

Chemical Investigation of Pyrope Garnets in the Stockdale Kimberlite Intrusion, Riley County, Kansas

FRANZ ROST¹, EBERHARD BEERMANN, AND GEORG AMTHAUER

Fachrichtung Mineralogie der Universität des Saarlandes, Saarbrücken, Germany

Abstract

The color variations between 41 separate pyrope garnet fractions from the Stockdale kimberlite are caused by differing chromium concentrations. Two main series may be distinguished. Series I shows a wide color range from pale orange to dark violet, corresponding to Cr₂O₃ content from 0.2 to 13 wt percent; the cell edge increases from 11.511 to 11.647 Å. Series II is characterized by light pink or red colors, Cr₂O₃ values below 2.5 wt percent, and TiO₂ contents greater than 0.5 wt percent. The larger cell edges in Series II are caused by higher content of Fe³⁺, which is proved by reflectance photometry and Mössbauer spectroscopy. The quantitative distribution of chromium in the Stockdale garnets is represented in a variation diagram.

Introduction

Many kimberlites characteristically contain pyrope garnets which originate from garnet peridotite and pyroxenite xenoliths, or are genetically related to kimberlite itself. Investigations on pyrope garnets from kimberlites by Nixon, Knorring, and Rooke (1963), Nixon and Hornung (1968), Meyer (1968; 1970), Sobolev, Lavrent'yev, Pospelova, and Sobolev (1969), Reid and Hanor (1970), Meyer and Boyd (1972), and Gurney and Switzer (1973) show colors ranging from pale orange to red and dark violet, caused by an increasing chromium content from 1 to 3 wt percent up to 10 wt percent of Cr₂O₃ and more. These garnets have been defined as "chrome pyropes." Similar variations of pyrope garnets from many European garnet peridotites have been investigated quantitatively (Rost and Grigel, 1969; Amthauer, Brenneis, Grigel, and Rost, 1971; Rost, Wannemacher, and Grigel, 1974).

In Riley County, Kansas, 6 kimberlite diatremes are known (Brookins, 1970), among which the kimberlite of Stockdale has the remarkable content of 4 percent pyrope garnets (Eastwood and Brookins, 1965; Rosa and Brookins, 1966). Bagrowski (1941) had been the first to identify as pyrope a red mineral in the Stockdale kimberlite, previously believed to be "ruby spinel." Discrepancies in the analysis and in

the calculated formula induced Brookins and others to reinvestigate the red garnet. Brookins' (1967) analysis of red pyrope yielded SiO₂, 44.11; TiO₂, 0.27; Al₂O₃, 21.50; Fe₂O₃, 1.37; Cr₂O₃, 2.77; FeO, 7.55; MgO, 20.57; CaO, 4.64; MnO, 0.37. Rosa and Brookins (1966) determined *a*₀ to be 11.535 Å for red pyrope and 11.558 Å for "green" pyrope. Brookins (1967) concluded that, because of the high value of the unit cell and refractive index, the "green pyrope" may be even more chromium rich than the red pyrope. Other garnets from eclogite xenoliths in the Stockdale kimberlite have pyrope-almandine composition and "appear unrelated to the pyrope garnets which occur as xenocrysts within the kimberlite" (Meyer and Brookins, 1971).

Methods

Preparation

About 20 kg of garnet-bearing kimberlite rock was crushed and sieved to grain sizes between 0.3 and 0.8 mm, and treated with dilute hydrochloric acid to dissolve carbonates and decompose serpentine and other minerals. Heavy minerals were separated by using Clerici solution (*D* = 3.5) and the garnets were concentrated by using a Frantz isodynamic separator. This portion was then heated with hydrochloric acid (HCl:H₂O = 1:2) on a magnetic agitator, thus producing grains with clean and polished surfaces. Those garnet grains without impurities and inclusions were finally picked out by hand (enlarge-

¹ Present address: Professor Dr. F. Rost, Fachrichtung Mineralogie der Universität des Saarlandes, D-6600 Saarbrücken, F. R. G.

ment of binocular microscope 16–25) to obtain about 21 g of pure garnet.

The discrimination of differently colored garnets is necessarily subjective. The authors, however, succeeded in selecting 41 garnet samples of like color—termed fractions—in different lots (See Fig. 1, Table 5).

Analytical Methods

Those garnet fractions totaling more than 400 mg were analyzed with a Philips X-ray vacuum spectrometer. For garnet fractions less than 400 mg, emission spectrography was used to determine FeO, CaO, MnO, TiO₂ and Cr₂O₃ (Rost and Hausner, 1954; Rost and Grigel, 1964; 1969). The standards used were predominantly common international standards and mixtures of these. The accuracy of both methods was estimated between 2 and 6 percent, depending on the element and its concentration.

Cell edges were determined by using the Guinier method, measuring the distance of 10.10.4 reflection of garnet against 4.4.4. reflection of pure silicon; the accuracy was 0.001–0.002 Å. Single grains were examined by using the Gandolfi camera (Gandolfi, 1967); the accuracy was 0.005 Å.

Results

Chemical Composition of the Stockdale Garnets

The analytical results for the various garnet fractions are arranged according to their chromium con-

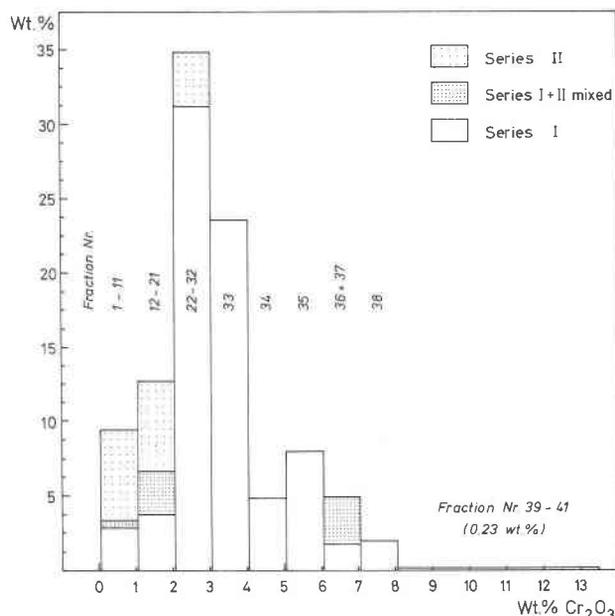


FIG. 1. Simplified histogram of the distribution of chromium content in the Stockdale garnets. Series III = Series I plus Series II, mixed.

centration in Tables 1, 2, and 3. Garnets which could only be separated in amounts of a few mg were examined by determination of their cell edges (Table 4).

By comparison of the results with the cell edge values, the pyrope garnets from the Stockdale kimberlite fall into two main series.

Each garnet fraction grouped into Series I (Table 1) possesses a definite value for a_0 ; with minor exceptions a_0 increases steadily from 11.521 to 11.581 Å as weight percent Cr₂O₃ increases from 0.46 to 7.20. Those garnet fractions grouped into Series II (Table 2) also have a definite value for a_0 but, unlike Series I garnets, their TiO₂ contents generally exceed 0.50 wt percent. For them a_0 shows a lesser range than for Series I, all but one being between 11.540 and 11.548 Å. Series II garnets have larger values of a_0 when compared to Series I garnets of approximately equal Cr₂O₃ content. The Cr₂O₃ content of Series II garnet fractions do not exceed 2.5 wt percent.

Garnet fractions 6, 18, and 20 in Table 3 yield two distinct cell edge values. Since one value corresponds to Series I and the other to Series II, fractions 6, 18, and 20 are probably mixtures of Series I and Series II garnets. Fraction 37 in Table 3 consists of violet-colored garnets that give a broad reflection in the Guinier camera and undoubtedly belong to Series I. Both pyropes studied by Rosa and Brookins (1966) and Brookins (1967) belong to Series I; the red garnet corresponds in Cr₂O₃ content and cell edge to garnet fraction 31 in Table 1.

On the basis of color and cell edge, the authors favor inclusion of the garnets in Table 4 into Series I. Thus fractions 39 to 41c compare to fractions 38 (Table 1) and 37 (Table 3); they show the "alex-

TABLE 1. Analyses of Stockdale Garnets, Series I

Nr.	SiO ₂	Al ₂ O ₃	FeO	MgO	CaO	MnO	TiO ₂	Cr ₂ O ₃	a_0
7	-	-	9.50	-	6.00	0.35	0.25	0.46	11.523
8	-	-	7.90	-	5.00	0.73	0.14	0.50	11.521
9	-	-	9.90	-	5.60	0.44	0.22	0.52	11.523
15	42.5	22.4	8.50	21.1	4.40	0.49	0.28	1.35	11.525
19	-	-	7.60	-	6.00	0.38	0.24	1.90	11.530
22	-	-	7.60	-	4.70	0.43	0.23	2.10	11.531
23	-	-	7.50	-	6.00	0.42	0.25	2.10	11.532
24	42.0	21.5	7.45	21.4	4.45	0.45	0.27	2.18	11.533
25	-	-	6.70	-	5.80	0.43	0.65	2.20	11.534
29	42.0	21.4	7.53	20.6	4.60	0.54	0.14	2.35	11.532
30	-	-	7.60	-	6.80	0.53	0.23	2.35	11.533
31	41.6	22.2	7.65	21.4	4.85	0.34	0.18	2.80	11.535
32	41.0	22.2	7.45	20.6	4.85	0.33	0.20	2.85	11.539
33	41.0	20.8	7.20	20.4	5.40	0.52	0.12	4.00	11.546
34	41.5	21.3	6.92	20.0	5.40	0.51	0.17	4.45	11.549
35	40.6	20.0	6.95	20.0	6.00	0.70	0.11	5.50	11.563
36	-	-	7.60	-	6.30	0.52	0.15	6.05	11.567
38	40.5	18.0	6.40	18.2	7.00	0.65	0.09	7.20	11.581
$\bar{\rho}$	41.3	21.3	7.55	20.57	5.26	0.47	0.26	3.18	-

Notes for Tables 2, 3 and 4:

Nr = number of garnet fraction

- = oxides by spectrographical method not determined

$\bar{\rho}$ = average composition of series

TABLE 2. Analyses of Stockdale Garnets, Series II*

Nr.	SiO ₂	Al ₂ O ₃	FeO	MgO	CaO	MnO	TiO ₂	Cr ₂ O ₃	a ₀
2	42.0	22.5	8.95	20.2	4.80	0.39	0.84	0.32	11.540
3	-	-	9.00	-	5.90	0.41	0.70	0.35	11.536
4	-	-	10.50	-	6.40	0.42	0.54	0.42	11.544
5	-	-	8.70	-	6.50	0.39	0.62	0.45	11.542
10	-	-	8.70	-	6.00	0.35	0.64	0.75	11.545
11	-	-	8.30	-	6.00	0.44	0.84	1.00	11.544
12	-	-	9.00	-	4.70	0.31	0.55	1.20	11.543
13	-	-	8.70	-	6.50	0.39	0.66	1.20	11.544
14	-	-	9.20	-	5.60	0.43	0.52	1.30	11.544
16	-	-	7.70	-	4.70	0.38	0.58	1.40	11.543
17	41.8	21.5	8.10	20.2	5.00	0.35	0.86	1.46	11.545
21	-	-	7.60	-	5.50	0.43	0.90	2.00	11.547
26	-	-	6.80	-	6.00	0.42	0.60	2.20	11.544
27	-	-	7.60	-	6.20	0.43	0.50	2.20	11.547
28	41.6	20.8	7.35	21.4	5.15	0.43	0.84	2.32	11.548
Ø	41.8	21.6	8.50	20.6	5.37	0.39	0.75	1.25	-

* for explanation of symbols, see footnotes to Table 2

TABLE 4. Cell Edge, Color, and Estimated Chromium Content of Some Peculiar Garnets*

Garnet No.	Color	Cell Edge (Å)	Wt percent Cr ₂ O ₃ *
1	Pale orange	11.511	0.2
39	Dark violet	11.595	8.5
40	" "	11.611	10.0
41a	" "	11.631	11.9
41b	" "	11.637	12.4
41c	" "	11.647	13.3

* Cr₂O₃ values estimated by extrapolation according to Figure 3.

andrite effect" (White, Roy, and Mck Crichton, 1967).

The histogram of Figure 1 shows the quantitative variation of chromium content in all garnet fractions collected in columns according to the Cr₂O₃ content in steps of 0.05–1.0, 1.05–2.0, . . . wt percent, etc. The variation corresponds approximately to a statistical distribution curve.

Average Chemical Composition and Formulas of Stockdale Garnets

Taking into account the weight portions of garnet fractions, the average chemical composition of the single series has been calculated (Table 5). Differences between Series I and II may be observed in the total content of iron—determined analytically as FeO—and in the higher titanium and lower chromium content in Series II.

According to the calculated formulas, the garnets in the Stockdale kimberlite, investigated herein, show a corresponding value of "pyrope" exceeding 72 mole percent only insignificantly. The analytical results show characteristic differences between the elements in the Y position of the garnet formula. The higher value of Fe³⁺ in Series II is of special importance and causes their higher values of a₀. A dependence of a₀ on the titanium content is not evident.

TABLE 3. Analyses of Garnets with Complex Composition*

Nr.	SiO ₂	Al ₂ O ₃	FeO	MgO	CaO	MnO	TiO ₂	Cr ₂ O ₃	a ₀
6	-	-	11.30	-	6.20	0.45	0.25	0.45	11.521/ 11.542
18	-	-	7.70	-	4.80	0.43	0.38	1.80	11.531/ 11.546
20	41.8	23.3	7.80	21.4	4.80	0.42	0.48	1.97	11.528/ 11.546
37	40.6	18.7	6.60	19.8	6.45	0.50	0.11	6.70	11.562/ 11.579
Ø	41.2	20.8	7.46	20.34	5.70	0.47	0.26	4.15	-

* for explanation of symbols, see footnotes to Table 2

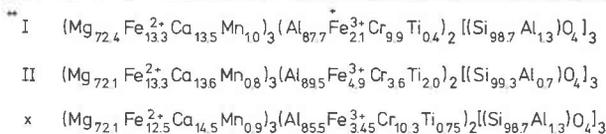
Reflectance Photometry and Mössbauer Studies on Stockdale Garnets

The reflectance spectra of 5 selected garnet fractions (Fig. 2) may be interpreted as follows: (1) The chromium content influences the color by the absorption bands near 410 nm and between 560 and 570 nm. (2) Garnets 17 and 27 from Series II have a more intensive absorption within the whole wavelength range, especially between 450 and 510 nm. The garnets of Series I in this range have higher reflectance values. (3) In the spectra of the garnets from Series II, a characteristic absorption peak near 367 nm occurs which belongs to Fe³⁺ in octahedral coordination. This assignment indicates higher content of Fe³⁺ in garnets of Series II (Amthauer, 1974).

Finally, Mössbauer studies on 4 garnets, whose reflectance spectra are given in Figure 2, gave further information about the differences of the Fe²⁺ and Fe³⁺ content in both main series. Although the determination of intensity according to the peak areas of Fe²⁺ and Fe³⁺ demonstrates only a low absolute content of Fe³⁺ compared to Fe²⁺, the Fe³⁺ value in gar-

TABLE 5. Average Composition and Formula of Garnets from the Stockdale Kimberlite

	Weight %	SiO ₂	Al ₂ O ₃	FeO*	MgO	CaO	MnO	TiO ₂	Cr ₂ O ₃
Series I	7750	413	213	741	2057	526	0.49	0.16	3.50
Series II	1587	418	216	850	2060	537	0.39	0.75	1.25
x	640	412	208	746	2034	570	0.47	0.26	4.15



* Total iron as FeO. *In the formulas some Fe²⁺ recalculated as Fe³⁺.
 ** Elements in the several positions X, Y and Z are calculated to the sum 100.
 x Average of garnets with complex composition (Table 3).

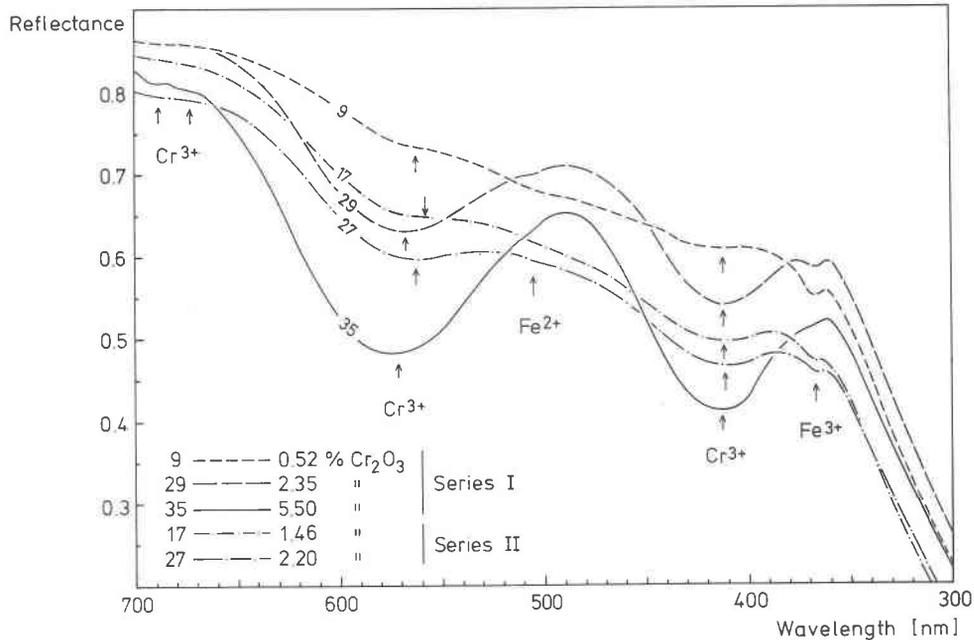


FIG. 2. Reflectance spectra of Stockdale garnets (Amthauer, 1974).

net 17 (Series II) is nearly twice as large as in the garnets of Series I (Amthauer, 1974). These discrepancies cannot be interpreted without further research. The results agree, however, at least relatively to the other results presented in this investigation on Stockdale garnets (Table 6).

Discussion

Series I pyropes from Stockdale kimberlite resemble similar garnets described from other kimberlites by O'Hara and Mercy (1963), Nixon *et al* (1963;

TABLE 6. Results of Mössbauer Investigation on Four Stockdale Garnets

Garnet Nr.	9	17	29	35	
Series	I	II	I	II	
% Cr ₂ O ₃	0.52	1.46	2.35	5.50	
Cell edge (Å)	11.523	11.545	11.532	11.563	
Mössbauer data					
Fe ²⁺ cub	IS ¹ (mm/sec)	1.42	1.42	1.43	1.42
	E _Q ² (mm/sec)	-3.67	-3.65	-3.65	-3.65
Fe ³⁺ oct	IS ¹ (mm/sec)	0.44	0.42	0.45	0.44
	E _Q ² (mm/sec)	0.26	0.29	0.28	0.32
Intensity ³	Fe ²⁺	94	89	94	93
	Fe ³⁺	6	11	6	7

¹ IS = isomere shift

² E_Q = quadrupole splitting

³ Intensity = relation of peak areas ($\pm 0.5\%$)

1968), Rickwood, Mathias, and Siebert (1968) and Gurney and Switzer (1973, Table 1) and the pyropes from peridotites of the Middle European Basement described by Rost and Grigel (1969)². These similarities include (1) a "pyrope content" between 70 and 73 mole percent, (2) a CaO content of at least 4 wt percent, and (3) a trend of cell edge values like that in Figure 3. Chromium contents of pyropes from garnet peridotites of Bohemia and Austria reach 7.6 percent Cr₂O₃ (Kleinpöchlarn, Austria) and 8.0 percent Cr₂O₃ (Drilling T 7 Linhorka, Bohemia) and exceed the value which Reid and Hanor (1970) have reported in Bohemian pyropes ("3.2 wt percent Cr₂O₃ in Mg-rich pyropes"). In the Stockdale pyropes of Series I the chromium content attains *ca* 13 wt percent (garnet 41c in Table 4); the highest chromium concentration of 17.47 wt percent Cr₂O₃ in garnet K 47 from a south African kimberlite caused Nixon and Hornung (1968) to designate this garnet as "knoringite." These authors consider it probable "that *PT* conditions such as obtained in the mantle are necessary for the formation of chromium-rich pyropes, exceeding 10 wt percent Cr₂O₃." These conditions are probably higher than in the deepest parts of an orogenic crust, where garnet peridotites may be formed (Rost and Grigel, 1969).

² Former publications about pyropes of this region, especially by Czechoslovakian authors, are taken into consideration in this paper.

Chromium concentrations in pyrope garnets included in or closely related to diamonds (Meyer and Boyd, 1972; Sobolev *et al.*, 1969; Gurney and Switzer, 1973) do not exceed the values in pyropes hitherto reported. This fact suggests that increasing *PT* conditions cause the trend towards higher chromium contents in pyrope-rich garnets, but the amount of chromium available for an isomorphous substitution in pyropes absolutely does not seem to increase at greater depths of the mantle, where diamonds originate.

The garnets of Series II from the Stockdale kimberlite contain equal values of CaO and MgO (*ca* 72 mole percent pyrope), but lower concentrations of chromium. They are also distinguished by a considerably higher content of TiO₂ and Fe³⁺ (in *Y* position). The authors surmise that these garnets originate in the same level of the upper mantle as garnets of Series I but in more basic environment, with a

higher supply of TiO₂ and a higher oxidation potential.

The pyrope garnets "related to or included in diamonds" show an evidently higher mole percent of Mg garnet than garnets in an environment missing diamonds; this percentage fluctuates between 75.1 and 87.8 (Gurney and Switzer, 1973; an average of 35 analyses gave 81.2 mole percent), 78.1–86.3 (Sobolev *et al.*, 1969; average of 11, 82.6 mole percent), and 81.9–88.9 (Meyer and Boyd, 1972; average of 11, 86.5 mole percent). Furthermore, these garnets have a negligible content of titanium and lower calcium concentration, which can cause the lower cell edge values of garnets in Figure 3 (Meyer and Boyd, 1972). Pyrope garnets genetically connected with diamonds "are considered to have a deeper provenance than the magnesian garnets commonly found as xenocrysts in kimberlite and in garnet peridotite xenoliths" (Gurney and Switzer, 1973).

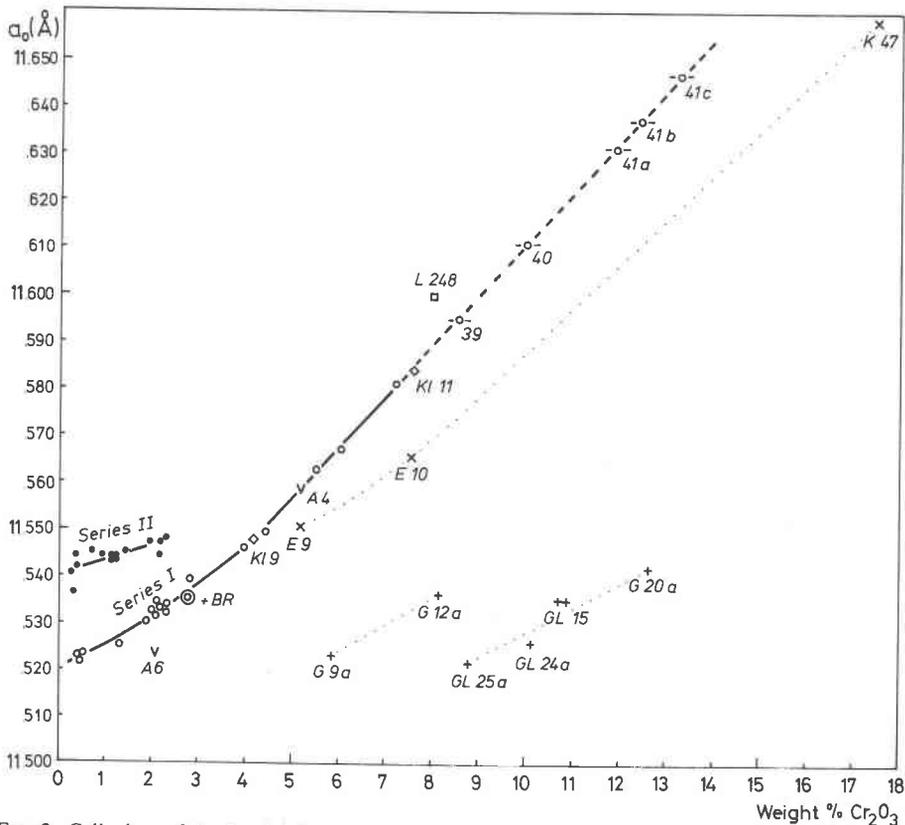


FIG. 3. Cell edges of the Stockdale garnet fractions (series I and II) plotted against chromium content. For comparison, plots of other pyrope garnets are added. (1) chromium-rich garnets from garnet peridotites: K19 and K111 (Kleinpöchlarn, Austria); L248 (Drilling T7, Linhorka, Bohemia) (Rost and Grigel, 1969). (2) Kimberlite garnets: (a) BR ("red garnet", Brookins *et al.*, 1966, 1967; from Stockdale); (b) A6 and A4 (O'Hara and Mercy, 1963); (c) E9, E10, and K47 (Nixon *et al.*, 1963, 1968); (d) G9a, G12a, GL15e+h, G20a, GL24a, and GL25a (Meyer and Boyd, 1972).

Acknowledgments

The authors would like to thank Dr. P. C. Franks, State Geological Survey, University of Kansas, Lawrence, Kansas, who kindly sent the kimberlite samples. The study was in part supported by the "Deutsche Forschungsgemeinschaft."

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Manuscript received, August 15, 1974; accepted for publication, February 21, 1975.