Stable Isotope Analysis of Small Amount of Carbon Dioxide and Its Application to the Microscale Isotopic Zoning of Graphite Crystals in Metamorphic Rocks

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A conventional dynamic mass spectrometer with an inlet system specially modified for microscale samples was used to measure carbon isotopic ratio of subsamples within individual graphite crystals collected from Hida metamorphic belt, central Japan. The graphite crystals with three different occurrences *i.e.*, in pelitic gneiss, skarn deposit, and crystalline limestone were examined for their isotopic zonation. Single graphite crystals collected from pelitic gneiss and hedenbergite skarn deposit has homogeneous isotopic distribution, whereas composite graphites of marble show complicated zonation which may imply the evolution of the metamorphic fluid during metamorphism.

1. Introduction

The Nier-McKinney-type mass spectrometers originally developed about half a century ago, have been improved to a great extent for precision and resolution with respect to stable isotope measurements. Introduction of a triple collector system has made possible to determine simultaneously carbon and oxygen isotopic compositions on a CO₂ sample. Commercially available mass spectrometers are now capable of measuring $\delta^{13}\text{C}$ values with precision as high as 0.01‰. The high level of precision is due to a dual inlet system and continuous gas pumping that maintains a stable ion beam. A statically operated mass spectrometer which has been recently developed for the measurements of extraterrestrial materials can provide isotopic analysis of ultra-small sized samples down to picomole of CO₂

and N₂.¹⁾ The instrument is capable of measuring $\delta^{13}\text{C}$ values of an individual CO₂ gas with a sample size of 10 pmol with a precision (1 σ) of $\pm 3\%$.²⁾

Ion probe mass spectrometry has been used to measure isotope ratio of carbon in extraterrestrial samples.^{3, 4)} The precision, however, is still unsatisfactory ($\pm 10\%$ at most).

The present paper describes some improvements and modifications of the microscale determination of carbon and oxygen isotopic compositions, including an easy handling of small-sized carbon dioxide. We apply these techniques to the microscale isotopic zoning in graphite crystals in metamorphic rocks. If the method for the isotopic determination of a small sample with a size as small as 0.1 μmol and high precision within 0.05‰, we will be able to discuss the behavior of isotopes in size of a single crystal

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in many crystalline rocks and/or within a single crystal *i.e.*, isotopic zoning in minerals.

2. Analytical Methods for a Microscale Sample

High precision of isotopic determination of microscale carbon dioxide using the conventional dynamic mass spectrometer can be obtained by adopting the following improvements in the preparation procedures and optimization of measurements; a) micro-inlet system for a small sample, b) correction for isotopic fractionation during capillary leak, c) pressure effect on isotopic ratios, and d) purification of carbon dioxide.^{5, 6)}

2.1. Micro-inlet system for small sample

A very small carbon dioxide sample is introduced to the mass spectrometer through the inlet system shown in Fig. 1. The volume of the sample inlet system can be varied from about 80 ml to 0.01 ml by changing the mercury level. The sample CO₂ gas is condensed around the cold finger using liquid nitrogen. Frozen CO₂ can easily vaporize with touching by mercury. With this inlet system, the dead volume of the inlet system is near zero, and the amount of a sample gas can be calculated from the volume and pressure of gas. It is also possible to monitor the rate of sample reduction during analysis.

Fig. 1. Schematic presentation of inlet system for a small amount of carbon dioxide slightly modified from Wada *et al.*⁵⁾ The gas reservoir is made of Pyrex glass. Mercury reservoir with bellows is made of stainless steel. The two reservoirs are connected with a flexible glass-end tube.

2.2. Isotopic fractionation through capillary leak

For the microscale sample, most of the sample gas will flow into mass spectrometer through the capillary leak during the isotopic analysis. The ion-beam intensity of a given mass number is dependent on the amount of gas leaked through the capillary under a constant ion source condition. The gas flow rate gives the limit of the sample amount that can be analyzed. In order to minimize the isotopic flow rate with a satisfactory precision of isotopic analysis (standard deviation better than 0.02‰), we should also minimize the isotopic fractionation during gas flow through the capillary leak. Therefore, it is necessary to maintain the gas flow to be viscous flow and the gas pressure constant. When the pressure of gas reservoir is 60 mmHg, the ion beam intensity of mass-45 is 1.2 volt on our mass spectrometer (MAT-250 instruction by Finnigan MAT Co., Ltd., recommends the ion beam intensity of mass-45 is about 8 volt) and the flow rate of gas leak is 9.22 $\mu\text{l/hr}$. At this rate, there is quite small isotopic fractionation between CO_2 effluented and that of reservoir lower than 0.1‰ in carbon and oxygen isotopes. Consequently, the following conditions are usually adopted on the MAT-250 mass spectrometer at the Shizuoka University. Total emission is 1.0 mA, gas flow rate is 9.22 $\mu\text{l/hr}$, and gas pressure is 60 mmHg.

2.3. Pressure effect on isotopic ratios

The ion-beam intensity ratios of mass-45/mass-44 or mass-46/mass-44 of carbon dioxide is fundamentally dependent on the pressure. Under the conditions mentioned above, we can observe the variation of the recorded ratios with ion-beam intensities although the effect is

Fig. 2. Variation in carbon and oxygen isotopic ratio with the difference in ion-beam intensity (ΔE) of mass-45 (volt) between sample and reference gases. Solid circles connected with a dotted line indicate the apparent $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values with no offset. Open circles with a solid line indicate $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values with offsets set at +3.0 mV for mass-45 and +1.2 mV for mass-46.

small. This effect was called as "pressure effect" by Craig.⁷⁾ Conventionally, there is no problem for the pressure effect on a sample with a sufficient amount. For a very small sample, the pressure of sample gas reservoir considerably decreases during measurement. Such pressure effect usually can be cancelled by same rate of pressure decrease in the reference and sample gas reservoirs using constant volume of micro-finger traps. Alternatively, we could keep the pressure of a sample gas equal to that of the reference gas by adjusting the mercury level of the inlet system. However, it is not easy to control the pressure of a small gas sample strictly equal to that of the reference gas. When we analyze a small sample gas with respect to a large-sized reference gas, the apparent $\delta^{13}\text{C}$ value changes with decreasing the ion-beam intensity due to the pressure reduction of sample gas during analysis. As pointed out by Craig,⁷⁾ the pressure effect could be eliminated by setting

a small potential bias (offset) on the smaller beam amplifier. The magnitude of the offset value is an inherent property of a mass spectrometer and the value of the offset is mainly dependent on the ion-beam intensity. As shown in Fig. 2, the apparent $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values slightly changed with the difference of ion-beam intensity between sample and reference. Actually the apparent $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values change by about 0.3‰ for carbon and 0.4‰ for oxygen with respect to the difference of about 0.2 volt between sample and reference (the ion-beam intensity of mass-45 is about 1.2 volt). The strict value of the offset can be calculated in proportion to the pressure effect between the conditions without offset and with an arbitrary offset value. When the 3.0 mV offset is applied for mass-45 and 1.2 mV for mass-46, one can obtain constant $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values for the voltage drop of ion-beam intensity of mass-45 in sample by 0.2 volt. Both offsets are given on the potentiometer of zero adjustment of mass-45 and mass-46 amplifiers or on the calculation of ion-beam intensity ratio using personal computer by addition of the offset on the ion-beam intensity from which was already subtracted background.

2.4. Purification of carbon dioxide

Conventionally, carbon dioxide prepared from carbonates by reaction with concentrated phosphoric acid and those from graphite combusted with oxidation reagent contains a variable amount of impurities. The CO_2 gas is usually purified by trap work at the dry-ice temperature (-70°C). During the trap work with a constant time, a constant amount of water vapor is trapped on the liquid nitrogen trap and mixed with sample gas. In the

case of a very small sample, relative amount of water vapor with respect to carbon dioxide will increase and it appears that the water vapor affects the output of mass-45 by production of $[\text{HCO}_2^+]$ ion in the ionization chamber of a mass spectrometer. Therefore, it is necessary to remove water vapor completely from carbon dioxide sample. Use of the dry-ice alcohol trap is not enough, but the *n*-pentane/liquid nitrogen mixture (about -130°C) is cool enough to remove water vapor completely. Actually, the $\text{H}_2\text{O}-\text{CO}_2$ separation was performed by two *n*-pentane traps in series is used. An additional electro-frozen trap (about -95°C) is installed in this separation vacuum line in order to trap the water vapor removed.⁶⁾

Graphite sample is combusted with vanadium pentoxide *in vacuo* in Vycor glass tube at $1,100^\circ\text{C}$, for about 1 hour. The batch combustion method originally developed by Steurmer *et al.*⁸⁾ and Sofer⁹⁾ is suitable for a very small sample. Vanadium pentoxide used is pre-heated at the temperature of 500°C in the air to decompose any organic impurities. The amount of background carbon dioxide from the Vycor glass tube can be reduced by heating prior to use over 10 hours at $1,100^\circ\text{C}$ in the air. Even through this pre-heating procedure of V_2O_5 and glass tube, however, at maximum volume of about $0.1\ \mu\text{l}$ of carbon dioxide was found to evolve from the glass tube.¹⁰⁾ In order to obtain accurate isotopic determination with precision less than $\pm 0.1\text{‰}$, use of the sample CO_2 that is more than $10\ \mu\text{l}$ is highly recommended.

3. Previous Works on Carbon Isotopes of Graphite

Graphite is a common accessory miner-

al of metamorphosed pelitic rocks and marbles. Graphite has been also found in the oldest metamorphic rocks of sedimentary origin from Isua, Greenland, and may be a key mineral to study the origin of life on the Earth.¹¹⁾ Graphite is one of the most important materials to play a role of controlling the oxygen fugacity in the crust of the Earth.¹²⁾

The isotopic composition of graphite depends mainly on the origin of carbon (e.g., organic or hydrothermal). Carbon isotopic exchange can take place between graphite in marble and the coexisting carbonate during metamorphism, providing a calcite-graphite geothermometer.^{13~15)} Rumble and Hoering,¹⁶⁾ Duke and Rumble¹⁷⁾ and Duke *et al.*¹⁸⁾ studied the evolution of hydrothermal and metamorphic fluid under the constraint by the presence of graphite in the scale of millimeter to meter. Recently Wada¹⁹⁾ reported that isotopic zonings of graphite and calcite crystals in marble. For graphite, only a few micrometers of the outer rims of crystalline graphite depleted in ^{13}C which due to a later stage isotopic exchange with ^{13}C depleted source of carbon in metamorphic fluid. Arita and Wada²⁰⁾ reported the precise isotopic compositions of individual graphite crystals in marble and showed that the crystallite formed secondary on the substrata of flaky graphite has lower $\delta^{13}\text{C}$ value than that of the hexagonal flaky graphite. The carbon isotopic composition in crystalline graphite is believed to be very resistant to later phase exchange reactions, so the isotopic variations of microscale samples of graphite crystals may have a possible key for application of precise carbon isotopic thermometry and for evolution of the metamorphic fluid from which graphite precipitated.

Furthermore, we can easily subdivide a

single crystalline graphite into subsamples along the direction perpendicular to its *c*-axis with a splitting technique described by Wada.¹⁹⁾

4. Samples

We found single and composite graphite crystals in rock specimens collected from the Hida metamorphic belt, central Japan, and analyzed their microscale carbon isotopic zonation within the graphite crystals using the analytical method given above.

There are three types in the occurrence of flaky graphite. The first type of the graphite occurs in pelitic gneiss. The graphite is anhedral and is intercalated into silicate minerals. The second type occurs in hedenbergite skarn found in the Kamioka mining district.²¹⁾ This skarn deposit is formed by the pyrometasomatism in which the crystalline limestone is accompanied with an extensive Pb-Zn ore depositions. Furthermore, the crystalline limestone is believed to have been subjected to progressive metamorphism up to granulite facies before the pyrometasomatism.²²⁾ The third one is the graphite occurred in crystalline limestone which is ubiquitously found in the Hida metamorphic belt.

5. Results and Discussion

The carbon isotopic results of a single crystal of the AM05A collected from the Amo graphite mine, Kawai, Gifu Prefecture, are shown in Fig. 3. The $\delta^{13}\text{C}$ values of graphite collected from biotite gneiss are almost constant with the average of -16.70‰ (v. PDB). The source rocks of the graphite bearing gneiss are considered to be of sedimentary origin. The range of $\delta^{13}\text{C}$ variation of graphite in the Amo area is from -11 to -18‰ .²²⁾ These

Fig. 3. A sketch of a graphite crystal (AM05) collected from biotite gneiss, Amo area, Kawai, Gifu Prefecture. Numerical figures in parentheses indicate $\delta^{13}\text{C}$ (‰ v. PDB) for each subsample in Figs. 3~6.

Fig. 4. A sketch of a graphite crystals (HW 74072903) collected from the hedenbergite skarn deposits, Kamioka mining district, Gifu Prefecture.

$\delta^{13}\text{C}$ values are evidently lower than those of graphite in limestone and skarns which will be mentioned later, but higher than those of typical organic carbon in sediments ($\sim -25\text{‰}$). Such variation in pelitic gneiss may be due to carbon isotopic exchange reaction with some carbonate minerals in pelitic rocks and/or isotopic change of carbonaceous material by releasing methane during graphitization processes.

Isotopic results of a single crystal in hedenbergite skarn are shown in Fig. 4. The $\delta^{13}\text{C}$ values in subsamples of a single crystalline graphite are in narrow range from -3.32 to -3.95‰ . The outermost graphite gave a slightly lower $\delta^{13}\text{C}$ value

Plate 1. A scanning electron photomicrograph (SEM) of the composite crystal (TK03A) collected from Takataki, Unazuki area, Toyama Prefecture.

than that of the core. The average $\delta^{13}\text{C}$ value of graphite in skarn minerals of the Kamioka mining district were reported by Wada.²¹⁾ The isotopic variation of this single graphite crystal agrees with the average value of graphite in skarn and ore deposition reported by Wada.²¹⁾ He concluded that the origin of the graphite in skarn and ore minerals was the remnant of graphite in limestone during the pyrometasomatic mineralization by which the limestone was replaced with skarn and ores. The morphology of this type of graphite is usually expanded form in the direction of *c*-axis and having a loose layered structure. These features have never been observed in graphite in marble and pelitic gneiss. The surface of the graphite shows an irregular pattern which is probably due to oxidation during pyrometasomatic mineralization. Thus there is no remarkable isotopic change in the remnant of graphite during the retrogressive pyrometasomatism and maintained its original isotopic composition fixed during the progressive metamorphism.

Fig. 5. Sketch of a composite graphite crystal (TK03A) in a marble collected from Takataki, Unazuki area, Toyama Prefecture. Localities of subsamples within the sample (TK03A) are indicated by A through F. The second figure indicates the localities of subsamples when removing subsamples A, B, and D.

Two graphite samples collected from the Unazuki area, Toyama Prefecture have a composite crystal from which shows many stages of crystal growth (Plate 1). The isotopic composition of subsamples of the composite graphite (TK03) shows a remarkable feature of large variation (Fig. 5). The subsamples TK03-E, -C and -F selected from the same layer of the composite crystal show almost constant $\delta^{13}\text{C}$ value (-1.40 to -1.67‰), whereas the upper layers of the TK03 graphite are gradually depleted in ^{13}C with the lowest value of -5.23 at the top (A). This isotopic variation may be due to the isotopic evolution of the metamorphic fluid during the graphite crystal growth.

Fig. 6. A sketch of composite graphite crystal (TK03B) in a marble collected from Takataki, Unazuki area, Toyama Prefecture.

The other example of a composite crystal of graphite is shown in Fig. 6. It also shows a wide variation of $\delta^{13}\text{C}$ values (-0.60 to -3.26‰). In this sample, the isotopic variation within a single crystal is appreciable. The weighted average of this composite graphite is -1.33‰ . In the subsample 1 of this graphite (Fig. 6), the $\delta^{13}\text{C}$ value of the central part (1-3) was lowest of -3.26‰ .

It has been demonstrated by Arita and Wada²⁰⁾ that calcite and graphite in marbles of the Utsubo area of Hida metamorphic belt attained in an isotopic equilibrium at a high temperature stage of the metamorphism. Individual graphite studied by them is not of composite crystal but of single crystal. Isotopic results on the composite graphite shown in the present study clearly indicate that there should have been small-scale isotopic disequilibrium despite the high grade of metamorphic rocks of the host rocks.

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Keywords

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