Isotopic ratios of carbonaceous materials incorporated in olivine crystals from the Hualalai Volcano, Hawaii - An approach to mantle carbon

SHUICHI WATANABE, KAZUNOBU MISHIMA and SADA0 MATSUO

Department of Chemistry, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152, Japan

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Carbon dioxide and graphitic carbon in olivine crystals from dunite nodules in the 1801 lava flow of the Hualalai Volcano, Hawaii were extracted by three methods, i.e., the pyrolysis under oxygen atmosphere, the ball-milling and the dissolution with hydrochloric acid. It is concluded that most of CO₂ extracted by the oxidative pyrolysis was derived from fluid inclusions, by comparing the isotopic ratios of CO₂ released by the oxidative pyrolysis and the ball-milling. Graphitic carbon was recovered from the evaporation residue after olivine crystals were dissolved in hydrochloric acid.

The averaged concentration of CO₂ extracted by the oxidative pyrolysis was 0.87 μ mole/g and $\delta^{13}\text{C}$ value was -3.2‰ . These of graphitic carbon were 0.51 μ mole/g and -26.9‰ , respectively. No appreciable amount of hydrogen-bearing species such as H₂, H₂O, CH₄, higher hydrocarbons and H₂S was detected in olivine crystals by both the oxidative pyrolysis and the ball-milling. Assuming all the extracted carbon is present in fluid inclusions in olivine crystals and the disproportionation reaction of CO ($2\text{CO} \rightarrow \text{CO}_2 + \text{C}$) has occurred in inclusions, we conclude that the major carbon-bearing species in the mantle beneath the Hawaiian Islands are CO and CO₂, and the CO/CO₂ ratio is estimated to be about 3 on the basis of the experimental data and that the $\delta^{13}\text{C}$ value of the carbon in upper mantle below the Hawaiian Islands is around -12‰ . Some additional data on Japanese olivines suggest that the $\delta^{13}\text{C}$ value of the mantle carbon may not be unique throughout the mantle.

INTRODUCTION

A number of studies have been attempted to determine the isotopic composition of the juvenile carbon. The $\delta^{13}\text{C}$ values of -8 to -5‰ found for carbonatite, diamond and carbonate in kimberlite have been believed to represent the juvenile or deep-seated carbon (HOEFS, 1978). Some diamonds, however, are much depleted in ^{13}C (e.g., SMIRNOV, *et al.*, 1979). DEINES (1980) could not find an adequate model that is compatible with the wide range of $\delta^{13}\text{C}$ of diamonds. Low $\delta^{13}\text{C}$ values have been found for reduced carbon in a variety of igneous rocks (e.g., CRAIG, 1953 and HOEFS, 1973). In particular, it is remarkable that reduced carbon in mafic and ultramafic rocks (FUEX and BAKER, 1973) and in Icelandic magmatic rocks (GALIMOV and GERASIMOVSKIY, 1978) have much lower $\delta^{13}\text{C}$ values, -30 to

-20‰ , than that of the so-called juvenile carbon.

PINEAU *et al.* (1976) found that the $\delta^{13}\text{C}$ value of CO₂ obtained by crushing fresh basalt of the Mid-Atlantic Ocean Ridge was -7.6‰ , but that of CO₂ released by stepwise heating after crushing was more depleted in ^{13}C . They attributed the difference to the isotopic fractionation during the outgassing process. The $\delta^{13}\text{C}$ value of CO₂ in volcanic gases from the Afar area, Ethiopia is about -6‰ (ALLARD, 1979) and is almost the same as that of the CO₂ extracted by crushing the fresh MORB.

JUNGE *et al.* (1975) assumed the $\delta^{13}\text{C}$ value of carbon in the upper part of the earth to be -4.5‰ by the material balance of carbonate carbon (0‰) and organic carbon (-25‰) with the abundance ratio of four to one. HOEFS (1973) also estimated the mean $\delta^{13}\text{C}$ value of the earth's crust and the upper mantle to be

around -7% on the basis of the material balance calculation of carbon in every possible reservoir.

The $\delta^{13}\text{C}$ value of the juvenile carbon of the earth may be related to that of meteoritic carbon which is in the range from -11.6 to -5.6% (SMITH and KAPLAN, 1970). However, the average $\delta^{13}\text{C}$ value of the mantle carbon with a variety of possible chemical forms such as CO_2 , CO, hydrocarbons, carbides, graphite, diamond and carbonates has not yet been adequately estimated. Especially, the vertical and lateral changes in the $\delta^{13}\text{C}$ value of the total carbon in the mantle is of great interest in connection with the mantle heterogeneity.

In this study, we adopted the olivine crystals of the Hualalai Volcano, Hawaii in order to determine the amounts and $\delta^{13}\text{C}$ values of carbon in different chemical forms. Based on the results obtained, $\delta^{13}\text{C}$ value of the mantle carbon in a hot spot was estimated.

EXPERIMENTAL

Samples and sample preparation Olivine crystals used in this study were obtained from dunite nodules in 1801 lava flow of the Hualalai Volcano, Hawaii. The Hualalai olivine has been studied by a number of researchers and was concluded to be transported from the mantle with an abundance of fluid inclusions consisting mostly of CO_2 (e.g., GREEN and RADCLIFFE, 1975).

Olivine crystals were hand-picked from dunite nodules crushed into the size of about 20 mesh. In order to avoid the contamination of carbon, we did not use heavy liquid to separate minerals. The collected crystals were treated with 6N HCl and 6N HNO_3 to remove surface contaminants, and washed several times with distilled water in a ultrasonic bath. After drying at about 100°C , the crystal grains were subjected to subsequent chemical treatments.

Procedure of carbon extractions Major chemical species of carbon included in olivine crystals have been known to be CO_2 and graphitic

or elemental carbon according to previous studies (e.g., ROEDDER, 1965, and FREUND *et al.*, 1980). For the extraction of carbon-bearing species, three methods have been applied, i.e., pyrolysis in oxygen atmosphere, ball-milling, and dissolution with hydrochloric acid.

CO_2 extracted by these methods was collected after purification in a MacLeod gauge modified for a small amount of CO_2 to determine the amount of CO_2 . The $^{13}\text{C}/^{12}\text{C}$ ratio was determined by a mass spectrometer, MM602C. The $^{13}\text{C}/^{12}\text{C}$ ratio is presented by $\delta^{13}\text{C}$ (‰) relative to the $^{13}\text{C}/^{12}\text{C}$ ratio of the Pee Dee Belemnite (PDB).

a) *Oxidative pyrolysis* This method was intended to extract total carbon in olivine crystals. The basic principle of this method is the oxidative destruction of the structure of olivine crystals under a designated oxygen partial pressure. The oxidation of Fe^{II} in the fayalite component of olivine brings about partial destruction of the crystal lattice, and gases incorporated in the destructed area are released. In this process, even reduced form of carbon is expected to be recovered in the form of CO_2 .

Approximately three grams of the pretreated olivine crystals was placed in a clean quartz tube and heated up to 850°C using a resistance furnace in vacuum for about 20 hours. Some contaminants and volatiles contained in a small amount of glass attached to crystal grains, which could not be separated by hand-picking are expected to be removed in this step. Fluid inclusions in crystals did not decrepitate under this condition (ROEDDER, 1965).

The clean oxygen gas evolved from CuO at $1,000^\circ\text{C}$ (SAKAI *et al.*, 1976) was introduced into the reaction tube. In the oxygen atmosphere of about 100 Torr, olivine crystals were kept at $1,000^\circ\text{C}$ for 20 to 24 hours.

The oxygen gas was then absorbed in $\text{Cu}_2\text{O}-\text{CuO}$ at 700°C to reduce p_{O_2} below 10^{-2} Torr, so that the collection of CO_2 extracted from olivine crystals was facilitated. The extracted gases were composed of CO_2 and H_2O . No SO_2 and SO_3 were detected mass spectrometrically

in the gases. The CO_2 was separated from H_2O by passing the gases through a dry ice-alcohol trap several times.

b) *Ball-milling* The purpose of this method is to collect CO_2 from the fluid inclusions and to compare its $\delta^{13}\text{C}$ value with that of CO_2 extracted by the oxidative pyrolysis to which a contribution of graphitic carbon is suspected.

A ball-mill designed by KITA (1981) was used in this study. The ball-mill consists of a Pyrex glass tube and an alumina ball.

About four grams of the pretreated olivine crystals was placed at the bottom of the tube with an alumina ball and evacuated at 300°C until detectable gas release stopped. The olivine crystals were then crushed by manual shaking of the mill for an hour at room temperature and the volatiles released were recovered while heating the mill externally at 300°C . After CO_2 was purified by trap works, its amount and $^{13}\text{C}/^{12}\text{C}$ ratio were measured.

c) *Dissolution method* The graphitic or non-volatile carbon in crystals was extracted exclusively by this method. One to two grams of olivine crystals was weighed in a quartz tube and pretreated by the same procedure as in the oxidative pyrolysis. 25 ml of conc. hydrochloric acid was introduced by distillation in vacuum into the tube which contained olivine crystals. The tube was kept in a water bath at 70 to 80°C for 3 days. After dissolution, the solution was evaporated in vacuum at about 70°C . In this step, gaseous carbon species derived from fluid inclusions and carbonate were removed together with HCl , H_2O and H_2S from sulfides, if any. The evaporation residue was preheated at 300°C for about 12 hours in vacuum to dryness and then oxidized at $1,000^\circ\text{C}$ in the oxygen atmosphere of about 100 Torr for more than 6 hours to recover graphitic carbon in the form of CO_2 . These steps were performed without breaking the vacuum. The evolved CO_2 was separated from other volatiles. HCl and Cl_2 were produced by thermal decomposition of the residue during oxidation. The gas including HCl and Cl_2

was circulated through CuO at 700°C to separate HCl and Cl_2 from CO_2 . HCl and Cl_2 were converted to CuCl_2 with the evolution of H_2O and O_2 on the surface of CuO at 700°C and separated from CO_2 . Negligible amount of CO_2 was recovered when $0.18\mu\text{mole}$ of pure HCl gas was circulated through CuO at 700°C . The amount and $\delta^{13}\text{C}$ value of purified CO_2 were measured.

RESULTS AND DISCUSSION

The dissolution method The content and $\delta^{13}\text{C}$ value of carbon extracted by the dissolution method are given in Table 2. The graphitic carbon content ranged from 0.4 to $0.6\mu\text{mole/g}$ and the $\delta^{13}\text{C}$ value was in the range from -29 to -26‰ . The $\delta^{13}\text{C}$ values are similar to those of the non-carbonate carbon of mafic and ultramafic rocks of -27 to -22‰ found by FUEX and BAKER (1973) and those of reduced form of carbon in Icelandic magmatic rocks of -32.6 to -24.5‰ given by GALIMOV and GERASIMOVSKIY (1978). The average values of the content and $\delta^{13}\text{C}$ of graphitic carbon were $0.51\mu\text{mole/g}$ and -26.9‰ , respectively.

The oxidative pyrolysis As given in Table 2, the average values of the content and $\delta^{13}\text{C}$ of CO_2 recovered by the oxidative pyrolysis were $0.87\mu\text{mole/g}$ and -3.2‰ , respectively.

The diffusion coefficient of O_2 gas in forsterite, which is estimated by extrapolation of the result reported by REDDY *et al.* (1980), is $1.9 \times 10^{-18} \text{cm}^2/\text{sec}$ in our experimental condition of $1,000^\circ\text{C}$. YUND *et al.* (1981) estimated that the diffusion coefficient of O_2 in albite

Table 1. Result of carbon extraction by pure heating and oxidative pyrolysis of run No. 4

Temperature ($^\circ\text{C}$)	C content ($\mu\text{mole/g}$)
200 - 850	0.27
850 - 1,000	0.12
1,000 - 1,100	0.04
1,000*	0.67

* In oxygen atmosphere about 100 Torr.

Table 2. Results of carbon extraction by the three methods

Method	C content ($\mu\text{mole/g}$)	$\delta^{13}\text{C}_{\text{PDB}}$ (‰)
Oxidative pyrolysis		
No. 1	0.90	-3.5
No. 2	0.95	-2.6
No. 3	0.94	-4.0
No. 4*	0.67	-2.6
av.	0.87	-3.2
Ball-milling		
No. 1	0.20	-4.1
No. 2	0.18	-5.5
Dissolution method		
No. 1	0.54	-25.8
No. 2	0.38	-25.6
No. 3	0.50	-27.3
No. 4	0.60	-29.0
av.	0.51	-26.9

* After stepwise heating.

along a dislocation core was five orders of magnitude greater than through the crystal lattice. Even if the diffusion coefficient of O_2 in

forsterite crystal of $2 \times 10^{-13} \text{ cm}^2/\text{sec}$ is assumed, the range of diffusion of O_2 is only several μm in a week. The diffusion of O_2 is so slow that the complete oxidation of Fe^{II} in the crystal is impossible under our experimental condition.

The powder X-ray diffraction analysis also supports the incomplete oxidation. There was no remarkable difference in the diffraction patterns between the original and the treated olivine in oxygen atmosphere at $1,000^\circ\text{C}$. Two minor differences, however, were detected, i.e., a weak diffraction due to hematite appeared and the diffraction pattern of the treated olivine shifted to that of pure forsterite. It is concluded by these observations that the crystal structure of olivine after oxidative pyrolysis was not drastically disturbed, because its lattice structure was retained, though a part of fayalite component was oxidized. Microscopic observation clearly indicated the oxidation of Fe^{II} . The actual size of a part which turned black by the formation of hematite was larger than the size

Fig. 1-a

expected from the range of O_2 diffusion.

It is conceivable, however, that oxidation takes place along dislocations or structural weakness in olivine crystals. As seen in Fig. 1-b and 1-c there are many cracks, channels and voids which connect several inclusions. The voids should have been formed by decrepitation of fluid inclusions through structural weakness caused by oxidation, so that gaseous components were more effectively extracted through these cracks and channels than in the case of ball-milling. Since the repeated oxidative pyrolysis of an identical sample gave negligible amount of CO_2 , we may conclude that the recovery of CO_2 from fluid inclusion was complete.

Fluid inclusions in olivine crystals decrepitate above $1,200^\circ C$ (ROEDDER, 1965). Some volatiles incorporated in basaltic glass can be released even below $1,000^\circ C$ (DELANEY *et al.* 1978). As given in Table 1, the amount of CO_2

extracted in vacuum decreased with increasing temperature. This suggests that the CO_2 thus collected can be derived mostly from surface contaminants of olivine crystals. The $\delta^{13}C$ values of CO_2 extracted from runs Nos. 1, 2 and 3 in vacuum up to $850^\circ C$ were centered at -23‰ , which also indicates that this CO_2 was derived mostly from organic carbon on the surface of crystals and/or in the glassy part attached to the crystal.

The average $\delta^{13}C$ value of CO_2 obtained by the oxidative pyrolysis was -3.2‰ (Table 2). This value is much higher than that of the carbon extracted by the dissolution method and is close to that of CO_2 collected by the ball-milling to be mentioned in the next section (see Table 2). These results indicate that carbon-bearing species extracted in the form of CO_2 by the oxidative pyrolysis contain little graphitic carbon.

The gas pressure of inclusions in the Hualalai

Fig. 1-b

olivine crystals has been estimated by MURCK *et al.* (1978) to be 3.4 kbar if entrapped at 1,200°C. When the release of CO₂ from inclusions is made by decrepitation through structural weakness, as mentioned previously, a jet-like stream of CO₂ is expected. After CO₂ is released, O₂ of 100 Torr penetrates through crooked channels into the interior of crystal grains. The penetration process of O₂ may have been sluggish, so that the oxidation of graphitic carbon present in the crystal was not effectively made.

Water and hydrocarbons in fluid inclusions should have been recovered together with CO₂ by this method. The amount of water extracted by this method, however, was almost the same as that of the blank run. As hydrogen in hydro-

carbons was converted to water and collected together with the original water, our result indicates that fluid inclusion in the Hualalai olivine crystal contains neither water nor hydrocarbons in detectable amount.

The ball-milling The amount and $\delta^{13}\text{C}$ values of CO₂ released from fluid inclusions are given in Table 2. Since CO₂ exists in fluid inclusions, it is worthy to compare its $\delta^{13}\text{C}$ value with that extracted by the oxidative pyrolysis.

The $\delta^{13}\text{C}$ values of CO₂ extracted by the ball-milling are -4.1 and -5.5‰ and lower by 1 to 2‰ as compared with those of the oxidative pyrolysis. It cannot be made clear whether or not this slight difference is due to isotopic heterogeneity of inclusions. This result,

Fig. 1-c

- Fig. 1. a) Photomicrograph of the original olivine crystal obtained from a dunite nodule in the Hualalai Volcano, Hawaii. Many inclusions are observed in the crystal.
 b) Photomicrograph of an olivine crystal after oxidative pyrolysis. Many cracks and channels are formed with partial oxidation in the olivine crystal.
 c) Channels and voids in an oxidized olivine crystal which connect several inclusions.

however, indicates that most of the CO_2 extracted by the oxidative pyrolysis should be derived from fluid inclusions.

A carbon-bearing species such as calcite decomposes on heating. The calcite formed at high temperature under isotopic exchange equilibrium with CO_2 has about the same isotopic ratio or slightly depleted in ^{13}C as compared with gaseous CO_2 (BOTTINGA, 1969). If calcite re-equilibrates with CO_2 at low temperature, calcite would be enriched in ^{13}C . When CO_2 from this calcite contributes to the CO_2 extracted by the oxidative pyrolysis, the $\delta^{13}\text{C}$ value of CO_2 extracted by the ball-milling should be lower than that by the oxidative pyrolysis.

The $\text{H}_2\text{O}/\text{CO}_2$ ratio obtained by the ball-milling was also too low to give a definite value for the Hualalai sample. It is evident that the Hualalai olivine has been crystallized under extremely water-deficient conditions.

The existence of graphitic carbon in fluid inclusions FREUND *et al.* (1980) suggested that atomic carbon can be retained in the lattice of olivine crystals on the basis of the study of synthetic forsterite and naturally occurring olivine crystals by a laser-induced mass spectrometry. On the other hand, MATHEZ and DELANEY (1981) proved the presence of carbonaceous materials in submarine basaltic glass and mantle-derived peridotite nodules in alkali basalt using electron microprobe techniques. Carbonaceous materials in peridotite nodules were detected in microcracks, grain boundaries and on the wall of fluid inclusions. They suggested that the carbonaceous materials consisted mostly of graphite and small amounts of organic matter.

Our observations by SIMS (Secondary Ion Mass Spectrometer) using O_2^+ beam as primary ions supported the existence of carbonaceous materials inside inclusions, because the more intense ion current at M/e of 12 (i_{12}) was detected in the area where the number density of inclusions was higher. The ion current of $^{24}\text{Mg}^{2+}$ overlaps that of $^{12}\text{C}^+$, so that we calculated

$i_{12\text{C}^+}$ to be equal to i_{12} (measured) $- i_{24\text{Mg}^{2+}}$ on the assumption that $i_{24\text{Mg}^{2+}}/i_{25\text{Mg}^{2+}} = i_{24\text{Mg}^{2+}}/i_{25\text{Mg}^{2+}}$. $i_{12\text{C}^+}$ can be estimated by measuring i_{12} , $i_{12.5}$, i_{24} and i_{25} . It has been proved that CO_2 in fluid inclusions does not contribute to i_{12} peak, even when an inclusion is broken by the primary ion beam.

The existence of CO in the mantle The existence of graphitic carbon in inclusions has been proposed first by ROEDDER (1965) and later by MATHEZ and DELANEY (1981) as the product of disproportionation reaction of CO, originally present in inclusions, $2\text{CO} \rightarrow \text{C} + \text{CO}_2$. If all the carbon obtained by the dissolution method (exclusively graphitic carbon) are the product from CO, the original CO/CO_2 ratio when inclusions of the Hualalai olivine were formed can be estimated roughly to be 3 on the basis of the average values of CO_2 and C contents (refer to Table 2). The equilibrium ratio of CO/CO_2 calculated thermodynamically is 4 under the condition of $1,200^\circ\text{C}$ and p_{O_2} of 10^{-12}atm which was measured directly by SATO (1978) for the Hualalai olivine. Considering the error and uncertainty involved in both calculations, the estimated CO/CO_2 ratio and the equilibrium ratio should be said to agree with each other. This result suggests that CO is one of the major gaseous components, among carbon-bearing species in the mantle. The possibility that the graphitic carbon is the most abundant species in the mantle, however, can not be ruled out from the thermodynamic point of view.

Carbon isotopic composition in the mantle

Since the Hualalai olivine crystals are concluded to have been originated from the mantle (GREEN and RADCLIFFE, 1975), the $\delta^{13}\text{C}$ value of total carbon in the mantle beneath the Hawaiian Islands can be estimated to be -12‰ on the basis of the data given in this study with the assumption that the mantle CO/CO_2 ratio has been retained in the inclusions when they were formed. This value was calculated by the isotopic mass balance of carbon extracted by the

oxidative pyrolysis (averaged values, $0.87 \mu\text{mole CO}_2/\text{g}$, -3.2‰) and by the dissolution method (averaged values, $0.51 \mu\text{mole C/g}$, -26.9‰).

As mentioned earlier, the gas pressure of inclusions in the Hualalai olivine crystals was estimated to be 3.4 kbar by MURCK *et al.* (1978). The depth assumed by the pressure of inclusions (about 11 km) is still within the crust of that area (EATON and MURATA, 1960), and the Hualalai nodules were deformed during passage to the surface (GREEN and RADCLIFFE, 1975). It is possible that the crustal carbon contamination to and loss of original carbon-bearing species from the inclusion occur during the ascending process. The crustal contamination, however, is inferred to have been small, because the pressure of inclusion should have been about 5 kbar before the disproportionation of CO in the inclusion took place during the cooling process. This estimated pressure corresponds to the boundary between the crust and the mantle underneath the Hawaii area. An extreme deficiency of water in fluid inclusions may indicate that the accumulation of the volatiles occurred in a relatively small and limited region in this particular area.

Our estimated $\delta^{13}\text{C}$ value of carbon of in the mantle -12‰ is lower by about 5‰ than the $\delta^{13}\text{C}$ value of the so-called juvenile carbon. The $\delta^{13}\text{C}$ value of CO_2 of volcanic gases from the lava lake of Aloi crater was approximately -15‰ (FRIEDMAN and O'NEIL, 1971), which indicates that CO_2 in the lava lake is fed with only slight contamination of crustal carbon.

Based on our results, we may estimate the $\delta^{13}\text{C}$ values of CO_2 and CO originally present in the mantle below the Hawaiian Islands. The results of calculation is schematically shown in Fig. 2. For this calculation, isotopic exchange equilibrium was assumed between CO and CO_2 at $1,200^\circ\text{C}$ when CO and CO_2 were entrapped in inclusions, so that $\delta^{13}\text{C}_{\text{CO}_2} - \delta^{13}\text{C}_{\text{CO}}$ was taken to be 5.5‰ (RICHEL *et al.*, 1977). Since the $\delta^{13}\text{C}$ value of the total carbon has been estimated to be -12.0‰ , those of the originally present CO and CO_2 were calculated to be -13.4 and -7.9‰ respectively. During the cooling process CO disproportionated into graphitic carbon and CO_2 . According to our calculation, no isotopic exchange equilibrium has been established between CO, CO_2 and graphitic carbon, because $\delta^{13}\text{C}_{\text{CO}_2} > \delta^{13}\text{C}_{\text{graphite}} > \delta^{13}\text{C}_{\text{CO}}$ (BOTTINGA, 1969 and RICHEL *et al.*, 1977), if the isotopic exchange equilibrium was established.

No information on isotopic fractionation has been reported so far with respect to this disproportionation process. We can not go further to discuss the kinetic mechanism that controls the isotopic fractionations.

CONCLUDING REMARKS

The Hualalai olivine is peculiar in its extraordinarily abundant fluid inclusions consisting mostly of CO_2 . This was the major reason why we adopted the Hualalai olivine for the exploitation of technique to extract a variety of carbon from the mantle substance. Actually, most of olivines with different localities and occurrences we examined contain almost no detectable amount of fluid inclusions. A certain amount of volatiles including H_2O has been

Fig. 2. Changes in amount and $\delta^{13}\text{C}$ of carbon-bearing species between the original mantle substance and present fluid inclusions. Figures in parentheses are the calculated value.

Table 3. Results of carbon extraction from Japanese olivines

Sample locality	Method	C content ($\mu\text{mole/g}$)	$\delta^{13}\text{CPDB}$ (‰)
Takashima	Oxidative pyrolysis	0.12	-14.3
	Dissolution	0.20	-29.4
Ichinomegata	Oxidative pyrolysis	n.d.	—
	Dissolution	0.14	-26.1

extracted from Ichinomegata olivine in Akita Pref., Japan by SUZUOKI *et al.* (1975). They concluded, however, that volatiles were derived mostly from glass inclusions in the olivine crystal. We have extracted a significant amount of H_2O from orthopyroxene in the peridotite nodule from the same locality (to be published elsewhere). In this case, $\text{H}_2\text{O}/\text{CO}_2$ ratio was quite high. The quite low $\text{H}_2\text{O}/\text{CO}_2$ ratio found in the Hualalai olivine needs to be elucidated by the future study.

Some additional results on carbon extraction from Japanese olivines are given in Table 3. As seen in Table 3, the Ichinomegata olivine gave no detectable amount of CO_2 by the oxidative pyrolysis. On the other hand, the graphitic carbon extracted by the dissolution method was measurable even for the $\delta^{13}\text{C}$ value which was the same as that of the Hualalai olivine. The other olivine sample separated from the olivine nodule of alkali-olivine-basalt in Takashima, Kyushu, Japan was characterized by a low $\delta^{13}\text{C}$ value of CO_2 extracted by the oxidative pyrolysis, yet the $\delta^{13}\text{C}$ value of graphitic carbon was within the range of graphitic carbon from the Hualalai olivine.

Combining these results with that of the Hualalai, we may conclude that the mantle is not homogeneous with respect to the carbon isotopic composition. If this is the case, the recycling of carbon with different chemical forms and $\delta^{13}\text{C}$ values in the upper part of the earth driven by global tectonics is expected to be realistic.

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