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Letter

Extreme closed system fractionation of volatile-rich, ultrabasic peralkaline melt inclusions and the occurrence of djerfisherite in the Kugda alkaline complex, Siberia

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ABSTRACT

Djerfisherite [$K_6(Cu,Fe,Ni)_{25}S_{26}Cl$] has been found as a daughter mineral in melt inclusions in melilite from a Kugda melilitolite. The inclusion mineral assemblage includes pyrrhotite, pentlandite, forsterite, diopside, monticellite, phlogopite, wollastonite, nepheline, sodalite, combeite, calcite, Na-K-Ca carbonate, and hydrated calcium silicates. The djerfisherite is Ni-rich rather than Cu-rich consistent with an ultimate upper mantle magma source. The djerfisherite-bearing assemblage formed from primary carbonate/alkali-rich, melilititic melt inclusions which underwent extreme, closed-system, magmatic to postmagmatic fractionation over a temperature range of >1000° to <500°C.

Keywords: fractionation, peralkaline inclusions, djerfisherite, Kugda, Siberia.

Introduction

Sulphides of the alkali metals are extremely rare mineral phases. Djerfisherite, a K-Fe-rich sulphide, was first described from meteorites by Ramdohr (1963) and investigated by El Goresy *et al.* (1971). It has subsequently been described from a variety of terrestrial magmatic occurrences ranging from ultramafic to peralkaline (Table 1), from Cu-sulphide ore deposits (Genkin *et al.*, 1970), and from contact metasomatized carbonate rocks (Jamtveit *et al.*, 1997). Peralkaline igneous rocks also contain other K-Fe sulphide phases [e.g. rasvumite (KFe_2S_3) and murunskite ($K_2Cu_3FeS_4$)], while others include erdite [$NaFeS_2.2H_2O$] (Table 1). Natrocarbonatites from Oldoinyo Lengai, Tanzania, contain an Mn- and F-bearing rasvumite (Jago and Gittins, 1999) as well as K-Fe sulphides which are stoichiometrically different from named K-Fe-S minerals (Dawson *et al.*, 1992; Mitchell, 1997).

Table 1 contains information on djerfisherite parageneses, together with their Ni and Cu affinities and petrogenetic information; representative analyses for magmatic occurrences described in the literature are given in Table 2. It is clear from Table 1 that most djerfisherites are closely associated with other sulphides, particularly pyrrhotite, pentlandite or chalcopyrite. Mantle-derived (mainly kimberlitic) magmatic occurrences tend to have djerfisherites with high Ni and low Cu, while those from alkaline and ultra-alkaline felsic rocks tend to be richer in Cu and poor in Ni (Tables 1,2). Djerfisherites in the most evolved magmatic and post-magmatic occurrences (e.g. Khibina pegmatite, Guli alkali carbonatite, Tazheran alkali metasomatite) are particularly Fe-rich and Cu- and Ni-poor. Representatives from sulphide ore deposits are Cu-rich (Genkin *et al.*, 1970). Most igneous-related occurrences have been attributed to formation during the latest magmatic stages and/or by deuteric/hydrothermal processes involving alkali-rich fluids, generally by alteration of pre-existing, alkali-free primary sulphides. Evidence of djerfisherite occurring as a primary mineral during the earlier stages of magmatic development is much less clear.

We have recently found djerfisherite in highly differentiated melt inclusions in melilitolites from the ultramafic-syenite Kugda massif, Maimecha-Kotui Province, Polar Siberia. This occurrence provides new information which helps to establish

TABLE 1. Occurrence of djerfisherite in igneous rock complexes

Locality	Rock type	Djerfisherite (Djf) associated with:	Djf-type	Origin?	Reference
Mantle					
Kimberlite, Yakutia, Russia	Eclogite nodule in kimberlite	Cpx, ilmenite, pyrrhotite, pentlandite, chalcopyrite, cubanite, mackinawite, Fe-Cu metal	Ni rich, Cu poor	Metasomatism of primary sulphides by K, Cu, Cl fluids; unclear whether in mantle or crust	Dobrovol'skya *et al.*, 1975
Kimberlite, N. Siberia, Russia	Eclogite nodule in kimberlite	Intergrown with diamond and olivine, associated with pyrrhotite, pentlandite	Ni rich, Cu poor	Metasomatic	Bulanova *et al.*, 1980
Frank Smith diatreme, South Africa	Megacryst in kimberlite	Blebs/veins in cpx/ilmenite megacryst, with pentlandite, pyrrhotite, mackinawite	Ni rich, Cu poor	Metasomatism of primary sulphides by K, Cu, Cl fluids; unclear whether in mantle or crust	Clarke *et al.*, 1977
Somerset Island, Canada	Monticellite kimberlite	Groundmass phase with spinel, perovskite, phlogopite, serpentine, pyrite	Ni rich, Cu poor	Late groundmass phase; primary	Clarke *et al.*, 1994
Alkaline ultramafic/basic complexes					
Napolean Bay, Baffin Island, Canada	Lamproites	Aegirine, arfvedsonite, phlogopite, kalsilite after leucite	Ni poor, Cu poor	Groundmass phase, ultimate origin unclear, some effects of hydrothermal processes	Hogarth, 1997
Ile Cadieux, Monteregian Hills, Canada	Alnoite	Phlogopite, monticellite, melilite, perovskite, pentlandite	Ni rich, Cu poor	Primary sulphides metasomatized by fluids during transport to surface	Hanois & Mineau, 1991
Coyote Peak, California	Potassic basic diatreme	Nepheline, phlogopite, pyrrhotite, magnetite, erdite, rasvumite, bartonite	Ni poor, Cu low to mod.	Late magmatic or metasomatic? Erdite replaces rasvumite	Czamanske *et al.*, 1978, 1979
Inagli complex, Aldan Shield, Russia	Peridotite	Phlogopite, ilmenite, apatite, pyrite, pyrrhotite, pentlandite, Cu-Fe metal	Ni poor, Cu low	Metasomatic involving addition of K	Eremeev *et al.*, 1982
Salmagorsky, NW Russia	Mineralized melteigite, ijolite	Aegirine, nepheline, apatite, pyrrhotite, pentlandite, cubanite, pyrite	Ni poor, Cu rich	Primary sulphides altered by post-magmatic fluids (S, Cu, Cl; K from mica)	Barkov *et al.*, 1997; Korobeinikov *et al.*, 1998
Alkali syenite complexes					
Khibina complex, Kola, Russia	Peralkaline syenites	Apatite, chalcopyrite, pyrrhotite, rasvumite	Ni poor, Cu rich/poor	Late magmatic to metasomatic	Sokolova *et al.*, 1971.
Lovozero complex, Kola, Russia	Agpaitic nepheline syenites	Na analogue (erdite), rasvumite, pyrrhotite, nosean, villiaumite, lamprophyllite, ussingite	Ni poor, Cu rich	Late- or post-magmatic	Ifantopulo *et al.*, 1978
Tazheran alkali syenite, Baikal, S Siberia	Alkali metasomatic skarns	Fe-rich monticellite, perovskite, pyrrhotite, cuspidine, graphite	Ni poor, Cu poor	Metasomatism of sulphides by K-bearing fluids	Konev *et al.*, 1972
Murun complex, Altai, Siberia	Mineralized K-rich syenites	Pyrrhotite, covellite, chalcopyrite, digenite, bornite, murunskite, idaite	Ni poor, Cu rich	Metasomatic	Dobrovol'skaya *et al.*, 1980
Carbonatitic complexes					
Guli complex, Polar Siberia	Calciocarbonatite	Inclusions in perovskite plus nyrereite (natrocarbonatite)	Ni poor, Cu poor	Associated with Na-K carbonate melt inclusions	Kogarko *et al.*, 1991
Kovdor complex, Kola, Russia	Carbonatite	Phlogopite, apatite, pyrrhotite, chalcopyrite, pentlandite, cubanite, mackinawite	Ni poor, Cu rich	Late magmatic to metasomatic	Balabonin *et al.*, 1980

TABLE 2. Representative analyses of djerfisherite from occurrences listed in Table 1

Sample	1	2	3	4	5	6	7	8	9	10	11	12
Wt.%												
K	9.46	9.10	8.89	9.46	10.32	10.37	9.00	10.99	10.11	8.92	8.8	9.1
Fe	47.35	36.73	40.16	42.85	37.67	51.8	45.4	52.51	42.17	34.21	35.1	53.1
Ni	3.92	18.88	15.63	12.77	–	–	1.41	0.58	0.12	1.04	0.25	n.a.
Cu	1.17	0.54	0.44	–	18.2	4.49	8.37	1.06	12.59	22.47	21.6	n.a.
S	34.37	33.08	32.32	34.92	32.36	32.87	33.8	34.25	34.51	31.88	33.2	31.0
Cl	1.41	1.45	1.28	–	1.35	1.41	1.26	1.37	1.51	1.31	1.43	1.3
Total	97.68	99.78	98.83	100.00	99.9	100.94	100.05	100.85	101.31	99.83	100.5	96.0

Including: (3) Co 0.11; (5) Co 0.09; (8) Co 0.09%

Analyses: (1,2) kimberlite, Elwin Bay, Canada; (3) kimberlite, Yakutia, Russia; (4) alnoite, Monteregian Hills, Canada; (5,6) urtite and pegmatite, respectively, Khibina, Russia; (7) alkali diatreme, Coyote River, USA; (8) alkaline peridotite, Inagli, Siberia; (9) K-rich syenite, Murun, Siberia ; (10) melteigite, Salmagorsky, Russia; (11) carbonatite, Kovdor, Russia; and (12) carbonatite, Guli, Siberia

the conditions of formation of this unusual mineral type which is the subject of the present communication.

Results and discussion

The Kugda intrusive complex forms a ring-like oucrop of ~4 km^2, and consists of a wide range of rock types including peridotite, melilitolite and urtite (Kogarko *et al.*, 1995). The melilitolites are intruded early and consist of melilite, olivine, clinopyroxene, titanomagnetite, monticellite and perovskite as the main phases. Accessory minerals include phlogopite, apatite and calcite. The melilite grains contain primary melt inclusions (50–80 μm across) which now consist of a proliferation of daughter minerals including forsterite, diopside, monticellite, wollastonite, larnite, titanite, phlogopite, nepheline, sodalite, titanomagnetite, apatite, perovskite, combeite ($Na_2Ca_2Si_3O_9$), a fibrous hydrated calcium silicate with Ca:Si of ~1:1 (analytical total ≈80 wt.%; tobermorite?), sylvine, sinjarite ($CaCl_2.2H_2O$), calcite, Ca-Na-K carbonate (nyerereite), and particularly important in the context of the present paper, djerfisherite, pyrrhotite, pentlandite, and chalcopyrite. Many of these phases have only been identified from their microprobe analyses. The djerfisherite sometimes occurs as discrete euhedral crystals and sometimes as rounded (spherical) composite grains with, or as overgrowths on, pyrrhotite and pentlandite. The alkali-rich and volatile-rich nature of the inclusion paragenesis is noteworthy. These micro-inclusions can be homogenized to a single melt-phase over the temperature range 950–1200°C (work in progress). Overall, this mineral and textural association points to *in situ*, closed system differentiation of a high-Ca, low-silica magma which shows a highly-extended fractional crystallization history towards peralkaline, carbonate-rich magmas related to its high volatile content (Cl, CO_2, S, H_2O).

Figure 1 shows two melt inclusions from a Kugda melilitolite. Table 3 gives representative analyses of djerfisherite and its associated sulphides, and Fig. 2 shows the variation of Fe, Ni and Cu in djerfisherites from our samples together with representative data from other localities (Table 2). The djerfisherite compositions show a fairly wide inter-grain variation with individual grains being relatively homogeneous. The compositions for euhedral grains vary from Ni-rich to those with moderate Ni- and Cu-contents, all with relatively high K and Cl, low Na and variable Ca. The most Ni-rich of our analyses are similar to those from kimberlite-nodule occurrences, but our Cu values are always much lower than those occurring in djerfisherites from peralkaline felsic rocks (Tables 1, 2 and 3). Our analyses of djerfisherite rims on composite pentlandite/pyrrhotite grains have lower K, higher Na and very low Cl compared with discrete grains from Kugda; this high-Na, low-Cl rim might have formed at a later stage than the euhedral djerfisherites.

The formation of djerfisherite during the late stages of fractionation of melilitic magmas is

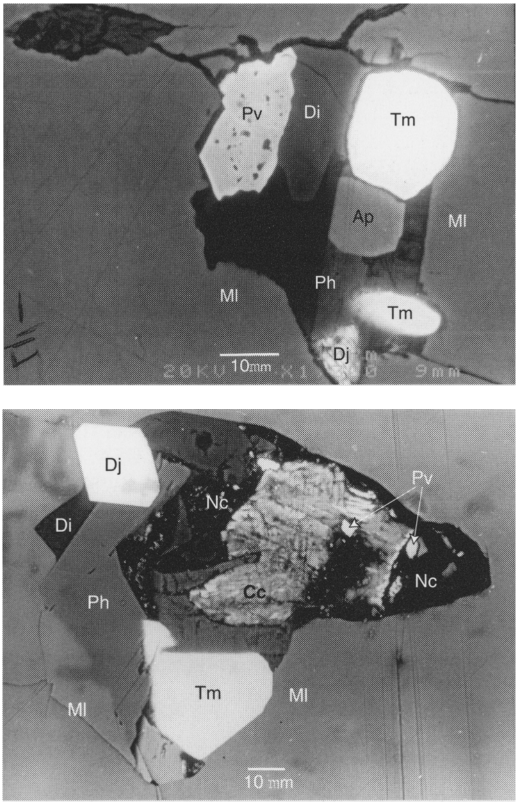

FIG. 1. Two micro-inclusions from melilite showing djerfisherites (Dj) and a range of other daughter minerals. Note the heterogeneous distribution of phases in individual sections through the inclusions. Abbreviations: Ml – melilite; Di – diopside; Ph – phlogopite; Tm – titanomagnetite; Pv – perovskite; Ap – apatite; Cc – calcite; Nc – Na-K-rich carbonate.

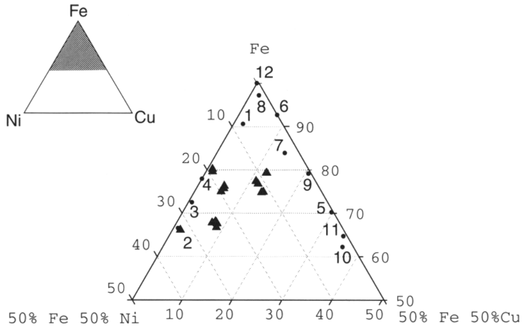

FIG. 2. Fe-Cu-Ni composition variations (at. %) in djerfisherites from Kugda (solid triangles) and other igneous localites (small solid symbols with numbers as in Table 2). Note that the most Ni-rich djerfisherites from Kugda have similar compositions to samples from kimberlites.

almost certainly related to the presence of residual alkali carbonatite melts enriched in volatiles and S which were probably similar in composition to the Oldoinyo Lengai natrocarbonatites (Dawson *et al.*, 1992; Nielsen *et al.*, 1997). The mineral assemblages present in the Kugda melilitolite bulk rock and in the 'melt inclusions' can be used to infer the conditions of fractional crystallization from the melilitic parental magma to the alkali carbonatite residual melt, together with the formation of djerfisherite, and into the subsolidus stage.

Homogenization temperatures of djerfisherite-bearing micro-inclusions are up to 1200°C with melting beginning in some inclusions at ~500°C. However, the assemblage monticellite + diopside + calcite was observed to be resorbed by the melt between 900 and 1000°C. These phases together with forsterite occur both in the micro-inclusions and the parent melilitolite allowing the univariant reaction:

$$\underset{\text{monticellite}}{3CaMgSiO_4} + \underset{\text{fluid}}{2CO_2} = \underset{\text{diopside}}{CaMgSi_2O_6} + \underset{\text{forsterite}}{Mg_2SiO_4} + \underset{\text{calcite}}{2CaCO_3}$$

to be defined. Using the temperature range above and the thermodynamic database of Shapkin *et al.* (1986) a $P(CO_2)$ of 1.12 $\pm$ 0.45 kbar is obtained, suggesting development in a magma chamber at a depth of 2–5 km if total pressure is assumed to be equal to $P(CO_2)$. Jamtveit *et al.* (1997) have recently studied a djerfisherite-bearing, contact metamorphic/metasomatic assemblage: calcite, wollastonite, phlogopite, diopside, melilite, kalsilite; and have inferred an equilibration temperature of 870°C and $X_{fluid}(CO_2)$ of 0.38, assuming a total pressure of 1 kbar with a mixed CO_2-H_2O fluid, in accordance with the data of Zharikov *et al.* (1977). This assemblage (kalsilite molecule in nepheline) also occurs in micro-inclusions in the Kugda melilite and similar *P/T* conditions could be inferred for this igneous occurrence.

The mineral assemblage Na,Ca,K-carbonate, melilite, nepheline, diopside, wollastonite, larnite, combeite, titanite, perovskite, sodalite, magnetite, sylvite, K-Fe-sulphide occurs in both the Oldoinyo Lengai natrocarbonatite (Dawson *et al.*, 1992; Dawson, 1998) and in the Kugda

TABLE 3. Analyses of sulphides from 'melt' inclusions in melilites from the Kugda complex

wt.%	1*	2*	3*	4*	5†	6*
Fe	34.00	42.85	41.84	36.68	61.5	32.12
Co	n.a.	n.a.	n.a.	0.17	n.d.	1.38
Ni	17.22	10.80	4.72	13.76	1.53	32.94
Cu	0.96	0.83	7.39	4.63	n.d.	0.03
K	8.92	8.93	8.91	8.06	n.d.	n.d.
Na	0.11	0.03	0.21	0.42	n.d.	n.d.
Ca	0.56	0.02	0.41	0.30	n.d.	n.d.
S	33.90	32.69	32.70	33.82	35.8	33.09
Cl	1.37	1.35	1.37	0.09	n.d.	n.d
Total	97.04	97.50	97.55	97.84	98.83	99.56

Analysed at Manchester University on: * CAMECA SX100; † JEOL JSM6400 fitted with an Oxford Instruments eXL analyser.
Standards: Cu, Fe, and S – chalcopyrite; Ni, Co – metals; K – orthoclase; Cl – halite; Ca – wollastonite. n.a. not analysed; n.d. not detected.
(1–3) separate djerfisherite grains; (4–6) composite sulphide grain: djerfisherite rim (4) on pentlandite (6), adjacent to pyrrhotite (5).

melilitolite micro-inclusions (this work). Dawson *et al.* (1992) reviewed various lines of evidence and concluded that the silicate-carbonate melt reaction at Oldoinyo Lengai occurred over the temperature range 600–800°C. Recent experimental work (Petibon *et al.*, 1998) on an Oldoinyo Lengai natrocarbonatite at 1 kbar places the solidus at about 550°C and the liquidus at about 900°C. By analogy with these studies, we deduce that the closed-system, carbonate-melt/silicate/sulphide mineral reactions in the Kugda micro-inclusions probably developed over a temperature range of ~1000–500°C in the presence of a mixed CO_2-H_2O-H_2S fluid. At lower temperatures still, the hydrated minerals (sinjarite, tobermorite?) were formed from anhydrous precursors.

We conclude that the melt inclusions in the Kugda melilitolite show a classic, closed-system, fractional crystallization sequence from an evolved melilititic magma through to a residual alkali carbonatite melt, with the reaction sequence being completed by deuteric alteration processes. The volatile phases CO_2, H_2O, Cl, H_2S/SO_2 played a crucial role throughout this sequence.

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References

Balabonin, N.L., Voloshin, A.V., Pakhomovsky, J.A. and Poljakov, K.I. (1980) The composition of djerfisherite in alkali complexes of the Kola Peninsula. *Mineral. J.*, **2**, 90–9. (in Russian).

Barkov, A.Y., Laajoki, K.V.O., Gehor, S.A., Yakovlev, Y.N. and Taikina-Aho, O. (1997) Chlorine-poor analogues of djerfisherite-thalfenisite from Noril'sk, Siberia and Salmagorsky, Kola Peninsula, Russia. *Canad. Mineral.*, **35**, 1421–30.

Bulanova, G.P., Shestkova, O.E., and Leskova, N.V. (1980) Djerfisherite from sulphide segregations in diamond. *Dokl. Akad. Nauk SSSR*, **255**, 430–3. (in Russian).

Clarke, D.B., Pe, G.G., Mackay, R.M., Gill, K.R., O'Hara, M.J. and Gard, J.A. (1977) A new potassium-iron-sulphide from a nodule in kimberlite. *Earth Planet. Sci. Lett.*, **35**, 421–8.

Clarke, D.B., Mitchell, R.H., Chapman, C.A.T. and MacKay, R.M. (1994) Occurrence and origin of djerfisherite from the Elwin Bay kimberlite, Somerset Island, Northwest territories. *Canad. Mineral.*, **32**, 815–23.

Czamanske, G.K., Lanphere, M.A., Erd, R.C. and Blake, M.C. Jr. (1978) Age measurements of potassium-bearing sulphide minerals by the $^{40}Ar/^{39}Ar$ technique. *Earth Planet. Sci. Lett.*, **40**, 107–10.

Czamanske, G.K., Erd, R.C., Sokolova, M.J., Dobrovol'skaya, M.G. and Dmitrieva, M.T. (1979) New data on rasvumite and djerfisherite. *Amer.*

Mineral., **64**, 776–8.

Czamanske, G.K., Leonard, B.F. and Clark, J.R. (1980) Erdite, a new hydrated sodium iron sulfide mineral. *Amer. Mineral.*, **65**, 509–15.

Dawson, J.B. (1998) Peralkaline nephelinite-natrocarbonatite relationships at Oldoinyo Lengai, Tanzania. *J. Petrol.*, **39**, 2077–94.

Dawson, J.B., Smith, J.V. and Steele, I.M. (1992) 1996 ash eruption of the carbonatite volcano Oldoinyo Lengai: mineralogy of lapilli and mixing of silicate and carbonate magmas. *Mineral. Mag.*, **56**, 1–16.

Dobrovol'skaya, M.G., Tsepin, A.I., Ilupin, I.P. and Ponomarenko, A.I. (1975) Djerfisherites from Yakutia kimberlites. In *Mineraly I Paragenezisy Mineralov Endogennykh Mestorozhdeniy* (P.M. Tamarinov, ed.). Izd. Nauka, Leningrad, (in Russian).

Dobrovol'skaya, M.G., Rogova, V.P., Tsepin, A.I. and Malov, V.S. (1980) About the sulphide mineralization in charoitic rocks (Murunsky massif). *Mineral. J. (Kiev)*, **2**, 3–13 (in Russian).

El Goresy, A., Grogler, N. and Ottemann, J. (1971) Djerfisherite composition in Bishopville, Pena Blanca Springs, St Marks amd Toluca meteorites. *Chem. Erde*, **30**, 77–82.

Eremeev, N.V., Dobrol'skaya, M.G. and Muravitskaya, G.N. (1982) The new occurrence of djerfisherite in alkaline series of the Inaglinsky complex (Aldansky shield). *Dokl. Acad. Nauk SSSR*, **263**, 1210–12 (in Russian).

Genkin, A.D., Troneva, N.V. and Zhuravlev, N.N. (1970) The first occurrence in ores of the sulfide of potassium, iron, copper, djerfisherite. *Geochem. Int.*, 693–701.

Hanois, L. and Mineau, R. (1991) Geochemistry of the Ile Cadieus monticellite alnoite, Quebec, Canada. *Canad. J. Earth Sci.*, **28**, 1050–57.

Hogarth, D.D. (1997) Mineralogy of leucite-bearing dykes from Napolean Bay, Baffin Island: multistage Proterozoic lamproites. *Canad. Mineral.*, **35**, 53–78.

Ifantopulo, T.N., Yushko-Zakharanova, O.E. and Dubakina, L.C. (1978). Djerfisherite from Lovozersky massif. *Dokl. Akad. Nauk SSSR*, **243**, 199–200 (in Russian).

Jago, B.C. and Gittins, J. (1999) Mn- and F-bearing rasvumite in natrocarbonatite at Oldoinyo Lengai Volcano, Tanzania. *Mineral. Mag.*, **63**, 53–5.

Jamtveit, B., Dahlgren, S. and Austrheim, H. (1997) High-grade contact metamorphism of calcareous rocks from the Oslo Rift, Southern Norway. *Amer. Mineral.*, **82**, 1241–54.

Kogarko, L.N., Kononova, V.A., Orlova, M.P. and Woolley, A.R. (1991) *Alkaline rocks and carbonatites of the world. Part 2: Former USSR*. Chapman & Hall, London, 226 pp.

Kogarko, L.N., Plant, D.A., Henderson, C.M.B. and Kjarsgaard, B.A. (1995) Na-rich carbonate inclusions in perovskite and calzirtite from the Guli intrusive Ca-carbonatite, polar Siberia. *Contrib. Mineral. Petrol.*, **109**, 124–9.

Konev, A.A., Afonin, L.A., Perfil'yeva, L.A. and Ushchapovskaya, Z.F. (1972). Djerfisherite from Tazheran skarns. In *Vopr. Mineral. Gorn. Porod. Rud. Vost. Sib.* (B.M. Shmakin, ed.), pp. 15–22. Akad. Nauk SSSR, Sib. Otd., Inst. Geokhim., Irkutsk, USSR, (in Russian).

Korobeinikov, A.N., Mitrofanov, F.P., Gehor, S., Laajoki, K., Pavlov,V.P. and Mamontov, V.P. (1998) Geology and copper sulphide mineralization of the Salmagorski ring igneous complex, Kola Peninsula, NW Russia. *J. Petrol.*, **39**, 2033–41.

Mitchell, R.H. (1997) Carbonate-carbonate immiscibility, neighbourite and potassium iron sulphide in Oldoinyo Lengai natrocarbonatite. *Mineral. Mag.*, **61**, 779–89.

Nielsen, T.F.D., Solovova, I.P. and Veksler, I.V. (1997) Parental melts of melilitolite and origin of alkaline carbonatite: evidence from crystallised melt inclusions, Gardiner complex. *Contrib. Mineral. Petrol.*, **126**, 331–44.

Petibon, C.M., Kjarsgaard, B.A., Jenner, G.A. and Jackson, S.E. (1998) Phase relationships of a silicate-bearing natrocarbonatite from Oldoinyo Lengai at 20 and 100MPa. *J. Petrol.*, **39**, 2137–51.

Ramdohr, P. (1963) The opaque minerals in stony meteorites. *J. Geophys. Res.*, **68**, 2011–36.

Shapkin, A.I., Garanin, A.V. and Khodakovskii, I.L. (1986) DIANIK GEOKHI. Russian Acad. Sci. Computer Complex for Chemical Thermodyamics Project. In *Direct and Inverse Thermodynamic Tasks*, pp. 80–88. Nauka, Novosibirsk, (in Russian).

Sokolova, M.N., Dobrovo'skaya, M.G., Organova, N.I., Kazakova, M.E. and Vasil'yeva, G.L. (1971) On the occurrence and distribution of djerfisherite in pegmatites from the Khibina massif. *Geol. Rudnykh Mestorozhd.*, **13**, 62–71 (in Russian).

Zharikov, V.A., Shmulovich, K.I., and Bulatov, V.K. (1977) Experimental studies in the system $CaO-MgO-Al_2O_3-SiO_2-CO_2-H_2O$ and conditions of high-temperature metamorphism. *Tectonophys.*, **43**, 145–62.

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