

## OCCURRENCE AND ORIGIN OF DJERFISHERITE FROM THE ELWIN BAY KIMBERLITE, SOMERSET ISLAND, NORTHWEST TERRITORIES

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### ABSTRACT

This paper focuses on a new occurrence of djerfisherite [approximately  $K_6(\text{Na,Li})(\text{Fe,Ni,Cu})_{24}\text{S}_{26}\text{Cl}$ ] from the Elwin Bay kimberlite on Somerset Island. The small (up to 10  $\mu\text{m}$ ), subhedral grains of djerfisherite occur individually and as clusters in the groundmass, suggesting that they are late primary magmatic phases of the kimberlite. Based on 84 compositions obtained with an electron microprobe, compositional ranges (weight percent) are: K (8.78–9.94), Fe (34.76–47.35), Ni (3.92–18.88), Cu (0.09–4.49), S (31.81–34.70), and Cl (1.25–1.57). Grain-to-grain compositional variation exists, as does variation within single zoned grains, characterized predominantly by a Fe-rich core and a Ni-rich rim. The analytical data indicate that Cl is an essential component of the Elwin Bay djerfisherite, as it is consistently present at a level of one atom per formula unit. The compositions also show a strong relation between the total number of transition-element cations (Fe, Ni, Cu) per formula unit and the number of *d*-shell electrons (DSE). There are two types of substitution: (i)  $2\text{Ni} \leftrightarrow (1+x)\text{Fe} + (1-x)\text{Cu}$ , where the value of *x* approaches 1, in the Early and Late stages, when the evolving composition of the magma controls the composition of the djerfisherite, and (ii)  $\text{Fe} \leftrightarrow 0.5\text{Cu} + 0.75$ ,  $\text{Ni} \leftrightarrow 1.5\text{Cu} + 0.25$ , and  $\text{Ni} \leftrightarrow 2.5 - 3\text{Fe}$ , reactions that stabilize the DSE at 6.50 in the intermediate stage. The stability of djerfisherite depends in part on fixing *d*-shell electrons in the cubic clusters of transition elements. The formula of the putative iron end-member of the Elwin Bay djerfisherite is approximately  $K_6\text{Fe}_{22.75}\text{S}_{26}\text{Cl}$ .

*Keywords:* djerfisherite, potassium, transition element, chlorine, sulfide, kimberlite, Elwin Bay, Northwest Territories.

### SOMMAIRE

Nous décrivons un nouvel exemple de djerfisherite, répondant à la formule approximative  $K_6(\text{Na,Li})(\text{Fe,Ni,Cu})_{24}\text{Cl}$ , dans la kimberlite de la baie d'Elwin, sur l'île de Somerset, Territoires du Nord-Ouest. De petite taille (10  $\mu\text{m}$  au plus), les cristaux sont soit isolés, soit regroupés dans la pâte, ce qui fait penser qu'il s'agit d'une phase tardi-magmatique. À la lumière de 84 compositions obtenues avec une microsonde électronique, la djerfisherite contient (en pourcentages pondéraux), K (8.78–9.94), Fe (34.76–47.35), Ni (3.92–18.88), Cu (0.09–4.49), S (31.81–34.70) et Cl (1.25–1.57). Nous décelons des variations d'un grain à l'autre, ainsi qu'à l'intérieur d'un seul grain; dans ce cas, le cœur est enrichi en Fe, tandis que la bordure est enrichie en Ni. D'après nos données, le Cl serait un composant essentiel de la djerfisherite de cet endroit, étant systématiquement présent au niveau d'un atome par unité formulaire. Les compositions montrent une forte relation entre le nombre de cations d'éléments du groupe de transition (Fe, Ni, Cu) par unité formulaire et le nombre d'électrons *d* dans la structure. Deux schémas de substitution seraient importants: (i)  $2\text{Ni} \leftrightarrow (1+x)\text{Fe} + (1-x)\text{Cu}$ , dans lequel la valeur de *x* se rapproche de 1, qui semble régir la composition des stades précoce et tardif de la croissance à partir du magma en évolution, et (ii)  $\text{Fe} \leftrightarrow 0.5\text{Cu} + 0.75$ ,  $\text{Ni} \leftrightarrow 1.5\text{Cu} + 0.25$ , et  $\text{Ni} \leftrightarrow 2.5 - 3\text{Fe}$ , qui stabilisent la structure ayant 6.50 électrons dans l'orbite *d* au stade intermédiaire de croissance. La stabilité de la djerfisherite dépend donc en partie de la proportion des électrons *d* associés aux métaux de transition en regroupements cubiques. La formule du pôle ferrifère de la djerfisherite de la baie d'Elwin se rapprocherait de  $K_6\text{Fe}_{22.75}\text{S}_{26}\text{Cl}$ .

(Traduit par la Rédaction)

*Mots-clés:* djerfisherite, potassium, élément de transition, chlore, sulfure, kimberlite, baie d'Elwin, île de Somerset, Territoires du Nord-Ouest.

## INTRODUCTION

Potassium, commonly regarded in geochemical terms as one of the classic *lithophile* elements, can

behave as a *siderophile* element under high-pressure conditions (Bukowski & Knopoff 1977), and also as a *chalcophile* element under conditions of high  $f(S_2)$  and low  $f(O_2)$ . This ability of potassium to assume

TABLE 1. SUMMARY OF DJERFISHERITE OCCURRENCES AND ORIGINS

Association	Example/Reference	Mineral Assemblage/ Texture	Deduced Origin*
Meteorites	Kota Kota and St. Marks (Fuchs 1966); Bishopville, Pena Blanca Springs, Toluca (El Goresy et al. 1971); EH chondrites (Kimura & El Goresy 1988); Khor Temiki achondrite (Ntaflos et al. 1988)	close spatial relationships with troilite, chalcopyrrhotite [ <i>sic</i> ], kamacite, graphite; some Djf grains appear primary, others secondary in veins	Djf either a normal member of primordial condensation sequence (caswellsilverite $[NaCrS_3]$ - roedderite $[(Na,K)_2(Mg,Fe)_2Si_2O_{10}]$ - plagioclase - djerfisherite), although the textures suggest a reaction between Fe-Ni metal and $K+H_2O$ gas, or a product of subsequent magmatic, metamorphic, or hydrothermal processes
Alkaline Mafic Rocks	kimberlites (Dobrovolskaya et al. 1975; Clarke 1979; Govorov et al. 1984; Distler et al. 1987; Spetsius et al. 1987; Solovyeva et al. 1988)	Djf apparently more common in megacrysts (Ol, Cpx, Ilm) and xenoliths (garnet peridotite, eclogite, alkremitite) than in the groundmass of host kimberlites; close spatial relationship with, and partial to complete replacement of, Po-Pn-Ccp	general consensus on metasomatic alteration of primary (magmatic) Po-Pn-Ccp by introduction of K-(Cu)-Cl-bearing fluid or vapor phases, but unclear whether the metasomatic event occurred in the mantle prior to formation of the kimberlite, or whether the kimberlitic fluid itself was the metasomatizing agent, and alteration of the inclusions occurred at a late stage in the diatreme
	Coyote Peak alkaline - ultramafic diatreme (Morgan et al. 1985)	Ol-Mag-Phl-Mel-Ne-Sdl-Prv- <i>Ap</i>	Djf, Rsv, and other K-sulfides are primary products of crystallization from melt
	Finero ultramafic complex (Bianconi et al. 1978)	Pn-Hzw-Po-Ccp	serpentinization, reduction, and sulphidization of peridotite - Djf secondary after blocky magmatic Pn
Alkaline Felsic Rocks and Mineral Deposits	Khibina alkaline complex (Sokolova et al. 1970)	several associations, including euhedral to subhedral grains in subgraphic intergrowths of Kfs and Aa, drop-shaped grains in massive urtite layers, and reaction rims on Po in alkaline pegmatites - coexisting sulfides include Po, Pn, Py, Ccp, Sp, Gn, Cub	apparently primary magmatic (subhedral to euhedral grains), immiscible (?) droplets, and metasomatic (reaction rims)
	skarns of the Tazheran alkaline syenite (Konev et al. 1972);	occurs in high-temperature Wo-Pl-Px-Hbl skarns as reaction rims on Tro	high chemical potential of potassium in iron ore-forming solutions produced kalsilite and Djf (as rims on Tro)
	Talnakh copper deposit (Genkin et al. 1970);	associate Cub and cubic Ccp (talnakhite) along boundary with Po + Pn ores	some euhedral Djf may be primary, but the rest results from reaction between late alkali sulfide fluids and metal sulfide minerals
	Jinchuan copper deposit (Zang & Chen 1985)	Pn + Hem + Au + platinum group minerals (Djf Ni/Cu > 10)	cocrystallization of Pn and Djf followed by their replacement by Po and Ccp(?)
Synthetic	Mt. Isa slags (Riley 1978)	euhedral grains associated with Mag-Tro-Ce-Bn-native Cu	primary crystallization of Djf from molten slag
	electrochemical experiments (Mrzacek & Battles 1977)	forms on positive FeS electrode in eutectic LiCl-KCl electrolyte	troilite and alkali halides react at 450-500°C to produce Djf
	evacuated silica tube experiments (Clarke 1979)	fine-grained assemblages of Djf, Po, Hz, $KFeS_3$ , KCl	decomposition products of K- and Cl-bearing starting materials react with troilite at 350-650°C to produce Djf

\*Origins are not always clear in primary references. Our comments include some inferences from described textures and figures.

Mineral Abbreviations (largely after Kretz, 1983): Ae - aegirine; Ap - apatite; Bn - bornite; Ce - chalcocite; Ccp - chalcopyrite; Cub - cubanite; Djf - djerfisherite; Gn - galena; Hbl - hornblende; Hem - hematite; Hzw - heazlewoodite; Kfs - K-feldspar; Mag - magnetite; Mel - melilitite; Ne - nepheline; Ol - olivine; Phl - phlogopite; Po - pyrrhotite; Pl - plagioclase; Pn - pentlandite; Prv - perovskite; Px - pyroxene; Py - pyrite; Rsv - rasvumite; Sdl - sodalite; Sp - sphalerite; Tro - troilite; Wo - wollastonite

radically different types of geochemical behavior has important implications for its distribution among the crust, mantle, and core of the Earth (Murthy & Hall 1970, Lewis 1971, Goettel 1973).

Although research chemists produced synthetic potassium sulfide compounds more than a century ago (Schneider 1888), the discovery of djerfisherite [approximately  $K_6(Na, Li)(FeNiCu)_{24}S_{26}Cl$ ] in meteorites established the first natural example of the *chalcophile* behavior of potassium (Fuchs 1966). Since that discovery, djerfisherite has been found in several other settings, notably in xenoliths from kimberlite diatremes and in various types of mineral

deposits (Table 1). Compositional variations in djerfisherite mostly involve the transition elements ( $Fe \rightleftharpoons Ni \rightleftharpoons Cu$  substitutions), although the possibility exists of  $Na \rightleftharpoons Li \rightleftharpoons Cu$  substitution in one of the transition-element sites, possibly coupled to  $S \rightleftharpoons Cl$  in the anion site. In general, djerfisherite compositions in meteorites are low in Ni and in Cu, those in mafic-ultramafic igneous rocks are high in Ni and low in Cu, and those in various types of mineral deposits compositionally reflect the type of deposit.

In this paper, we describe a new occurrence of djerfisherite from the Elwin Bay kimberlite on Somerset Island, and consider its origin on the basis

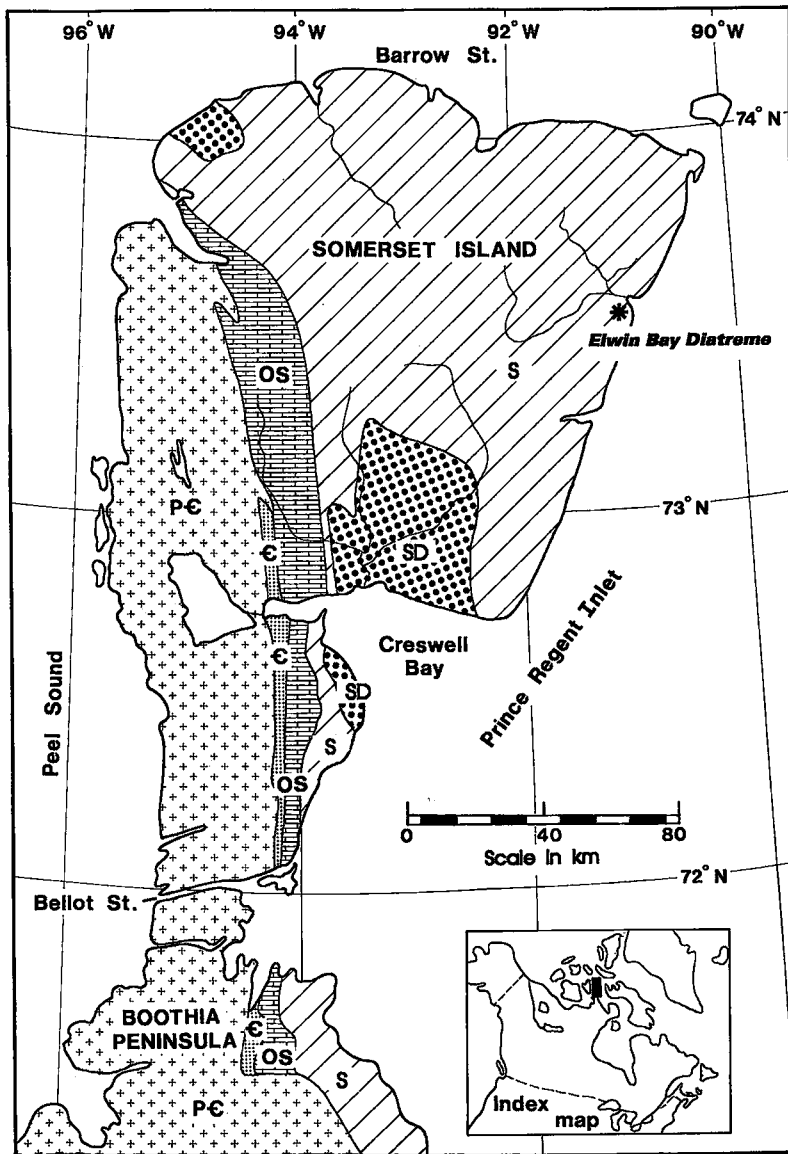


FIG. 1. Location map for the Elwin Bay kimberlite diatreme (after Clarke & Mitchell 1975). Symbols: PC Precambrian basement, C Cambrian sandstone and dolomite, OS Ordovician and Silurian dolomite and dolomitic sandstone, S Silurian limestone and shaly dolomitic limestone, D lower Devonian conglomerate, sandstone, and siltstone.

of textural and chemical data. Also, the wide range of djerfisherite compositions at this locality lead to an examination of the mechanisms of substitution, and a probable formula of djerfisherite.

#### GEOLOGICAL SETTING AND PETROLOGY

The Elwin Bay diatreme (73° 30' N, 91° 7.5' W; Fig. 1) forms a small circular intrusion *ca.* 200 m in diameter lying near the east coast of Somerset Island, Northwest Territories (Mitchell 1976, 1978). The ultramafic rocks apparently intrude the surrounding Silurian limestones, but their surface exposures are expressed only as frost-heaved regolith. Uranium-lead age determinations on perovskite grains from related kimberlitic rocks elsewhere on Somerset Island yield a Cretaceous age in the interval from 88–110 Ma (Heaman 1989, Smith *et al.* 1989).

The Elwin Bay diatreme is a hypabyssal root-zone intrusion of monticellite – calcite – serpentine kimberlite (Mitchell 1986). It contains abundant rounded macrocrysts of serpentized olivine, rare rounded macrocrysts of phlogopite, and titanian pyrope with a kelyphitic rim, in a predominantly uniform, fine-grained groundmass consisting of spinel, perovskite, and pyrite set in a mesostasis of phlogopite-kinoshitalite, calcite, and primary serpentine. Coarser-grained segregations of phlogopite-kinoshitalite and calcite are common.

The grains of djerfisherite occur as small subhedral to skeletal crystals in the kimberlite groundmass (Fig. 2), suggesting that they are late primary magmatic phases of this diatreme. This contrasts with most described examples of djerfisherite, which occur in

mantle-derived xenoliths entrained by kimberlite, and in which they are normally secondary after pyrrhotite and pentlandite. To date, djerfisherite has been found in only one hand specimen (EL-8) at Elwin Bay.

#### MINERAL CHEMISTRY

##### Analytical methods

A JEOL 733 electron microprobe equipped with an Oxford Link eXL energy-dispersion system was used for the analyses. Resolution of the energy-dispersion detector was 137 eV at 5.9 keV. Operating conditions (accelerating voltage 15 kV, beam current 13 nA, and beam diameter *ca.* 1  $\mu\text{m}$ ) resulted in a count rate of  $\sim 11\,000$  cps on chalcopyrite; counting times were 40 seconds. The raw data were corrected using the Link ZAF matrix-correction program. Instrument calibration was performed on cobalt metal ( $\pm 0.5\%$ ), and accuracy for major elements is  $\pm 1.5$  to 2.0% relative. Geological standards and pure metals were used as controls: chalcopyrite for Fe, Cu and S, arsenopyrite for As, tugtupite for Cl, cobaltite for Co, sphalerite for Zn, barite for Ba, galena for Pb, sanidine for Si, Al, and K, kaersutite for Ti and Mg,  $\text{MnO}_2$  for Mn, synthetic Ag–Au alloy for Ag, and pure metals for Mn and Cr. Images were collected using a two-part, annular type *pn*-junction back-scattered detector at a  $512 \times 512$  pixel resolution.

##### Chemical compositions

Compositional ranges based on 84 analyses of djerfisherite from Elwin Bay are (in wt.%):

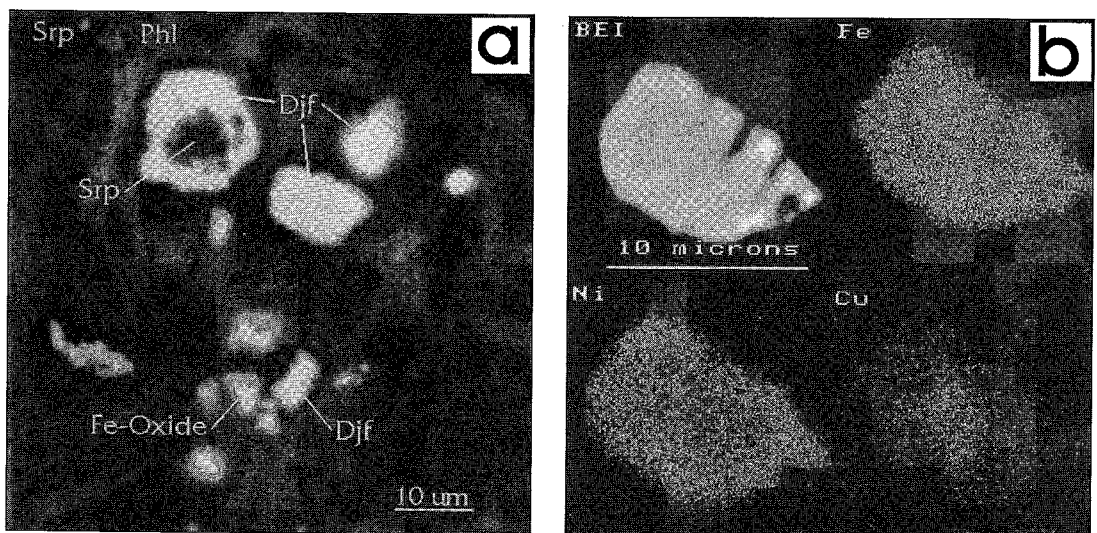


FIG. 2. Back-scattered electron images and X-ray maps. (a) Djerfisherite and coexisting phases in the groundmass of the Elwin Bay kimberlite. (b) Typical single grain of djerfisherite showing zoning from Cu-rich interior to Ni-rich rim.

TABLE 2. REPRESENTATIVE COMPOSITIONS OF DJERFISHERITE FROM ELWIN BAY

Grain	1	2	3	4	5	6	7	8
<i>Analysis (wt. %)</i>								
K	9.46	9.30	9.49	9.57	9.62	9.35	9.04	9.10
Fe	47.35	47.17	45.59	42.09	42.57	39.99	38.46	36.73
Ni	3.92	4.63	6.49	8.08	9.52	12.06	15.91	18.88
Cu	1.17	1.29	3.36	4.10	3.27	1.56	1.39	0.54
S	34.37	33.90	33.21	33.36	33.78	33.85	33.48	33.08
Cl	1.41	1.28	1.37	1.46	1.57	1.48	1.44	1.45
Total	97.68	97.57	99.51	98.66	100.33	98.29	99.72	99.78
<i>Cations per formula unit (S=26)</i>								
K	5.87	5.85	6.09	6.12	6.07	5.89	5.76	5.87
Fe	20.57	20.77	20.49	18.83	18.81	17.64	17.15	16.57
Ni	1.62	1.94	2.78	3.44	4.00	5.06	6.75	8.11
Cu	0.45	0.50	1.33	1.61	1.27	0.60	0.54	0.21
S	26.00	26.00	26.00	26.00	26.00	26.00	26.00	26.00
Cl	0.96	0.89	0.97	1.03	1.09	1.03	1.01	1.03
<i>TTE = Total Transition Elements (per formula unit)</i>								
TTE	22.63	23.21	24.60	23.89	24.09	23.30	24.44	24.90
<i>DSE = Number of D-Shell Electrons (per transition element)</i>								
DSE	6.20	6.23	6.39	6.49	6.49	6.51	6.62	6.68

Na contents &lt; 0.1%

Li not determined

TTE = Total Transition Elements (per formula unit)

DSE = Number of D-Shell Electrons (per transition element)

K 8.78–9.94, Fe 34.76–47.35, Ni 3.92–18.88, Cu 0.09–4.49, S 31.81–34.70, and Cl 1.25–1.57. Grain-to-grain compositional variation exists, as does variation within single grains, characterized predominantly by an Fe-rich core and a Ni-rich rim. Table 2 presents eight representative compositions of djerfisherite from the Elwin Bay kimberlite. These data show that Cl is an essential component of djerfisherite at the level of one atom per formula unit, that probably no  $S \rightleftharpoons Cl$  substitution occurs, and that Na is not an essential component in these samples. We cannot analyze for lithium, but Li concentrations in the hosts of most djerfisherite-bearing rocks (meteorites, kimberlites, mineral deposits), including the Elwin Bay kimberlite (kimberlite mean: 29 ppm Li; Mitchell 1986), are generally so low that Li is probably present only in trace amounts in most naturally occurring djerfisherite, unlike the compositions of some synthetic djerfisherite (e.g., Tani *et al.* 1986).

## DISCUSSION

*Origin of djerfisherite at Elwin Bay*

Almost all of the djerfisherite grains at Elwin Bay have a Cu-poor, Ni-rich rim, unlike zoned djerfisherite from kimberlites described by Dobrovol'skaya *et al.* (1975), which are zoned outward to a Cu-rich rim. Figures 3a–c show bivariate plots of the three transition elements, and an interpretation of the growth history of these grains. We recognize three stages in their growth: (i) Early stage: high Fe, low Ni; all transition elements negatively correlate with each other; substitution is of the type  $2Ni \rightleftharpoons (1+x)Fe + (1-x)Cu$ , where the value of  $x$  approaches 1; (ii) Intermediate stage: intermediate Fe, intermediate Ni; Fe–Ni and

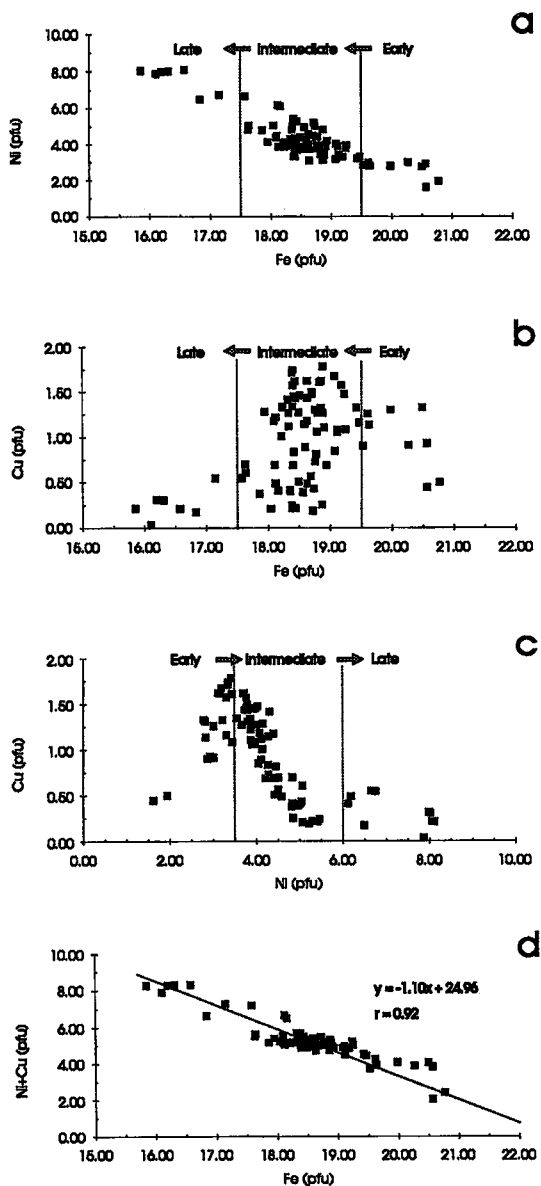


FIG. 3. Transition-element (Fe–Ni–Cu) variations in samples of djerfisherite from Elwin Bay. Positive and negative interelement correlations govern the selection of boundaries demarcating Early, Intermediate, and Late stages (see text). Scales in numbers of cations per formula unit (pfu) based on 26 atoms of sulfur.

Ni–Cu negatively correlate, but Fe–Cu positively correlate; substitution in the three-component system is of the type  $Fe \rightleftharpoons 0.5 Cu + 0.75 Ni$ ,  $Ni \rightleftharpoons 1.5 Cu + 0.25 Fe$ , and  $Ni \rightleftharpoons 2.5 - 3Fe$ , forming a straight line in Fe–Ni–Cu space; and (iii) Late stage: low Fe, high Ni; Fe–Ni

negatively correlate, but Fe–Cu and Ni–Cu positively correlate; substitution is of the type  $2\text{Ni} \rightleftharpoons (1+x)\text{Fe} + (1-x)\text{Cu}$ , where again the value of  $x$  approaches 1 (Fig. 3d).

Overall, Figure 3d shows a substitution approximating  $2\text{Fe} \rightleftharpoons \text{Ni} + \text{Cu}$ . In summary, the skeletal to subhedral nature of the grains, and the occurrence of djerfisherite in the groundmass, suggest that it is a late primary phase of the Elwin Bay kimberlite. The compositional zoning indicates rapid (*i.e.*, disequilibrium) growth.

#### Transition-element substitution and chemical formula

The debate concerning the nature of the mechanism of substitution in all structural positions in djerfisherite is largely unresolved for two reasons: (1) restricted ranges of djerfisherite composition from single localities, and (2) interlaboratory analytical differences that prevent rigorous comparison of djerfisherite compositions from different occurrences. Our analyses of the Elwin Bay djerfisherite grains allow us to circumvent both of these problems, and permit us to comment on possible mechanisms of transition-element substitutions in this mineral.

The general formula of djerfisherite is  $A_{6-x}B_{24-y}S_{26}Z_{1-x}$ , where  $A = \text{K}$ ;  $B = \text{Li}, \text{Na}, \text{Cu}$ ;  $M = \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}$ ;  $S = \text{S}$ ; and  $Z = \text{Cl}$  (Tani *et al.* 1986). The structure of djerfisherite consists of cubic clusters of eight transition element atoms bonded to 14 sulfur atoms. Evans & Clark (1981) noted the similarity of these  $\text{Fe}_8\text{S}_{14}$  clusters in djerfisherite, bartonite, and pentlandite. Published analytical data on djerfisherite (Dmitrieva 1976, Czamanske *et al.* 1979, Tani *et al.* 1986) show that the sum of the transition elements ranges from slightly less than 23 (randomly occupying the 24 available sites) to slightly more than 24. A central question is whether the control on transition-element occupancy is charge balance or, given the metallic bonds among the transition elements in the cubic clusters, whether the control is constancy of  $d$ -shell electrons and, if so, at what number of  $d$ -shell electrons.

Figure 4 shows the relation between the number of transition element atoms (Fe, Ni, Cu) per formula unit and the average number of  $d$ -shell electrons (DSE) per transition element. Most samples have compositions close to  $\text{DSE} = 6.50$ , suggesting compositional control by stabilization of the number of  $d$ -shell electrons at 52 per  $(\text{FeNiCu})_8\text{S}_{14}$  cluster; however, considerable departure from  $\text{DSE} = 6.50$  occurs in the Early- and Late-stage compositions, suggesting control by some other factor, such as variation in the composition of the rapidly fractionating kimberlitic magma.

Figure 5 includes four plots showing variation in the level of transition elements. Figures 5a–c show each of the transition elements as a function of the

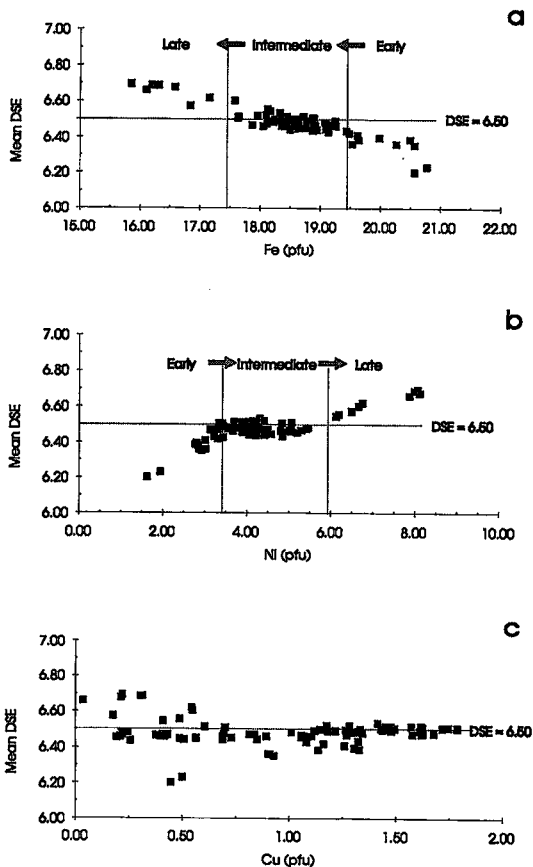


FIG. 4. Variation in level of individual transition elements with calculated mean  $d$ -shell electron (DSE) densities. Crystallization-stage boundaries as in Fig. 3. Constant  $\text{DSE} (= 6.50)$  characterizes the Intermediate stage.

total number of transition element atoms (per formula unit), and Figure 5d shows that for constant  $\text{DSE} = 6.50$ , the total number of transition elements (per formula unit) ranges from 23.25 to 24.25 (mean  $23.78 \pm 0.27$ ,  $n = 68$ ). The role of Cu substitution appears to be critical in maintaining the constancy of  $d$ -shell electrons as Fe increases and Ni decreases.

These data seem to confirm that djerfisherite is *not* stoichiometric with respect to transition elements. In the Elwin Bay samples, a plateau of stability occurs at  $\text{DSE} = 6.50$ , where the substitution is generally  $\text{Fe} + \text{Cu} \rightarrow 2\text{Ni}$ , as suggested by Dmitrieva (1976), although in that particular example stability occurred at  $\text{DSE} \approx 7$ . Rajamani & Prewitt (1973) concluded that  $\text{DSE} = 7$  in the metallicly bonded, cubic clusters of transition elements stabilized the composition of pentlandite at  $\sim \text{Fe}_{4.5}\text{Ni}_{4.5}\text{S}_8$ . The pure iron end-member djerfisherite ( $\text{DSE} = 6$ ) also is stable (Clarke 1979),

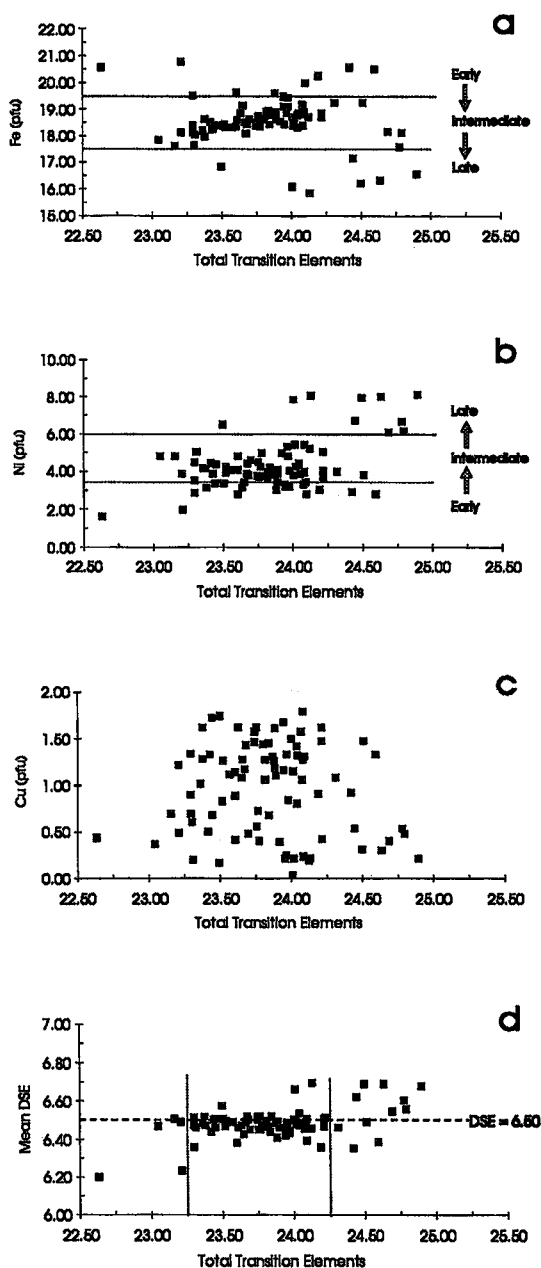


FIG. 5. Variation of total number of atoms of transition elements (TTE) per formula unit (pfu) with concentration of individual cations and mean DSE. Note the scatter of Cu (important in stabilizing DSE at 6.50, depending on the amount of Fe and Ni), and the constancy of DSE between a TTE of 23.25 and 24.25.

raising a question about the systematic stabilization of such compounds, where plateaus of stability may occur at  $DSE = 6.0 + n \cdot (0.25)$ , where  $n$  is an integer.

Garanin *et al.* (1988, Fig. 10) showed a compilation of djerfisherite compositions; those lying close to the Fe–Cu join cluster at values of DSE of 6.25, 6.50, and 7.00, whereas those lying close to the Fe–Ni join scatter near DSE = 6.50.

Finally, returning to Figure 3d, linear regression of the data yields a Pearson correlation coefficient  $r = 0.92$ , an intercept of  $22.74 \pm 0.21$  on the Fe axis, and an intercept of  $24.96 \pm 0.95$  on the (Ni + Cu) axis (note that, in the case of the Elwin Bay djerfisherite, Cu probably equals zero at the extremes of Fe and Ni concentration). Thus, in general terms, the putative Fe end-member djerfisherite at Elwin Bay could have the formula  $K_6Fe_{22.75}S_{26}Cl$  (DSE = 6.00, but not charge-balanced, unless some Fe occurs as  $Fe^{3+}$ ), or possibly  $K_6LiFe_{22.75}S_{26}Cl$ . These structural formulae are virtually identical to that proposed for synthetic djerfisherite (Tani *et al.* 1986). With the inability of the electron microprobe to detect Li, we cannot distinguish between these two alternatives.

#### CONCLUSIONS

The presence of djerfisherite in the Elwin Bay kimberlite is unusual in two respects. First, the djerfisherite appears to be a primary magmatic phase belonging to the late stages of kimberlite crystallization, like those in the Coyote Peak diatreme (Table 1), and unlike most known occurrences in kimberlite xenoliths, which are secondary after pyrrhotite and pentlandite. Secondly, it shows a wide degree of chemical zonation consistent with disequilibrium conditions of crystallization. The chemical zoning permits an investigation of the mechanisms of transition-element substitutions in djerfisherite, which correspond to three stages in the crystallization of the kimberlite groundmass. There are two types of substitution: (i)  $2Ni \rightleftharpoons (1+x)Fe + (1-x)Cu$ , where the value of  $x$  approaches 1, in the Early and Late stages, when the evolving composition of the magma controls the composition of the djerfisherite, and (ii)  $Fe \rightleftharpoons 0.5 Cu + 0.75 Ni \rightleftharpoons 1.5 Cu + 0.25 Ni \rightleftharpoons 2.5 - 3Fe$  reactions that stabilize at DSE = 6.50 in the Intermediate stage. Also, from an analysis of the chemical data, we conclude that the chemical formula of pure iron end-member djerfisherite may be approximately  $K_6Fe_{22.75}S_{26}Cl$ , or possibly  $K_6LiFe_{22.75}S_{26}Cl$ .

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