SOBO-NV 71-037

Contr. Mineral. and Petrol. 31, 1–12 (1971)
© by Springer-Verlag 1971

Isomorphic Sodium Admixture in Garnets Formed at High Pressures

N. V. Sobolev, Jr. and Ju. G. Lavrent'ev

Institute of Geology and Geophysics, Siberian Branch of the USSR Academy of Sciences, Novosibirsk, USSR

Received January 4, 1971

Abstract. Na_2O contents were determined by electron microprobe analysis in 124 garnets from diamonds, xenoliths of peridotites, eclogites from kimberlitic pipes and metamorphic complexes. Na_2O content ranges between 0.01 and 0.22% with the limit of detection at about 0.01%. In the garnets of diamond-bearing eclogites and orange garnets from diamonds a regular increase in the Na_2O content has been established, varying from 0.09 to 0.22, as compared to garnets from eclogites of metamorphic complexes (range 0.01 to 0.06). It is assumed that the increased Na_2O content in the garnets of eclogites is mainly connected with higher pressure, whereas isomorphism of sodium is connected with the initial stages of the transition from Si^4 to Si^6 in the garnet structure: $CaAl \rightleftarrows NaSi$.

The study of the sodium content of garnets has shown that all the orange-coloured garnets from diamonds so far studied are related to eclogite assemblage. Determination of the Na_2O content of individual inclusions of chrome pyropes from diamonds permits a conclusion on the type of assemblage (with or without clinopyroxene). Proceeding from these data, the importance of garnet-olivine paragenesis within the stability field of diamond has been revealed.

Some clear distinctions in the sodium content of the garnets from xenoliths of the kyanite eclogites from the Zagadochnaya pipe in Yakutia and the Roberts Victor mine in South Africa confirm the relation of these eclogites to different subfacies.

A conclusion is drawn as to the possibility of utilizing the Na/Na+Ca distribution in the garnets and pyroxenes of eclogites of especially deep-seated origin as a pressure indicator and to the necessity for experimental testing of the dependence of the distribution of these elements in garnets and pyroxenes on pressure, presumably in the range of 30–100 kbars.

Introduction

The application of modern analytical methods, particularly electron probe microanalysis, offers great possibilities for determining peculiarities in the content and distribution of individual elements in the minerals. This may, for instance, be applied to some minor elements whose role in minerals can hardly be explained on the basis of chemical analyses of powdered material because of the probability of mechanical impurities of other phases.

The present paper deals with the study of the minor sodium content and its peculiarities of distribution in the pyrope-almandine-grossular garnets, coexisting with clinopyroxenes containing Na_2O, i.e. from eclogite-peridotite assemblages and in individual garnet inclusions in diamonds, mainly of unknown assemblage.

Analytical Methods

Sodium determination was carried out with local electron probe analysis using a microanalyzer MS-46 produced by "CAMECA". The accelerating voltage was 15 kV, the sample current being −150 nA. The $K\alpha$-line of sodium was recorded at ten different points on the

MAY 8 1972

Table 1. *Reproducibility of Na_2O content determinations in the pyrope sample 0–145*

Number of Analysis	Na_2O (wt %)
1	0.023
2	0.011
3	0.017
4	0.024
5	0.012
6	0.025
7	0.022
8	0.018
9	0.025
$\bar{x}$	0.020
s	0.0055

$\bar{x}$ = arithmetic mean; s = standard deviation.

samples studied, the time of each count being 20 sec. The same procedure was applied to measurements of the background spaced at 0.16 A (3 mm of the scale) from the long-wave side of the line.

Determination of low sodium content is rather complicated. One of the factors likely to affect the accuracy of the analyses is the possibility of the evaporation of sodium from the radiating microvolume under the electron beam. At the relatively high current required for attaining the desired sensitivity of scanning and a beam diameter of about 5–10 mc, an insignificant decrease in the radiative intensity of sodium was observed within the exposure time for albite, which was used as a standard. A slow displacement of the sample during analysis eliminated this phenomenon as a whole. Small garnet grains largely restricted the possibility of displacement. However, repeated analysis of one of more large grains with maximal Na_2O content (0.20%) carried out with sample displacement revealed perfect convergence, and hence, the absence of evaporation. This confirms the opinion of Smith (1965) and Siivola (1969) that evaporation does not significantly affect the analytical results of silicates containing high Mg, Ca and Fe.

Special care was paid to accounting for possible inclusions of sodium-bearing minerals in the garnets. The counts recorded were checked for homogeneity by the 3σ criterion, and unsatisfactory ones were discarded; in general, the number of such measurements was insignificant. Then the dispersion of measurements for each sample (S^2) was compared by Fisher's criterion (Nalimov, 1960) with that of the Poisson statistics (σ^2). In most cases the compared dispersions could be regarded as equal to the probability exceeding 5%. Thus the results of the measurements can be regarded as free of the effect of possible inclusions of mineral impurities in the garnet.

The F-criterion check provides a possibility for calculating the limit of detection of the Na content in the garnets for statistical registration of errors only, while instrumental error (Lavrent'ev and Vainstein, 1965) is regarded as negligibly small. Under the above-stated conditions of analysis, the background value was 1.4 pulse/sec and 1% of sodium corresponded to 60 pulses/sec, which agrees with the limiting Na_2O concentration of about 0.01%. The reproducibility of the analyses in the region of extremely low Na_2O content may be seen from

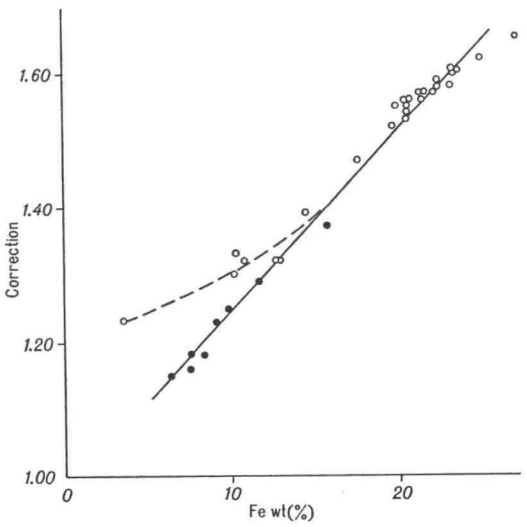


Fig. 1. Dependence of correction value of Na content on Fe content in pyrope-almandine garnets (open circles) and on Cr+Fe content in pyropes (black circles)

Table 1, which lists the results of parallel measurements of Na_2O content in the 0–145 garnet sample used as a reference.

Absorption corrections after Philibert (1963) were introduced in directly measured values of Na concentration (K) as well as corrections for the atomic number by the method of Duncumb and Reed (1968). When garnets were fully analysed by electron probe, corrections were computed using a number of approximations. In a number of cases, complete analyses were impracticable so corrections were introduced according to the empirically found dependence on the Fe content of garnet (Fig. 1). For chrome pyropes, chromium concentration was taken into account and reduced to the iron absorption level.

Analytical Results

In accordance with the methods stated above, the Na_2O content was determined in 124 garnets of eclogite and peridotite assemblages, including garnets coexisting with diamonds as inclusions and grown-in (Table 2). Although the total Na_2O content in the studied garnets is low, the range of variation is rather wide (<0.01–0.22%), which permits one to distinguish some regularities.

The peculiarities in the Na distribution are considered in: 1) pyrope-almandine garnets with variable f-value[1] and Ca content from eclogites and diamonds and 2) chrome-bearing pyropes with low f-value and mainly low Ca content. Clinopyroxenes having higher Na_2O contents coexist with the first type of garnets (3–8.0%) while chrome-diopsides with $Na_2O = 1$–2% mainly coexist with the second type of garnets. The wide variations in Na content are especially typical of the first type and some regularities in its distribution may be determined for some distinctly differing rock groups (Fig. 2).

This finding can be largely applied to diamond-bearing eclogites which represent a unique rock group with a peculiar character of pyroxenes (Sobolev, 1968). As may be seen from the diagram in Fig. 2, the garnets of these eclogites (14 samples are from the Mir pipe and 2 from South Africa) form a separate group with

1 $FeO/FeO + MgO$.

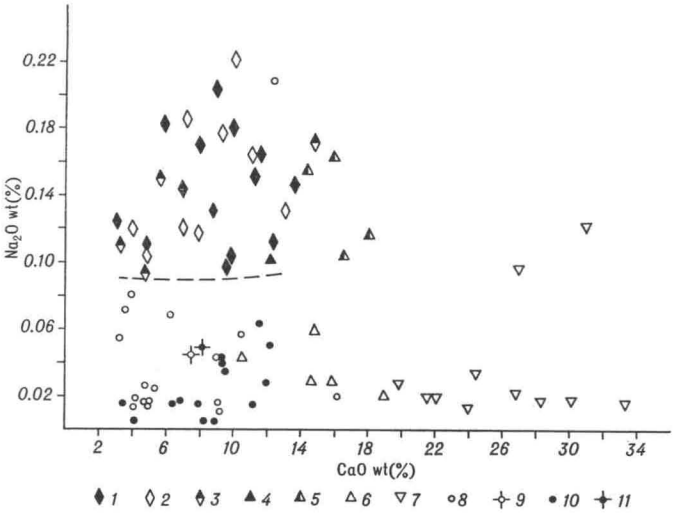


Fig. 2. Weight per cent Na_2O content versus weight per cent CaO content in pyrope-almandine-grossular garnets from diamonds and eclogitic assemblages: 1. from diamond-bearing eclogite; 2. garnet inclusions in diamonds; 3. grown in with diamonds; 4. from diamond-bearing kyanite eclogite; 5. from kyanite eclogites of the Roberts Victor pipe; 6. from kyanite eclogites of the Zagadochnaya pipe, Yakutia; 7. those from grospydites; 8. garnets from eclogite xenoliths; 9. garnet from eclogite xenolith contained graphite; 10. garnets from eclogites of metamorphic complexes; 11. from quartz-garnet-jadeite rock, South Urals

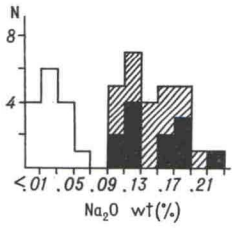


Fig. 3. Histogram of Na_2O (weight %) content in garnets from diamonds (black); diamond-bearing eclogites (shaded) and from eclogites of metamorphic complexes (white)

maximum Na_2O content (0.09–0.20%). Similar peculiarities in the Na content along with some other peculiarities in the composition are also typical of the yellow-orange and orange garnets found as inclusions and grown-in with diamonds (Table 2).

Another tendency in the Na distribution is typical for the garnets from eclogites of different metamorphic terranes. Na content in these garnets is similarly low both in the eclogites of gneiss complexes and in eclogites associated with glaucophane schists (Table 2) from different regions of the globe: Urals, Kazakhstan, Tien-Shan (USSR), Norway, Scotland, California, Swiss Alps. In more than half of such garnets studied, the Na_2O content was found within the limits of detection to be equal to 0.01–0.02%.

It should be stressed that some of the attempts to determine Na_2O content in garnets of this type by chemical analyses (Bryhni *et al.*, 1969) have led to obviously overestimated results caused by an impurity of omphacite in the analyzed

Table 2. *Mean Na_2O contents (weight %) in pyrope-almandines, and magnesian garnets from diamonds, peridotites and eclogites of different types*

Number	Rock type	N	$\bar{x}$	s	Range of variation
1	Diamond-bearing eclogites	16	0.142	0.030	0.097–0.205
2	Yellow-orange garnets from diamonds of Yakutia and Urals	12	0.146	0.037	0.094–0.220
3	1 + 2	28	0.143	0.036	0.094–0.220
4	Kyanite eclogites, from Roberts Victor pipe	5	0.128	0.025	0.103–0.163
5	Kyanite eclogites, from Zagadochnaya pipe	5	0.036	0.013	0.020–0.059
6	Grospydites, Zagadochnaya pipe	11	0.038	0.035	0.014–0.123
7	Eclogites and garnet pyroxenites from kimberlites of Yakutia	18	0.044	0.044	0.010–0.209
8	Eclogites of metamorphic complexes	16	0.027	0.017	0.010–0.063
9	Diamond-bearing serpentinites, Aikhal pipe, Yakutia	3	0.027	0.012	0.017–0.044
10	Chrome pyropes included in diamonds, Yakutia and Urals	12	0.015	0.011	0.010–0.047
11	Pyrope-diamond intergrowths, Yakutia	5	0.063	0.012	0.049–0.081
12	Pyrope-clinopyroxene-diamond intergrowths, Yakutia	2	0.085		0.041–0.128
13	Pyrope-olivine-chromediopside assemblage included in diamond, Yakutia	1	0.035		
14	Pyrope peridotites from kimberlites of Yakutia	12	0.034	0.018	0.010–0.067
15	Green garnets rich in Ca and Cr from kimberlites of Yakutia	7	0.049	0.030	0.010–0.113

N = number of analyses; $\bar{x}$ = arithmetic mean; s = standard deviation.

material. We obtained for two samples of Norwegian eclogite garnets less than 0.01% Na_2O.

The sharp distinction observed in the Na content of garnets from eclogites of different types is illustrated by the histograms in Fig. 3.

A much lower mean Na_2O content is typical of the chromium-bearing pyropes of peridotite xenoliths and inclusions in diamonds. With the exception of one sample (garnet-cpx intergrowth with diamond) containing 0.13% Na_2O, all the garnets studied (36 samples) contain from 0.01 to 0.08% Na_2O. It may be interesting to note that chrome-rich, Ca-poor garnets from the Yakutian diamonds, for which we suggested assemblage with olivine without clinopyroxene (Sobolev, Lavrent'ev *et al.*, 1969), are characterized by the practically total lack of Na_2O (Table 2) as well as garnets of serpentinized diamond-bearing olivinites (Sobolev, Nai *et al.*, 1969) (Fig. 4).

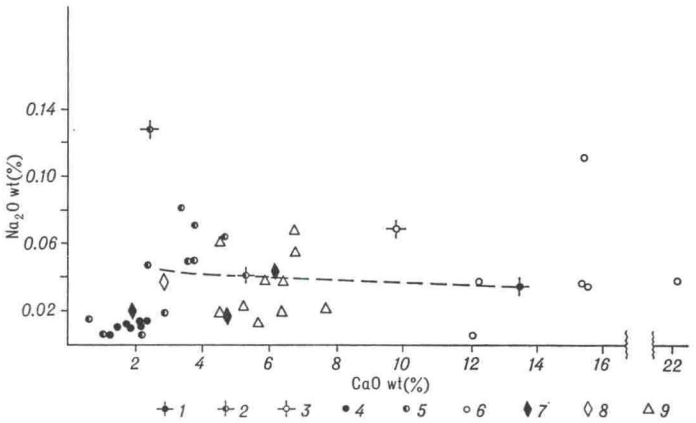


Fig. 4. Weight per cent Na_2O versus weight per cent CaO in pyropes: 1. from an individual diamond (coexistent with diopside and olivine); 2. from the garnet-diopside-diamond intergrowth; 3. from garnet-diopside intergrowth from kimberlite; 4. inclusions in diamonds; 5. garnet-diamond intergrowths; 6. from kimberlitic concentrate; 7. from diamond-bearing olivinites; 8. from olivinite; 9. from peridotite xenoliths

Discussion

The distinctions revealed in the Na content of the garnets of eclogites of different types cannot be associated with the peculiarities in the rock composition, i.e. Na content. The only Na-containing mineral in eclogites is omphacite, whose Na_2O content varies from 3 to 8.0%. Such omphacites are typical of both the eclogites from metamorphic complexes (Dobretsov, 1968), the diamond-bearing eclogites (Sobolev, 1968) and the kyanite eclogites and grospydites (Sobolev, Kuznetsova and Zyuzin, 1968).

The data listed above permit one to suggest a possible dependence of the sodium admixture in garnets on pressure, fixed in this case by their association with diamond. We do not mean the pressure of about 10 kbar which is the lower limit of eclogite formation, but much higher pressure close to at least that required for the graphite-diamond transition (Leipunskii, 1939) and even higher. Such an assumption is in satisfactory agreement with the specific features of a possible isomorphic admixture of Na in garnets, which may enter the garnet structure only as replacing two-valence cations. By analogy with pyroxenes of diopside-jadeite composition, an assumption on the $Na \rightleftarrows Ca$ substitution may be offered. The theoretical possibility of such a substitution in the garnet structure was experimentally shown by hermanate of the compostition: $(Ca,Na_2)Ti_2Ge_3O_{12}$ (Geller, 1967). In this example Na and Ca are joined together with Ti to form hypothetic end members $CaTi_2Ge_3O_{12}$ and $Na_2Ti_2Ge_3O_{12}$.

In the pyrope-almandine garnets the substitution can evidently proceed after $NaSi \rightleftarrows CaAl$ for which it is necessary that part of Si^4 changes into Si^6, which is possible only when pressure substantially increases (Ringwood, 1967), but this may be also combined with the effect caused by some admixture of TiO_2 in garnets. In experiments carried out by A. E. Ringwood (1967) the jump-like increase of garnet content from 40% to 80% and even up to 95% was fixed when pressure

was raised from 110 to 150 kbar. The phase X-ray analysis and data on the a_0 value of the garnet phase were the basis for fixing the variations. But these methods cannot be used to determine the initial stages of the transition from Si^4 to Si^6.

For the composition of natural basalts similar to eclogites, the pressure required for the total rock garnetization strongly depends on the Na_2O content of the initial composition (Ringwood, 1967). This is connected with the stability of jadeite up to the highest pressures (Ringwood and Major, 1967) as the more sodium is present in the rock, the larger the amount of jadeite present in the products. This permits A. E. Ringwood to assume that alkalis cannot enter the garnet structure. However, it has been shown in principle that alkalis do enter the garnet structure (Geller, 1967). The high K_2O content (more than 5%) was determined in garnet in the experiments at high pressures (Kushiro, Syono and Akimoto, 1967), but recently Erlank and Kushiro (1970) showed by repeated analysis of the same probe section that the earlier data were in error. In a recent contribution by Ringwood and Lovering (1970) it is suggested that some Na_2O may enter the garnet at pressures of about 100 kbar, but it is combined only with Ti and not with Si. Thus, at present, direct experimental data are lacking concerning Na entering the pyrope-almandine garnets at high pressures, as experimental products were not analyzed for sodium content.

As implied by the above results of garnet analyses for Na content, the garnets coexisting with diamonds are distinguished by a higher Na_2O content than eclogite garnets of the metamorphic complexes (Table 2). If one proceeds from the relation between Na_2O (0.1–0.2%) and Si contents (and partially Ti), then about 0.5% of all the contained Si would change coordination, or SiO_2 contents in the garnet may increase roughly by 0.2–0.4%. Such an increase in the SiO_2 cannot be verified using a microprobe technique, for analytical error in the Si determination would constitute up to 2% of its contents.

This leads to the conclusion that the initial stages of the $Si^4 \rightarrow Si^6$ transition may be fixed only by the content of Na_2O in the garnet, or by peculiarities in the sodium distribution in garnets and coexisting clinopyroxenes. For an additional test of the possible connection between the sodium content in the garnet and pyroxene, it was necessary to calculate the Na/Na+Ca ratio in the available pairs as well as the distribution coefficient of these ratios (K_D^{Na}) by means of the widespread methods originally applied in mineralogy by Kretz (1961). As has been pointed out by various authors, the value of the distribution coefficient depends on various factors, some of which relate to the compositional features and conditions of formation. However, the dependence on pressure, for a given specific case, evidently relates to the main factors.

The value of the K_D^{Na} was calculated by the general formula: $K_D = \frac{x_1(1-x_2)}{(1-x_1)x_2}$ (Kretz, 1961) where $K_D = K_D^{Na}$; $x_1 = Na/Na + Ca$ ratio in garnet and $x_2 = Na/Na + Ca$ ratio in pyroxene.

K_D^{Na} was calculated for the garnet-pyroxene pairs having at least 0.03% Na_2O in the garnet. At lower Na_2O, which is near to the limit of detection for this method, the resulting error rises sharply. The highest possible values of K_D^{Na} are characteristic of the garnet-pyroxene pairs of diamond-bearing eclogites. For

15 pairs, K_D^{Na} values range from 0.013 to 0.110 (mean 0.039 ± 0.027). It may be interesting to note that the garnet-omphacite assemblage from a single diamond from the Urals described by Sobolev, Gnevushev *et al.* (in press) is also typical of the high $K_D^{Na} = 0.06$. Proceeding from this example, as well as the observed stable high Na content in the yellow-orange garnets coexisting with the Uralian and Yakutian diamonds as inclusions and intergrowths (Figs. 2, 5), a suggestion (Sobolev and Kuznetsova, 1966) that all the garnets of this type contained in diamonds belong to the eclogite assemblage is confirmed. Evidently all the garnets of eclogitic type from African diamonds so far known to have been analyzed must also obey the found regularity. This relates to the samples D15, GL16 (Meyer and Boyd, 1970) and the sample 20f (Meyer and Boyd, 1969). A final reply may be given only after checking the Na content of these samples[2].

For half the analyzed samples of garnets of eclogite (grospydite) xenoliths from kimberlitic pipes, without diamonds, an Na_2O content within the range 0.01–0.03% is typical. The garnets of "eclogite" nodules from the breccias of Oahu, Hawaii and Kakanui, New Zealand in which $Na_2O = 0.02$–0.03% are also included in this group. In considering the peculiarities of the Na_2O content in the garnets of xenoliths of eclogitic composition (Fig. 2), it may be interesting to note that the higher content is typical only of several xenoliths from the kimberlitic pipes from which the diamond-bearing eclogites are known. This may be applied to some of the samples from the Mir pipe and Roberts Victor pipe which may be considered as belonging to the diamond-bearing group (Fig. 2).

There are some extremely interesting distinctions in the Na contents in the garnets of kyanite eclogites from the Roberts Victor pipe in South Africa and the Zagadochnaya pipe in Yakutia. Among the kyanite eclogites from the former pipe, two samples containing diamonds were found (Dawson, 1968; Switzer and Melson, 1968). A small amount of garnet from one of these samples, 111060, has become available from the collection of Dr. G. Switzer, National Museum, USA, along with 110752 and 87375 garnet samples from diamond-free kyanite eclogites from the same pipe and data on their composition (Switzer, personal communication). The mean Na_2O content in the garnets of these xenoliths from the Roberts Victor pipe from 5 samples, including the diamond-bearing eclogite, was much higher than in 5 samples of garnets of similar composition from the Zagadochnaya pipe (Table 2). The same low mean Na_2O content is found in garnets from grospydites of this pipe (Table 2). However, in two grossularites a higher Na_2O content was found, equal to 0.10 and 0.12% (Fig. 2). In comparing the data, an empirical dependence is found in the Na/Na+Ca value in the garnets from the Zagadochnaya pipe with an increase in their f-value (Fe/Fe+Mg) (Fig. 5). The same feature is also shown for the garnets from metamorphic eclogites (Fig. 5). For comparison, the Na/Na+Ca ratios are plotted for garnets from above-noted eclogites of the Roberts Victor pipe, with a tendency to higher values.

Thus, in addition to the well-established fact of diamond-bearing kyanite eclogites from the Roberts Victor pipe, peculiarities in the Na content of the

2 A summary of our data on the Na content of garnets was reported at the Upper Mantle Symposium in Flagstaff. Lately Dr. F. R. Boyd analyzed some of the above-listed garnets for Na with results in accord with ours: D15–0,09% Na_2O; GL16–0.19% Na_2O and chrome pyrope GL25a–0.02% Na_2O (Boyd, personal communication).

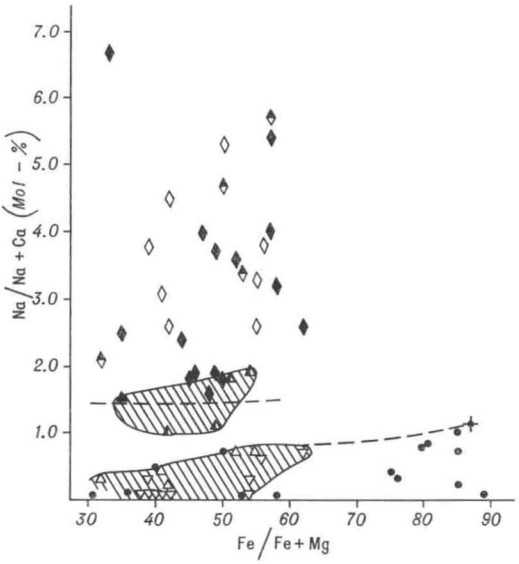


Fig. 5. Na/Na+Ca versus Fe/Fe+Mg ratios in the garnets from eclogites and diamonds. The symbols are the same as in Fig. 2

garnets also confirm that these rocks formed at higher pressure as compared to similar assemblages of the Zagadochnaya pipe, and the latter pipe is free of diamonds. The mean K_D^{Na} value for 3 pairs from the Roberts Victor pipe is also higher than that for 5 pairs from the Zagadochnaya pipe: 0.014 ± 0.003 and 0.006 ± 0.002 correspondingly.

Less clear are the peculiarities of sodium distribution in garnets and clinopyroxenes for assemblages contained in chrome-bearing pyrope. Lower Na_2O contents in garnets are mainly associated with low Na_2O contents in pyroxenes (for various xenoliths of peridotites), while in diamond assemblages both minimum ($<0.01\%$) and maximum (to 0.13%) contents of Na_2O have been found (Fig. 4).

For the garnets coexisting with diamonds, the total lack of Na or a low content may be explained by the peculiarities in the chemical composition of the medium, i.e. low Na content and corresponding peculiarities of their assemblage. In this case a dominating role is played by the garnet-olivine (forsterite) assemblage, as proved by the peculiarities in the garnet composition (Sobolev *et al.*, 1969). However, garnets with low Ca content may coexist not only with olivine but may also be stable in the paragenesis with diopside-jadeitic pyroxene (Sobolev, Zyuzin and Kuznetsova, 1966; Sobolev, Kuznetsova and Zyuzin, 1968; Banno, 1967). The latter may be easily distinguished by the Na content of the garnets. A fair example of this is the garnet-clinopyroxene-diamond intergrowth from the Mir pipe, with Na_2O in garnet $= 0.13$ and in pyroxene $= 6.52\%$, and CaO in this chrome-bearing pyrope about 2.45% (Sobolev *et al.*, in press). The garnets of pyrope olivinites and Ca-poor pyropes included in the diamonds differ sharply in their Na_2O content. The K_D^{Na} value for this pair is of the same order of magnitude as for the pairs of diamond-bearing eclogites (0.087).

An example of a much lower Na content in the garnet and pyroxene is the sample of garnet-olivine-chromediopside assemblage included in a single diamond (Sobolev *et al.*, 1970), with $Na_2O = 0.04\%$ in garnet and $K_D^{Na} = 0.037$.

Wide sodium content variations in the garnets (from 0.01 to 0.07% Na_2O) are typical of xenoliths of peridotites containing subcalcic clinopyroxene from the Udachnaya pipe, reflecting the specific deep-seated nature of the so-far known peridotite assemblages containing no diamonds (Sobolev, 1970).

Proceeding from the Na_2O determinations in the garnets of various assemblages shown in Fig. 4 and Table 2, a rough boundary may be suggested for the Na_2O content in the garnets in paragenesis with olivine (below the boundary) and clinopyroxene (above the boundary); some garnets studied, coexisting with diamonds as intergrowths, differ from most Ca-poor garnet in their Na content. A dominating distribution of garnet-olivine assemblage in the diamond stability field, as confirmed by the Na content of the garnets, seems to be very important. Determination of Na content provides additional important evidence for the conditions of formation of the garnet-clinopyroxene intergrowths, often with chromite, which rarely occurs in the kimberlitic concentrate. The examination of a single sample of this kind from the Mir pipe, Yakutia, containing 0.07 Na_2O in the garnet (Fig. 4) permits one to assume that its crystallization proceeded in the diamond stability field ($K_D^{Na} = 0.04$).

Similar evidence may be obtained for conditions of formation of garnets rich in Cr and Ca, of rare occurrence as separate green grains in the kimberlite concentrate. These garnets can be related to the assemblage with olivine and clinopyroxene in the peculiar wehrlites (Sobolev *et al.*, 1970). Examination of 6 samples of such garnets (Fig. 4) showed that for one sample an especially deep-seated nature of formation may be assumed, while all the remaining ones showed a low Na content.

Conclusions

The study of the Na_2O content of garnets related to eclogite and peridotite assemblages, as well as that of garnets coexisting with diamonds, revealed a series of regularities in its content and distribution in garnets and clinopyroxenes.

The Na_2O content in the garnets of diamond-bearing eclogites and yellow-orange garnets from diamonds ranges from 0.09 to 0.22%. An analysis of the Na/Na+Ca distribution for the garnet and pyroxene inclusions from a single diamond crystal from the Urals and a comparison with the data dealing with diamond-bearing eclogites support the assumption that all the yellow-orange garnets of the diamonds belong to the eclogite assemblage.

The peculiarities in the Na_2O contents of these garnets suggest their possible association with clinopyroxenes containing from 3–8% Na_2O. It must be stressed that a possible association with diopside containing 1.4% Na_2O as inclusions in one of the African diamonds (Meyer and Boyd, 1969) must have been of second importance, as chromium-free iron-bearing garnet coexisting with such a pyroxene may contain only 0.03–0.05% Na_2O.

The specific nature of the Na distribution in chromium-bearing pyropes, related to the assemblage containing no clinopyroxene (garnet-olivine), as well as with diamond and clinopyroxene, permits one to determine the type of assemblage for the single garnets included in the diamond from the Na content of the garnet alone. It has been confirmed that most of such garnets associated with diamonds relate to the garnet-olivine assemblage without clinopyroxene.

As the Na_2O content in the pyrope-almandine garnets of the diamond-bearing eclogites and diamonds as well as K_D^{Na} for the corresponding garnet-pyroxene pairs are much higher than in the garnets of eclogites from the metamorphic complexes, an experimentally check must be made of the correlation between the Na content of the garnets and pressure. Such a test must incorporate a series of experiments with eclogite (basaltic) compositions having different Na contents, at different pressures, presumably within the range 30–100 kbar. The phase obtained, garnet and pyroxene, must be studied by electron probe for its Na and Ca content.

It is not impossible that this method would aid in more accurate outlining of the boundary of the crystallization field of assemblages containing natural diamonds and would give data on the Na-Ca distribution in garnets and pyroxenes as a function of pressure for a P-T region in which phase transformation phenomena are completely lacking.

Acknowledgements. The authors wish to thank Prof. V. S. Sobolev for numerous helpful suggestions during the work and critical reading of the manuscript. We are also indebted to Drs. D. S. Coombs, M. A. Lappin, M. J. O'Hara, E. P. Saggerson, G. Switzer for their kindness in supplying specimens.

References

Banno, S.: Effect of jadeite component on the paragenesis of eclogite rocks. Earth and Planet. Sci. Letters **2**, 249–254 (1967).

Boyd, F. R.: Personal communication.

Bryhni, I., Bollingberg, H. J., Graff, P. R.: Eclogites in quartzo-feldspatic gneisses of Nordfjord, West Norway. Norsk Geol. Tidsskr. **49**, 194–225 (1969).

Dawson, J. B.: Recent researches in kimberlite and diamond geology. Econ. Geol. **63**, 504–511 (1968).

Dobretsov, N. L.: Paragenetic types and composition of metamorphic pyroxenes. J. Petrol. **9**, 358–377 (1968).

Duncumb, P., Reed, S. J. B.: Quantitative electron probe microanalysis. Nat. Bur. Std. Spec. Publ., N **298**, 133 (1968).

Erlank, A. J., Kushiro, I.: Potassium contents of synthetic pyroxenes at high temperatures and pressures. Carnegie Inst. Wash. Year Book **68**, 235 (1970).

Geller, S.: Crystal chemistry of the garnets. Z. Krist. **125**, 1–47 (1967).

Kretz, R.: Some applications of thermodynamics to coexisting minerals of variable compositions. Examples: orthopyroxene-clinopyroxene and orthopyroxene-garnet. J. Geol. **69**, 361–387 (1961).

Kushiro, I., Syono, Y., Akimoto, S.: Stability of phlogopite at high pressures and possible presence of phlogopite in the earth's upper mantle. Earth and Planet. Sci. Letters **3**, 197–203 (1967).

Lavrent'ev, Ju. G., Vainstein, E. E.: The effect of instrumental error on the precision and sensitivity of X-ray spectrographic analysis [in Russian]. Zh. Analit. Khim. **20**, 918–926 (1965).

Leipunskii, O. I.: On artificial diamonds [in Russian]. Usp. Khim. **8**, N 10 (1939).

Meyer, H. O. A., Boyd, F. R.: Mineral inclusions in diamonds. Carnegie Inst. Wash. Year Book **67**, 130–135 (1969).

— — Inclusions in diamonds. Carnegie Inst. Wash. Year Book **68** (1970).

Nalimov, V. V.: Utilization of mathematical statistics at the matter analysis [in Russian]. Fizmatgiz (1960).

Philibert, J.: Method for calculating the absorption corrections in electron probe microanalysis, X-ray optics and X-ray microanalysis, vol. 3, p. 379. New York: Academic Press 1963.

Ringwood, A. E.: The pyroxene-garnet transformation in the earth's mantle. Earth and Planet. Sci. Letters **2**, 255–263 (1967).
— Lovering, J. F.: Significance of pyroxene-ilmenite intergrowths among kimberlite xenoliths. Earth and Planet. Sci. Letters **7**, 371–375 (1970).
— Major, A.: Some high-pressure transformations of geophysical significance. Earth and Planet. Sci. Letters **2**, 106–110 (1967).
Siivola, J.: On the evaporation of some alkali metals during the electron microprobe analysis. Bull. Geol. Soc. Finl. **41**, 85–91 (1969).
Smith, J. V.: X-ray emission microanalysis of rock-forming minerals. 1. Experimental techniques. J. Geol. **73**, 830–864 (1965).
Sobolev, N. V., Jr.: Eclogite clinopyroxenes from the kimberlite pipes of Yakutia. Lithos **1**, 54–57 (1968).
— Eclogites and pyrope peridotites from the kimberlites of Yakutia. Phys. Earth. Planet. Interiors **3**, 398–404 (1970).
— Bartoshinsky, Z. V., Efimova, E. S., Lavrent'ev, Ju. G., Pospelova, L. N.: Olivine-garnet-chromediopside assemblage from a single diamond of Yakutia [in Russian]. Dokl. Acad. Sci. USSR **192**, 1349–1352 (1970).
— Gnevushev, M. A., Mikhailovskaya, L. N., Futergendler, S. I., Shemanina, E. I., Lavrent'ev, Ju. G., Pospelova, L. N.: Composition of garnets and clinopyroxenes from the diamonds of the Urals [in Russian]. (In press.)
— Kuznetsova, I. K.: Mineralogy of diamond-bearing eclogites [in Russian]. Dokl. Acad. Sci. USSR **167**, 1365–1368 (1966).
— — Zyuzin, N. I.: The petrology of grospydite xenoliths from the Zagadochnaya kimberlite pipe in Yakutia. J. Petrol. **9**, 253–280 (1968).
— Lavrent'ev, Ju. G., Pospelova, L. N., Sobolev, E. V.: Chrome pyropes from the diamonds of Yakutia [in Russian]. Dokl. Acad. Sci. USSR **189**, 162–165 (1969).
Sobolev, V. S., Nai, B. S., Sobolev, N. V., Lavrent'ev, Ju. G., Pospelova, L. N.: Xenoliths of diamond-bearing pyrope serpentinites from the Aikhal pipe, Yakutia [in Russian]. Dokl. Acad. Sci. USSR **188**, 1141–1143 (1969).
Switzer, G.: Personal communication.
— Melson, W. G.: Partially melted kyanite eclogite from the Roberts Victor mine, South Africa. Smithsonian Contrib. Earth Sci. N **1**, 1–9 (1969).

Dr. N. V. Sobolev, Jr.
Dr. Ju. G. Lavrent'ev
Institute of Geology and Geophysics
Siberian Branch of the USSR Academy of Sciences
Novosibirsk-90, USSR