences; 1: from Salmagorsky (djerfisherite and AD; this study), 2: from alkaline rocks and carbonatites at Khibina, Kovdor, Lovozero and Murun (Ifantopulo *et al.* 1978, Balabonin *et al.* 1980, Dobrovol'skaya *et al.* 1980), 3: from serpentinite and peridotite at Kovdor and Inagli (Balabonin *et al.* 1980, Yermeev *et al.* 1982), 4: from kimberlites and xenoliths in kimberlites, Yakutia (Dobrovol'skaya *et al.* 1975, Distler *et al.* 1987) and Elwin Bay, Northwest Territories (Clarke *et al.* 1994), 5: from eclogite (xenolith in kimberlite), Yakutia (Govorov *et al.* 1984), 6: from Cu–Ni sulfide ores at Noril'sk (Genkin *et al.* 1981), 7: from magnesian skarns in the Yoko–Dovyren layered intrusion, Pribaikal'e (Kislov *et al.* 1994), 8: from a skarn at Tazheran, Siberia (Konev *et al.* 1972).

Figure 4 shows compositional data for djerfisherite from various terrestrial occurrences, compared with that from Salmagorsky. In general, examples of djerfisherite from alkaline rocks display the highest concentrations of copper. However, djerfisherite from ultramafic rocks in alkaline ultramafic complexes may be very Cu-poor (Balabonin *et al.* 1980, Yermeev *et al.* 1982). The Salmagorsky djerfisherite is particularly rich in Cu (up to 21.9 wt.%), being among the richest known to date. Lesser amounts of Cu are reported for djerfisherite from Noril'sk (up to 16.6 wt.% Cu: Genkin *et al.* 1981) and the Murun alkaline complex, Siberia (16.4 wt.% Cu: Dobrovol'skaya *et al.* 1980). Djerfisherite from other occurrences, including kimberlites, xenoliths in kimberlites and skarns, are typically poor in Cu (Fig. 4). Djerfisherite from kimberlites and xenoliths in kimberlites (Clarke *et al.* 1977, 1994, Clarke 1979), along with djerfisherite from the disseminated pyrrhotite-rich Noril'sk ores (Genkin *et al.* 1981), show the highest level of enrichment in Ni (Fig. 4). Djerfisherite associated with various skarns is characteristically Fe-rich (Konev *et al.* 1972, Orsoev *et al.* 1993, Kislov *et al.* 1994).

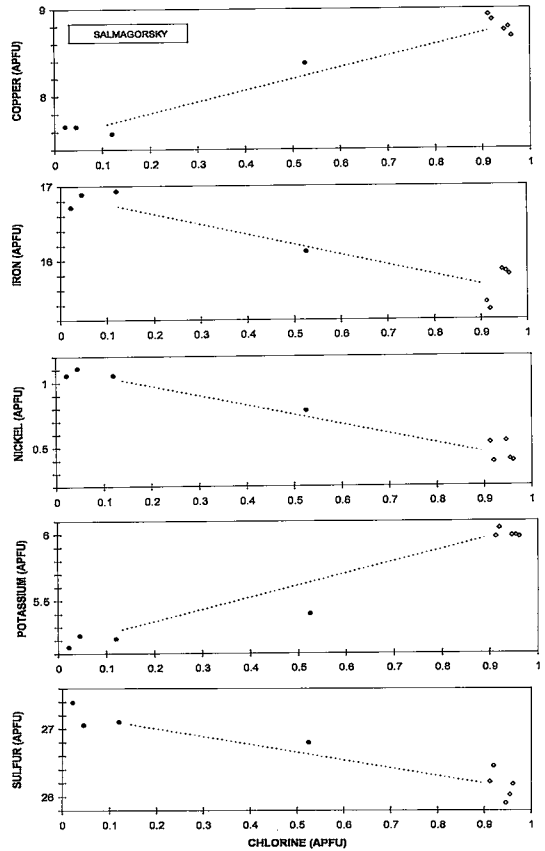


FIG. 5. Plot of chlorine versus copper, iron, nickel, potassium and sulfur contents (apfu; Σ atoms = 58) in djerfisherite (open symbol) and associated Cl-poor analogue of djerfisherite (solid symbol) from the Salmagorsky complex.

Cl-poor analogue of djerfisherite from Salmagorsky

Compared with the djerfisherite from Salmagorsky, the coexisting AD is characterized by: (1) low Cl (0.03–0.72 wt.% Cl; 0.02–0.52 apfu Cl), (2) low K, (3) higher Ni and Fe, (4) lower Cu, (5) higher totals of transition elements, and (6) higher S (Table 4). These distinctions are illustrated in Figures 5 and 6. If calculated on the basis of Σ atoms = 58, the total of S and Cl is close to 27 apfu in both djerfisherite and Cl-deficient sulfide (Tables 3, 4). This implies the existence of the S-for-Cl substitution, as previously noted in ADT from Noril'sk.

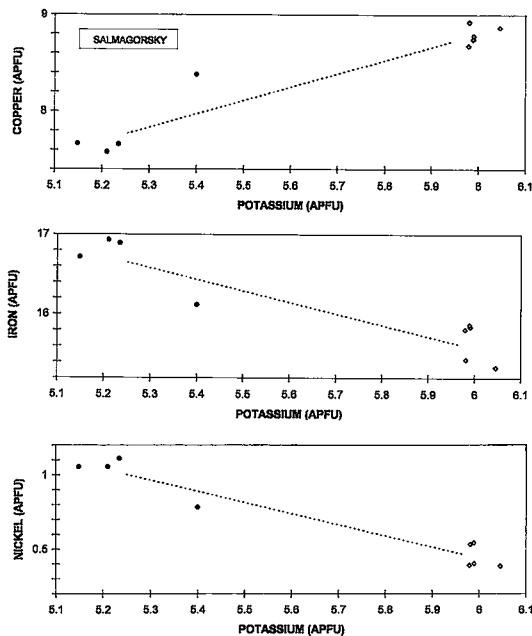


Fig. 6. Plot of potassium *versus* copper, iron and nickel contents (*apfu*; Σ atoms = 58) in djerfisherite (open symbol) and associated Cl-poor analogue of djerfisherite (solid symbol) from the Salmagorsky complex.

DISCUSSION

The occurrences of Cl-deficient K-(Tl-Pb)-bearing sulfides in the Noril'sk and Salmagorsky complexes provide evidence for the existence of Cl-free analogues of djerfisherite and thalfeisite, both of which normally contain about 1 *apfu* Cl (Czarnaske *et al.* 1979, Rudashevsky *et al.* 1979, Clarke *et al.* 1994). However, a synthetic Cl-free djerfisherite-like compound has been reported by Gorbachev & Nekrasov (1980).

In accordance with the "50% rule" in mineral nomenclature (*e.g.*, Nickel 1992), the Cl-poor djerfisherite and thalfeisite analogues with $S > Cl$ in the Cl site can be proposed to represent new mineral species. Unfortunately, no X-ray studies could be carried out because of the small grain-size of the Cl-poor phases at Noril'sk and Salmagorsky. By analogy with (Cl-free) owensite, these and related phases also appear to be structurally similar to djerfisherite and belong to the djerfisherite group.

Evidence from Noril'sk

The *ADT* from Noril'sk are distinct from djerfisherite-thalfeisite in that they are Cl-deficient and invariably contain essential lead (4.2–9.6 wt.% Pb; 0.6–1.3 *apfu*), which is absent in thalfeisite and

djerfisherite (Rudashevsky *et al.* 1979, Clarke *et al.* 1994, and references therein). The presence of Pb^{2+} substituting for K^+ and Tl^+ in the *ADT* structure seems to be of considerable significance in order to compensate the charge imbalance in the probable S^{2-} -for-Cl-substitution. Thus, the following coupled substitution is suggested to occur: $Pb^{2+} + S^{2-} \rightarrow K(Tl)^+ + Cl^-$. This is not inconsistent with owensite, which is Cl-free and contains only divalent cations in the Ba site. The other important substitution in the *ADT* is homovalent: $K^+ \rightarrow Tl^+$.

In spite of the fact that the *ADT* occur in a copper-rich environment (chalcopyrite-rich ore) and form as inclusions in chalcopyrite, they are rather poor in Cu (4.1–6.3 wt.% Cu). This feature suggests that a factor(s) other than the extent of Cu-(Ni-Fe) enrichment has controlled their composition.

The rims of argentopentlandite (Fig. 1a) deserve attention, since similar textures have not previously been reported, and similarities exist between the djerfisherite and argentopentlandite structures. Probably, silver was an incompatible element during growth of the *ADT* crystals, and became sufficiently concentrated at the border to form argentopentlandite. Since the latter is only stable up to 455°C (Mandziuk & Scott 1977), the rims presumably were formed below this temperature. Morales-Ruano & Fenoll Hach-Alí (1996) proposed a generalized formula for argentopentlandite: $(Fe_{5 \pm 0.77}Ni_{3 \pm 0.75})_{\Sigma 8 \pm x}Ag_{1 \pm y}S_{8 \pm z}$, with $0 < x < 0.30$, $0 < y < 0.23$, and $0 < z < 0.30$. The compositions in our study yield Fe and Ni values in the ranges 5.8–5.9 and 2.15–2.2, respectively, *i.e.*, close to the ideal formula $(Fe_6Ni_2)AgS_8$.

The presence of submicroscopic grains of galena (?) along the periphery of *ADT* crystals (Figs. 2a, b) also is of interest. They appear to have formed after the *ADT*. Probably excess Pb could not be incorporated into crystal structure of the *ADT* under the conditions of growth, and was precipitated separately. Although the *ADT* contain as much as 21 mol.% of a hypothetical lead-rich end-member $Pb_6(Fe,Ni,Cu)_{25}S_{27}$, the observed solid-solution series essentially does not extend toward the Pb end-member (Fig. 3a). However, this fact cannot be taken as evidence for the absence of a more extensive solid-solution series involving K-, Tl- and Pb end members. A lead-rich base-metal sulfide, shadlunite (and related manganese-shadlunite), which occurs at Noril'sk, is reported to belong to the pentlandite group (Evstigneeva *et al.* 1973). However, it is also possible that these minerals are akin to the djerfisherite group. It is noteworthy that initial interpretation of the owensite stoichiometry was Me_9S_8 , and it was only possible to understand the true stoichiometry after the crystal-structure study (Laflamme *et al.* 1995, Szymański 1995). Assuming an essential Me^{2+} -for-Pb substitution in shadlunite, the representative composition given in Evstigneeva *et al.* (1973) and Genkin *et al.* (1981), *i.e.*, Pb 16.6, Cd 3.9, Cu 27.5, Fe 24.1, S

27.4, total 99.5 wt.%, may be recalculated on the basis of Σ atoms = 58 to the formula $(\text{Pb}_{2.53}\text{Me}^{2+}_{2.34}\text{Cd}_{1.10})_{\Sigma 5.97}(\text{Cu, Fe})_{\Sigma 25.00}\text{S}_{27.03}$, where $\text{Me} = \text{Fe}^{2+}$ or Cu . The fact that Mn can readily replace Pb in the (manganese)-shadlunite structure may imply the possibility of Fe-for-Pb substitution in these minerals. Since shadlunite can contain up to 9.1 wt.% Cd (Karpenkov 1974; cited in Genkin *et al.* 1981), the existence of the Cd-predominant member also is possible. It seems that all these Noril'sk minerals under discussion may represent the K-, Tl-, Pb-, Mn- and Cd (?) -predominant, Cl-free members of the djerfisherite group, akin to owensite; this possibility should be tested in further studies. In addition, the possible incorporation of a transition element (Ni) in the K site of a Cl-poor djerfisherite-like mineral is implied by the findings from the Salmagorsky complex.

Evidence from Salmagorsky

Unlike many compositions of djerfisherite reported in the literature (Clarke *et al.* 1994, and references therein), the Salmagorsky examples are in excellent agreement with the ideal formula. In contrast, the AD differs in composition, and shows a relative depletion in K, an increase in Ni (and Fe), a somewhat lower Cu content, and an excess in total transition elements (Table 4, Figs. 5, 6). The empirical S (+ Cl) values in the formulae are close to 27 *apfu*, like those in the ADT from Noril'sk and in owensite. We conclude from these observations that (1) there is a Cl-poor natural analogue of djerfisherite, which is characterized by significant (probably unlimited) S-for-Cl substitution (in the Cl site); a transitional variety with 0.5 *apfu* Cl was encountered at Salmagorsky; (2) the incorporation of S instead of Cl into the structure also involves an essential increase in the content of a transition element (Ni) and a decrease in K. A comparison between the Cl-bearing and Cl-deficient compositions in Table 4 implies a minor substitution of Fe for Cu. Assuming that Ni is incorporated in the K site, the empirical formula for a representative composition (anal. 8, Table 4) may be written $(\text{K}_{5.23}\text{Ni}_{0.77})_{\Sigma 6.00}(\text{Fe}_{16.89}\text{Cu}_{7.66}\text{Ni}_{0.34})_{\Sigma 24.89}(\text{S}_{27.06}\text{Cl}_{0.05})_{\Sigma 27.11}$ (basis: Σ atoms = 58). Consequently, by analogy with the ADT from Noril'sk, the charge balance for the heterovalent substitution of S^{2-} for Cl^- could be maintained by the substitution of Me^{2+} for K^+ , *i.e.*, a coupled substitution of $\text{Ni}^{2+} + \text{S}^{2-} \rightarrow \text{K}^+ + \text{Cl}^-$.

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