

A NEW CHROMIUM GARNET END MEMBER,
KNORRINGITE, FROM KIMBERLITE

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ABSTRACT

Analysis by electron probe confirms that a garnet from Kao kimberlite pipe in Lesotho contains a large proportion of the component $Mg_3Cr_2(SiO_4)_3$. This is now called knorringite and thus replaces the name hanleite which has been discredited (= uvarovite). The garnet from Kao, with 17.4% Cr_2O_3 , is green, $a = 11.65$, $n = 1.803$, G (obs) = 3.756, G (calc) 3.852.

The properties of this and other "chromium pyropes" from kimberlites are described and their significance discussed.

INTRODUCTION

Pyrope garnets containing chromium have long been known to occur in kimberlites (Wagner, 1914; Williams, 1932). They characterise the ultrabasic nodules of these bodies, chrome-spinel peridotites, their higher level equivalents being much less common. (Nixon *et al.*, 1963).

Typically pyropes contain about 2-3 percent Cr_2O_3 equivalent to 5 to 8 percent of the uvarovite molecule, but greater amounts are found. A partial analysis of chromium pyrope from E9 lherzolite nodule from Lihobong, Lesotho, gave 5.14 percent Cr_2O_3 and a full analysis of chromium pyrope from E10 serpentinitised nodule from Sekameng, Lesotho gave 7.52 percent Cr_2O_3 (table 1) (Nixon *et al.*, 1963). E10 garnet contains 8.7 percent $Mg_3Cr_2(SiO_4)_3$ as calculated in terms of end members of the garnets, there being insufficient calcium to match the high chrome content. If one calculates all the chromium as magnesium chromium garnet instead of calculating first the uvarovite molecule, then considerably more of the new component is seen to be present.

Magnesium-chrome garnet has until recently been called hanleite after Fermor's (1952) interpretation of an old analysis of a green garnet found in 1864 near the Hanle monastery in Rupshu, Kashmir. Hanleite has since been shown to be uvarovite (Sastri, 1963).

A bluish-green garnet, K47 from Kao kimberlite pipe, Lesotho, whose physical properties indicate a high chrome content (Nixon *et al.*, 1963) but which was only qualitatively analysed due to the very small amount of material available, has now been proved to contain a major proportion of $Mg_3Cr_2(SiO_4)_3$. The end member is named knorringite² for Oleg

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² Approved by Commission on New Minerals and Mineral Names, I.M.A. before publication.

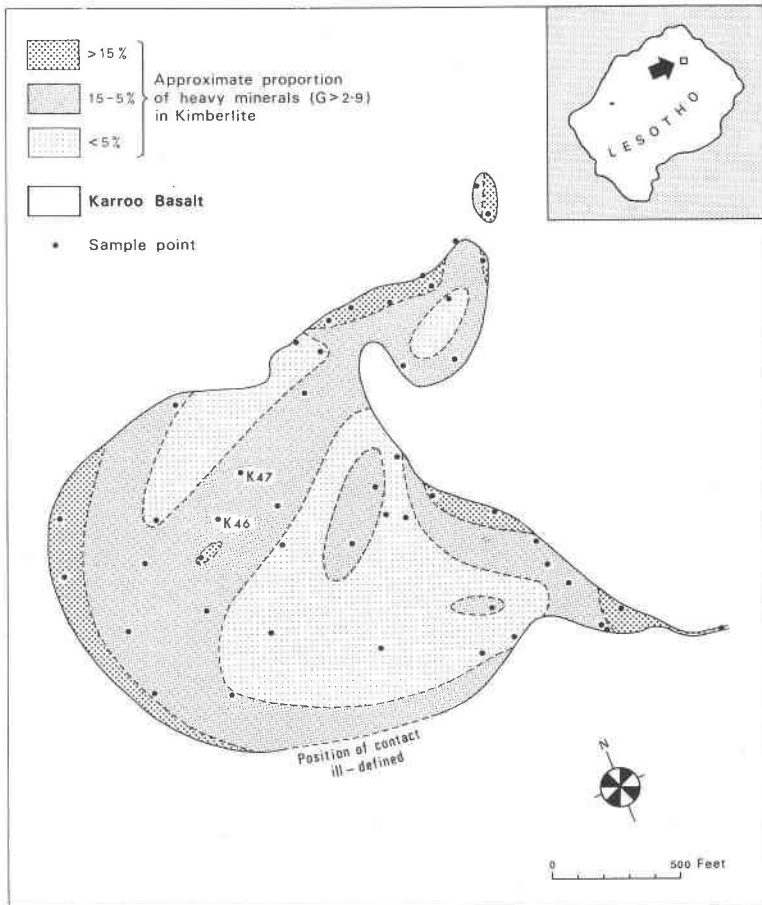


FIG. 1. Distribution of heavy minerals in soft surface kimberlite, Kao, Lesotho.

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GEOLOGICAL SETTING OF KNORRINGITE RICH GARNETS

K47 garnet was recovered from one of 55 concentrated kimberlite samples taken from scattered localities at Kao pipe by J. B. Dawson and P. H. Nixon in 1957 (Fig. 1). The heavy minerals separated from the serpentinous matrix were olivine, enstatite, chrome-diopside, chromium pyrope, chromium spinel (from disintegrated ultra-basic nodules), ilmenite, a more iron rich olivine, bronzite, diopside, pyrope, perovskite,

zircon, diamond, (cognate with kimberlite), omphacite, pyrope-almandine, rutile and others (from eclogite and other crustal inclusions). The bulk of kimberlite itself is made up of serpentine, carbonates and micas.

The highest proportion of heavy minerals occurs near the periphery of the pipe, with the exception of a north-easterly trending strip of 'highs' (Fig. 1). This distribution probably arises from the manner in which the kimberlite was intruded. Uneven distributions of inclusions in pyroclastic diatremes have been discussed by Shoemaker and Moore (1956) who explain these features in terms of varying velocity gradients within a fluidised magma system. Such a system would appear to have operated in kimberlites also. The NE-SW 'high' crossing the Kao pipe can be interpreted as indicating a screen of country rock or division of the pipe either in depth or above the present erosional level of the pipe.

An ultrabasic nodule which was fragmented during the waning stages of the intrusion is thought to have been the host of the knorringite-rich garnet recovered from K47 concentrate. Fragments of lilac-coloured garnets of intermediate properties between those of K47 and normal chromium pyropes were recovered from an adjacent concentrate, K46 (Fig. 1).

MINERALOGY

The chemical composition of the garnet was determined by electron probe analysis. Five fragments of the garnet, between 50–300 μ in diameter were recovered from a sample of the concentrate K47 and mounted in araldite. Samples of E10 analysed garnet, and an analysed uvarovite were mounted in identical fashion and, after polishing, all three were simultaneously vacuum coated with carbon. Preliminary examinations with an A.E.I. SEM 2 microprobe indicated that E10 was homogeneous and suitable for use as a standard, but that the uvarovite was zoned and unusable and that of the five unknown grains, three had a sufficiently good surface to be analysed and were uniform in composition whereas two were unusable.

It was clear that the unknown and E10 samples were close in composition and justified direct comparison to deduce an answer without the necessity for the usual correction procedures. The analysis which was performed at 20 kV with 1000 times magnification, gave the following: SiO₂, 40.2; TiO₂, 0.1; Al₂O₃, 13.7; Cr₂O₃, 12.0; Fe as FeO, 4.3; MnO, 0.6; MgO, 20.9; CaO, 8.7; total, 100.5. The analysis, although indicating without doubt the existence of Mg₃Cr₂(SiO₄)₃, showed a slight divergence from the garnet 3:2:3 ratio (3.03:2:3.29), whereas an extrapolation of a curve based on physical properties against chromium content placed the garnet near to the intermediate K46-type (Nixon *et al.* 1963).

Several other grains were therefore carefully selected from the K47

concentrate on the basis of refractive index (>1.800) and greenish color. These were treated briefly in HF acid to dissolve or loosen and remove kelyphitic alteration products and then mounted in the same manner as the previous group. The Cr content of each grain was investigated, and the grain with the highest Cr was then fully analysed, again using the E10 garnet as a standard.

The composition of this grain differed somewhat from the standard, and therefore corrections were applied for the absorption, fluorescence, and atomic number effects experienced in microanalysis. The absorption correction was that of Duncumb and Shields (1966) modified Philibert correction; the fluorescence correction was according to Reed (1965); and the atomic number correction was from a report by Duncumb and Reed.¹ The corrections were made by computer program devised by Mr. T. Padfield of the Department of Earth Sciences, University of Leeds. The results of the analysis are given in Table 1.

The analysis of K47 garnet (Table 1) shows that it is composed dominantly of the $Mg_3Cr_2(SiO_4)_3$ component even when Cr is abstracted with Ca (uvarovite) prior to calculating $Mg_3Cr_2(SiO_4)_3$ (knorringite).

The physical properties are significantly different from the more usual chrome pyropes and they bear a definite relationship to the amount of Cr (knorringite) replacing Al (pyrope) in the crystal lattice (Fig. 2). The refractive index and cell edge length curves are nonlinear. This is ascribed to the influence of calcium which increases from about 5 percent CaO in the normal chromium pyropes to 6.27 percent in E10 garnet and 8.14 percent in K47 garnet. This increase takes place at the expense of magnesium (Table 1) and can be regarded as additional uvarovite "molecule." Extrapolation of the chemical data gives a uvarovite bearing knorringite. One wonders whether an old reference (Wagner, 1914, p. 65) to yellowish green "demantoids" and dirty green trapezohedra from kimberlite were in fact such a garnet.

The calculated densities of the garnets show a linear relationship to the number of Cr atoms in their unit cells (Fig. 2). The observed density of K47 lies some way from this line and appears to be too low. Due to the small amount of material the density was measured by floating several grains in Clerici solution which was then diluted until it was judged that most grains were suspended in the liquid, whose density was then determined by pycnometer method. We now realise that the grains measured were probably of two types, the high Cr variety K47, and the type recorded above in the first analysis, with a lower Cr content.

The calculated density of the latter, using the K46 cell edge value of

¹ From an unpublished report (1967) of the Tube Investments Laboratories, Hinxtoy, Cambridge, England, P. Duncumb, and S. J. B. Reed.

TABLE 1. CHEMICAL COMPOSITIONS AND PHYSICAL PROPERTIES OF THREE CHROMIUM BEARING GARNETS FROM KIMBERLITE PIPES.

	K47		E10		E11	
SiO ₂	39.92		41.90		42.77	
TiO ₂	0.11		0.11		0.30	
Al ₂ O ₃	9.74		16.92		21.91	
Cr ₂ O ₃	17.47		7.52		1.90	
Fe ₂ O ₃	1.20 ^a		1.24		1.25	
FeO	6.53		6.17		6.79	
MnO	0.60		0.59		0.26	
MgO	16.97		19.64		20.70	
CaO	8.14		6.27		4.65	
	100.68		100.36		100.53	

Number of atoms (O=96) in garnet unit cell							
	K47		E10		E11		<i>Theoretical</i>
O	96		96		96		96
Si	24.07		24.27		24.07		24.20
Ti	.04		.03		.13		
Al	6.91		11.54		14.54		16
Cr	8.33		3.44		.84		
Fe ³⁺	.54		.56		.54		24
Fe ²⁺	3.30		2.99		3.21		
Mn	.33		.28		.41		23.71
Mg	15.24		16.93		17.55		
Ca	5.25		3.89		2.81		24

Composition in terms of end member "molecules" calculated from the cation percentages in two orders, A and B.									
A		B		K47		E10		E11	
A	B	A	B	A	B	A	B	A	B
Spessartine	Sp	1.4	1.4	1.1	1.1	0.6	0.6		
Andradite	And	3.4	3.4	3.5	3.5	3.4	3.4		
Uvarovite	<i>Knorr</i>	18.7	52.7	12.7	21.5	5.4	5.4		
Grossularite	Gr	—	18.7	—	12.7	3.0	8.4		
Almandine	Alm	13.9	13.9	12.4	12.4	13.5	13.5		
Pyrope	Py	28.7	9.9	61.6	48.8	74.1	68.7		
<i>Knorringite</i>	—	33.9	—	8.7	—	—	—		

Physical properties (mostly from Nixon <i>et al.</i> 1963)						
	K47		E10		E11	
$n \pm 0.002$	1.803		1.758		1.743	
$a \text{ \AA}, \pm 0.01$	11.659		11.565		11.528	
G(obs)	3.756 ^b		3.715		3.712	
G(calc)	3.852		3.748		3.698	
Color index	6G3/2		5RP3/2		8R5/2	

- K47. Blue-green garnet, rich in magnesium and chromium (Knorringite) from Kimberlite concentrate, Kao pipe, Lesotho. Analyst: G. Hornung.
 E10. Chromium-rich pyrope from serpentinised nodule, Sekameng pipe, Lesotho. Analyst: O. von Knorring (Nixon *et al.* 1963, Table 5).
 E11. Chromium pyrope, lherzolite nodule, pipe at Farm Lawrence, nr. Gibeon S.W. Africa. Analyst: J. R. Baldwin (Nixon *et al.* 1963, Table 5).

^a Ferric iron arbitrarily taken as 1.2% by analogy with E10 and E11.

^b FeK α radiation

11.59 Å as an approximation agrees reasonably with the observed density, The true density of K47 may therefore be taken as the value calculated from the unit-cell measurements, 3.85.

The X-ray data of knorringite-rich garnet K47 and normal chromium pyrope (E11) have already been presented (Nixon *et al.* 1963).

Together with an increase in the refractive index, cell size and density

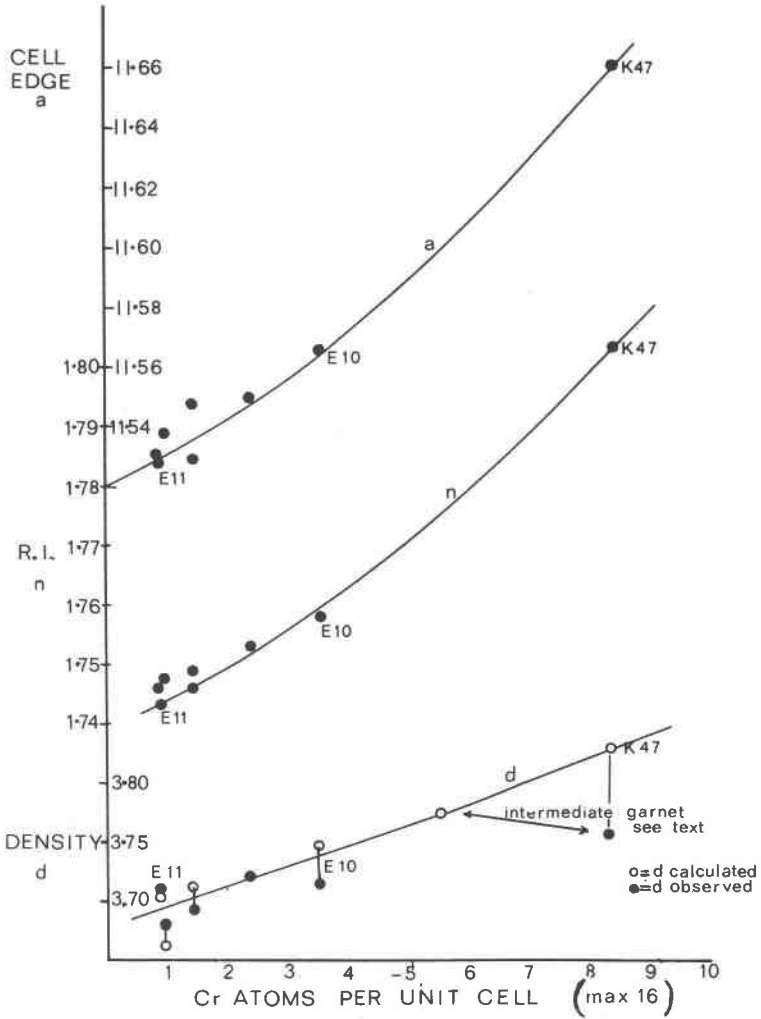


FIG. 2. Physical properties of Cr-bearing garnets from kimberlitic ultrabasic nodules, plotted against Cr atoms in the unit cell. K47=magnesium chromium garnet (Knorringite).

there is a marked change in color (hue). Normal chromium pyropes are blood red with a purple tinge. With a higher chromium content the hue is lilac or purple passing ultimately to the greenish hue of K47. Accompanying this change there is a decrease in the light value, i.e. the color becomes darker, but the chroma value (the degree of brightness) remains more or less constant about 2.

SIGNIFICANCE OF KNORRINGITE

Like E3 subcalcic chromium diopside from Thaba Putsoa (Nixon *et al.*, 1963, Davis and Boyd, 1966), K47 knorringite is a rare variety of the common or type species found in kimberlitic ultrabasic nodules. E3 diopside appears to be a high temperature equivalent of the common and normal chromium diopsides. The accompanying garnet in E3 nodule is a normal chromium pyrope which suggests that the chromium (knorringite) content is unrelated to the temperature of formation. Nor does the larger unit cell of knorringite (Fig. 2) favour a higher than usual load pressure during its crystallisation, when compared with pyropes and chromium pyropes. Pure magnesium-chromium garnet has been synthesized under 20,000 kg/cm² pressure at 800°C (Roy and Tuttle 1965) but a P. T. stability field does not appear to have been defined experimentally. Although it is probable that PT conditions such as obtained in the mantle are necessary for the formation of knorringite it is difficult to explain why the mineral is so rare, a problem also applying to subcalcic diopside. One possible explanation is that knorringite is particularly susceptible to breakdown or kelyphitization, when the surrounding kimberlite ascends to shallow depth in the earth's crust. Its preservation in this instance may be due to its enclosure up to a late stage in an unusually large nodule which retarded ingress of the potentially reactive water vapor from the surrounding kimberlite magma.

The occurrence in an adjacent pit of an intermediate chromium-rich lilac colored garnet (K46) (Fig. 1) is perhaps indicative of the disruption of an unusually large chromium-rich garnet bearing body; even so, the wide range in chromium content of the garnets is difficult to explain when in other nodules, admittedly much smaller, there is no significant compositional variation in the constituent minerals. It would appear that in the region of pits K46 and K47 there was an unusual enclave in the kimberlite in which chromium was concentrated and partly took over the role of aluminium, in the garnet structure. Unfortunately no co-existing chromium-rich pyroxene such as the chromium acmite, NaCrSi₂O₆, Ureyite (Fron del and Klein, 1965) found in meteorites was detected in the concentrates. The chromium diopside from the nodule accompanying E10 garnet, however, contains a significantly high propor-

tion of chromium acmite, ureyite, $\text{NaCrSi}_2\text{O}_6$ (2.42% Na_2O and 2.68% Cr_2O_3 ; Nixon *et al.* 1963).

Recent discoveries in kimberlites in the U.S.S.R. (Sobolev *et al.* 1966) include chromium kyanite in which Cr substitutes for Al. It is clear that a fuller assessment of the role of chromium in basic and ultrabasic rocks under high P-T conditions is desirable.¹

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¹ Our attention has been drawn to an article in press in *Science*, by H. O. A. Meyer (Geophysical, Laboratory, Washington), describing Cr-rich pyropes as inclusions in diamonds which are similar to those described by us.