



Carbon isotope fractionation between graphite and diamond during shock experiments

Teruyuki MARUOKA,^{1†*} Christian KOEBERL,¹ Jun-ichi MATSUDA,²
and Yasuhiko SYONO³

¹Department of Geological Sciences, University of Vienna, Althanstrasse 14, A-1090, Vienna, Austria

²Department of Earth and Science, Graduate School of Science, Osaka University, Toyonaka, Osaka 560–0043, Japan

³Institute for Materials Research, Tohoku University, Katahira, Aoba-ku, Sendai 980, Japan

[†]Present Address: Laboratory for Space Sciences, Physics Department, Washington University, 1 Brookings Drive, St. Louis, Missouri 63130–4899

*Corresponding author. E-mail: teruyuki@wuphys.wustl.edu

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Abstract—Carbon isotopic compositions were measured for shock-produced diamond and shocked graphite formed at peak pressures ranging from 37 to 52 GPa. The $\delta^{13}\text{C}$ values of diamonds produced in a sealed container were generally lower than that of the initial graphite. The differences in the carbon isotopic composition between initial graphite and shocked graphite/diamond may reflect kinetic isotopic fractionation during the oxidation of the graphite/diamond and/or analytical artifacts possibly induced by impurities in the samples. The pressure effect on the isotopic fractionations between graphite and diamond can be estimated from the $\delta^{13}\text{C}$ values of impurity-free diamonds produced using a vented container from which gases, including oxygen, in pore spaces escaped during or after the diamond formation (e.g., $0.039 \pm 0.085\text{‰}$ at a peak pressure of 52 GPa). Any isotopic fractionation induced by shock conversion of graphite to diamond is too small to be detected in natural shock-induced diamond-graphite systems related to terrestrial impact cratering processes.

INTRODUCTION

A number of recent studies suggested that, theoretically, the pressure dependence of some isotopic equilibrium fractionation factors may not be negligible (e.g., Driesner 1997; Polyakov and Kharlashina 1994). Horita et al. (1999, 2002) actually observed the pressure effect on hydrogen isotope fractionation between the mineral brucite, $\text{Mg}(\text{OH})_2$, and pure water. A pressure effect implies that molar volume changes with isotopic substitution (Sheppard 1997). A difference in bond length has been observed between D_2O and H_2O (Kuchitsu and Bartell 1962). Although the effect is more extreme for hydrogen than for all other elements, the pressure effect should not be limited to hydrogen isotopes. A change of the lattice constant with isotopic composition was actually observed for diamond (Holloway et al. 1991; Yamanaka et al. 1994; Fujihisa et al. 1996). The difference in the lattice constants of ^{12}C and ^{13}C diamonds is quite small at atmospheric pressure (0.015%; Holloway et al. 1991). However, the difference becomes noticeable at pressures higher than about 20 GPa (Fujihisa et al. 1996). At ~ 35 GPa, the difference in lattice constraints between ^{12}C and ^{13}C diamonds is $\sim 0.1\%$. Therefore, this could lead to isotopic fractionation between

diamond and co-existing graphite at high pressure, as has been theoretically proposed (Polyakov and Kharlashina 1994). To study the pressure effect on the isotopic fractionation between the two phases and to apply it to a natural graphite-diamond system related to impact shocks (which has applications in terrestrial impact cratering and in meteorite studies), we analyzed the isotopic compositions of diamonds produced in shock experiments (Matsuda et al. 1995).

EXPERIMENTAL PROCEDURES

The shock-produced diamond samples used in this study were prepared by Matsuda et al. (1995). These authors did not use all their diamond samples for their noble gas analyses. Therefore, we used the remainder of their run products for our carbon isotopic analyses. Here, we summarize the experimental procedures for the preparation of the diamond residues, which are described in more detail by Matsuda et al. (1995). Natural finely powdered graphite (purity 99.9%, less than 25 μm grain size) was mixed with copper powder (purity 99.8%, 100 μm grain size) and pressed into a pellet. The mixing ratio of graphite to copper was 1:9 by weight (about 1:1 in volume). The compressed pellet of the graphite-copper

mixture was encased in copper or stainless steel containers. Isotopic compositions were determined for diamond produced in 2 different types of containers (type-1 and type-2, as described by Matsuda et al. 1995). Considerable amounts of noble gases were found to be trapped in the diamonds produced in the type-1 containers, while none were trapped in those produced in the type-2 containers (Matsuda et al. 1995), although both types of containers were sealed before the shock experiments and contained similar amounts of air. As noble gases were not trapped in the diamonds produced in the containers with venting holes, Matsuda et al. (1995) concluded that the type-1 containers were sealed, while the type-2 containers were vented during the diamond formation.

Shock loading experiments (37–52 GPa) were made by using a 25 mm bore, single-stage powder propellet gun at Tohoku University, Japan (Goto and Syono 1984). The shock pressures were determined from the projectile velocity by the shock-impedance match method (Goto and Syono 1984). The errors in the pressure values were estimated to be about 2 rel%. The stainless steel container was dissolved in 12 M HCl, and then, the copper powder and container were dissolved in 14 M HNO₃. The remaining carbon material was boiled in a H₂SO₄ and KNO₃ solution to oxidize the graphite. The residue was rinsed and centrifuged several times and identified by X-ray diffraction (XRD). The oxidation procedures were repeated until it was confirmed by XRD that the oxidation of graphite was complete. Two graphite-diamond mixtures, after shock-loading with the type-1 container (SP63DG and SP67DG), were also analyzed to examine the isotopic compositions of shocked graphite.

The isotopic compositions of carbon were measured at the Stable Isotope Lab of the Department of Geological Sciences (formerly the Institute of Geochemistry), University of Vienna, using a continuous flow isotope ratio mass spectrometer (CF-IR-MS; Micromass Optima; e.g., Preston and Owens 1985; Maruoka et al. Forthcoming). The samples were weighed into 8 × 5 mm 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, that promote the complete oxidation of the sample. Excess oxygen was removed and nitrogen oxides were converted to nitrogen by copper wires at 650°C in the reduction chamber. The water produced during oxidation was removed by a water trap of magnesium perchlorate. Carbon dioxide and nitrogen were separated by gas chromatography at 50°C and were then introduced into the mass spectrometer.

The ion signals of CO₂⁺ with the molecular weights of 44, 45, and 46 were counted to determine the carbon amount and C isotopic composition. Intensities of ion signals were compared with those of a reference CO₂ gas pulse that was introduced into the mass spectrometer before the sample CO₂ gas arrived. The $\delta^{13}\text{C}$ value compared with those of the reference gas were converted to those of a V-PDB scale based

on comparison with the analytical results for 2 standards (USGS-24, $-15.994 \pm 0.105\%$; NBS-18, $-5.029 \pm 0.049\%$; IAEA-TECDOC-825, 1995) and determined with a reproducibility of $\pm 0.04\%$ (1 σ). In this report, we did not take into consideration the errors related to the reference $\delta^{13}\text{C}$ values (i.e., $\pm 0.105\%$ for USGS-24; $\pm 0.049\%$ for NBS-18), which is acceptable because we do not compare our data with any literature data but only discuss small differences between the $\delta^{13}\text{C}$ values of our various samples. The number of samples that we analyzed at the same analytical conditions was limited by the amount of ash that remained in the combustion tube after sample combustion. To increase the number of shocked diamonds and graphites that could be analyzed under the same analytical conditions, we used just 2 (USGS-24 and NBS-18) reference standard materials as working standards for this study. Although we used a carbonate reference material (NBS-18) as one of the laboratory standards, we determined whether or not the species difference between the reference materials (i.e., carbonate and graphite) affected the observed $\delta^{13}\text{C}$ values. Figure 1 shows a comparison between the measured $\delta^{13}\text{C}$ values and reference $\delta^{13}\text{C}$ values for 3 carbonate (NBS-18, NBS-19, and IAEA-CO-9) and 1 graphite (USGS-24) reference materials. All of the measured $\delta^{13}\text{C}$ values in Fig. 1 are average values for analyses of 80–120 μg of carbon (Table 1). The datum for the graphite reference material was located on the regression line determined from data of 3 carbonate reference materials. This means that the species difference does not affect the observed $\delta^{13}\text{C}$ values. Therefore, no problem exists with using a carbonate reference material, NBS-18, as one of the laboratory standards to determine the isotopic compositions of graphite and fine-grained diamond.

The carbon isotopic compositions obtained for 4 reference materials were roughly correlated to the amount of carbon (Fig. 2). The slopes of these correlations were typically $0.002 \pm 0.001\%$ per 1 μg of carbon. This instrumental fractionation also affects the results for shocked diamond and graphite. To minimize this instrumental fractionation, we had to prepare samples with a small range of weights. Actually, we weighed the samples with a weight difference of less than 3 μg (i.e., $\pm 1.5 \mu\text{g}$). This range of the weight difference might cause isotopic variation of less than 0.01‰ as a result of instrumental isotopic fractionation. As this variation is less than the typical reproducibility

Table 1. Carbon isotopic compositions of reference standards.

Reference		$\delta^{13}\text{C}$ (‰) ^a	$\delta^{13}\text{C}$ (‰) ^b
NBS-19	calcite	1.950	1.444 ± 0.053
NBS-18	calcite	-5.029 ± 0.049	-5.407 ± 0.066
IAEA-CO-9	BaCO ₃	-47.119 ± 0.149	-47.078 ± 0.062
USGS-24	graphite	-15.994 ± 0.105	-16.209 ± 0.052

^aReference carbon isotopic composition relative to V-PDB (IAEA-TECDOC-825, 1995). Errors are 1 σ .

^bCarbon isotopic compositions obtained using 80–120 μg of carbon relative to our reference gas with unknown isotopic composition. Errors are 1 σ .

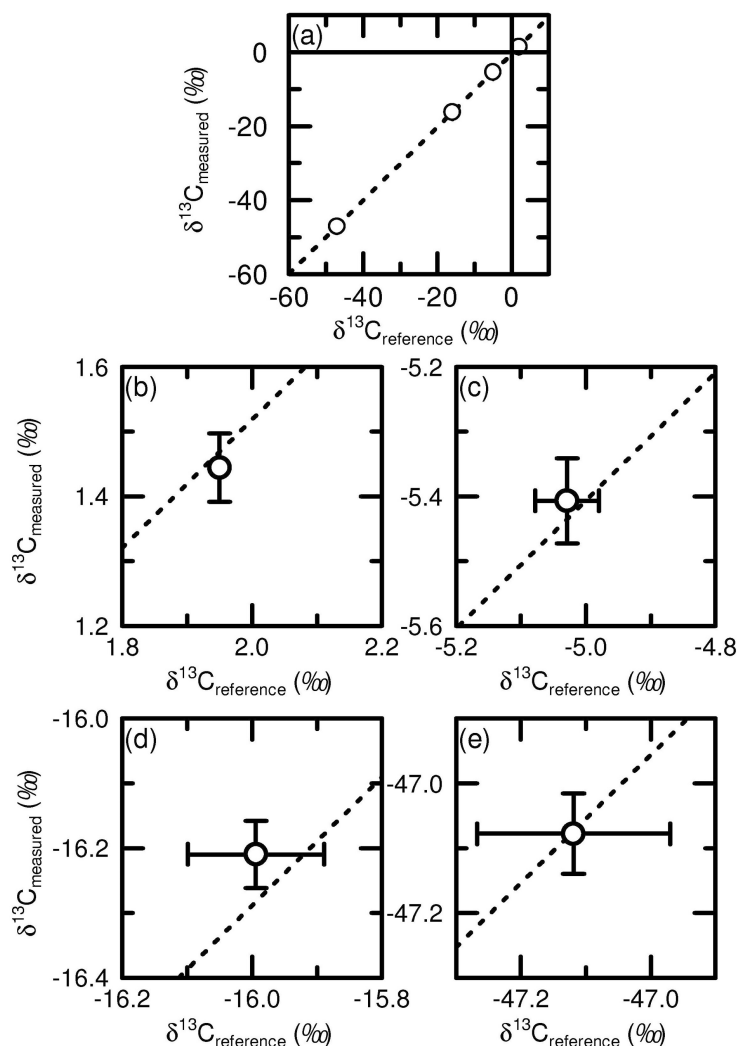


Fig. 1. a) Comparison of measured and reference $\delta^{13}\text{C}$ values for 4 reference standard materials and enlarged diagrams of (a) around data for standard materials; b) NBS-19; c) NBS-18; d) USGS-24; and e) IAEA-CO-9. The measured $\delta^{13}\text{C}$ values are determined relative to the $\delta^{13}\text{C}$ value of a reference gas. The reference $\delta^{13}\text{C}$ values are relative to V-PDB. The dotted lines represent a regression line based on data for 3 carbonate reference materials (NBS-18, NBS-19, IAEA-CO-9).

($\pm 0.04\text{‰}$), we did not apply any correction for this instrumental fractionation.

Tin capsules were heated at 150°C for more than 1 week before their use to oxidize organic matter on the surface of the capsules. As a result of the heating, the amount and isotopic compositions of blank CO_2 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 corresponded to $1.26 \pm 0.10 \mu\text{g}$ of carbon with a $\delta^{13}\text{C}$ value of $-26.78 \pm 0.66\text{‰}$, based on 35 blank measurements. This blank CO_2 amount corresponded to about 2% of the typical sample amount of $70 \mu\text{g C}$. The variation of blank amounts and their isotopic compositions can produce a maximum variation of $\pm 0.04\text{‰}$ in the analytical results. As this maximum $\delta^{13}\text{C}$ variation was similar to the reproducibility of standard and sample analyses (i.e., about 0.04‰), the variations in the

blank amount and its isotopic composition are the main factors determining the reproducibility of the $\delta^{13}\text{C}$ data in this study. The observed isotopic compositions were calculated based on the following relation:

$$\delta^{13}\text{C}_{\text{sample}} = \frac{y_{\text{USGS-24}} - y_{\text{NBS-18}}}{x_{\text{USGS-24}} - x_{\text{NBS-18}}} x + \frac{x_{\text{USGS-24}} y_{\text{NBS-18}} - x_{\text{NBS-18}} y_{\text{USGS-24}}}{x_{\text{USGS-24}} - x_{\text{NBS-18}}}$$

where x_i and y_i represent measured and reference $\delta^{13}\text{C}$ values, respectively, for the standard material i (i.e., USGS-24 and NBS-24) and x represents the averaged $\delta^{13}\text{C}$ values for the sample. The errors of the $\delta^{13}\text{C}$ value of a sample, e_{sample} , were given from the error propagation as follows:

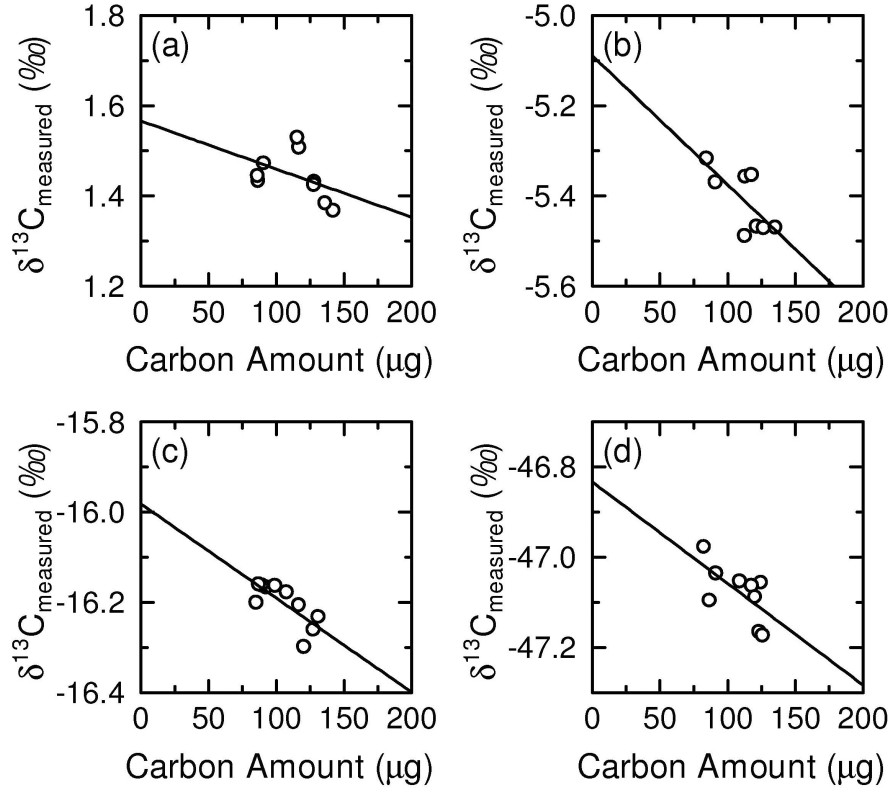


Fig. 2. $\delta^{13}\text{C}$ data versus carbon amount for reference standard materials (a) NBS-19, (b) NBS-18, (c) USGS-24, and (d) IAEA-CO-9. The solid lines represent regression lines. The $\delta^{13}\text{C}$ values are not corrected for instrumental isotopic fractionation.

$$e_{\text{sample}} = \sqrt{\left[\left(\frac{\partial \delta^{13}\text{C}_{\text{sample}}}{\partial x_{\text{USGS-24}}} \right) e_{\text{USGS-24}} \right]^2 + \left[\left(\frac{\partial \delta^{13}\text{C}_{\text{sample}}}{\partial x_{\text{NBS-18}}} \right) e_{\text{NBS-18}} \right]^2 + \left[\left(\frac{\partial \delta^{13}\text{C}_{\text{sample}}}{\partial x} \right) e_{\text{measured}} \right]^2}$$

where the standard deviation from repeated analyses of the standard i and the sample are used for e_i and e_{measured} , respectively. The errors reported here were calculated based on this equation. We can obtain the following expressions from the definition of $\delta^{13}\text{C}_{\text{sample}}$.

$$\begin{aligned} \frac{\partial \delta^{13}\text{C}_{\text{sample}}}{\partial x_{\text{USGS-24}}} &= \frac{(x_{\text{NBS-18}} - x)(y_{\text{USGS-24}} - y_{\text{NBS-18}})}{(x_{\text{USGS-24}} - x_{\text{NBS-18}})^2} \\ \frac{\partial \delta^{13}\text{C}_{\text{sample}}}{\partial x_{\text{NBS-18}}} &= \frac{(x_{\text{USGS-24}} - x)(y_{\text{NBS-18}} - y_{\text{USGS-24}})}{(x_{\text{NBS-18}} - x_{\text{USGS-24}})^2} \\ \frac{\partial \delta^{13}\text{C}_{\text{sample}}}{\partial x} &= \frac{y_{\text{NBS-18}} - y_{\text{USGS-24}}}{x_{\text{NBS-18}} - x_{\text{USGS-24}}} \end{aligned}$$

The CO_2 yields during the combustion of diamond samples ranged from 80 to 100%. The accuracies of the CO_2 yields are 1–2 rel%. As the accuracies are comparable to the errors of the sensitivity for our mass spectrometer during

analyses for this study, the discrepancy between the CO_2 yield and the values expected for pure diamond (i.e., 100%) should be indigenous for our samples. Some samples may contain trace residues of stainless steel from the projectile or alloy produced from copper and stainless steel.

RESULTS AND DISCUSSION

The $\delta^{13}\text{C}$ values (relative to V-PDB) of the shocked diamonds and the diamond-graphite mixtures are listed in Table 2. These values are averages determined by analyses that were repeated at least 3 times, and the errors are based on 1σ . The errors for all diamond samples are comparable to the errors of repeat analyses of standard materials. This indicates that the samples were adequately homogenized by the chemical treatment after the shock experiments. Figure 3 shows $\delta^{13}\text{C}$ data versus the porosity of the initial graphite for a diamond and a diamond-graphite mixture, which were produced at a shock pressure of about 40 GPa in a type-1 container. The porosity of the initial graphite ranged from 11 to 37% by volume. Figure 4 shows $\delta^{13}\text{C}$ data versus the maximum pressure for a diamond and a diamond-graphite

Table 2. Carbon isotopic compositions of shock-produced diamonds.

Sample name	Pressure (GPa)	Vessel Type	Material ^a	Porosity ^b (%)	Yield ^b (%)	$\delta^{13}\text{C}_{\text{V-PDB}}^{\text{c}}$ (%)	CO_2 Yield ^c (%)
SP4	52	1	Cu	11	9.3	-9.811 ± 0.057	97.4 ± 1.2
SP5	51	1	Cu	11	7.2	-9.862 ± 0.047	96.4 ± 1.4
SP51	45	1	Cu	11	8.3	-9.906 ± 0.059	88.0 ± 2.6
SP52	40	1	Cu	11	4.8	-9.922 ± 0.044	79.0 ± 2.3
SP55	51	1	Cu	11	12.0	-9.882 ± 0.062	98.3 ± 3.4
SP62	38	1	Cu	11	6.4	-9.895 ± 0.085	84.1 ± 2.5
SP63 DG ^d	39	1	Cu	11	—	-9.866 ± 0.050	101.5 ± 1.7
SP64	37	1	Cu	18	8.5	-9.811 ± 0.055	88.2 ± 1.3
SP65	37	1	Cu	24	6.8	-9.936 ± 0.064	94.4 ± 1.4
SP66	37	1	Cu	35	14.0	-9.861 ± 0.070	94.5 ± 1.4
SP67 DG ^d	37	1	Cu	35	—	-9.689 ± 0.064	97.9 ± 2.5
SP28	39	2	Cu	35	17.4	-9.720 ± 0.045	96.6 ± 2.1
SP29	46	2	SS	11	3.3	-9.766 ± 0.048	92.0 ± 2.5
SP30	52	2	SS	11	7.6	-9.720 ± 0.074	101.0 ± 2.9
SP31	39	2	Cu	18	7.8	-9.766 ± 0.049	95.6 ± 1.7
G#1 ^e						-9.684 ± 0.027	

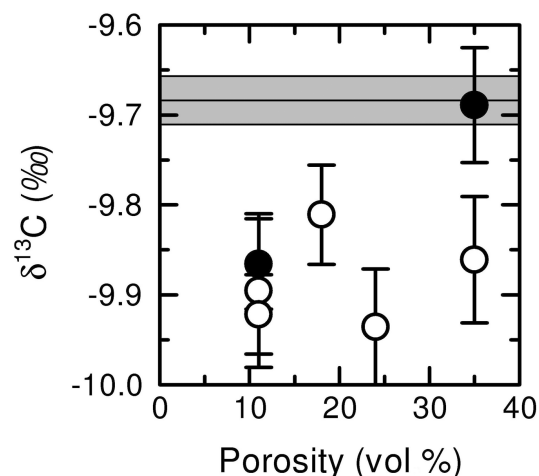
^aSS represents stainless steel.^bData from Matsuda et al. (1995).^cErrors are 1σ .^dGraphite-diamond mixtures. Graphite was not dissolved.^eInitial graphite.

Fig. 3. $\delta^{13}\text{C}$ data for diamonds and diamond-graphite mixtures for a shock pressure of about 40 GPa with a type-1 container versus the porosity of initial graphite in vol%. The open and closed circles represent data for diamonds and diamond-graphite mixtures, respectively. The gray zone represents the $\delta^{13}\text{C}$ value of the initial graphite used in the shock experiments ($-9.684 \pm 0.027\text{‰}$).

mixture, which were produced from the graphite with an initial porosity of 11% by volume with the type-1 container. Both of these figures show that the diamond produced using the type-1 container has $\delta^{13}\text{C}$ values slightly lower than those of the initial graphite ($-9.684 \pm 0.027\text{‰}$). On the other hand, the diamond produced using a type-2 container has $\delta^{13}\text{C}$ values similar to those of the initial graphite (Fig. 5).

Matsuda et al. (1995) showed that noble gases in the pore spaces escaped before diamond formation in the type-2

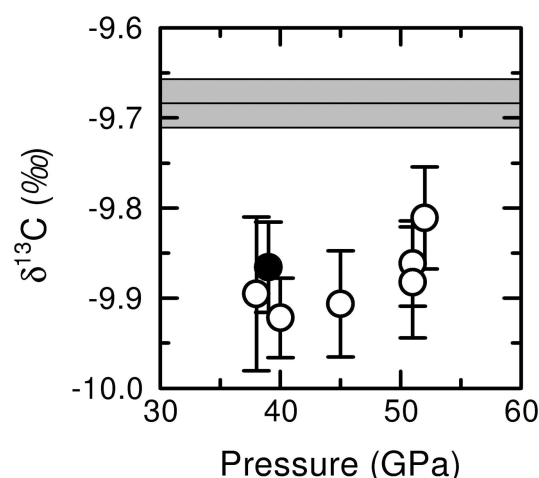


Fig. 4. $\delta^{13}\text{C}$ data for diamonds and diamond-graphite mixture for an initial porosity of 11 vol% with a type-1 container versus the shock pressure. The open and closed circles represent data for diamonds and diamond-graphite mixtures, respectively. The gray zone represents the $\delta^{13}\text{C}$ value of the initial graphite used in the shock experiments ($-9.684 \pm 0.027\text{‰}$).

container, while they did not escape during the shock experiments in the type-1 container and were trapped in the shock-produced diamond and graphite without elemental fractionation. This may imply that the isotopic difference of diamonds produced using the type-1 and type-2 containers is a function of the presence or absence of gas in the pores. Oxygen in the pore spaces or from the reduction of copper oxide on the surface of the copper grains should have escaped through the holes through which the noble gases also escaped

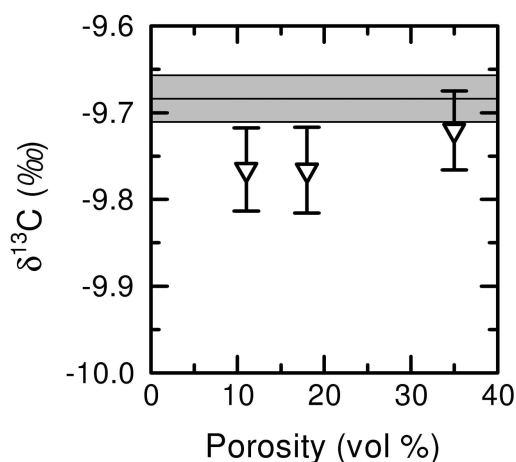


Fig. 5. $\delta^{13}\text{C}$ data for diamonds for a shock pressure of about 40 GPa with a type-2 container versus the porosity of initial graphite. The gray zone represents the $\delta^{13}\text{C}$ value of initial graphite used in the shock experiments ($-9.684 \pm 0.027\text{‰}$).

when employing the type-2 container. In contrast, oxygen should not have escaped when employing type-1 containers and should be available to oxidize some of the graphite and diamond. This difference of oxygen availability can cause at least part of the isotopic difference between the shocked diamond produced using the type-1 and type-2 containers.

In addition, the CO_2 yields for the diamond samples produced in the type-1 container are generally lower than those expected for pure diamond (Fig. 6). Therefore, the isotopic difference between the shocked diamond produced using the type-1 and type-2 containers may also reflect an analytical artifact induced by impurities in the diamond samples.

The $\delta^{13}\text{C}$ values of the diamond produced using the type-1 container (Figs. 3 and 4) are not suitable to study the pressure effect of the isotopic fractionation because they reflect isotopic fractionation resulting from the oxidation of graphite and diamond and/or an analytical artifact possibly induced by impurities in the samples. However, the $\delta^{13}\text{C}$ values of the diamond produced in the type-2 container (Fig. 5) are suitable for this purpose because oxygen, as well as noble gases, escaped from the container (Matsuda et al. 1995) and because impurities in the samples are generally lower than those in the diamond produced in the type-1 container (Fig. 6).

Here, we must discuss other possible mechanisms that could have affected the isotopic compositions of shocked diamonds. During carbon dissolution in metal (and subsequent carbide formation), the isotopic composition of graphite might be affected due to isotopic fractionation (e.g., Banholzer and Anthony 1992; Deines 2002). As the initial graphite was mixed with copper powder, carbon could be dissolved in the copper. Actually, dissolution of carbon in copper at high temperatures has been observed before (e.g., McLellan 1969; Oden and Gokcen 1992). The dissolved carbon is precipitated as graphite during cooling, as observed during shock experiments by Burkhard et al. (1994). The

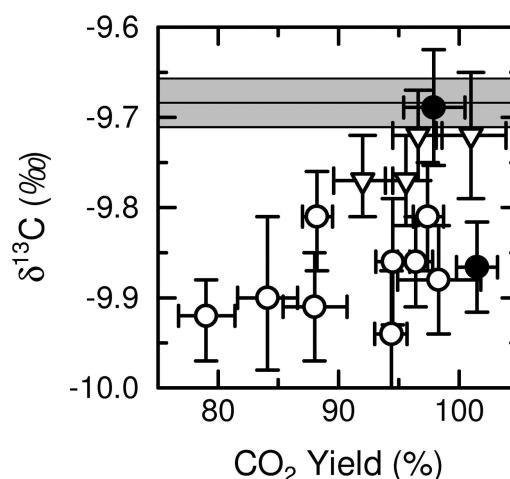


Fig. 6. $\delta^{13}\text{C}$ data for diamonds and diamond-graphite mixtures versus the CO_2 yield during carbon isotopic analyses (i.e., carbon concentrations in the samples). The open and closed circles represent data for diamonds and diamond-graphite mixtures, respectively, produced in type-1 (sealed) containers. The triangles represent data for diamonds produced in type-2 (vented) containers. The gray zone represents the $\delta^{13}\text{C}$ value of the initial graphite used in the shock experiments ($-9.684 \pm 0.027\text{‰}$).

graphite precipitated from dissolved carbon might have an isotopic composition different from that of the original graphite. However, the effect of the C dissolution in the copper should be trivial on the isotopic compositions of diamond because the diamond formation (and, therefore, isotopic fractionation between graphite and diamond) occurs before the graphite-copper reaction. Diamond transformation from initial porous graphite occurs within about 10^{-8} sec (DeCarli 1979), while solid-phase reactions during shock experiments generally occur during a time interval of 10^{-7} – 10^{-6} sec (Batsanov and Marquis 2001).

Graphite in the graphite-diamond mixture after the shock experiments was dissolved in a KNO_3 and H_2SO_4 solution. This solution might also have dissolved trace amounts of diamond. Graphite is dissolved in the KNO_3 and H_2SO_4 solution in the form of graphite intercalation compounds, such as $(\text{C}_{24n})^+\text{HSO}_4^-\cdot 2\text{H}_2\text{SO}_4$ (Ubbelohde 1969) and $(\text{C}_{24n})^+\text{NO}_3^-\cdot 3\text{HNO}_3$ (Loughin et al. 1978; Avdeev et al. 1997, 1999). As large numbers (≥ 24) of carbon atoms have a joint behavior, no selectivity of carbon isotopes should be expected during the intercalation reaction process. Therefore, even if diamonds are partially etched by the KNO_3 and H_2SO_4 solution, this process should not be accompanied by the isotopic fractionation between dissolved and residual diamonds.

Therefore, the isotopic compositions of the shocked diamonds produced in the type-2 container most likely reflect mainly isotopic fractionation between graphite and diamond at high pressures.

The isotopic differences between graphite and diamond ($\Delta^{13}\text{C} \equiv \delta^{13}\text{C}_{\text{graphite}} - \delta^{13}\text{C}_{\text{diamond}}$) at a high pressure were

expected to be positive, based on the calculation with a pressure correlation for the isotopic fractionation between graphite and diamond (Polyakov and Khalashina 1994). If we assume that the artifact effect induced by sample impurities is insignificant for diamonds produced in the type-2 container, the isotopic fractionation, $\Delta^{13}\text{C}$, can be determined as follows:

$$\Delta^{13}\text{C} = (\delta^{13}\text{C}_{\text{initial}} - \delta^{13}\text{C}_{\text{diamond}})/(1 - X) \quad (1)$$

where $\delta^{13}\text{C}_{\text{initial}}$ and X represent the $\delta^{13}\text{C}$ values of the initial graphite and diamond yield from Matsuda et al. (1995), respectively. Equation 1 is based on a mass balance between graphite and diamond during shock conversion from graphite to diamond. The isotopic fractionations between graphite and diamond can be estimated to be 0.068 ± 0.044 , 0.085 ± 0.057 , and $0.039 \pm 0.085\%$ for maximum pressures of 39, 46, and 52 GPa, respectively. For the isotopic fractionation at a maximum pressure of 39 GPa, the value represents the average of 2 experiments (i.e., SP28 and SP31). The assumption stated above should be correct at least for the sample SP30, which was produced at the maximum pressure of 52 GPa, because the sample consisted of pure diamond, based on the CO_2 yield of $101.0 \pm 2.9\%$ (Table 2).

Several possible mechanisms for the shock transformation from graphite to diamond have been proposed, including martensitic transformation of graphite (e.g., DeCarli and Jamieson 1961; Erskine and Nellis 1991) and nucleation and growth (diffusive reconstruction) from a glass-like structure (e.g., Pujols and Boisard 1970) or through a liquid phase (e.g., DeCarli 1979; Kleiman et al. 1984; Burkhard et al. 1994). The mechanism controlling diamond formation depends on shock conditions and starting materials. For our shock experimental settings (Matsuda et al. 1995), diamond yield increases with the porosity of the initial graphite. This means that the diamond yield is controlled by the temperature of local "hot spots" rather than by the pressure. This observation suggests that the diffusive reconstruction process is the dominant mechanism for the transformation from graphite into the diamond that was analyzed in this study. This conclusion is consistent with those obtained in similar experiments using porous initial graphite (e.g., Yoshida and Thadhani 1992; Hirai et al. 1995). Therefore, the isotopic fractionation discussed above should be associated with the diffusive reconstruction process.

We cannot rule out the possibility that the $\delta^{13}\text{C}$ values of some diamonds produced in type-2 containers, as well as those in the type-1 containers, could be affected by some impurities within the samples. However, irrespective of any such possible artifacts, any isotopic fractionation during shock conversion from graphite to diamond is expected to be quite small (less than 0.1‰, based on the estimation above) and, therefore, cannot be detected in natural shock-induced diamond-graphite systems, such as those related to terrestrial impact cratering processes (e.g., Hough et al. 1995; Koeberl et al. 1997; Gilmour 1998). Naturally occurring graphite has

an original isotopic heterogeneity that is much larger than the isotopic variation reported in this study (e.g., 3.5‰ within gneiss of the Popigai impact structure; Gilmour 1998).

However, our results can be used to constrain the origin of diamonds in ureilites. The origin of the diamond in ureilites is still a matter of debate (e.g., Rai et al. 2002, 2003). Some mechanisms have been proposed, including a chemical vapor deposition (CVD) (e.g., Fukunaga et al. 1987; Matsuda et al. 1991, 1995; Fukunaga and Matsuda 1997) or high-pressure conversion of graphite (e.g., Lipschutz 1964; Nakamuta and Aoki 2000). An important observation is that diamond and graphite in ureilites have the same C isotopic composition (Vdovykin 1970; Grady et al. 1985). This does not necessarily mean that the ureilite diamonds were produced by high-pressure conversion of graphite. Although the isotopic fractionations between the starting material and the diamond produced by chemical vapor deposition (CVD) were much larger (e.g., Derjaguin and Fedoseev 1973) than the isotopic fractionation between graphite and the diamond produced at high pressure, no isotopic difference between graphite and diamond should be expected if they were deposited at the same time. This is because the isotopic separation occurs between the plasma and vapor phases (e.g., Chu et al. 1990, 1991). Therefore, the comparison of $\delta^{13}\text{C}$ values between graphite and diamond cannot explain the origin of diamonds in ureilites.

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