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Isotope fractionation related to kimberlite magmatism and diamond formation

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Abstract—This paper deals with a model of carbon isotope fractionation presumed to accompany the movement of mantle fluids. In the first part of the article, the experimental data and the relationships revealed are generalized and discussed; the remainder of the paper describes the model. The isotope compositions of different forms of carbon related to kimberlite magmatism vary widely. In diamonds, $\delta^{13}C$ values range from −34.5 to +2.8‰. Carbonate-bearing autholiths in kimberlites occur enriched in ^{13}C up to +35‰. Organic matter, including that occurring in fluid inclusions of magmatic minerals of kimberlites, is depleted in ^{13}C down to −30‰. It is concluded that the $\delta^{13}C$-distribution for diamonds is specific for a particular occurrence (different kimberlite pipes, different regions, etc.). Principal differences in isotopic distribution patterns for diamonds of ultrabasic and basic paragenesis exist. Isotopically light diamonds are related only to the latter. When a diamond consists of several sequential generations of growth (coated diamonds, diamond-in-diamond), $\delta^{13}C$ values of the early generation vary widely, whereas the isotopic composition of the latter is more uniform.

The intention of the model is to explain the observed variations of carbon isotope composition of diamond and other carbonaceous substances related to kimberlite magmatism. The model is based on the interaction of reduced sub-asthenospheric fluid with the relatively oxidized lithosphere. It is suggested that diamonds of ultrabasic paragenesis (lherzolite and harzburgite mineral assemblages) are produced during interaction of the fluid with sheared garnet lherzolite which is considered to be primitive mantle rock. During contact with the more oxidized mantle, reduced carbon (CH_4) may partially be converted to CO_2. Isotope exchange in CO_2-CH_4 system, combined with Rayleigh distillation, may provide a significant isotope fractionation. Diamonds of the basic (eclogitic) paragenesis are considered to be related to this fractionated carbon. Also, occurrence of carbonate material highly enriched in ^{13}C is explained by the model.

INTRODUCTION

Historical Background

THE FIRST DATA ON THE carbon isotope composition of diamonds appeared in the 1950s (CRAIG, 1953; WICKMAN, 1956). With one exception (+2.4), the $\delta^{13}C$-values for several diamond crystals fell within the relatively narrow range of −9 to −2‰. VINOGRADOV et al. (1966) found the same range of carbon isotopic composition for Yakutia diamonds and reported $\delta^{13}C$ values lower than −25‰ for several samples of carbonado from Brazil.

Diamonds unusually enriched in the light carbon isotope were first found by KOVAL'SKIY et al. (1972). In particular, one diamond from the Mir pipe had a $\delta^{13}C$ value of less than −32‰.

Subsequently, systematic studies of diamonds from East Siberia and elsewhere (GALIMOV, 1978; GALIMOV et al. 1978a,b, 1980a,b; KRAVTSOV et al., 1978b; GURKINA et al., 1979; SOBOLEV et al., 1979; SMIRNOV et al., 1979) established that diamonds are characterized by a wide range of isotopic composition from −34.5 to +2.8‰.

In addition, it was shown that the isotopically light diamonds occurred more frequently in placers than in kimberlite pipes, that all of the diamonds which revealed significant deviation from the mean $\delta^{13}C$ value were of eclogite paragenesis, that yellow diamonds containing uncoupled nitrogen atoms were often isotopically light, and cubic diamonds and polycrystals were, on average, isotopically lighter than octahedrons. The limits of variation of $\delta^{13}C$ values and the mode and the shape of the $\delta^{13}C$ distribution patterns were generally established by 1978 based on about 300 analyses.

DEINES (1978) reported a newer set of data for South African diamonds. He did not find isotopically light crystals among them. In a later paper, DEINES (1980) compiled his and our previous data and discussed the wide range of variation of $\delta^{13}C$ of diamonds. In particular, Deines considered possible isotope fractionation in the system CO_2-C-CH_4-CO under *P-T* conditions of the mantle and concluded that it could not account for the observed range of $\delta^{13}C$ values for diamond.

MILLEDGE et al. (1983) and SWART et al. (1983) recorded significantly negative $\delta^{13}C$ values (down to −31‰) for diamonds, but they did not reveal the sampling locality. They also studied internal variations of carbon isotope composition within diamond crystals. JAVOY et al. (1984, 1986) studied carbon and nitrogen isotope composition of diamonds from Zaire. Many other studies have been published recently (BOYD et al., 1987; DEINES et al., 1984, 1987, 1989; JAQUES et al., 1988; OTTER et al., 1989; GALIMOV et al., 1985, 1989b,c,d, 1990a,b; SOBOLEV et al., 1989; ZAKHARCHENKO and GALIMOV, 1986) and are discussed further below.

A histogram comprising $\delta^{13}C$ analyses for more than 2000 diamonds is presented in Fig. 1.

Apart from carbon, the isotope compositions of nitrogen (WAND et al., 1980; BECKER and CLAYTON, 1977; JAVOY et al., 1984; BOYD et al., 1987; MALTSEV, 1989), noble gases (OZIMA et al., 1983; HONDA et al., 1987), and sulphur (CHAUSSIDON et al., 1987) have been studied. Thus, there

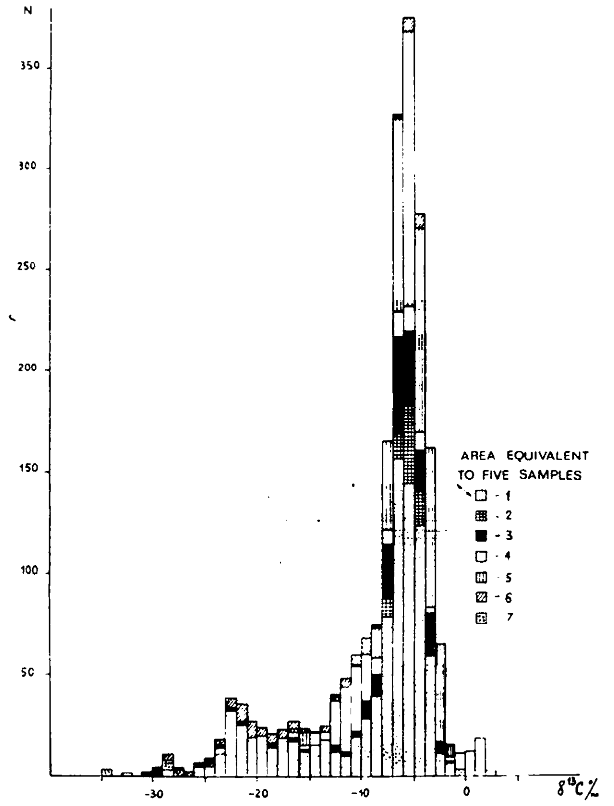

FIG. 1. Histogram of carbon isotope composition of diamonds from worldwide sources: 1 = Siberia (Galimov, 1978, 1984, Galimov et al., 1978a,b, 1980a,b, 1989b, and unpubl. data); 2 = China and India (Galimov et al., 1990a, and unpubl. data); 3 = Ural and Northeastern Europe (Galimov et al., 1989d; Zakharchenko and Galimov, 1986, and unpubl. data); 4 = West Australia and South Australia (Jaques et al., 1988; Sobolev et al., 1989; Galimov, 1984); 5 = Africa (Deines, 1980; Deines et al., 1984, 1987; Craig, 1953; Javoy et al., 1986; Boyd et al., 1987, Smirnov et al., 1979); 6 = North America (Otter et al., 1989); 7 = South America (Galimov et al., 1985). When several fragments of the same crystal were measured only the average value was adopted.

currently exists a substantial data base which characterizes the isotope composition of various elements, related to diamond formation.

DIAMOND

Relation to Geological Setting

Deines (1989) pointed out a very remarkable similarity between the $\delta^{13}C$ distributions of South African diamonds and diamonds from "Russian kimberlites." This is true as a first approximation; however, it is even more remarkable that differences exist among $\delta^{13}C$ distributions for diamonds from different regions. Figure 2 shows some of our recently obtained data. Note that the shape of the distribution is characteristic of each source. Even spatially related kimberlite bodies (e.g., Mir and its satellite pipe) can have distinctive $\delta^{13}C$ distributions. This implies that the observed isotope variations are not simply due to isotope heterogeneity of the mantle carbon. Rather, the $\delta^{13}C$ patterns are related to peculiarities of magmatism leading to the formation of a particular diamond bearing source.

From Figs. 1 and 2, it is clear that the global $\delta^{13}C$ distribution for diamonds is composed of individual distributions, which are themselves distinctive. Therefore, it is not appropriate to represent the general $\delta^{13}C$ distribution by a single model curve (e.g., Deines, 1989). Rather, it is more correct to consider the general distribution as the superposition of $\delta^{13}C$ distributions, which are characteristic of genetically different groups of diamonds. In its main features, the $\delta^{13}C$ distribution pattern for diamonds from a particular geological location depends on the relative proportion of diamonds which originated from an isotopically uniform carbon source (related to ultrabasic mineral assemblages) and isotopically fractionated carbon sources (related to eclogitic and transitional mineral assemblages), with the fractionation being different under various conditions (see below).

As shown earlier, diamonds from sources located on the periphery of a craton tend, on average, to be isotopically lighter than diamonds from its central part (Fig. 3).

Metamorphic rocks are a recently discovered source of diamonds. The first data obtained for microcrystals of dia-

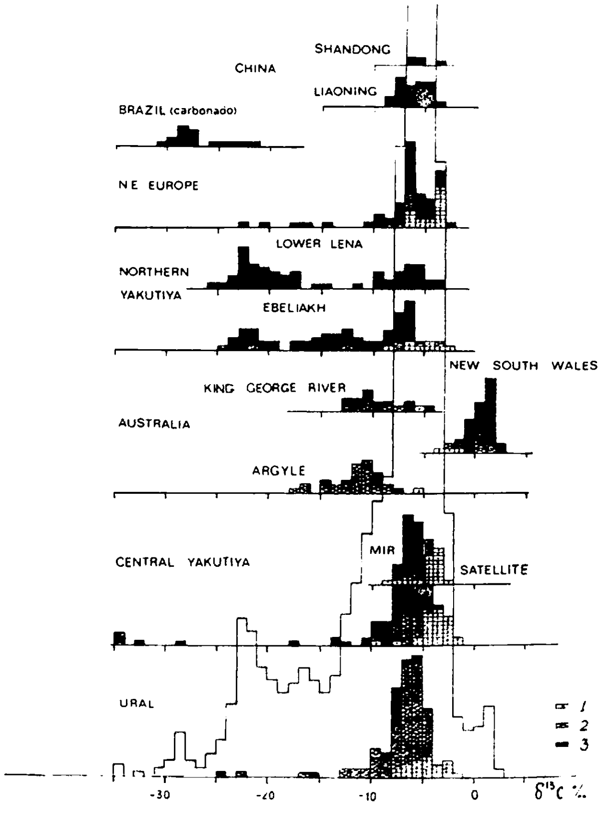

FIG. 2. Carbon isotope composition of diamonds from different fields: placer Ural (Galimov et al., 1989d); coupled kimberlite pipes Mir and Sputnik (Galimov et al., 1989b); lamproite pipe, Argyle, and King George River placer (Sobolev et al., 1989); Ebeliakh and Lower Lena placers (Galimov, 1984, and unpubl. data); kimberlite pipes of Northeastern Europe (Zakharchenko and Galimov, 1986, and unpubl. data); Brazil carbonado (Galimov et al., 1985); kimberlite pipes from Shandong and Liaoning provinces, China (Galimov et al., 1990a).

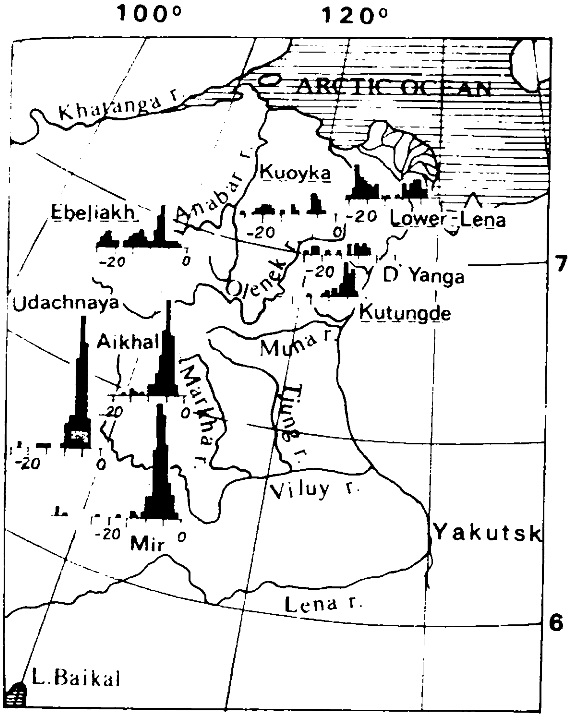

FIG. 3. Diamond $\delta^{13}C$ distribution patterns from kimberlite pipes and placers of Central and North Yakutiya. The names of placers are underlined.

monds found in the rocks of the eclogite-gneiss complex of Kazakhstan showed that these diamonds were characterized by a range of $\delta^{13}C$ values from −17.5 to −10.6‰ (YEKIMOVA et al., 1981). It is noteworthy that the isotopic composition of diamond correlated with that of coexisting graphite. It has been suggested that the formation of metamorphic diamonds was due to high pressures which could arise on a microscale during geodynamic events. Minerals forming under exceptionally high pressure sometimes occur in metamorphic rocks, e.g., coesite in dolomite-eclogite and kyanite-eclogite pods in the Western Gneiss Region of Norway (SMITH and LAPPIN, 1989).

Relation to Physical Properties

Several correlations have been established between the carbon isotope composition and the habit, color, and nitrogen aggregation state of diamonds (GALIMOV, 1984). It should be noted, however, that based on data for South African diamonds DEINES et al. (1984) concluded that there was no difference in the carbon isotope composition of diamonds of different shape and color. These authors dealt mainly with octahedrons, macles, dodecahedrons, and irregular forms, which were found to be isotopically indistinguishable. However, this conclusion is not valid for other forms and colors. There are statistically significant differences between diamonds of cubic habit and octahedrons. Ballases and some other polycrystals frequently show relative enrichment in the light carbon isotope (GALIMOV and KAMINSKIY, 1982). Diamonds of brown or rose color are statistically indistinguishable in carbon isotope composition from colorless crystals (GALIMOV, 1984). However, yellow diamonds, especially of cubic shape (variety II in Orlov's classification), and greenish-gray diamonds (variety III in Orlov's classification) have lower average $\delta^{13}C$ values than colorless ones.

Apparently, there is no appreciable correlation between carbon isotope composition of diamond and the content of nitrogen impurity (GALIMOV, 1984; DEINES et al., 1987). However, a relationship exists between the carbon isotope composition and the state of aggregation of nitrogen. Diamonds containing nitrogen in the completely nonaggregated form, i.e., as single atoms (type Ib in Robertson's classification), have $\delta^{13}C$ values which significantly deviate from the average of the $\delta^{13}C$ distribution. Over 70% of such diamonds have $\delta^{13}C$ values less than −10‰ (GALIMOV, 1984). It was also found that there was a higher proportion of more highly aggregated forms of nitrogen among the isotopically heavy diamonds ($\delta^{13}C > -10‰$). DEINES et al. (1987) disputed these findings (p. 1232). They did not find a correlation between the fraction of nitrogen in the B-centers of diamonds and their carbon isotope composition. However, they compared the samples within a narrow range of $\delta^{13}C$ values (−5.81 to −3.56‰, see their Table 3), i.e., entirely within the realm of "isotopically heavy" diamonds. In fact, as one can see from their Table 1, which contains all the data, the nitrogen aggregation state has been analyzed only for one isotopically light diamond (−15.73‰) and the content of nitrogen in the B-center was low (23 ppm). Moreover, even the diamonds with $\delta^{13}C$ less than −6‰ tend to have a relatively low nitrogen content in the B-centers (<75 ppm), whereas all cases with high concentration (>200 ppm) are related to diamonds heavier than −5.8‰.

The relationships between the isotope composition of diamonds and their physical properties have been discussed in more detail previously (GALIMOV, 1984, and references therein). In general, the less perfect the diamond crystal, the higher the probability of finding it enriched in the light carbon isotope.

Relation to Paragenesis of Mineral Inclusions

There is a clear relationship between the carbon isotope composition of diamond and the type of paragenesis of mineral inclusions (Fig. 4). All studied diamonds belonging to an ultrabasic paragenesis (containing olivine, pyrope, chromite) have $\delta^{13}C$ values within the range −10 to −1‰. In contrast, when the isotopic composition of a diamond deviates significantly (more than 5‰) from the mode of the general $\delta^{13}C$ distribution curve (−4.6‰), it is always related to an eclogite paragenesis (typically represented by orange garnet, omphacite, coesite) or to a transitional paragenesis (pyroxenite, websterite). Examples of the $\delta^{13}C$ distributions for diamonds of eclogite and ultrabasic paragenesis for individual sources are shown in Fig. 2. JAQUES et al. (1988) recently provided new data for diamonds from Western Australia. The $\delta^{13}C$ values of the Western Australian diamonds of ultrabasic paragenesis vary from −9 to −4.4‰, whereas the majority (83%) of diamonds containing eclogite mineral inclusions have $\delta^{13}C$ values from −16 to −9‰, thus confirming the results of SOBOLEV et al. (1979) and GALIMOV (1984).

In contrast, DEINES (1980, 1989) and DEINES et al. (1984, 1987) did not find any significant difference in the carbon

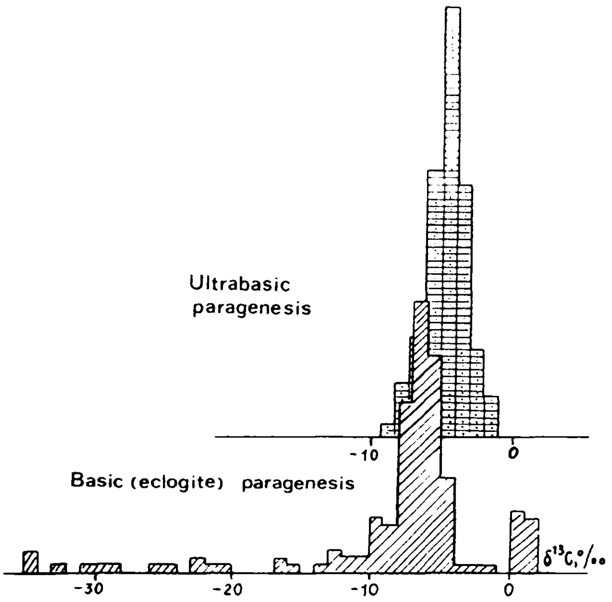

FIG. 4. $\delta^{13}C$ distributions for diamonds of ultrabasic and basic paragenesis (SOBOLEV et al., 1979, 1989; GALIMOV, 1984; GALIMOV et al., 1989d, and unpubl. data).

isotopic compositions of diamonds of eclogitic and ultrabasic paragenesis. They concluded that "for the kimberlites studied the carbon isotopic composition of diamonds is not related to their color, shape, deformation, type of mineral occluded, or type of mineral paragenesis occluded" (DEINES et al., 1984, p. 340). However, it can be seen from their own data (see, e.g., DEINES et al., 1987) that all isotopically light diamonds are related to eclogitic paragenesis. In a recent paper DEINES (1989) referred to several examples of diamonds of ultrabasic paragenesis which are isotopically light. These might be an exception among several hundreds of samples which display the relationship. SOBOLEV (pers. comm., 1989) has examined some of these specimens and concluded that their paragenesis is either doubtful or transitional (facies of magnesium enriched eclogites and websterites) rather than purely ultrabasic. In such facies even olivine (generally with increased iron content) sometimes occurs. It should be mentioned that the isotopically lightest diamonds studied so far (from pipe Mir with $\delta^{13}C$ values lower than $-34‰$) are also of a pyroxenite paragenesis. OTTER et al. (1989) described a diamond with a $\delta^{13}C$ value of $-21.9‰$, which contained two inclusions related to different types of paragenesis: olivine and eclogitic garnet. The location of the inclusions within the diamond crystal was not reported. However, the model proposed below admits to the possibility that diamond initially of eclogite paragenesis may be enclosed by a rim which grew in the ultrabasic paragenesis.

Thus, we distinguish two populations of diamonds distinctive in their $\delta^{13}C$ distribution patterns: ultrabasic (comprising lherzolite and harzburgite-dunite assemblages) and basic (including eclogite and pyroxenite-websterite assemblages). As identification of mineral paragenesis by different authors might be different, Fig. 4 represents only our data.

Apart from the wider range, the average $\delta^{13}C$ value for diamonds of basic paragenesis is more negative than for diamonds of ultrabasic paragenesis. This is true not only for the general distribution but also for those in particular kimberlite bodies. For example, one can see in Fig. 2 the difference between $\delta^{13}C$ distributions for diamonds of ultrabasic and basic paragenesis in two closely spaced kimberlite pipes (Mir and its satellite), with the difference between mean $\delta^{13}C$ values of the distributions for diamonds of ultrabasic and basic types being slightly different for the two pipes.

Isotopic Variations within Diamond Crystals

Significant variations of carbon and nitrogen isotope composition within individual diamond crystal have been discovered (SWART et al., 1983; BOYD et al., 1987). Earlier we studied so-called coated diamonds (IVANOVSKAYA et al., 1980; GALIMOV, 1984). Such diamonds typically consist of octahedron cores and cubic shells having different isotopic characteristics. The shells of diamonds collected from different kimberlite pipes showed a rather uniform isotopic composition between -6 and $-8‰$, whereas the isotopic composition of the internal parts varied broadly from -4 to $-17‰$. Recently, BOYD et al. (1987) also studied coated diamonds and made similar observations. They suggested that this might be related to habit, i.e., that the $\delta^{13}C$ values of cubic diamonds are less variable. In order to clarify the subject, we studied diamonds whose host phase and inclusions were both of octahedron habit (GALIMOV et al., 1990b). They exhibited the same relationship as that for which the habits differed (Figs. 5 and 6). Thus, it appears that the earlier generation of diamond (inclusion) originated from fractionated carbon, whereas the later (host) was derived from an isotopically homogeneous carbon source.

We also studied the internal carbon isotope distribution within diamond crystals with no signs of internal structural heterogeneity (GALIMOV et al., 1989c). The thin layer was cut by laser, and spatially fixed fragments of the layer were analyzed. An example is presented in Fig. 7(a and b). One can see that there exist small variations of 1–1.5‰, which obviously reflect the scale of isotope effects accompanying diamond growth. Significant differences which occur between the isotope composition of core and shell of coated diamonds and within other diamonds having a multistep history of formation must be due to changes in the carbon source.

CARBONATE CARBON

The most widespread carbon-bearing component of kimberlite is carbonate. In Fig. 8, $\delta^{13}C$ is plotted against $\delta^{18}O$ for carbonate in kimberlite from the Udachnaya pipe. The cross in the left part of the drawing corresponds to assumed mantle values of $\delta^{13}C$ and $\delta^{18}O$. The former is assumed to equal the mode of the $\delta^{13}C$ distribution for diamond ($-4.6‰$), and the latter ($+7‰$) is the oxygen isotope composition of calcite in high temperature equilibrium with mantle peridotite ($C_{\text{calcite-forsterite}} = 1.002$ under 1100°C (KIEFFER, 1982); $\delta^{18}O$ of mantle ultrabasic rock is known to be close to $+5‰$). The isotope composition of the carbonate component of kimberlite behaves as if it starts from this point. The change in oxygen isotope composition is due to low temperature isotope exchange of carbonate oxygen with water oxygen. The

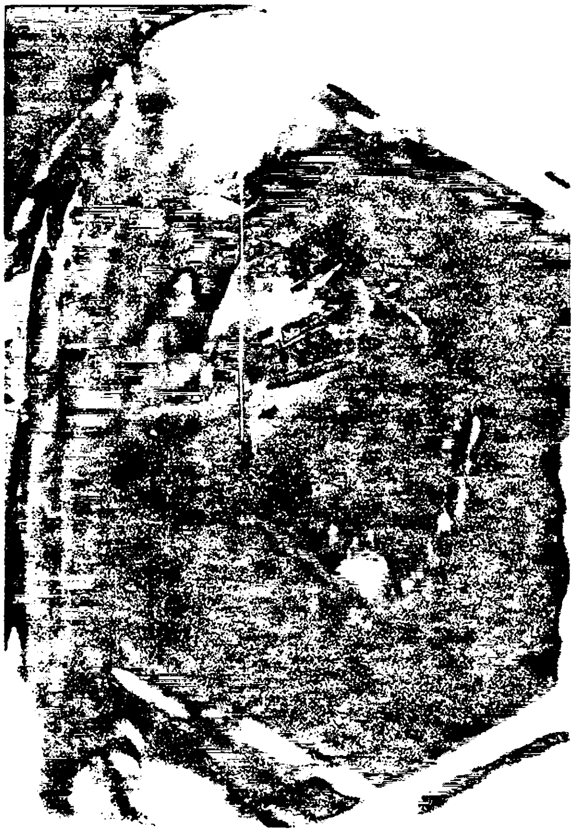

FIG. 5. Octahedral diamond crystal containing a diamond inclusion of octahedral habit (reproduced from GALIMOV et al., 1990b). The enlargement is 25×; $\delta^{13}C$ of the inclusion is −6.71‰; that of the host crystal is −5.59 to −4.43‰.

spreading of the $\delta^{13}C$ values is due to admixture of sedimentary carbonate and organic carbon (GALIMOV and UKHANOV, 1989).

A comparison of the $\delta^{13}C$ distributions for diamonds and the magmatic carbonate component of kimberlites from the same pipe shows that their modes are very close (Fig. 9).

An interesting result of our study was the discovery of autoliths exceptionally enriched in the heavy carbon isotope (one value of $\delta^{13}C$ was greater than +30‰; Fig. 9). Autoliths are spherical bodies consisting of concentric layers of calcite and are believed to precipitate from moving fluidized magma. Isotopically heavy calcite in a kimberlite pipe was reported earlier (MAMCHUR, 1980). However, its source was not identified and its origin was ascribed to low temperature hydrothermal processes. As autoliths are of magmatic origin, the question arises as to what process could be responsible for such a significant isotope fractionation in magmatic systems. P. Wyllie showed me a sample of a mica peridotite with carbonate inclusions which were earlier reported as being enriched in ^{13}C up to +25‰ (DEINES, 1968). Some of these inclusions look very much like the autoliths described here. It is possible that all occurrences of isotopically heavy carbonates in kimberlite and kimberlite-like rocks are manifestations of the same phenomenon. A possible mechanism is proposed below.

ORGANIC CARBON

Kimberlites also contain reduced carbon in the form of organic compounds, including extractable organic material, so-called bitumen. Its isotopic composition varies widely from −30 to −10‰. However, the origin of this organic matter is ambiguous.

Recently L. Kodina and I (unpubl. data) studied bitumen extracted from the Udachnaya and Mir kimberlite pipes using a technique which we developed to identify oil source rock in sedimentary basins. As seen in Fig. 10a, the isotope distribution curves are similar for both kimberlite pipes (despite a significant distance between them) and differ from those which characterize oil and organic matter in sedimentary rocks (GALIMOV, 1986). However, this cannot be considered as evidence of the endogenous origin of the bitumen in kimberlites, since a similar isotope distribution was found during experimental oxidation of petroleum from a conventional deposit (Fig. 10b). It is likely that the source of bitumen in kimberlites was the sedimentary host rocks. Obviously the trapped organic substances were subjected to thermal alteration and oxidation during hydrothermal processes accompanying emplacement of the kimberlite body. However, this does not mean that there is no hydrocarbon material actually

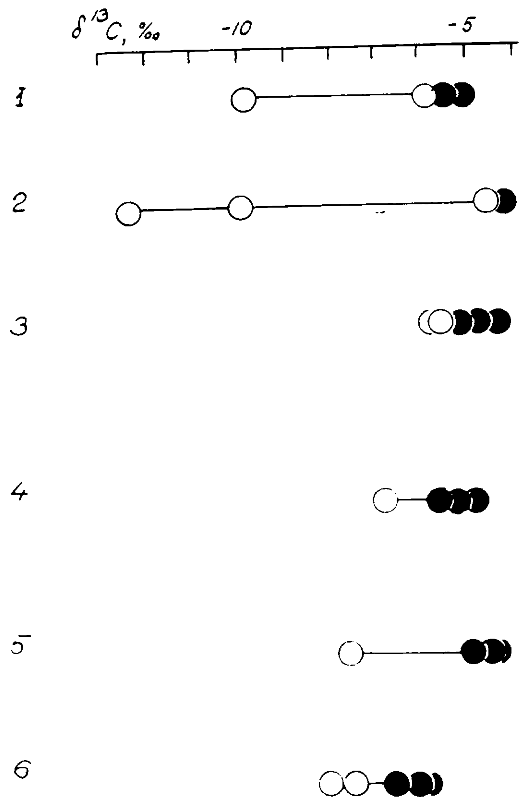

FIG. 6. $\delta^{13}C$ of "diamond-in-diamond" samples (filled circles = host crystals; open circles = inclusions). 1 = octahedron containing octahedron; 2 = octahedron containing irregular growth of two octahedra; 3 = octahedron containing complex growth of octahedra (aggregate); 4 = octahedron containing octahedron (photo in Fig. 5); 5 = octahedron containing irregular growth of two octahedra; 6 = octahedron containing irregular growth of two octahedra. All samples are from the Udachnaya pipe, East Siberia.

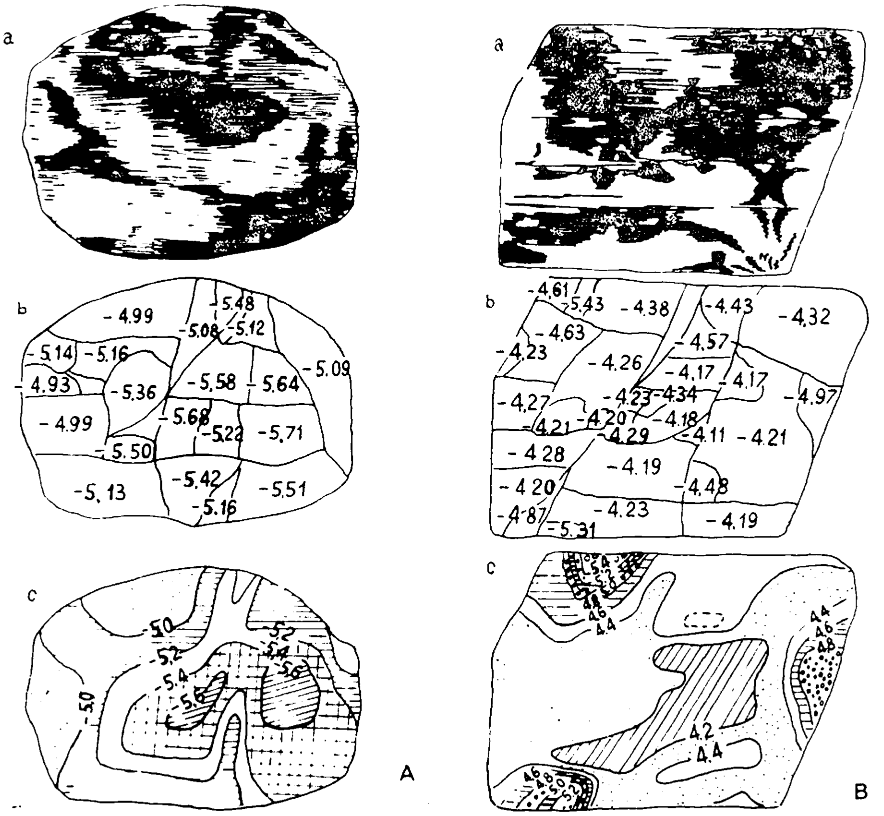

FIG. 7. Variations of $\delta^{13}C$ in section of diamond crystal: A is sample 1: a = birefringence pattern; b = measured $\delta^{13}C$ values of the fragments of the thin layer; c = isolines of $\delta^{13}C$ values. B is sample 2. Both samples are octahedra from the Udachnaya pipe.

related to kimberlite magmatism. Garnet and olivine crystals containing fluid inclusions were found in kimberlites (KRAVTSOV et al., 1978a; BOTKUNOV et al., 1985). The inclusions are visible under a microscope and are filled with yellow carbonaceous material.

The carbon isotope composition of this material is light

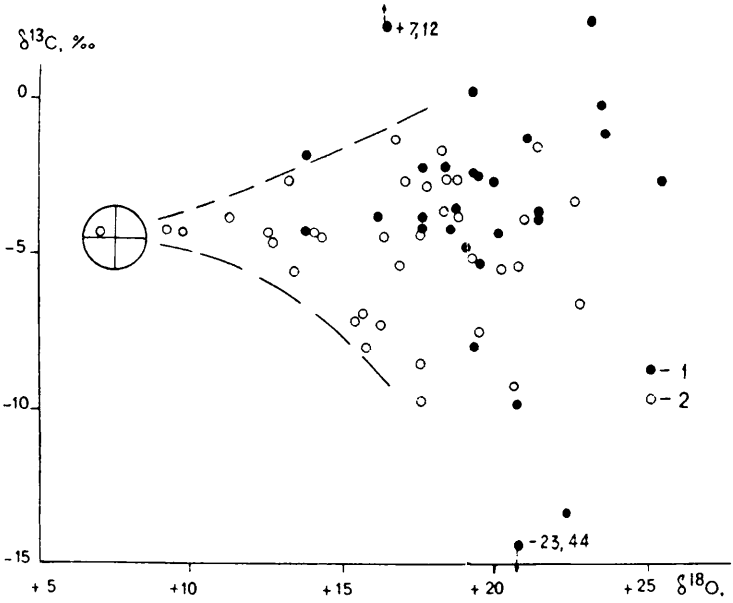

FIG. 8. $\delta^{13}C$ vs. $\delta^{18}O$ of carbonate for kimberlite from the Udachnaya pipe: 1 = brecciated kimberlites; 2 = massive kimberlites.

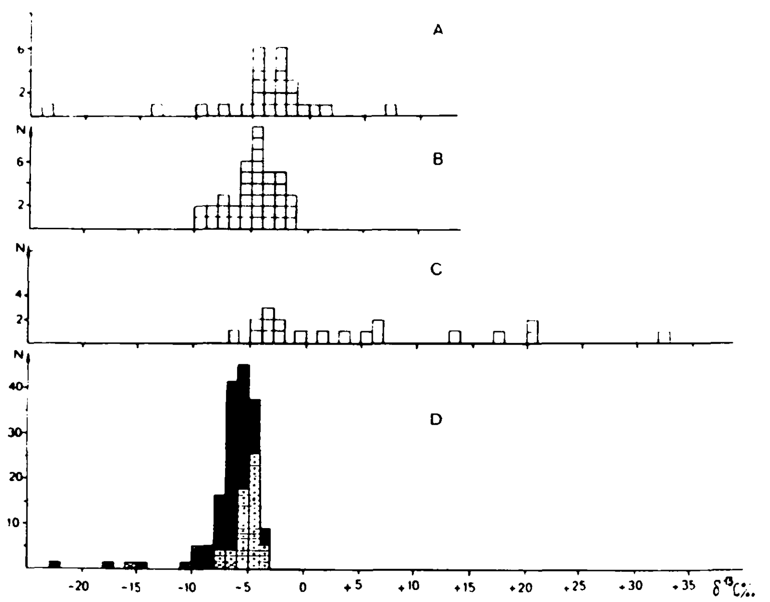

FIG. 9. $\delta^{13}C$ distributions for carbonate material of kimberlites compared with that for diamonds from the same pipe (Udachnaya): a = brecciated kimberlites; b = massive kimberlites; c = autoliths; d = diamonds (the designations are the same as in the Fig. 2).

(GALIMOV et al., 1988). The inclusions contain several phases. The gas phase is most likely methane ($\delta^{13}C$ is −23.68‰). A volatile liquid phase, probably consisting of unidentified hydrocarbons, has $\delta^{13}C$ of −31.84‰. Bitumen was also extracted by a benzene-methanol (1:1) mixture ($\delta^{13}C$ is −29.06‰).

Inclusions containing reduced carbon compounds were also found in olivine crystals from the Udachnaya kimberlite pipe (GALIMOV et al., 1989a). Mass-spectra showed the presence of hydrocarbon-like material in olivines enriched in iron. Apart from carbonaceous matter, the inclusions contained nitrogen (but not CO). CO_2 was a minor component. The trapped hydrocarbons (as well as the garnet) were enriched in the light carbon isotope. The fraction condensable at −196°C had a $\delta^{13}C$ value of −28 [illegible]‰, and that which was not condensable, −26.56‰.

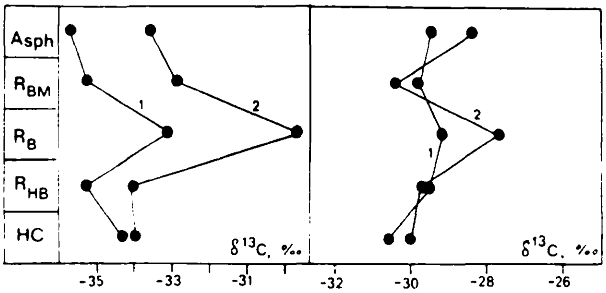

FIG. 10. Carbon isotope distribution between the fractions of different polarity: Asph = asphaltenes; R_{BM} = fraction eluted by benzene-methanol (1:1) mixture; R_B = fraction eluted by benzene; R_{HB} = fraction eluted by hexane-benzene mixture; HC = hydrocarbons (fraction eluted by hexane). The left curve is for bitumen, extracted from kimberlite pipes: 1 = Mir; 2 = Udachnaya. The right curve is for products of the oxidation experiment: 1 = crude oil; 2 = the oil oxidized during 24 h under 350°C in the presence of sulfate.

We believe that the carbon compounds contained in the inclusions are endogenous. The crystals collected for the study were free of any traces of alteration. However, it cannot be ruled out that the hydrocarbons were trapped not at the stage of crystallization of the minerals but during secondary processes.

Thus, the data obtained to date can be summarized in the following statements:

1. The isotope composition of the different forms of carbon related to kimberlite magmatism varies widely: from −35 to +35‰, in particular:
   a) the carbon isotope composition of diamonds varies from −34.5 to +2.8‰;
   b) the average value for $\delta^{13}C$ of magmatic carbonates in kimberlites practically coincides with that which characterizes diamonds in the same body (Udachnaya pipe);
   c) autoliths in kimberlites can be extremely enriched in ^{13}C, up to +35‰;
   d) hydrocarbons occurring in fluid inclusions of magmatic minerals of kimberlites are depleted in ^{13}C down to −30‰.
2. Variations of carbon isotope composition of diamonds are not random. They exhibit the several regularities, in particular:
   a) the $\delta^{13}C$ distribution is specific for a particular occurrence of diamonds (different kimberlite pipes, different regions, etc.);
   b) principal differences exist between the isotope distribution patterns for diamonds of ultrabasic and basic (eclogite) paragenesis;
   c) carbon isotope composition varies within a diamond crystal;
   d) when a diamond consists of several sequential generations of growth (coated diamond, diamond-in-dia-

mond) the $\delta^{13}C$ of the early generation varies widely, whereas $\delta^{13}C$ of the later growth is more uniform;

e) the less perfect a diamond, the greater the probability that its isotope composition deviates from the mode of the general $\delta^{13}C$ distribution of diamonds.

THE MODEL

One possible cause of the observed isotope variations is believed to be the incorporation of the crustal carbon into the mantle. Indeed, the wide range of isotope variations in diamonds, the relation of the isotopically light diamonds to the basic assemblage of minerals, and the fact that the isotopically light diamonds occur more frequently in the periphery of cratons rather than at their center can be explained, in principal, on this basis.

However, this idea is inconsistent with the major facts:

1) The isotopic composition of carbon in sediments of the oceanic crust, including both carbonate and organic carbon, varies mostly from 0 to −25‰, being very rare beyond these limits, while magmatic carbon in kimberlites varies from +35 to −35‰. It is well known that carbon in sedimentary rocks reveals a clear trend to isotopic homogenization during metamorphism. Therefore, it is unlikely that the subducted carbon would retain the isotope heterogeneity in full scale.
2) The regularities observed, including the isotope heterogeneity within the same crystal, the difference between internal and external parts of coated diamonds, peculiarity of isotope distribution of diamonds for different kimberlite bodies, as well as some other relationships, cannot be readily explained by this idea.
3) Sm-Nd isotopic data for eclogite and garnet lherzolite xenoliths from kimberlite pipes show that they derived from a highly depleted mantle. The $\epsilon_{Nd(T)}$ values are +19.8 and +36.7 at T = 2.9 10^9 years (MCCULLOCH, 1982), which are not characteristic of crust material. $^{143}Nd/^{144}Nd$ ratios of kimberlites themselves differ from their basic and ultrabasic xenoliths but are close to the chondritic evolution curve, indicating that even though kimberlite is highly enriched in incompatible elements it originated from undifferentiated primitive source (BASU and TATSUMOTO, 1980). In other words, neither kimberlites nor their xenoliths (including eclogites) reveal evidence of recycled crust material.

The alternative explanation of the isotope variations is based on the possibility of significant isotope fractionation in the mantle.

Isotopic fractionation involving batch equilibrium at high temperature is small and may have been responsible for a maximum fractionation of 3-5‰, depending on temperature and composition of C-H-O system, but not for the whole range of the observed variations. However, even small isotope fractionations under the conditions of extensive reaction (Rayleigh distillation type behavior) may provide large isotopic effects. Earlier JAVOY et al. (1986) used Rayleigh distillation mechanism in order to explain isotope fractionation during degassing of magma. In the present paper degassing is not considered to be appropriate. Another model is suggested which uses the Rayleigh fractionation concept (Fig. 11).

I start from the assumption that the mantle below the asthenosphere boundary is reduced approximately to the level defined by the iron-wustite (IW) buffer, while the lithosphere is relatively oxidized, with a redox condition (i.e., fO_2) between wustite-magnetite (WM) and fayalite-magnetite-quartz (FMQ) buffers. This is the opposite of the suggestion of HAGGERTY (1986).

Then, I assume that a fluid rises from the sub-asthenosphere. Under conditions of IW buffer the fluid would contain carbon in a reduced form, mostly in the form of methane (RYABCHIKOV, 1980; KADIK and LUKANIN, 1986). When this reduced fluid comes in contact with more oxidized upper mantle rocks, the CH_4 begins to oxidize, producing H_2O and CO_2. The rock melts due to interaction with the fluid. If the buffering capacity of the fluid exceeds of that of the rocks only part of the methane oxidizes. The newly formed CO_2 is redistributed between melt and carbonate, whereas the methane will be distributed between fluid and melt. Because of this difference CH_4-rich vapor may be separated from a CO_2-rich melt/crystal assemblage during movement of the fluid. The isotope fractionation factor between CO_2-CH_4 is about 1.004 at 1100°C. Therefore, upon separation of vapor, the CO_2-rich melt-crystal assemblage is enriched by 4‰ and the fluid becomes isotopically lighter.

Calculation using the Rayleigh formula ($^{13}C = [(V/V_0)^{1-c/c} - l] \cdot 10^3$) shows that when 1% of the initial fluid remains (V/V_0 = 0.01) the residual carbon is enriched in the light isotope relative to its initial composition by about 20‰. Eventually the composition of the residual fluid may approach the most negative $\delta^{13}C$ values observed for diamonds and hydrocarbon inclusions in magmatic minerals.

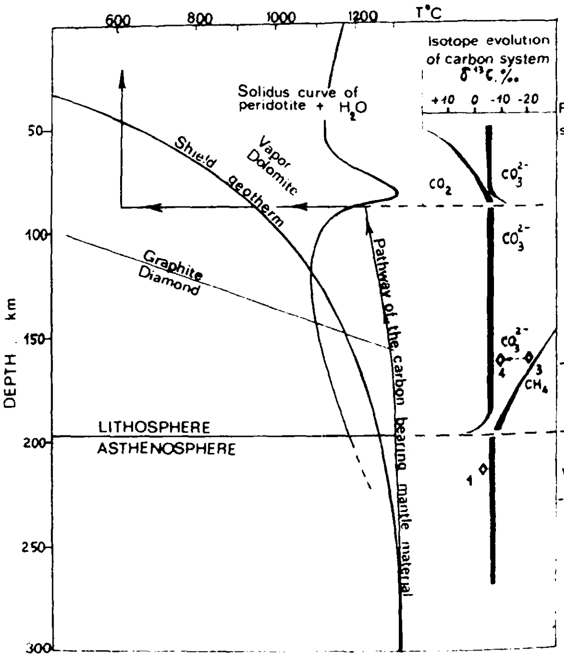

FIG. 11. The model of carbon isotope fractionation during evolution of the carbon-bearing mantle fluid.

It should be noted that the $\delta^{13}C$ distribution, like that presented in Fig. 1, may not be representative of the diamond population as a whole, since the sampling procedure was not random. Diamonds containing mineral inclusions of eclogite paragenesis and some other exotic diamonds have been analyzed in an unduly high proportion. Therefore, the shape of the presently established $\delta^{13}C$ distribution cannot be used as a proof of an isotope fractionation mechanism. However, the mode of the distribution actually corresponds to diamonds of the most frequently occurring carbon isotope composition. I assume that this value (−4.6‰) is characteristic of the carbon isotope composition of the initial fluid which invades the upper mantle. It is reasonable to attribute variations of ±4‰ about this mean to possible kinetic isotope effects accompanying crystallization of diamond, and variations of isotope fractionation depending on the composition of carbon system, temperature, and pressure. It should be mentioned that a diamond in equilibrium with graphite is isotopically lighter than graphite under any pressure higher than 20 kbar (POLYAKOV and KHARLASHINA, 1989). That is in contrast to the calculations of BOTTINGA (1969), who neglected a pressure effect.

I assume also that sub-asthenosperic fluids are the main source of carbon in the upper mantle. Hence, the isotopic composition of the main reservoir of mobile carbon in the mantle is about −4.6‰. I use a term "mobile" carbon to distinguish it from the finely dispersed carbon, enriched in the light isotope. Existence of two forms of the mantle carbon—concentrated, mobile, and isotopically heavy on the one hand, and dispersed, relict, and isotopically light on the other—was suggested by GALIMOV (1967) and is discussed in more detail elsewhere (GALIMOV, 1988).

I consider sheared garnet lherzolite to be the primitive mantle rock before interaction with the fluid. When such an interaction occurs the temperature of solidus decreases and the sheared lherzolites melt. The coarse-grained garnet lherzolites or harzburgites represent the residue from which the partial melt was extracted. I believe that diamonds of ultrabasic paragenesis are precipitated on this stage. Their isotope composition should vary around −4.6%. As the carbon of the fluid is considered to be the primary source of diamonds, the sheared lherzolites per se cannot be expected to contain diamonds. This is consistent with the observations of SOBOLEV et al. (1984).

The melt and the fluid being separated from the crystallized rocks can evolve further upon contact with other, undifferentiated or differentiated, rocks. As mentioned, this may be accompanied with an isotope effect. Also, it follows from stoichiometry consideration that interaction with a CO_2-containing fluid and formation of a carbonate may lead to a change in the composition of a silicate system from an ultrabasic to a basic one:

$$(MeO)_2SiO_3 + CO_2 = MeO \cdot SiO_2 + MeCO_3.$$

In other words, the same process leads to the isotope fractionation of carbon in the fluid and to formation of a basic melt, which can crystallize in the field of stability of eclogite. Discussion of petrological aspects of this process is beyond my competence. However, I believe that this might explain why the isotopically light diamonds are associated with the basic assemblage of the mineral inclusions.

The coated diamonds in this context represent crystals which begin to form in the fluid from carbon which can be isotopically fractionated to different extents. Therefore, $\delta^{13}C$ values of the internal part of these diamonds vary from −4.6 to +4‰ at the beginning of the fluid evolution to values as low as −30‰ at the latest stages. These crystals make up the first generation. They include diamonds of the basic paragenesis. Because they were deposited from the fluid, they can reside in the ambient mantle rocks. Under favorable conditions they can continue to grow. The external parts of such diamonds grow at the expense of carbon in the main carbon reservoir, whose isotopic composition is thought to be close to the mantle average (see Fig. 11). This could explain the relatively uniform isotope compositions of the shells of coated diamonds. During this process the diamond can trap inclusions of the ultrabasic assemblages. In this way, diamonds of the "mixed" paragenesis can form.

In contrast to diamonds of an ultrabasic paragenesis, those of the basic paragenesis are frequently generated in the moving fluid. Often, the newly formed diamonds were immediately erupted with kimberlite magma. Therefore, they escaped the annealing process, which leads to aggregation of nitrogen and recrystallization of polycrystal forms (GALIMOV, 1985). Hence, imperfect forms occur more often among diamonds of basic paragenesis, in particular among those which are enriched in the light carbon isotope.

The ultrabasic melts acquire a carbonate component after interaction with the fluid. The isotopic composition of the carbonate carbon coincides with that of the original fluid since most of the carbon in the fluid eventually reacts to form carbonate, that has a $\delta^{13}C$ value of about −5‰.

When the carbonate-bearing rocks or melts get to the shallower depths corresponding to the boundary of stability of carbonate (at a pressure of approximately 25 kbar) the carbonate decomposes and CO_2 gas is released. This must cause propagation of a fracture through which the fluidizing magma rushes to the surface.

Expansion of the gas results in an adiabatic drop in temperature (see Fig. 11). When temperature decreases to about 700–800°C, carbonates again become stable and CO_2 reacts with the silicates (even at a low pressure). This reaction may be accompanied by an isotope effect, and the residual CO_2 may be enriched in ^{13}C.

In order to check whether an isotope effect actually occurs in such a process we undertook the following experiment (see GALIMOV et al., 1990c, for full details). In a small vessel, calcite was decomposed under vacuum at about 1000°C. The temperature was decreased to 700°C and CO_2 was allowed to react with CaO. The residual CO_2 was actually found to be enriched in the ^{13}C isotope. $\delta^{13}C$ of the CO_2 was +2.5, +4.4, +5.6, and +6.6 when V/V_0 (the ratio of residual CO_2 volume to initial CO_2 volume) was 0.5, 0.4, 0.3, and 0.15, respectively. The calculated fractionation suggests that this is a single-step reaction and showed a dependence on the reaction progress. This is taken as evidence that the reaction actually involves several steps. We suggest three steps: gas diffusion to the surface, chemical binding of the CO_2, and diffusion of the CO_2 from the surface inside the sample. The first stage has been described by the Stephen flow equation (FRANC-KAMENETSKII, 1967), and the second and the third stages by equations for heterogeneous reaction of gas with powdered material (ZELDOVICH, 1939). Using these equations shows that the best fit with the experimental data is achieved when the above stages are characterized by the isotope fractionation factors: 1.0030, 1.0105, and 1.0030 (at 700°C). The detailed experimental data and theory are discussed elsewhere (GALIMOV et al., 1990a).

Thus, when chemical binding (stage 2) is a limiting step, the isotope effect might be as high as 10.5‰. With an isotope effect of this magnitude, the Rayleigh distillation process may result in enrichment of the residual CO_2 greater than +40‰, when less than 1% of the CO_2 remains unbound. Hence, one can explain the occurrence of the ^{13}C-enriched nature of calcite in kimberlite autoliths. The mineralogical peculiarities of the latter, which are believed to indicate that they crystallized from turbulent flow of a fluidized magma, are in agreement with the mechanism of their enrichment in ^{13}C suggested here.

Adiabatic cooling also provides a possible explanation for several other curious features of kimberlite magmatism. It is known that kimberlite magma, despite moving rapidly from a high-temperature zone, is relatively cool. The walls of the kimberlite pipes and the xenoliths of sedimentary rocks falling into the magma during its emplacement do not bear any evidence of strong thermal alteration. Even pieces of coal remain preserved. Besides, since kimberlites are rich in a CO_2-component, many believe that a kimberlite magma is essentially degassed during the formation of a kimberlite pipe and consequently loses a large amount of CO_2. However, there exists an almost stoichiometric correspondence between CO_2 and CaO content in different kimberlites. Thus, kimberlite magma may lose little (if any) of its CO_2 component.

CONCLUDING REMARKS

The model proposed implies that isotope heterogeneity of the mantle carbon is mainly due to isotope fractionation processes.

Diamond formation is related to the movement of the mantle fluids. Diamonds of the ultrabasic paragenesis are derived from a primary, unfractionated carbon source, which is surprisingly uniform throughout the world.

The question arises about the source of the deep reduced mantle fluid. I think that such a fluid may derive from the relict reservoir of volatiles, retained since the time of formation of the Earth (GALIMOV, 1990). If the upper shell of the Earth (300–400 km) completely melted during its formation, the solidification must have proceeded from below and from above. This could have resulted in a concentration of volatiles in the residual melt and the formation of a volatile- and incompatible element–rich layer, such as occurs in layered magmatic intrusions. Primitive helium with high $^3He/^4He$ ratios should be characteristic of this layer. During interaction of the fluid with the mantle rocks, incompatible elements, including uranium, would be concentrated in the accompanying melt. Therefore, both low and high $^3He/^4He$ ratios ought to be characteristic of diamonds related with the fluid. Actually, the $^3He/^4He$ values vary in diamonds from 1.5×10^{-4} to 5×10^{-6} (OZIMA et al., 1983; HONDA et al., 1987), these extremes being related to the isotopically light diamonds of eclogitic paragenesis.

The essence of this model is the interaction of a reduced fluid with the relatively oxidized lithosphere. This is a necessary prerequisite for significant carbon isotope fractionation. However, oxidized lithosphere could not have been present from the beginning, and the mechanism of isotope fractionation described above could not have operated, and isotopically light diamonds could not have formed at that time. Moreover, if the appearance of the eclogite assemblage related to the same process, diamonds of eclogite paragenesis could not occur among the most ancient diamonds. In the extreme case, which cannot be ruled out, the ancient diamonds could be predominantly (if not entirely) of ultrabasic paragenesis while the younger diamonds would be predominantly (if not entirely) of eclogitic paragenesis. The boundary between "the ancient" and "the younger" depends on the actual history of the evolution of the redox state of the mantle. It might be elucidated by a carbon isotope study of diamonds combined with geochronology of their mineral inclusions. Meaningful results have already been obtained by RICHARDSON et al. (1984) and RICHARDSON (1986).

Isotopic fractionation in the mantle carbon may be manifested in other situations as well. For instance, interaction with the fluid may result in metasomatic alteration of mantle rocks. Carbon related to these rocks must show evidence of the isotope fractionation. In order to check this idea several samples of metasomatized xenoliths from kimberlites were collected and the carbon isotope composition of their graphite was determined (GALIMOV et al., 1989e). These were two garnet websterites from pipe Udachnaya and one spinel websterite from pipe Obnazhonnaya (East Siberia). Intercrystalline space between pyroxene grains in the garnet websterites was filled up by garnet and clinopyroxene and also by phlogopite intergrown with graphite. The graphite was undoubtedly deposited from the metasomatic fluid. The $\delta^{13}C$ values were −7.8 and −10.8‰ for two different xenoliths. Graphite from the spinel websterite gave $\delta^{13}C = -22.7‰$. Spinel websterites belong to shallower facies than garnet websterites; therefore, their metasomatism might be related to the later stage of evolution of the fluid. This is in accordance with the carbon isotope composition of the graphite in the studied samples. Systematic study of metasomatized mantle rocks combined with appropriate geothermobarometry studies would provide an approach to understanding the evolution of the mantle fluids and the isotope fractionation related to this process.

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