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Isotopic composition of carbon in diamonds of diamondites: Record of mass fractionation in the upper mantle

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Abstract—Carbon isotope data have been obtained for diamonds in diamondites (framesites, polycrystalline diamond) of unknown origin (presumably from southern Africa), which contain minor amounts of garnet (plus rare clinopyroxene). The carbon isotope abundance ratios show wide inter- and intra-sample ranges. The $\delta^{13}\text{C}$ variations of diamonds from diamondites with “peridotitic” or “eclogitic” garnets are indistinguishable from each other, with a range from -3.2 to -27.9% , and a peak around -18% , indicating a depletion in ^{13}C relative to most silicate-bearing single crystal diamonds. This ^{13}C depletion could have been produced by mass fractionation of C from an isotopically homogeneous mantle source in a C-O-H fluid system. Fluids traveling between regions of varying redox conditions in the mantle could have provided the necessary vehicle. The variations of $\delta^{13}\text{C}$ can be explained by different degrees of oxidation during the fluid/melt ascent. Copyright © 2004 Elsevier Ltd

1. INTRODUCTION

Carbon in the solar system has many different sources; it was not homogenized in the solar nebula and, consequently, has astonishingly variable isotopic compositions in various meteoritic components (e.g., Kerridge, 1985; Cronin et al., 1988; Sugiura, 1998; Mostefaoui et al., 2000). Carbon was, however, apparently isotopically homogenized within the Earth (e.g., Deines and Gold, 1973; Javoy et al., 1986; Deines, 2002). Large variations found among different rocks or phases are apparently due to fractionation processes operating during C distribution between various C-bearing phases, both inorganic and organic. As a consequence, presumably the largest C reservoir on Earth, the Earth's mantle, is believed to have a homogenous C isotopic composition of $\delta^{13}\text{C} \sim -5\%$, the common composition also found in bulk carbonaceous chondrites (e.g., Deines and Wickman, 1973; Kerridge, 1985). The overwhelming majority of rock samples from the Earth's upper mantle contains C of this isotopic composition. Also, the most precious C phase from the Earth's mantle, diamond, has an isotopic composition mostly around $\delta^{13}\text{C} \sim -5\%$ (e.g., Deines, 1980, 2002; Galimov, 1991; Deines et al., 1993, 1997, 2001). However, there are a few samples of diamonds from the Earth's mantle that have considerably lighter isotope ratios, with $\delta^{13}\text{C}$ reaching ca. -34% (Sobolev et al., 1979). The carbon isotope compositions of diamonds with silicate inclusions correlate with their silicate paragenesis (e.g., Kirkley et al., 1991b). Inclusion assemblages in silicate-bearing single-crystal diamonds parallel the mineralogy of the two major categories of mantle xenoliths, “peridotitic” and “eclogitic” parageneses (e.g., Prinz et al., 1975; Meyer, 1987). Single-

crystal diamonds with peridotitic inclusions have a restricted range of $\delta^{13}\text{C}$ from -10 to -1% , with a sharp maximum in the distribution near -5% , whereas single-crystal diamonds with eclogitic inclusions have $\delta^{13}\text{C}$ values between -34 and -3% , with a small maximum near -5% (e.g., Kirkley et al., 1991b).

As the C isotopic composition of the diamonds with eclogitic inclusions approximates that of the Earth's biosphere, these diamonds were believed to have formed from biogenic C that was subducted into the lower upper mantle (e.g., Kirkley et al., 1991b). This is certainly a possible explanation for a small diamond population. However, growing evidence points towards a different direction, namely that the isotopic variety encountered among diamonds might be due to mass fractionations taking place in the upper mantle between fluids and solids and between reduced and oxidized C species (e.g., Deines, 1980; Galimov, 1991; Cartigny et al., 1997, 1998, 2001; Taylor et al., 2000).

Diamondites (framesites) are fine- ($<100 \mu\text{m}$) to coarse-grained ($>1 \text{mm}$) rocks consisting almost entirely of diamonds with abundant pores and cavities (Gurney and Boyd, 1982; Kirkley et al., 1991a; Kurat and Dobosi, 2000; Dobosi and Kurat, 2002). The walls of the open cavities are covered by euhedral diamond crystals that are commonly simple octahedra, but octahedra with terraced faces are also present. The silicates are mostly interstitial or occupy the space in cavities and often contain inclusions of euhedral diamonds, giving evidence for a cogenetic origin of these phases. The most common silicate is pyrope, which occurs in different colors and chemical compositions (Kurat and Dobosi, 2000; Dobosi and Kurat, 2002), i.e., orange and purple garnets similar to those known from upper mantle eclogites and garnet peridotites, respectively (e.g., Nixon, 1987). However, olivine, which is the most common mineral of the upper mantle, is not present in diamondites.

The trace element contents of hypothetical fluids in equilibrium with the peridotitic garnets are similar to the trace ele-

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ments contents of kimberlitic and carbonatitic liquids (Dobosi and Kurat, 2002). Thus, crystallization of these diamondites from a highly alkaline liquid in the presence of carbonates can be suggested – similar to what has also been found for Jwaneng fibrous diamonds (e.g., Schrauder et al., 1996). Recent high-temperature and high-pressure experiments support this observation and showed that diamond can be grown from carbonatitic fluids (Akaishi et al., 1990; Litvin et al., 1997, 1998a,b, 2001; Pal'yanov et al., 1999, 2002a,b; Sokol et al., 2000, 2001a) or CO₂-H₂O fluid (Kumar et al., 2000; Pal'yanov et al., 2000; Yamaoka et al., 2000; Akaishi et al., 2001; Sokol et al., 2001b).

Hypothetical melts in equilibrium with eclogitic garnet are highly magnesian, but depleted in light rare earth elements and highly incompatible elements relative to the typical kimberlitic, lamproitic, or carbonatitic liquid (Dobosi and Kurat, 2002). This is surprising, as eclogites should be richer in trace elements than peridotites, and fluids in equilibrium with these rocks should reflect this. Therefore, the different trace element contents of fluids that precipitated peridotitic and eclogitic garnets must be the result of differences in the properties of these fluids, rather than of different source rocks (Kurat and Dobosi, 2000; Dobosi and Kurat, 2002). From trace element abundances in silicates from diamondites, Kurat and Dobosi (2000) and Dobosi and Kurat (2002) concluded that these silicates and diamonds must have formed from carbonate-rich fluids/melts.

The chemical compositions of eclogitic and peridotitic garnet analyzed so far from our batch of diamondites differ only in Cr and Ti content, but not in the Fe/Mg ratio, which is low and similar in both types, indicating a peridotitic source (see Dobosi and Kurat, 2002). The signature of the C isotopes should allow a conclusion regarding the source of these diamonds to be reached. Here we present the results of our study of carbon isotope abundances in diamonds from diamondites with peridotitic and eclogitic garnets, which allow constraining the diamond (and silicate) formation mechanisms of such rocks.

2. SAMPLES AND EXPERIMENTAL PROCEDURES

Ten diamondite samples, selected from a lot of ~50, were described by Kurat and Dobosi (2000) and Dobosi and Kurat (2002). These rocks consist principally of diamonds with minor amounts of garnets and rare clinopyroxene. Diamonds and silicates are intimately intergrown, with the former frequently also being enclosed by the latter. Trace element contents and abundant fluid inclusions suggest formation from carbonatitic fluids/melts. The diamondite samples were bought from a diamond dealer and the exact locality from which they originate is unknown, but must be in southern Africa because similar samples have previously been described from there (Gurney and Boyd, 1982; Kirkley et al., 1991a).

The color of the garnet reflects its chemical composition (Prinz et al., 1975; Sobolev, 1977; Meyer, 1987; Kirkley et al., 1991a; Kurat and Dobosi, 2000; Dobosi and Kurat, 2002). Purple and orange garnets are Cr-rich (>2 wt% Cr₂O₃) and Cr-poor (usually < 1 wt% Cr₂O₃), respectively, and in the following we refer to purple (Cr-rich) and orange (Cr-poor) garnets as peridotitic and eclogitic garnets, respectively, as proposed by Prinz et al. (1975) and Sobolev (1977) (Fig. 1). Thirty-five diamondites have been selected for the present study, with 13 containing peridotitic garnets, 19 containing eclogitic garnets and 3 being free of garnets. Samples of masses ranging between 30 and 200 µg were taken from diamondites for carbon isotope analyses. The

samples were washed with acetone in an ultrasonic bath and dried in an oven at ~105°C overnight.

The isotopic composition of carbon was measured at the Department of Geological Sciences, University of Vienna, using a continuous flow isotopic ratio mass spectrometer (CF-IR-MS; Micromass Optima; Maruoka et al., 2003). The samples were weighed into tin capsules, which were introduced by an autosampler into the combustion chamber heated at 1020°C with helium gas flowing at 100 mL/min, and were oxidized by a pulse of oxygen. The combustion chamber contained the chemicals, including chromium trioxide and silvered cobaltous cobaltic oxide, which promoted the complete oxidation of carbon species in the sample. Excess oxygen was removed and nitrogen oxides were converted to nitrogen by copper wires at 650°C in the reduction chamber. Water produced during oxidation was removed by a magnesium perchlorate water trap. Carbon dioxide and nitrogen were separated by gas chromatography at 50°C, and then were introduced into the mass spectrometer. The ion signals of CO₂⁺ with molecular weights of 44, 45 and 46 were counted to determine the C isotopic compositions.

Tin capsules were heated at 150°C for more than 1 week before their usage to oxidize organic matter on the surface of the capsules. As the results of the heating, the amount and isotopic compositions of blank CO₂ gas, which were obtained by the same procedure as sample runs with a tin capsule, but without a sample, became relatively constant. Each blank gas corresponds to 1.26 ± 0.10 µg of carbon.

Diamonds are resistant to combustion and memory effects were monitored by multiple runs for a single sample until gas amount of the run became comparable to the blank CO₂ gas stated above. Most of the samples could be oxidized by a single combustion, but some samples could not be oxidized completely in a single combustion. However, cumulative CO₂ yields of 99.3 ± 4.7% were achieved after two burns for such samples, except one analyses of Dia014 (61%). The error of the average yield (± 4.7%) is similar to that of the sensitivity of our apparatus during analyses for this study. Therefore, complete oxidation can be achieved after two successive combustions for the samples that cannot be oxidized by a single combustion. For such samples, the isotopic compositions are calculated as a weighted mean of the isotopic composition obtained for each run.

The carbon isotopic composition is given by

$$\delta^{13}\text{C} = \left(\frac{(^{13}\text{C}/^{12}\text{C})_{\text{sample}}}{(^{13}\text{C}/^{12}\text{C})_{\text{V-PDB}}} - 1 \right) \times 1000 \quad (1)$$

The δ¹³C values were calculated relative to the C isotopic composition of the Pee Dee Belemnite (latest V-PDB definition; ¹³C/¹²C = 0.0111802; Zhang and Li, 1990; Coplen, 1996) based on comparison with the analyses of four standards (NBS-19, +1.95‰; NBS-18, -5.01‰; USGS-24, -16.1‰; IAEA-CO-9, -47.1‰; IAEA AQCS CATALOGUE 1998/99) and determined with a precision of better than 0.2‰ (1σ). When available, several grains were analyzed from the same diamondite rock.

3. RESULTS AND DISCUSSION

3.1. Comparison of δ¹³C Values of Diamondites with Peridotitic and Eclogitic Garnets

Averaged δ¹³C values relative to V-PDB of diamonds from diamondites are listed in Table 1. The δ¹³C values range from -3.24 to -24.4‰ for 13 diamondites with peridotitic garnets and from -5.27 to -22.2‰ for 19 diamondites with eclogitic garnets. The δ¹³C frequency distributions for diamondites with peridotitic and eclogitic garnets studied here are shown in Figure 2. The δ¹³C values obtained for diamondites in this study are generally lower than those previously reported from silicate-bearing diamonds (e.g., Kirkley et al., 1991a; Deines et al., 1997) and diamondites from Yakutia (δ¹³C from -6.1 to -2.6‰ with an average of -4.5‰; Reutskii et al., 1999; Fig. 2j), but similar to those reported for diamondites from southern Africa (Fig. 2e for all southern African diamondites; δ¹³C from

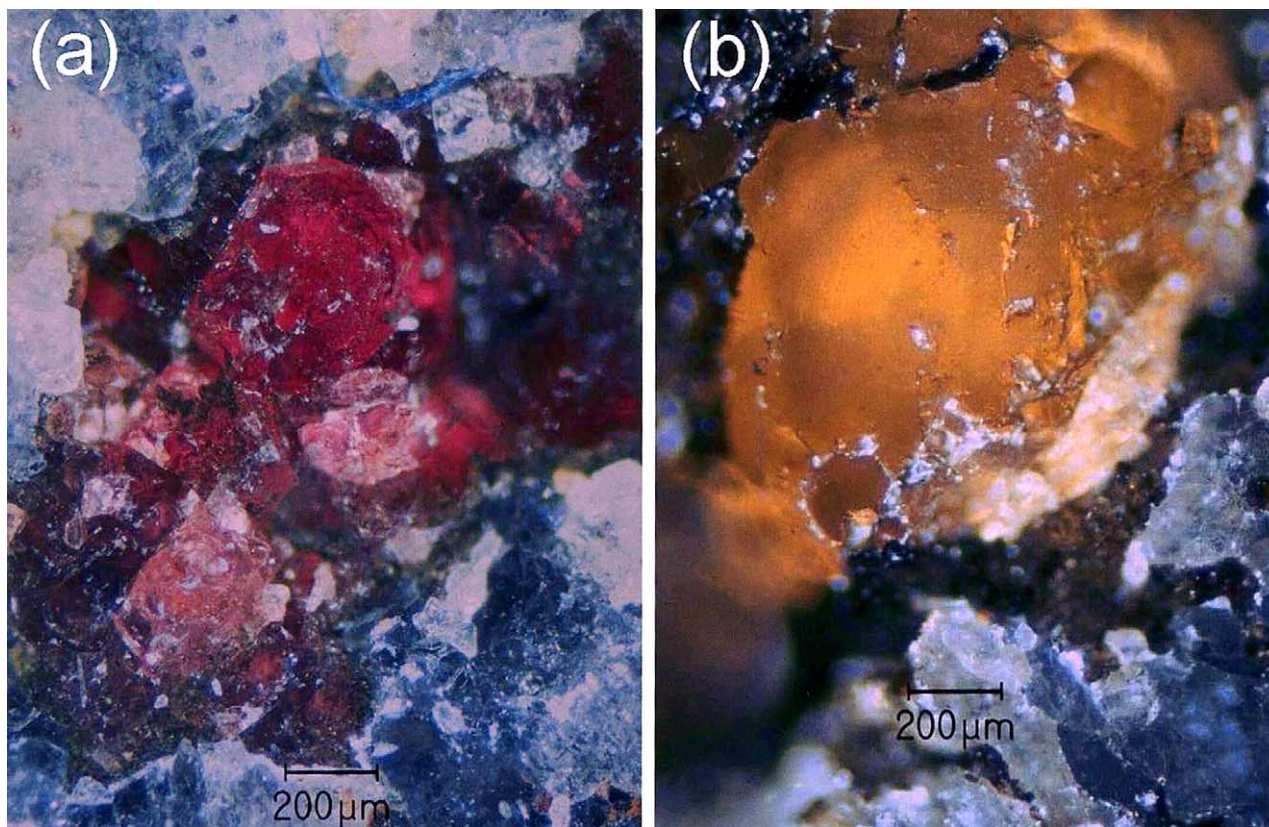


Fig. 1. Optical microscope image of garnets in diamondites. (a) Purple “peridotitic” garnet from Dia015 embedded in diamonds (gray to blue) and also enclosing diamond (gray to white small grains). (b) Orange “eclogitic” garnet in diamondite Dia013 containing numerous diamond inclusions (white grains). Images were taken from polished sections in reflected light with crossed polarizers.

–3.8 to –23.5‰ for Orapa mine, McCandless et al., 1989, Deines et al., 1993, Burgess et al., 1998, Fig. 2f; $\delta^{13}\text{C}$ from –5.5 to –23.6‰ for Jwaneng mine, Burgess et al., 1998, Kirkley et al., 1991a, Fig. 2g; and $\delta^{13}\text{C}$ from –15.8 to –23.4‰ for Venetia mine, Jacob et al., 2000, Fig. 2h). Figure 2 demonstrates that the $\delta^{13}\text{C}$ frequency distributions are indistinguishable for the diamondites with peridotitic and eclogitic garnets that we analyzed in this study, and that both show maxima at about $\delta^{13}\text{C} \sim -18\text{‰}$. It is surprising that most of the diamonds in the diamondites with peridotitic garnets have such low $\delta^{13}\text{C}$ values, because only a few single-crystal diamonds with peridotitic silicate inclusions analyzed by Kirkley et al. (1991b) showed $\delta^{13}\text{C}$ values as low. If the difference between the peridotitic and eclogitic garnets in the diamondites results from the source material, the $\delta^{13}\text{C}$ values of the diamond in diamondites should also reflect the $\delta^{13}\text{C}$ values of the source material. As eclogites have $\delta^{13}\text{C}$ values that are different from those of peridotites, the $\delta^{13}\text{C}$ values of the diamonds in diamondites with the peridotitic garnet should be distinct from those with the eclogitic garnet. However, this is not the case for our diamondites. This means that the difference of the chemical compositions of the garnets does not reflect a difference in the source rock, as was already suspected by Kurat and Dobosi (2000).

In their geochemical study of diamondites, Kurat and Dobosi (2000) and Dobosi and Kurat (2002) concluded that the compositional difference in minor and trace elements between the peridotitic and eclogitic garnets must be the result of different fluid processing. According to them, the high Cr content in the peridotitic garnet is a characteristic of the carbonatitic or kimberlitic fluid/melt that was able to extract Cr effectively from the source. Also, fluids/melts that precipitated the eclogitic garnet were poor in Cr probably because of their inability to mobilize chromium or because they came from a source already depleted in Cr. However, a source depleted in Cr has to be excluded, because such a source should also be strongly depleted in incompatible trace elements (e.g., Kurat et al., 1980), which is not indicated by the composition of the garnets. Thus, a specific feature of these fluids, yet to be explored, made them Cr-poor and allowed the precipitation of only eclogitic garnets. Kurat and Dobosi (2000) and Dobosi and Kurat (2002) discussed also the possibility that precipitation of Cr (chromite?) had occurred before garnet was precipitated.

The similarity of the $\delta^{13}\text{C}$ frequency distributions of diamondites with peridotitic and eclogitic garnets suggests that the isotopic fractionation of C did not occur during the fluid/melt extractions from their source rock but rather must be due to consecutive processes. The C isotopic composition also sug-

Table 1. Averaged carbon isotope data for diamonds in diamondites (relative to V-PDB in ‰).

Sample	$\delta^{13}\text{C}^{\text{a}}$	N ^b	Silicates ^c
Diamondites with "Peridotitic" garnets			
Dia074	-3.24	1	gt
Dia056	-16.46 ± 0.09	5	gt
Dia006	-17.39 ± 0.15	3	gt
Dia055	-18.30 ± 1.67	8	gt, cpx
Dia054	-18.59 ± 0.27	4	gt, cpx
Dia019	-18.75 ± 0.11	3	gt
Dia017	-19.06 ± 0.21	2	gt
Dia075	-19.29 ± 0.12	2	gt
Dia065	-20.92 ± 0.10	3	gt
Dia012	-21.92 ± 0.07	2	gt, cpx
Dia005	-22.70 ± 0.03	2	gt
Dia066	-23.59 ± 0.09	4	gt, cpx
Dia050	-24.36 ± 0.12	2	gt
Diamondites with "Eclogitic" garnets			
Dia068	-5.27 ± 0.07	2	gt
Dia020	-11.13 ± 0.02	3	gt
Dia061	-13.95 ± 0.56	8	gt
Dia051	-16.05 ± 0.05	2	gt
Dia052	-16.24 ± 0.09	4	gt
Dia030	-16.60 ± 0.17	3	gt
Dia011	-17.16 ± 0.10	2	gt
Dia073	-17.24 ± 0.12	2	gt
Dia022	-17.28 ± 0.65	5	gt
Dia014	-18.21 ± 0.15	3	gt
Dia001	-18.70 ± 0.16	3	gt
Dia063	-18.98 ± 0.13	4	gt
Dia060	-19.01 ± 0.09	2	gt
Dia018	-19.13 ± 0.03	3	gt
Dia058	-19.91 ± 0.14	4	gt
Dia062	-20.36 ± 0.12	3	gt
Dia053	-20.84 ± 0.52	5	gt
Dia057	-21.39 ± 0.13	5	gt
Dia059	-22.22 ± 0.26	2	gt
Diamondites without garnets			
Dia064	-5.44 ± 0.17	3	
Dia067	-13.54 ± 0.69	2	
Dia071	-27.87 ± 0.23	3	

^a Errors are 1 σ .

^b Number of grains for determination of the averaged values.

^c gt and cpx denote garnet and clinopyroxene, respectively.

gests derivation of fluids/melts that precipitated either peridotitic or eclogitic garnets from the same source.

Different degrees of partial melting of a common source can also not be responsible for the formation of diamondites with peridotitic and eclogitic garnets, respectively. Such a process should lead to different variabilities of C isotope abundances in diamondites with eclogitic (low degree partial melting) and peridotitic (high degree partial melting) garnets, which is not observed (Fig. 2). The standard deviation of the $\delta^{13}\text{C}$ values for the diamondites with eclogitic garnets from all values except the highest one (-5.27‰), is 2.7‰, whereas that for the diamondites with peridotitic garnets for all values except the highest one (-3.24‰) is 2.5‰. This means that the $\delta^{13}\text{C}$ variations of diamondites do not reflect different degrees of fluid/melt extraction from a common source. Our data indicate similar degrees of C extraction from a common source for both types of diamondites.

3.2. Common Source for Diamondites with Peridotitic and Eclogitic Garnets

Regarding a common reservoir for both types of diamondites, i.e., diamondites with peridotitic and eclogitic garnets, three possibilities exist, based on the observed $\delta^{13}\text{C}$ variations. These possible scenarios differ in the timing of the isotopic fractionation. First, each part of the source mantle, from which the fluids/melts that produced diamondites were extracted, could have had a different isotopic composition and, therefore, the $\delta^{13}\text{C}$ distribution observed for diamondites might reflect the heterogeneity of the source. This heterogeneity could have been produced by a process, such as mantle metasomatism (e.g., Yaxley et al., 1991; Rudnick et al., 1993). This process also requires fluids/melts to produce the isotopic heterogeneity, but these fluids/melts have altered the source mantle and need to be different from the fluids/melts that produced subsequently the diamondites. As a mm- or cm-scale of the isotopic heterogeneity should be erased by the successive fluid/melt processes producing the diamondites, the observed isotopic variation could reflect the heterogeneity of the source region on a much larger scale (≥ 100 m). The frequency for a certain $\delta^{13}\text{C}$ value of the diamondites (Fig. 2) might have reflected the distribution of the materials with the $\delta^{13}\text{C}$ value in the source region. The average of the $\delta^{13}\text{C}$ value in the source should have been -18‰, which corresponds to the maximum in the isotopic composition frequency distribution (Fig. 2). Such a component with an isotopic composition of just above -20‰ was proposed by Deines (2002) for southern African diamonds with eclogitic silicate inclusions, although such a component has never been observed in other mantle rocks. Even if such a ^{13}C -depleted component exists in the Earth's mantle, it should not originate from subducted oceanic crust with a biogenic ^{13}C -depleted carbon. As the *mg* numbers for garnet in both types of diamondites with peridotitic and eclogitic garnets are similar to those of upper mantle peridotites (Kurat and Dobosi, 2000; Dobosi and Kurat, 2002), such garnets cannot be produced from a subducted oceanic crust. Therefore, the isotopic variation in the isotopically heterogeneous source proposed here should reflect an isotopic fractionation process rather than heterogeneous mixing between homogeneous mantle source and subducted oceanic crust.

Second, the source and, therefore, the initial melts/fluids could have had a homogeneous $\delta^{13}\text{C}$ value of less than -28‰ (i.e., the minimum $\delta^{13}\text{C}$ value in this study). The isotopic variation of carbon in diamondites might be explained by mixing of a normal component with $\delta^{13}\text{C}$ of -5‰ and the proposed component with $\delta^{13}\text{C}$ of less than -28‰ during migration of the fluids/melts to the Earth's surface. The source, from which the first fluids/melts were extracted, had a $\delta^{13}\text{C}$ of -28‰ and these fluids/melts were diluted by a component with a $\delta^{13}\text{C}$ value of -5‰ during migration. The frequency distribution with a peak around -18‰ should mean that the two components mixed relatively homogeneously, i.e., at similar mixing ratios.

Third, the source could have a homogeneous $\delta^{13}\text{C}$ value of about -5‰, which corresponds to the isotopic composition of the upper mantle C as manifested in MORBs, carbonatites, carbonate from kimberlites, and gem diamonds with peridotitic

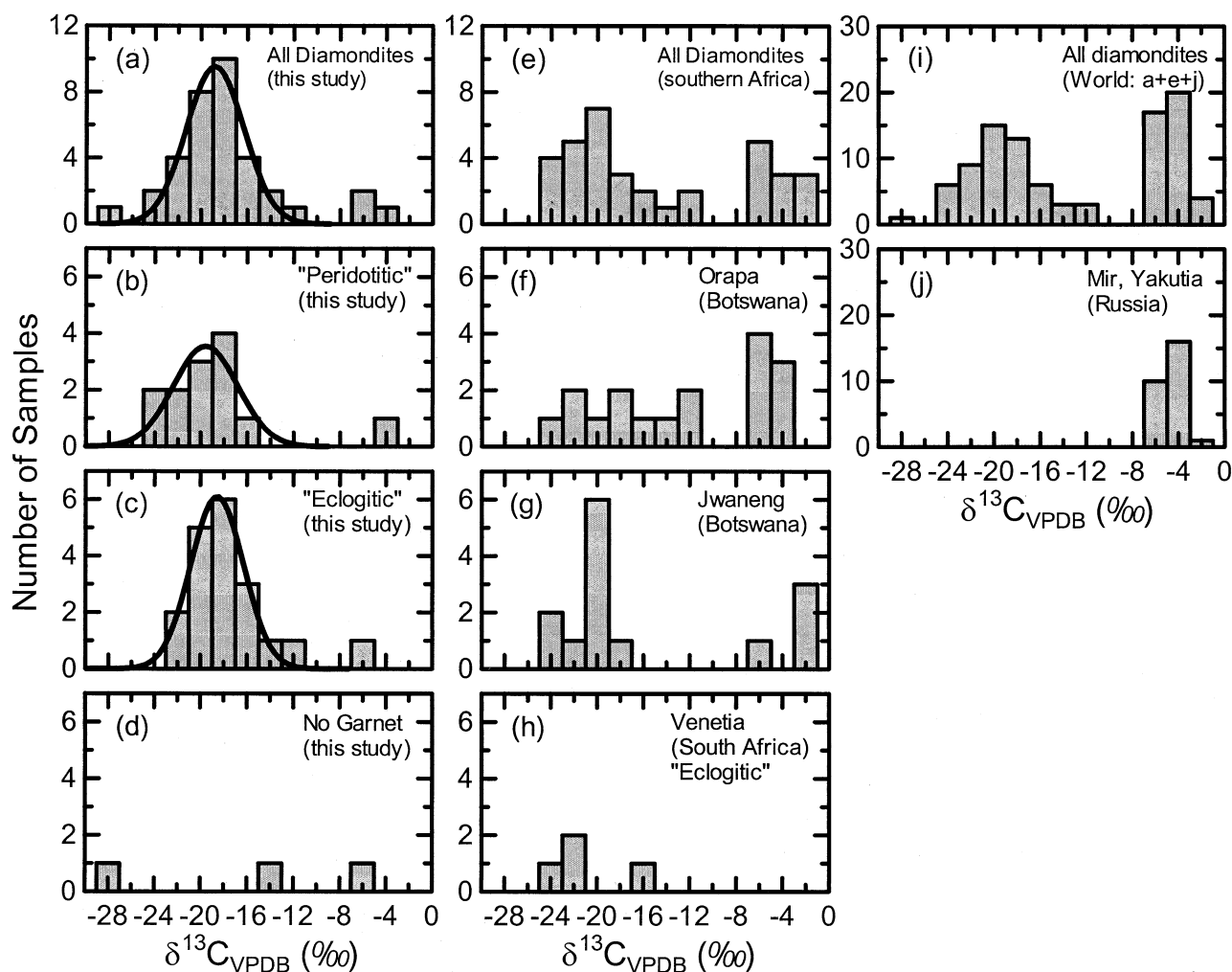


Fig. 2. $\delta^{13}\text{C}$ histogram for (a) all, (b) diamondites with “periodic” garnets, (c) diamondites with “eclogitic” garnets, and (d) diamondites without garnet that we analyzed in this study. Solid curves represent a gaussian regression curve. $\delta^{13}\text{C}$ distribution for diamondite from (e) southern Africa mines: (f) Orapa, Botswana (McCandless et al., 1989; Deines et al., 1993; Burgess et al., 1998); (g) Jwaneng, Botswana (McCandless et al., 1989; Kirkley et al., 1991); (h) Venetia, South Africa (Jacob et al., 2000). (i) All diamondites worldwide; (j) Mir, Yakutia, Russia (Reutskii et al., 1999).

silicate inclusions (e.g., Deines and Gold, 1973; Javoy et al., 1986; Matthey, 1987; Javoy and Pineau, 1991; Galimov, 1991). The isotopic variation for diamondites could be explained by variable degrees of isotopic fractionation from such homogeneous starting material during extraction or migration of the fluids/melts.

Our data do not allow to discriminate between the three proposed scenarios. In any case, a process producing ^{13}C -depleted carbon must have been involved. As suggested in the recent review of Deines (2002), C with $\delta^{13}\text{C}$ of about -5‰ has been identified as a major carbon component in the Earth’s mantle. Thus, it is reasonable to discuss a process that can produce ^{13}C -depleted carbon from the largest available reservoir with a $\delta^{13}\text{C}$ value of -5‰ , although it is uncertain whether any ^{13}C -depleted component existed before or after extraction of the fluid/melt from which diamondites would precipitate. In the next section, we discuss a possible scenario to produce ^{13}C -depleted carbon from the mantle. As all the

three possible scenarios stated above do not allow the existence of the diamondites with a $\delta^{13}\text{C}$ value higher than -5‰ (i.e., -3.24‰ for Dia074 with peridotitic garnets), we also discuss a possible mechanism for the creation of such a higher $\delta^{13}\text{C}$ value in the next section.

3.3. Possible Scenario for C Isotopic Fractionation in Diamondites

It is likely that the carbon isotope abundances in diamondites somehow reflect isotopic fractionation during diamond growth from a fluid/melt. Fractionations of a few‰ within a diamond were reported for synthetic diamonds (Boyd et al., 1988), where fractionation was observed between zones with different crystal habit. A similar type of isotopic fractionation could explain the small isotopic variations within individual diamondites (Table 2). This process also could have produced the diamondite with the highest $\delta^{13}\text{C}$ value observed by us

Table 2. Carbon isotopic composition of individual diamond grains from diamondites (relative to V-PDB in ‰).

Sample	$\delta^{13}\text{C}$	Color	Averaged $\delta^{13}\text{C}^a$	Type ^b
Dia022	-16.26		-17.28 ± 0.65	E
	-17.04			
	-17.54			
	-17.65			
	-17.89			
Dia053	-20.03	Black	-20.84 ± 0.52	E
	-20.84	Black		
	-20.84	White		
	-21.03	White		
	-21.46	Black		
Dia055	-16.41		-18.30 ± 1.67	P
	-16.50			
	-16.95			
	-17.30			
	-19.12			
	-19.59			
	-20.20			
	-20.32			
	-20.32			
Dia061	-13.46	Black	-13.95 ± 0.56	E
	-13.49	White		
	-13.50	White		
	-13.59	Black		
	-13.95	Black		
	-14.13	Black		
	-14.45	Black		
	-15.00	Black		

^a Errors are 1σ .

^b P = diamondites with peridotitic garnets; E = diamondites with eclogitic garnets

(-3.24‰), which cannot be produced from a component with a $\delta^{13}\text{C}$ value of -5‰ in the three possible scenarios outlined above. However, such fractionation can explain only a small part of the C isotopic variation observed among diamondites. Therefore, another mechanism is needed to create the very large isotopic variations found among diamondites. Such large $\delta^{13}\text{C}$ variations probably reflect isotopic fractionation resulting from redox reactions of CH_4 (or graphite/diamond) and CO_2 , which are expected to occur in the Earth's mantle (Taylor and Green, 1989). Fluid inclusions in diamonds and trace element abundances in coexisting silicates support this view, as they demonstrate the presence of CO_2 during diamond formation (e.g., Schrauder and Navon, 1993; Kurat and Dobosi, 2000; Dobosi and Kurat, 2002).

A $\text{CH}_4\text{-H}_2\text{O}$ fluid is stable at low oxygen fugacity conditions (e.g., Taylor and Green, 1989). As f_{O_2} tends to decrease with increasing depth (Saxena, 1989; Ballhaus and Frost, 1994; Simakov, 1998), such a $\text{CH}_4\text{-H}_2\text{O}$ fluid is likely to be an important species at great depth in the upper mantle and in the lower mantle. During migration of the $\text{CH}_4\text{-H}_2\text{O}$ fluid to the upper parts of the mantle, the methane in the fluid will be oxidized to graphite (or diamond) and CO_2 (e.g., Deines, 1980). The latter can react with silicates (e.g., Luth, 1993; Knoche et al., 1999) and, therefore, be removed from the fluid in the form of solid phases (carbonates). Atomic C can be dissolved in the fluid phase (Kumar et al., 2000) and, therefore, would remain in the fluid phase. This process can cause the separation of CO_2 from graphite (diamond) and methane in the mantle, accompa-

nied by a large isotopic fractionation of C. If the separation occurred simultaneously and continuously after the oxidation of graphite (and methane) to CO_2 , this isotopic fractionation can be considered a Rayleigh-type fractionation. In this case, the carbon isotopic compositions in the residual fluid phase (R) can be given as follows, provided that the isotopic fractionation factor α is constant (Rayleigh, 1902):

$$R/R_0 = f^{\alpha-1} \quad (2)$$

where R_0 is the $^{13}\text{C}/^{12}\text{C}$ ratio of the initial reservoir and f is the ratio of the residual phase to initial reservoir. For instance, at a temperature range from 1300 to 1500°C, which can be considered as a typical temperature for the asthenospheric mantle (Fig. 3), the separation of 95 and 98%, respectively, of carbon as CO_2 from the fluid phase can cause an isotopic fractionation of 13‰. This can shift the C isotopic composition of the residual C in the fluid from the initial $\delta^{13}\text{C}$ of -5‰ to $\delta^{13}\text{C}$ of -18‰ , as observed for the average of diamondites (Fig. 4). This simple estimate implies that a sufficient amount of carbon remains in the fluid phase and available for diamond formation after the separation of CO_2 from the fluid/melt. The observed variation of $\delta^{13}\text{C}$ in diamonds of diamondites can be explained by different degrees of fluid oxidation before diamond formation.

All proposed geotherms become steep at depths larger than ~ 200 km (gray lines in Fig. 3). Most of them intersect with solidi of a volatile-rich peridotite-C-O-H system (Taylor and

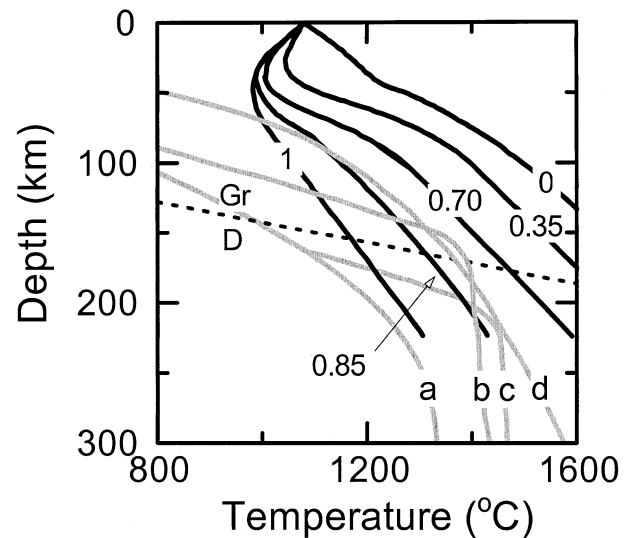


Fig. 3. Solidi of the C-O-H-peridotite system and some proposed geothermal gradients. Solid curves represent solidi of C-O-H-peridotite for water activities of 0 (water-absent), 0.35, 0.70, 0.85 and 1 (water-saturated), respectively (Taylor and Green, 1988). The numbers near the curves represent the water activity for the solidi. Gray curves represent a variety of proposed geothermal gradients as compiled by Wyllie (1995). The geotherms "a" and "c" are based on geothermobarometry of mantle xenoliths from kimberlites erupted through cratons. The geotherm "b" is based on conduction and convection heat-transfer. The geotherm "d" is based on conduction heat-transfer. The dotted line represents the boundary between diamond and graphite stability fields (Kennedy and Kennedy, 1976).

Green, 1988). It is worthwhile to note that the intersections are located near the diamond formation field (5–7 GPa and 900–1300°C; e.g., Meyer, 1987). As carbonate is incorporated into the upwards-migrating fluid phase after the intersection (point “c” in Fig. 5), solid carbonate formation from the fluid (and, therefore, heavy-isotope separation from the migrating fluid) would not occur after the passage of the intersection of solidus and geotherms. Instead, carbonatitic or kimberlitic melt would be produced and be incorporated in the fluid/melt phases. Also,

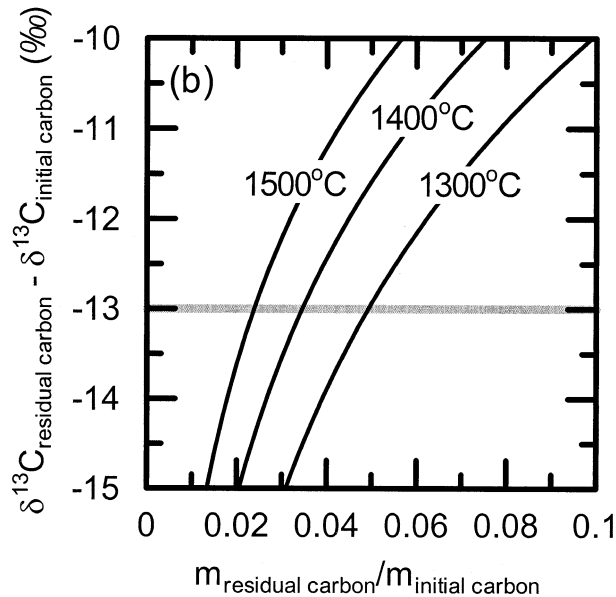
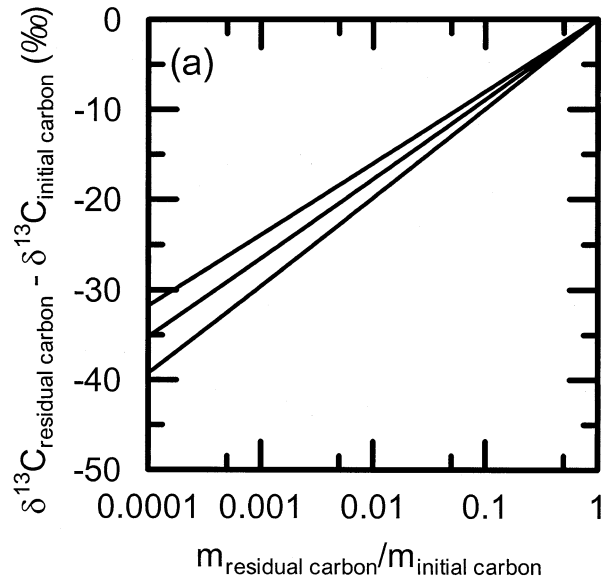


Fig. 4. (a) Estimated carbon isotopic fractionation between residual and initial fluid vs. mass ratio of residual and initial fluid for 1300, 1400, 1500°C. (b) Enlarged view of the region around isotopic difference of -13% between residual and initial carbon. Isotopic fractionation factors between CO_2 and CH_4 determined by Horita (2001) were used for these estimates.

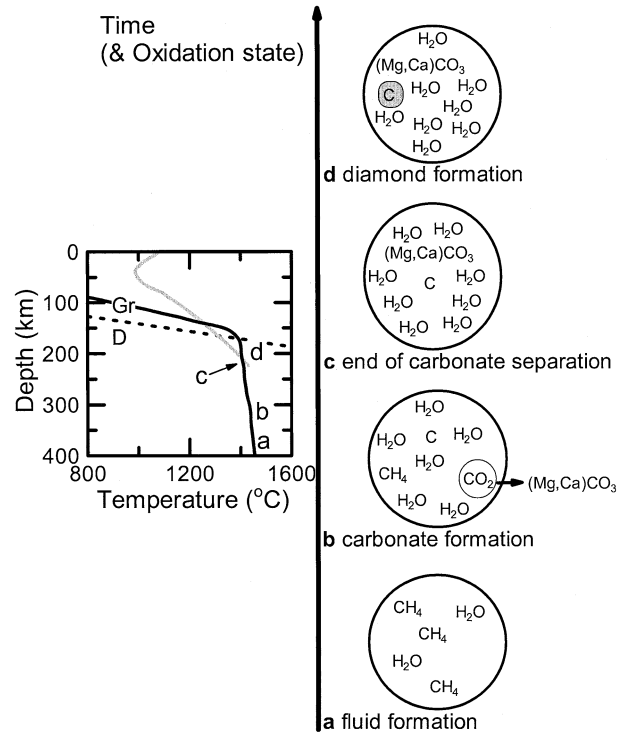


Fig. 5. Schematic diagram for diamondite formation. Solid curve in graph represents a proposed geothermal gradient (Wyllie, 1995). The geotherm is based on conduction and convection heat-transfer (“b” in Figs. 3). Gray curve represents the solidus for the C-O-H-peridotite system ($a_{\text{H}_2\text{O}} = 0.85$; Taylor and Green, 1988). The dotted curve represents the boundary between diamond and graphite stability fields (Kennedy and Kennedy, 1976).

diamond formation would start around that point. Therefore, diamond in diamondites may have been produced from a carbonate-rich (carbonatitic or kimberlitic) fluid, as previously suggested by Kurat and Dobosi (2000) and Dobosi and Kurat (2002), in agreement with experiments of Sokol et al. (2001a,b), Pal’yanov et al. (2002a,b), and Litvin et al. (2001). As is evident in Figure 3, a H_2O -rich fluid is required to decrease the solidus temperature of the asthenospheric peridotites sufficiently to intersect with the local geotherm. Such a fluid can be produced by oxidation and carbonate-separation of methane-rich upwards-migrating fluid.

In the scenario proposed above, the chemical composition of the migrating fluid at the time interval from fluid formation to carbonate separation (a–b in Fig. 5), e.g., the $\text{H}_2\text{O}/\text{CH}_4$ ratio, should vary due to oxidation of the methane-rich fluid and carbonate separation. Differences in fluid composition influence the peridotite solidus temperatures and, therefore, determine the depth at which carbonate separation from the fluid ceases. In addition, the depth controls the degree of heavy-isotope separation from the fluid. As the isotopic compositions of C in diamondites with peridotitic and eclogitic garnets are similar, the fluids producing these two types of diamondites should have the same chemical composition at least at the time of carbonate separation (point “c” in Fig. 5). Diamondites with peridotitic and eclogitic garnets with the same isotopic compo-

sition should have originated from very similar migrating fluid. The differences in the chemical compositions of the fluids that produced peridotitic and eclogitic garnets, respectively, in the diamondites should, therefore, reflect an environmental difference after end of carbonate separation (“d” in Fig. 5).

Although the range of the $\delta^{13}\text{C}$ values for the eclogitic diamonds and for diamondites are similar, the $\delta^{13}\text{C}$ -distributions observed for diamondites are completely different from those of eclogitic diamonds (e.g., Deines, 1980, 2002; Kirkley et al., 1991b). The distributions of $\delta^{13}\text{C}$ values for diamondites show a symmetrical (gaussian) peak with a maximum at -18% (Fig. 2), whereas those for eclogitic single-crystal diamonds show a peak at -5% and are skewed towards negative values. To obtain the distributions observed for eclogitic diamonds, Deines (1980, 2002) proposed a Rayleigh fractionation model in which he had to assume a certain probability for producing diamonds with certain $\delta^{13}\text{C}$ values. He assumed that the lower frequency for low- $\delta^{13}\text{C}$ diamonds was induced by the volume loss of carbonaceous material. The initial material to produce low- $\delta^{13}\text{C}$ diamonds had the same volume as the material that produced high- $\delta^{13}\text{C}$ diamonds. We see no reason to apply this model also to diamondite formation. Therefore, there is no necessity for diamondites to show $\delta^{13}\text{C}$ distributions similar to those of eclogitic diamonds as predicted by Deines (1980, 2002).

4. SUMMARY AND CONCLUSIONS

Variations in the $\delta^{13}\text{C}$ values of diamonds from diamondites with peridotitic and eclogitic garnet are almost identical and show maxima in their frequency distribution at about -18% . These observations suggest that the difference between the peridotitic and eclogitic garnets in the diamondites does not reflect different source rocks. In addition, the carbon isotopic composition excludes different degrees of fluid/melt extraction from a source to be responsible for the formation of the compositionally different peridotitic and eclogitic garnets in diamondites. As we do not observe any difference in the $\delta^{13}\text{C}$ distribution between the diamondites with peridotitic and eclogitic garnets, the C isotopic variation supports the model derived from trace element data, namely, that diamondites with peridotitic and eclogitic garnets were precipitated from carbonate-rich fluids that had a similar, peridotitic source. The C isotopic variation can have been achieved by simple Rayleigh fractionation from an isotopically homogeneous reservoir with an isotopic composition identical to that of the Earth's upper mantle (-5%) during oxidation of upwards-migrating fluids. The separation of CO_2 from the fluid/melt phase by reaction with silicates (formation of carbonates) can cause C isotopic fractionations similar to those observed in diamonds from diamondites, changing the $\delta^{13}\text{C}$ from upper mantle values (-5%) to the values actually observed (about -18%). The total variation of $\delta^{13}\text{C}$ in diamonds of diamondites can be explained by variable degrees of oxidation of the originally reduced fluid phase.

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