NASA TT F-13,819

ASSOCIATION OF OLIVINE, GARNET AND CHROME-DIOPSIDE IN A YAKUSTK DIAMOND

N. V. Sobolev, Z. V. Bartoshinskiy, E. S. Yefimova, Yu. G. Lavrent'yev, and L. N. Pospelova

Translation of "Assotsiatsiya Olivin-Granat-Khromdiopsid iz Yakutskogo Almaza", Doklady Adademii Nauk SSSR, Vol. 192, 1970, pp. 1349-1353.

CASEFILE

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION WASHINGTON, D.C 20546 NOVEMBER 1970

## ASSOCIATION OF OLIVINE, GARNET AND CHROME-DIOPSIDE IN A YAKUSTK DIAMOND (1)

N. V. Sobolev, Z. V. Bartoshinskiy, E. S. Yefimova, Yu. G. Lavrent'yev, and L. N. Pospelova

ABSTRACT. Diamonds from the "Udachnaya" vein were found to contain olivine (2 inclusions) chrome-diopside, garnet (2 inclusions) and concretions of garnet and chrome-diopside. These data make possible a more exact evaluation of the distribution of scattered concentrations of  $K_2^0$  at high pressures in the pyroxene phase.

In the past few years, use of an electronic microprobe has already produced the first data on a direct determination of the chemical composition of minerals that are included in diamonds [6, 16, 17]. These data point to the special role of the minerals in the process of forming minerals deep under the earth. However, in spite of the relatively significant quantity of analyzed syngenetic inclusions (about 50), there are no data on such an important mineral as chrome-diopside. Information on the composition of inclusions of various minerals from one diamond crystal is also very limited; it is only available for the following pairs: olivine and garnet, olivine and enstatite, olivine and chromite, and garnet and chromite [17]. However, the most significant information for deciding on the crystallization conditions could be obtained by studying a pair of pyroxenes or pyroxenes with garnet.

/1349

<sup>\*</sup>Numbers in the margin indicate pagination in the original foreign text.

(1)
Presented by Acadmician V. S. Sobolev, 25 December 1969.

For this reason there is great interest in the study of various inclusions that are found in diamonds from the "Udachnaya" vein in Yakutiya (Sample No. 57/9). After this crystal was crushed, the following minerals were extracted: olivine (2 inclusions) chrome-diopside, garnet (2 inclusions), and also concretions of garnet and chrome-diopside. The studied selection of inclusions is unique in the quantity of the various minerals that are contained.

The diamond was an almost isometric octahedron, about 8 mm in diameter; it weighed 0.851 g (4.25 carats). The facets of the octahedron were covered with a series of thick flakes of a ditrigonal form of growth. The flakes were intermixed with each other with respect to orientation to the facets and to the top of the cyrstal. A thin system of cracks had developed around the inclusions.

The idomorphous inclusions of olivine and garnet, that were extracted from the diamond, were subjected to a goniometric investigation in a double-circle goniometer GD-1. The olivine crystal (Figure 1) was significantly extended along the [001] axis; its dimensions were 0.25 x 0.14 x 0.18 mm. Because of the insignificant dimensions of the crystal and the weak signals with diffuse contours from most of the facets, the spherical coordinates of the facets were registered from reflections. Thus, the difference between the measured and calculated values of the  $\varphi$  and  $\rho$  coordinates was as much as 2° for various forms.

The central parts of the facets in the vertical band appeared smooth and flat, but the peripheral parts were rounded. In essence, there were narrow cylindrical surfaces at the edge locations, but some places had rather wide cylindrical surfaces. The roughest facets were the a $\{010\}$  planes. The u $\{540\}$  and  $\{140\}$  facets appeared to be well developed, but had significantly smaller dimensions than the a $\{010\}$  plane. The r $\{130\}$  and z $\{140\}$  planes had the form of very narrow flat bands. All of these forms, except z $\{140\}$  had been observed earlier in olivine, and are usual for individual types of this mineral. The facets on the crown had significantly smaller dimensions than the facets on the vertical band, and were lightly curved in some degree.

Among them, the following forms were established: 0(304), h(499), s(432), y(452), z(472), p(224),  $\varphi(442)$ ; up to now, such forms have not been encountered in olivine crystals of other genetic types. The roughest facets were s(132) and x(172); the rest were very fine (see Figure 1).

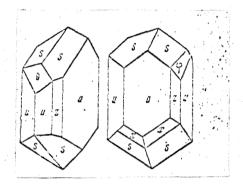


Figure 1. An olivine crystal from a diamond.

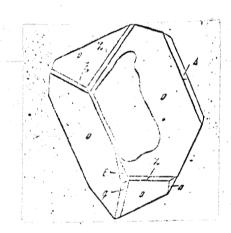


Figure 2. A garnet crystal from a diamond.

The garnet inclusion was a narrow crystal of octrahedral appearance with dimensions of 0.30 x 0.19 x 0.17 mm; it was strongly elongated along one of the L, axes (Figure 2). This distortion resulted in rather long, smoothly rounded, false edges at the top of the octahedron. The equally sized facets dominated the crystal and gave very clear and sharp signals on the goniometer. One of these facets 0{111} had a rough outgrowth that had a laminated structure. The narrow cylindrical surfaces had developed at the edges of the octrahedron, along with extremely thin longitudinal striations, which gave goniometer signals in the form of thin rectangular beams. One rather clear, but diffuse, signal was registered on each of these beams. Measurements of these reflections showed that they were very close to trigon-trioctahedrons  $q(331), \xi(551), \chi(991)$  and  $\Delta(774)$ , according

to their crystallographic position. Moreover, slightly rounded tetragon-trioctahedrons n{445} and a hexatetrahedron E{453} were encountered in some cases. Garnets of octahedral appearance are very rare [11]. Only rhombododecahedrons were found visually in garnets from diamonds [2]. This form, along with the tetragon-trioctahedron, was observed in synthetic pyropes [1].

/1350

X-ray analysis of the inclusions was carried out on the MS-46 microanalyzer under conditions described previously [4, 6]. Philibert's Method [19] was used to correct the measured intensity ratio for x-ray absorption in the sample. Corrections for the effect of the atomic number of the radiator were made according to Duncumb and Reed [10]. Corrections for the flourescence of the characteristic spectra were made according to Reed [20]. The corrections were calculated on an electronic computer by the method of successive approximations.

Table 1 shows the results of the analysis of olivine, which was subjected to a preliminary goniometric investigation (Column 1); the roughest inclusion of garnet that was isolated, which was 0.8 mm along the axis (Column 2); chrome-diopside (Column 4), and an inclusion in the chrome-diopside (Column 6). The compositions of the garnet (Column 3) and the chrome-diopside from the concretion (Figure 3) were also studied.

Colorless olivine is characterized by a high content of forsterite (94%). It is analogous to diamonds in the amount of admixed  ${\rm Cr_2^0}_3$  [18], but different from olivines that come from kimberlites and hyperbasic rocks.

The garnet, which had an unusual inky blue color when it was still in the diamond, was first identified from x-rays. After it was extracted from the diamond, the color of the garnet turned out to be bluish violet. The compositions of the two garnets were essentially different, within the errors of the analysis. The main difference from chrome-containing garnets from diamonds and xenolites of diamond-bearing peridotites was the very high content of a calcium component (about 36%) [4, 6, 16]. The garnets in this study were close to some rare forms of pyrope-uvarovites of garnets from kimberlites [6, 23]. However, they differ from kimberlite garnets in that they have a lower iron content. The composition (in mol-%) of the garnets in this study are as follows: 57.1% and 58.0% pyrope, 5.8% and 5.7% almandine, 0.6% and 0.6% spessarite, 7.0% and 6.8% grossular, 5.9% and 6.1% andradite, and 23.6% and 22.8% uvarovite. N meas = 1.769; N calc = 1.768 [21].

<u> 135</u>1

TABLE 1. CHEMICAL COMPOSITION OF MINERALS, EXTRACTED FROM DIAMOND (SAMPLE NO. 59/7)

	Olivine	Garnets		Chrome- diopsides		Inclusions in chrome-diopside
	í	2 .	3 ;	4 .	5	6
SiO <sub>2</sub> TiO <sub>2</sub> Al <sub>2</sub> O <sub>3</sub> Cr <sub>2</sub> O <sub>4</sub> FoO MnO MgO CaO N,O K <sub>2</sub> O	41,4 0,02 0,06 6,00 0,11 52,9 0,04 0,02 (NiO 0,34)	41,0 0,46 16,2 8,00 4,66 0,30 15,2 13,5 0,07 0,00	41,0 0,42 16,3 7,82 4,64 0,29 15,5 13,3 0,06 0,00	55,4 0,07 1,75 1,65 1,36 0,03 16,6 21,4 1,40 0,15	54,1 0,10 1,50 1,62 1,11 0,03 16,8 22,1 1,31 0,14	62,0 0,7 0,7 1,6 27,0 9,3 0,4
Total  Si AlIV  Ti AlVI  Cr Fe <sup>3+</sup> *** Fo <sup>2+</sup> Mn  Mg Ca Ca Ca Fo/(Fe + Mg) (/), % Ca/(Ca + Mg), %*** Cr/(Cr + Al), %	100,39 0,991 	99,39 3,034 0,026 1,413 0,470 0,117 0,172 0,018 1,676 1,071 0,008 44,6 50,4 24,9	99,33 3,031 0,024 1,422 0,456 0,122 0,167 0,018 1,711 1,053 0,008 14,5 35,6 24,3	99,81 1,599 .0,001 0,002 0,072 0,041 .0,893 0,893 0,100 0,007 4,4 48,1 39,3	98,81 1,979 0,021 0,002 0,045 0,048 0,032 0,917 0,866 0,092 0,007 3,5 48,6 42,1	101,7 2,09  0,03 0,02 0,04 1,36 0,34 0,02 3,0 20

<sup>\*</sup>All iron in the form of FeO.

Chrome-diopside (Table 1, Columns 4 and 5) is characterized by the practically complete absence of  ${\rm Al}^4$ , the increased value of the  ${\rm Cr/(Cr+Al)}$  ratio, and a tendency to accumulate  ${\rm K}_2{\rm 0}$  that is analogous to pyroxenes from diamond-bearing eclotites [3]. The compositions of the two pyroxenes were very close, with insignificant differences in the amounts of alumina and iron.

Fine (5-10  $\mu$ ) rounded deposits were observed in the isolated chromediopside inclusion. Analysis of these deposits (Table 1, Column 6) showed that they belonged to the pigeonite type of pyroxene, but with a higher Ca/(Ca+Mg) ratio and with a lower iron content.

<sup>\*\*</sup>Only for garnets in additions to 2.0.

<sup>\*\*\*</sup> For garnets — concentration of calcium component.

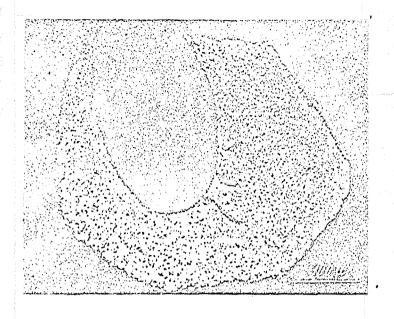


Figure 3. Concretion of garnet and chromediopside from a diamond irradiated by A]K $\alpha$ -radiation.

The first question that arises in interpreting these results is whether the characterized minerals in one diamond can be considered to be in an equilibrium phase.

The following factors can serve to confirm the equilibrium character of the minerals:

(1) the presence of garnet and chrome-diopside concretions, and (2) the fact that the compositions of the isolated inclusions (Columns 2 and 4) are identical to the

compositions of the same minerals in the concretion (Columns 3 and 5). Data on the composition of two garnets (Sample 15) from one diamond and of two chromites (Sample 3) from one diamond can provide additional confirmation [17]. Also, data obtained by us (N. V. Sobolev, new data) gave identical compositions for two chromic garnets from one diamond. Finally there are analogous data from S. I. Futergendler (verbal communication).

/1352

The originally measured very high calcium content (36%) is most unusual for garnet in natural association with olivine, as compared to 11-18% for a peridotite association in the presence of enstatite [5, 8]. This peculiarity of the garnet makes it possible to exclude enstatite as a possible mineral in this association, since the garnet composition in equilibrium with enstatite, forsterite, and diopside depends very little on pressure [8]. While the range of garnet composition in the paragenesis of diopside-forsterite is close to the measured value for pressures on the order of 20 kbar, it increases greatly at increased pressure [14] to 45% calcium at P = 45 kbar and  $T = 1300^{\circ}$  C.

The absence of enstatite in the paragenesis makes it impossible to evaluate the temperature from the Ca/(Ca+Mg) ratio in the diopside [9]. The lower temperature limit can be evaluated from the existence of pigeonite growths with an unusual composition. Experimental data [13] show that, even at atmospheric pressure, such a decomposition is possible at temperatures under 1100°, if it is considered in this case that the decomposition can occur after the pressure decreases. The pressure can be evaluated to be above 40 kbar from the data of MacGregor [14].

Thus, in addition to the two known diamond-containing associations of olivine + Cr-pyrope and garnet + omphacite, we have characterized a new, third type of association which contains diamond, and which is different in mineral composition from the parageneses known in nature. Currently, it is difficult to determine how widespread this association is in the stability field of diamonds. However, establishing this association allows us to assume that it is possible to find single inclusions of chrome-diopside in diamonds, and that these inclusions will have a high Ca/(Ca+Mg) ratio (close to 0.5), analogous to most of the chrome-diopside grains in kimberlite concentrate [7].

The increased value of  $K_d$ Cr/(Cr-Al) for garnet and pyroxene from individual inclusions and a concretion, respectively (0.52 - 0.44) agrees with our preliminary conclusion [22] and with MacGregor's data [15] on the effect of pressure on the relative increase in Cr content in coexisting phases of pyrope peridotites.

In conclusion, we should remark that these data open the possibility for a more exact evaluation on the preeminent distribution of scattered concentrations of  $K_2^0$  at high pressures in the pyroxene phase [12]. There is also interest in observing  $Na_2^0$  in garnet.

Received by the editors 28 Oct 1969

Institute of Geology and Geophysics

Siberian Department of the USSR Academy of Sciences Novosibirsk

Lvov Government University, imeni Ivan Franko

## REFERENCES

- 1. Medvedeva, M. S. and S. V. Popova. Geokhimiya. No. 11, 1969.
- 2. Orlov, Yu. L. Tr. Mineral. muzeys (Transactions of the Minerology Museum). No. 10, 1969.
- 3. Sobolev, V. S., et al. In: Problemy kristallochimii mineralov i endogennogo mineraloobrazovaniya (Problems of Crystal Chemistry of Minerals and Endogenic Mineral Formation). 1967.
- 4. Sobolev, V. S., et al. Doklady Akad Nauk, Vol. 188, No. 5, 1969.
- 5. Sobolev, N. V. Parageneticheskiye tipy granatov (Paragenic Types of Garnets). Science Publishing House, Moscow, 1964.
- 6. Sobolev, N. V., et al. Doklady Akad Nauk, Vol. 198, No. 1, 1969.
- 7. Boyd, F. R. American Journal of Science. Shairer Vol., 267-A, 1969.
- 8. Boyd, F. R. Carnegie Institute Year Book. Vol. 68, 1970.
- 9. Davis, B. T. C. and F. R. Boyd. Journal of Geophysics Research. Vol. 71, 1966, p. 3567.
- 10. Duncumb, P. and S. J. B. Reed. Quantitative Electron Microprobe Microanalysis, National Bureau of Standards, Special Publication No. 298, 1968, p. 133.
- 11. Goldschmidt, V. Kristallographische Winkeltabellen (Crystallographic Angle Tables). Berlin, 1897.
- 12. Ito, K., T. Matsumoto and N. Kawai. Journal of Geoscience. Osaka City University, No. 11, Article 1, 1968.
- 13. Kushiro, II. American Journal of Science. Schairer Volume, 267A, 1969.
- 14. MacGregor, I. D. Carnegie Institute Year Book. Vol. 64, 1965.
- 15. MacGregor, I. D. International Symposium on Phase Transformations, Abstract Volume 80, 1969.
- 16. Meyer, H. O. A. Science. Vol. 160, 1968, p. 1446.
- 17. Meyer, H. O. A. Carnegie Institute Year Book. Vol. 67, 1969.
- 18. Meyer, H. O. A. and F. R. Boyd. Carnegie Institute Year Book. Vol. 68, 1970.

- 19. Philibert, J. X-ray Optics and X-ray Microanalysis. New York, 1963, p. 379.
- 20. Reed, S. J. B. British Journal of Applied Physics. Vol. 16, No. 913, 1965.
- 21. Skinner, B. I. American Mineralogist. Vol. 41, No. 5-6, 1956.
- 22. Sobolev, N. V. Physics Earth. Planet. Inter. Canberra Proc., 1969.
- 23. Sobolev, N. V., et al. J. Petroleum. Vol. 9, No. 2, 1968.

Translated for Goddard Space Flight Center under Contract No. NASw 2035, by SCITRAN, P. O. Box 5456, Santa Barbara, California, 93103.