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COMPARISON OF ^{14}C COLLECTED BY PRECIPITATION AND GAS-STRIP METHODS FOR DATING GROUNDWATER

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ABSTRACT

Dissolved inorganic carbon (DIC) in groundwater is used to estimate the residence time based on ^{14}C concentration. DIC is usually extracted by a gas-strip or precipitation ($SrCO_3$ or $BaCO_3$) method. In this study, gas-strip and precipitation methods of DIC were applied to both artificially prepared $NaHCO_3$ solutions and natural groundwater to estimate the certainty of the two methods for ^{14}C dating. ^{14}C values obtained by the gas-strip method for $NaHCO_3$ solutions with distinct salinity, DIC and ^{14}C concentrations were close to the theoretically predicted ^{14}C value based on the ^{14}C value of $NaHCO_3$ powder. Conversely, the ^{14}C value obtained by the precipitation method always showed higher values than the predicted values. The difference in ^{14}C value between gas-strip and precipitation methods was assumed to arise owing to contamination of modern carbon in the NaOH solution used in the precipitation method. The contamination of modern carbon derived from NaOH solution during precipitation was found to range from less than 1 mg/L to about 1 mg/L. The applicability of the precipitation method for groundwater should be considered carefully according to the DIC, ^{14}C concentration of groundwater and purpose of the study being conducted.

INTRODUCTION

The ^{14}C of dissolved inorganic carbon (DIC), which is one of the most powerful tools for dating groundwater samples, has been applied in many previous studies (Geyh 2000; Iwatsuki et al., 2000). DIC in water samples is usually extracted and collected by either a gas-strip method or a precipitation method. Both of these methods have frequently been used for groundwater studies (gas-strip method: Dulinski et al., 2013; Dorsett et al., 2011; Stewart 2012; precipitation method: Corcho et al., 2013; Sültenfuβ et al., 2010; Stewart 2012).

In the precipitation method, water samples are alkalinized with NaOH or ammonium followed by the addition of $BaCl_2$ or $SrCl_2$, after which DIC is precipitated as $BaCO_3$ or $SrCO_3$. These precipitation procedures are occasionally conducted during groundwater sampling in the field. This procedure enables the amount of samples to be reduced significantly, and facilitates the transport of the samples from the field to the laboratory. However, the precipitation might be contaminated by the alkaline solution because CO_2 readily dissolves in alkaline solutions (Aggarwal et al., 2014). In addition, it could be difficult to extract carbon from groundwater samples with very low DIC concentrations because sometimes precipitation could not be visually confirmed in such samples and this makes the collection of the precipitation difficult. Furthermore, precipitation sometimes might not quantitatively remove carbon due to interfering reactions (Minami and Takahashi, 2015). In such cases, ^{14}C might be fractionated. Possible contamination and potential ^{14}C fractionation need to be quantitatively determined to assess the reliability of the precipitation method in groundwater $DI^{14}C$ dating.

In the gas-strip method, water samples are acidified by phosphoric acid and DIC is collected as CO_2 (Atekwana and Krishnamurthy 1998). This method can be applied to a wide variety of groundwater samples, although they must be brought to the lab for processing. This can be the only method to collect DIC in cases where the precipitation method cannot be applied. To validate the method, the possibility of contamination during the gas-strip extraction and DIC recovery from solutions with low DIC concentration needs to be investigated.

In this study, the reliability of these two methods in the determination of ^{14}C groundwater ages are examined, with special attention given to potential contamination. To accomplish this: (1) a preliminary comparison of ^{14}C values obtained by the two preparation methods using a set of $NaHCO_3$ solutions was made, (2) contamination in sample preparations were identified, and (3) the two methods were applied to natural groundwater samples.

METHODS

(1) Preliminary comparison of ^{14}C values obtained by two preparation methods using $NaHCO_3$ solutions

Comparison of ^{14}C results obtained by the two preparation methods for $NaHCO_3$ solutions allows us to determine the precision and accuracy of each preparation method. This is accomplished by preparing ^{14}C DIC standards, given the DIC concentrations of the solutions and ^{14}C content of the $NaHCO_3$ powder. Four types of $NaHCO_3$ standard solutions were prepared (Table 1), and both the gas-strip and precipitation methods were applied to extract and collect DIC from them. The ^{14}C content of the DIC extracted from the solutions was measured by accelerator mass spectroscopy (AMS). Solutions 1–4 were prepared to simulate the following: 1) an old (~25,000 B.P.) groundwater with low salinity, 2) younger (~10,000 B.P.) groundwater with low salinity, 3) younger groundwater with low DIC and salinity, and 4) younger groundwater with high salinity. For each solution, two samples, one obtained by gas-strip and one by precipitation were compared.

All procedures except weighing the $NaHCO_3$ powder were carried out in a glove box (GB) under an Ar atmosphere. A CO_2 absorbent (Lithoryme: Allied Healthcare Products, St. Louis, MO, USA) was placed in the GB to ensure the CO_2 concentration was low. Deionized water was placed in the GB and purged with Ar gas for at least 12 hours to reduce the DIC in the water. A fraction of this water was used for the DIC measurements after purging. $NaHCO_3$ powder was subsequently added to the purged water and stirred until completely dissolved. A commercial $NaHCO_3$ powder was used for Solution 1, while a second batch of $NaHCO_3$ was prepared by bubbling air through NaOH for Solutions 2–4. In the case of Solution 4, a simulated sea water (SSW) was prepared by adding NaCl, KCl, $MgSO_4$ $7H_2O$, $MgCl_2$ $6H_2O$ and $CaCl_2$ into the purged water and a $NaHCO_3$ solution was prepared by dissolution of $NaHCO_3$ into SSW.

The four $NaHCO_3$ solutions were sent to Beta Analytic (Miami, FL, USA). Two sample bottles were used for the gas-strip method, while the remaining samples were extracted by precipitation method for ^{14}C analyses. Both the DIC collection and ^{14}C measurements were conducted by Beta Analytic.

(2) Identification of contamination during sample preparation

Preliminary comparison of ^{14}C in the $NaHCO_3$ solutions showed the possibility of significant contamination with modern carbon during the precipitation procedure (see Results and Discussion). Therefore, a gas-strip line was employed to test NaOH and $SrCl_2$ solutions used in the DIC precipitation procedure. This step was taken to identify the source and amount of contamination associated with the precipitation method. NaOH and $SrCl_2$ solutions were prepared as follows. Dissolved gas in deionized water was purged with Ar in a GB, as described above. Two types of NaOH solutions were then prepared, one under atmospheric conditions and the other in the GB with the addition of granular NaOH to deionized water. $SrCl_2$ solutions were subsequently prepared by adding $SrCl_2$ reagent to deionized water under atmospheric conditions.

DIC extraction using the gas-strip method was optimized by application of a vacuum gas-strip line (Fig.1) in JAEA (Japan Atomic Energy Agency) and the following procedure was established. Prior to sample preparation, the air in the gas-strip line was removed under a vacuum of less than 0.1 Pa. Next, 2 mL of phosphoric acid was added to the water sample to convert the DIC to CO_2 gas. CO_2 gas was subsequently stripped from the water sample by bubbling with carrier gas (pure N_2 or Ar) at a flow rate of 500 cc/min and collected in a cold trap of liquid N temperature. After 5 minutes of gas circulation, the carrier gas was evacuated and trapped CO_2 was purified and directed into a glass tube at the gas sampling port. The yield of CO_2 relative to DIC in the water samples was 90%. The DIC concentration in NaOH and $SrCl_2$ solutions were estimated by the gas (CO_2) pressure in the gas-strip line.

(3) Application of the 2 methods to natural groundwater samples

Both the precipitation and gas-strip methods were applied to natural groundwater samples to identify ^{14}C differences between each method. Groundwater samples were obtained from depths of 200–500 m in granitic rock at the Mizunami Underground Research Laboratory (MIU), Gifu Prefecture, Japan (Fig.2). The groundwater chemistry was Na-Ca-Cl or Na-Cl dominant with a salinity of less than 1 g/L (Iwatsuki et al. 2005; 2015). Groundwater samples were collected into 1 L airtight glass vessels for precipitation. Next, 10 mL of 5N NaOH solution and 10 mL of 2N $SrCl_2$ solution were added into the vessel to precipitate $SrCO_3$, after which the samples were stored at 4°C. Precipitated $SrCO_3$ was collected into small sample vessels by pipette in a CO_2–free glove box for freeze-dry storage. In parallel, groundwater samples for gas-strip method preparation were collected into 0.5 L airtight glass vessels and stored at 4°C, while CO_2 gas was collected by the aforementioned gas-strip method for ^{14}C measurement. In the case of natural samples, the DIC collection was carried out in Tono Geoscience Center of JAEA and ^{14}C was measured by AMS in JAEA (JAEA-AMS-TONO).

RESULTS AND DISCUSSION

Preliminary comparison of ^{14}C values obtained by both preparation methods using $NaHCO_3$ solutions

^{14}C and ^{13}C values of the $NaHCO_3$ powder used for Solution 1 were measured twice and the results were 0.5 pMC, −18.6‰ and 0.4 pMC, −17.1‰, respectively. The ^{14}C and ^{13}C values of $NaHCO_3$ powder prepared for solutions 2–4 were also measured twice and found to be 26.6 pMC, −18.9‰ and 26.1 pMC, −18.1‰, respectively. $NaHCO_3$ solutions were prepared by dissolving $NaHCO_3$ powders into deionized water or SSW. Therefore, the ^{14}C in the DIC sample solutions can be calculated by equation (1):

$$ {}^{14}\mathrm{C}_{\mathrm{s}} = \frac{{}^{14}\mathrm{C}_{\mathrm{p}} \times [\mathrm{C}]_{\mathrm{p}} + {}^{14}\mathrm{C}_{\mathrm{w}} \times [\mathrm{C}]_{\mathrm{w}}}{[\mathrm{C}]_{\mathrm{p}} + [\mathrm{C}]_{\mathrm{w}}} \qquad (1) $$

where, ${}^{14}C_w$ is the ${}^{14}C$ value (pMC) of DIC in the deionized water or SSW used for preparation of the $NaHCO_3$ solutions, ${}^{14}C_p$ is the ${}^{14}C$ value of $NaHCO_3$ powder, $[C]_p$ and $[C]_w$ are the concentrations of DIC (mg/L) provided from $NaHCO_3$ powder and DIC in the deionized water, respectively, and $[C]_p$ is found from the difference between the DIC concentration of the sample solutions and $[C]_w$.

${}^{14}C_w$ is considered to be the ${}^{14}C$ of CO_2 in air. According to previous studies (Taylor, 2004; Levin et al., 2013), the value of ${}^{14}C_w$ is between 100 and 110 pMC. The $[C]_w$ and DIC concentration of sample solutions before the experiment (i.e., sum of $[C]_p$ and $[C]_w$) were determined using a TOC analyzer and the measurements included a maximum error of 5%. The ${}^{14}C$ concentrations of the powder $NaHCO_3$ reagent were 0.4 and 0.5 pMC; thus, the correct value of ${}^{14}C_w$ was considered to be between 0 and 1 pMC. Similarly, the correct values of ${}^{14}C_w$ for prepared $NaHCO_3$ solutions 2–4 were assumed to be between 26 and 27 pMC. The values indicated above were put into equation (1) and a possible range of ${}^{14}C_s$ (correct value of ${}^{14}C$ in the sample solution) was calculated. The possible ranges of ${}^{14}C_s$ for solution 1–4 were 3.1 to 5.2, 26.0 to 28.0, 26.0 to 29.0 and 26.0 to 28.0 pMC, respectively. The calculated ranges of ${}^{14}C_s$ are compared to the measured ${}^{14}C$ values in Table 2.

Table 2 shows the ${}^{14}C$ and ${}^{13}C$ values of DIC measured by the gas-strip ($_{\text{gas strip}}$) and precipitation ($_{\text{precip}}$) methods for $NaHCO_3$ solutions. In solution 1 and 2, the differences between ${}^{14}C_{\text{gas strip}}$ and ${}^{14}C_{\text{precip}}$ ranged from 4 to 7 pMC. However, the ages estimated by the gas-strip and precipitation methods differed significantly (by 7000 to 12,000 years) for solution 1, and by 1000 to 1200 years for solution 2. These results indicate that the uncertainty of ^{14}C age becomes larger when the age of old groundwater is estimated, as expected. The difference between $^{14}C_{gas\ strip}$ and $^{14}C_{precip}$ in solution 3 was about 10 pMC, which was twice that of solution 1 and 2. This result indicates the difference become more significant in the case of solution with low DIC. Furthermore, the difference in solution 4 was 17 to 33 pMC, indicating a very large difference compared to other solutions. This result shows that the ionic strength and/or ion composition of the sample water can significantly affect ^{14}C values of the precipitation method. There is also a possibility that the ^{14}C values might be controlled by relative relationships between carbonate and the other ion concentrations.

As shown in Table 2, the $^{14}C_{gas\ strip}$ values were close to the possible range of $^{14}C_s$ values calculated from equation (1), although measured $^{14}C_{gas\ strip}$ values were always slightly (~1 pMC) higher. Conversely, $^{14}C_{precip}$ always showed much higher values relative to the calculated range of $^{14}C_s$ values. Thus, the gas-strip method is shown to be reliable for many types of groundwater samples with minimal error. $^{14}C_{precip}$ always showed significantly higher values than $^{14}C_s$. Therefore, the precipitation method should be applied carefully to groundwater samples and potential errors in $^{14}C_{precip}$ results should be explicitly assessed.

The effects of DIC concentration were investigated by comparing the ^{14}C values in solutions 1, 2 and 3. The averaged differences between $^{14}C_{precip}$ and $^{14}C_s$ in solutions 1, 2 and 3 were 5.0, 5.1, and 10.4 pMC, respectively. These results clearly indicate that the relative difference in ^{14}C estimated by the 2 methods increases with decreasing DIC concentration. These findings can be explained if we assume that a certain amount of modern carbon contaminated the sample during precipitation. If 0.6 to 0.7 mg of modern C contaminates 1 L of sample solution during the precipitation procedure, the observed differences between $^{14}C_{precip}$ and $^{14}C_{s}$ will occur.

Comparison of solutions 2 and 4 show the affect of salinity on $^{14}C_{precip}$. The difference between $^{14}C_{gas\ strip}$ and $^{14}C_{precip}$ was greater in solution 4 than in solution 2. If contamination by modern carbon from the air was the dominant cause of this phenomenon we would expect that the ^{13}C values would be close to −8‰ (Taylor, 2004). However, the $^{13}C_{precip}$ values in the solution 4 test samples were −23.7 and −27.3 ‰, significantly lower than the ^{13}C value of $NaHCO_3$ powder (−18.5‰). Thus, the difference between $^{14}C_{gas\ strip}$ and $^{14}C_{precip}$ in saline water can not be explained by contamination of modern carbon from the air alone.

Identification of contamination in samples prepared by the precipitation method

The preliminary comparison experiments described above indicate that contamination by modern carbon might occur during the precipitation procedure. Modern carbon contamination from air to alkaline and $SrCl_2$ solutions was assumed to be the most likely source of contamination during the precipitation procedure. The background DIC concentrations in NaOH and $SrCl_2$ solutions were analyzed using a gas-strip line to confirm this possibility. Table 3 shows the DIC concentrations of each solution. Degassed deionized water with H_3PO_4 contained 0.01 mg/L DIC. The $SrCl_2$ solution is estimated to contain 0.04 mg/L DIC. Similarly, the DIC content of the NaOH solution (1 L of degassed deionzed water with 5 mL of 5N-NaOH solution) was estimated to range from 0.2 to 0.3 mg/L, when 5N NaOH solutions were prepared under atmosphere conditions. On the other hand, NaOH solutions prepared under inert conditions contained approximately 0.2 mg/L DIC, that was as same as prepared in atmosphere condition. Accordingly, the modern carbon contamination of solutions appears to originate from the NaOH granules. Such background contamination of modern carbon probably also occurs for other alkaline solutions, such as ammonium solutions. Contamination with modern carbon in preliminary experiments using $NaHCO_3$ solutions could also originate from the NaOH solution used in the precipitation method.

Conversely, modern carbon contamination might occur in the gas-strip method during the addition of H_3PO_4 into the groundwater prior to carrier gas circulation because deionized water with H_3PO_4 contained minor but measurable DIC. This would be expected to influence the $^{14}C_{\text{gas strip}}$ result from the $NaHCO_3$ solutions, which deviate by about 1 pMC from $^{14}C_s$ (Table 2).

Application of the two methods to natural groundwater sample

^{14}C values of DIC in groundwater samples prepared by both the gas-strip and precipitation methods are shown in Table 4. ^{13}C values of DIC are also listed in Table 4. $^{14}C_{precip}$ values were approximately 0.4–9.5 pMC higher than those obtained using the gas-strip method. By assuming that $^{14}C_{gas\ strip}$ is less contaminated by modern carbon and the ^{14}C value of contaminated modern carbon in samples obtained by the precipitation method is 100 pMC, the mass balance equation describing contamination in the precipitation methods ($^{14}C_{precip.}$) can be expressed by the following equation:

$$\mathrm{DIC_{gw}} \times {}^{14}\mathrm{C_{gasstrip}} + \mathrm{DIC_{contami}} \times 100 = \left(\mathrm{DIC_{gw}} + \mathrm{DIC_{contami}}\right) \times {}^{14}\mathrm{C_{precip}} \qquad (2)$$

where, $DIC_{contami}$ is the amount of DIC contamination with modern carbon (mg), and DIC_{gw} is the amount of DIC (mg) in groundwater samples analyzed before addition of NaOH solution. The amounts of modern carbon contamination during the precipitation procedure (described as $DIC_{contami}$ above) were estimated to be 1 mg for all groundwater samples, regardless of the $^{14}C_{gas\ strip}$ and DIC_{gw} values (Table 4). These findings suggest that modern carbon contamination during preparation of the precipitation method significantly influenced the ^{14}C value according to the DIC content and ^{14}C concentration of sampled water.

The $^{14}C_{gas\ strip}$ value of groundwater at depths of 200 to 500 m were estimated to range from 2 to 29 pMC, with a tendency to become lower with increasing depth. We were not able to collect the DIC in groundwater at 500 m depth (12MI33 borehole) by the precipitation method. The reason that the DIC did not precipitate is not clear, but is likely related to the low DIC concentration (4.9 mg/L) and high salinity (about 450 mg/L) of the sample. The groundwater residence time at that depth is estimated to be about 31,000 year by the $^{14}C_{\text{gas strip}}$ value. However, the groundwater flow around this large underground facility (MIU) has been influenced by water drainage for more than ten years (Iwatsuki et al., 2015), and the analyzed ^{14}C values might reflect mixed shallow and deep groundwater sources.

When we discuss about the groundwater ages with ^{14}C, the ^{14}C values should be corrected considering the geochemical reactions that could affect to the ^{14}C values (Clark and Fritz, 1997; Kalin, 2000). However in this manuscript groundwater ages are estimated without correction of geochemical reactions because our main purpose is to indicate the difference between precipitation and gas-strip methods.

Applicability of the precipitation method for groundwater dating

As indicated above, contamination with modern carbon probably occurs during the DIC precipitation procedure. The effects of contamination varied significantly depending on the DIC and ^{14}C concentrations of the groundwater samples. Equation (2) was applied to estimate error in cases in which modern carbon contaminated groundwater with various DIC concentrations. For example, Fig. 3a and 3b show ^{14}C values after contamination of 1 L of groundwater with 0.5 or 1 mg modern carbon as estimated by Equation (2). The error from the true ^{14}C value became more significant as the DIC and ^{14}C concentrations of sampled groundwater decreased. Constraints for DIC and ^{14}C of groundwater that should be analyzed within 10 %

error are estimated in Fig. 3c. Because background contamination with modern carbon was estimated for each preparation method, the uncertainty in ^{14}C analysis could be inferred by the DIC concentration and probable ^{14}C content of the groundwater. As described above, 1 L of $NaHCO_3$ solutions and groundwater samples were contaminated with about 0.7 mg and 1 mg of modern carbon, respectively.

As shown in Fig.3b, if we want to control the ^{14}C age error from the precipitation procedure within 10%, the concentration of DIC and $^{14}C_{gw}$ contents should be higher than 20, 10 and 1 mg/L and 32, 47 and 83 pMC, respectively. If the error has to be controlled within 20%, the concentration of DIC and $^{14}C_{gw}$ should be higher than 20, 10 and 1 mg/L and 19, 31 and 71 pMC, respectively.

Because our purpose was to determine the effects of both methods on estimation of groundwater age, the relationships between expected groundwater age estimated by ^{14}C (without considering the effect of geochemical reaction) using the precipitation method and DIC concentrations are compared in Fig.4. The expected groundwater age estimated by ^{14}C using the precipitation method was calculated by the following equations:

$$^{14}\mathrm{C\ age}_{\mathrm{ex}}\ (\mathrm{y}) = \frac{5730}{\ln 2} \times \ln\left(\frac{^{14}\mathrm{C}_{\mathrm{precip}}}{100}\right) \tag{3}$$

$$^{14}\mathrm{C}_{\mathrm{preip}} = \frac{^{14}\mathrm{C}_{\mathrm{gw}} \times [\mathrm{DIC}]_{\mathrm{gw}} + {}^{14}\mathrm{C}_{\mathrm{contami}} \times 1.0}{[\mathrm{DIC}]_{\mathrm{gw}} + 1.0} \tag{4}$$

Equation (3) is frequently used for estimation of groundwater age from ^{14}C (Mook and Plicht, 1999; Clark and Fritz, 1997). ^{14}C age $_{ex}$ is the expected ^{14}C age after precipitation and $^{14}C_{precip}$ is the ^{14}C concentration after precipitation with 1 mg modern carbon contamination. $^{14}C_{gw}$ and $^{14}C_{contami}$ are the concentrations of

DI^{14}C in the groundwater samples and modern carbon, respectively. The value of $^{14}C_{contami}$ is set to 100 pMC. $[DIC]_{gw}$ is the concentration of DIC in the groundwater samples.

The acceptable error depends on the purpose of the study. When we applied the precipitation method to estimate groundwater age, the acceptable error for the study and conditions that affect the ^{14}C age (DIC and ^{14}C concentrations in targeted groundwater) had to be considered. The information provided in Fig. 3 and 4 is useful to determine if the precipitation method is applicable for a targeted groundwater. According to the results of ^{14}C values for $NaHCO_3$ solutions and groundwater samples treated using the precipitation method, we could assume that the amount of modern carbon contamination to be about 1 mg. However this value might depend on the atmosphere of the laboratory and reagents used for the precipitation procedure. Thus, quantitative estimation of contamination by modern carbon in each laboratory during the precipitation procedure should be evaluated if the precipitation method is chosen.

CONCLUSION

In this study, the difference in ^{14}C values of samples prepared by gas-strip and precipitation methods were compared in artificially prepared and natural groundwater samples. The ^{14}C values obtained by the gas-strip method were very similar to the theoretically predicted ^{14}C values in chemically-distinct waters, indicating that this method can be applied to variety groundwaters. Conversely, the ^{14}C value obtained by the precipitation method showed higher than predicted ^{14}C values. In the case of natural groundwater samples, ^{14}C obtained by the precipitation method always showed higher values than those from the gas-strip method. It was assumed that an average of 1 mg/l of modern carbon contaminated the samples during the precipitation procedure. This contamination affects the estimation of groundwater ages, especially when DIC concentrations and ^{14}C contents are low. Thus, the applicability of the precipitation method should be considered according to the required accuracy and/or purpose of the study. The amount of contamination with modern carbon might differ among laboratories and should therefore be estimated in each laboratory to evaluate the applicability of the precipitation method.

For solutions with high salinity, the differences between ^{14}C measured from precipitation samples and predicted ^{14}C values increased. Thus, for groundwater with low DIC concentration and/or high salinity and old groundwater, the gas-strip method should be applied to estimate the groundwater age by $DI^{14}C$.

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FIGURE CAPTIONS

Figure 1 Gas-strip line to extract DIC from groundwater.

Figure 2 Groundwater sampling point at Mizunami underground research laboratory.

Figure 3 Error in ^{14}C analysis for contamination by modern carbon for groundwater with initial DIC concentrations of 0–20 mg/L. ^{14}C value of contaminated modern carbon is assumed to be 100 pMC. (a)

Contamination by modern carbon is 0.5 mg/L. (b) Contamination by modern carbon is 1 mg/L. Shaded area shows error within 10% of known ^{14}C value. (c) Constraint for DIC and ^{14}C of groundwater that should be analyzed within 10% error in the case of modern carbon contamination with 0.5 and 1 mg/L.

Figure 4 Relationships between concentration of DIC in groundwater and expected ^{14}C ages (^{14}C age$_{ex}$) for samples prepared by the precipitation method where groundwater ^{14}C ($^{14}C_{gw}$) is 10, 50 and 80 pMC. ^{14}C age$_{ex}$ were calculated by equations (3) and (4).

TABLE CAPTIONS

Table 1 Solutions for preliminary comparison of ^{14}C values obtained by two preparation methods

Table 2 Comparison of measured ^{14}C and possible range of ^{14}C for $NaHCO_3$ solutions

Table 3 Background DIC concentration of solutions used for precipitation method

Table 4 Comparison of ^{14}C of groundwater samples prepared by gas-strip and precipitation methods

Table 1 Solutions for preliminary comparison of ^{14}C values obtained by 2 preparation methods

Solution name	DIC concentration (mg/l)	$NaHCO_3$ used for preparation	Salinity (g/L)	Extraction method	Sample Name for ^{14}C measurement
Solution 1	9.0	Purchased (with low ^{14}C concentration)	0.06	Gas-strip	Sample1-1-1
					Sample1-2-1
				precipitation	Sample1-1-2
					Sample1-2-2
Solution 2	9.0	Prepared* (with relatively high ^{14}C concentration)	0.06	Gas-strip	Sample1-1-1
					Sample1-2-1
				precipitation	Sample1-1-2
					Sample1-2-2
Solution 3	4.5	Prepared* (with relatively high ^{14}C concentration)	0.03	Gas-strip	Sample1-1-1
					Sample1-2-1
				precipitation	Sample1-1-2
					Sample1-2-2
Solution 4	9.0	Prepared* (with relatively high ^{14}C concentration)	41.16	Gas-strip	Sample1-1-1
					Sample1-2-1
				precipitation	Sample1-1-2
					Sample1-2-2

*$NaHCO_3$ used for solution 2 to 4 was prepared as follows; NaOH solution was bubbled with air to obtain precipitation of $NaHCO_3$ and this $NaHCO_3$ was mixed with purchased one.

Table 2 Comparison of measured ^{14}C and possible ranges of ^{14}C for $NaHCO_3$ solutions

Sample Name	Extraction method	δ ^{13}C (‰)	^{14}C (pMC)	^{14}C year B.P.	Possible range of $^{14}C_s$* (pMC)	Deviation from ^{14}Cs (pMC)
Sample-1-1-1	Gas-strip	-20.0	2.0 ± 0.1	31,430 ± 180	3.1 to 5.2	-1.1
Sample-1-2-1		-19.3	3.7 ± 0.1	26,320 ± 110		-
Sample-1-1-2	Precipitation	-19.6	9.0 ± 0.1	19,290 ± 70		+3.8
Sample-1-2-2		-20.2	11.4 ± 0.1	17,340 ± 60		+6.2
Sample-2-1-1	Gas-strip	-19.9	29.0 ± 0.1	9,947 ± 32	26.0 to 28.0	+1.0
Sample-2-2-1		-17.6	28.7 ± 0.1	10,025 ± 32		+0.7
Sample-2-1-2	Precipitation	-19.0	33.3 ± 0.1	8,842 ± 33		+5.3
Sample-2-2-2		-17.1	32.8 ± 0.1	8,956 ± 34		+4.8
Sample-3-1-1	Gas-strip	-19.3	30.5 ± 0.1	9,534 ± 37	26.0 to 29.0	+1.5
Sample-3-2-1		-19.3	30.3 ± 0.1	9,591 ± 37		+1.2
Sample-3-1-2	Precipitation	-19.9	39.5 ± 0.2	7,459 ± 32		+10.5
Sample-3-2-2		-19.7	39.3 ± 0.2	7,502 ± 32		+10.3
Sample-4-1-1	Gas-strip	-17.8	29.2 ± 0.1	9,890 ± 38	26.0 to 28.0	+1.2
Sample-4-2-1		-17.4	29.9 ± 0.1	9,706 ± 38		+1.9
Sample-4-1-2	Precipitation	-23.7	62.6 ± 0.2	3,770 ± 22		+34.6
Sample-4-2-2		-27.3	47.4 ± 0.2	5,994 ± 27		+19.4

*Calculated by equation (1)

Table 3 Background DIC concentration of solutions used for precipitation method

Sample name	Preparation of solution	Composition of solution			DIC concentration in solution (mg/L)
		5N-NaOH (ml / 1L water)	2N-$SrCl_2$ (ml / 1L water)	H_3PO_4 (ml / 1L water)	
Pure water	In the atmosphere	0.0	0.0	2.0	0.01
$SrCl_2$ solution		0.0	5.0	2.0	0.04
NaOH solution1		5.0	0.0	2.0	0.21
NaOH solution2		5.0	0.0	4.0	0.29
NaOH solution3		10.0	0.0	8.0	0.45
NaOH solution4	In inert atmosphere	5.0	0.0	4.0	0.18

Table 4 Comparison of ^{13}C and ^{14}C of groundwater samples prepared by gas-strip and precipitation methods

Borehole-zone No. (date)	$\delta\,^{13}\mathrm{C}_{\mathrm{precip}}$* (‰)	$\delta\,^{13}\mathrm{C}_{\mathrm{gas\ strip}}$* (‰)	$^{14}\mathrm{C}_{\mathrm{precip}}$* (pMC)	$^{14}\mathrm{C}_{\mathrm{gas\ strip}}$* (pMC)	$(^{14}\mathrm{C}_{\mathrm{precip}}) - (^{14}\mathrm{C}_{\mathrm{gas\ strip}})$ (pMC)	Concentration of DIC in sample (mg/L)	$\mathrm{DIC}_{\mathrm{contami}}$** (mg)
07MI07-1 (2012/10)	-17.35	-16.83	34.57	29.07	5.50	17.6	1.48
07MI07-3 (2012/10)	-16.13	-17.43	32.16	24.23	7.93	12.1	1.41
07MI07-5 (2012/10)	-15.61	-14.91	26.45	16.95	9.50	8.9	1.15
09MI20-1[1] (2012/10)	-14.98	-14.88	29.27	24.34	4.93	15.4	1.07
09MI20-1[2] (2012/10)	-14.28	-14.47	27.46	23.38	4.08	15.4	0.87
09MI20-1[3] (2012/10)	-14.34	-14.77	27.24	22.05	5.19	15.4	1.10
09MI20-1 (2014/9)	-14.02	-13.88	23.97	18.14	5.83	14.3	1.10
09MI20-3 (2012/10)	-13.38	-14.04	24.97	20.12	4.85	15.4	1.00
09MI20-3 (2014/9)	-13.19	-10.89	24.12	10.43	13.69	13.2	2.38
09MI20-5 (2012/10)	-11.73	-11.52	21.20	15.50	5.70	15.4	1.11
09MI20-5 (2014/9)	-12.31	-11.95	19.82	12.02	7.80	10.3	1.01
10MI26-1 (2012/10)	-7.39	-6.79	10.25	9.86	0.39	15.4	0.07
10MI26-3 (2012/10)	-8.89	-8.09	15.33	7.90	7.43	15.4	1.35
10MI26-5 (2012/10)	-13.47	-12.77	27.18	19.09	8.09	15.4	1.71
12MI33-4 (2015/2)	No precipitation	-11.43	No precipitation	2.10	-	4.9	-
						Average	1.04

* $\delta\,^{13}\mathrm{C}_{\mathrm{precip}}$, $\delta\,^{13}\mathrm{C}_{\mathrm{gas\ strip}}$, $^{14}\mathrm{C}_{\mathrm{precip}}$ and $^{14}\mathrm{C}_{\mathrm{gas\ strip}}$ are measured ^{13}C or ^{14}C of samples prepared by precipitation and gas strip method, respectively.

** $\mathrm{DIC}_{\mathrm{contami}}$ is the amount of DIC contamination of modern carbon calculated by equation (2)

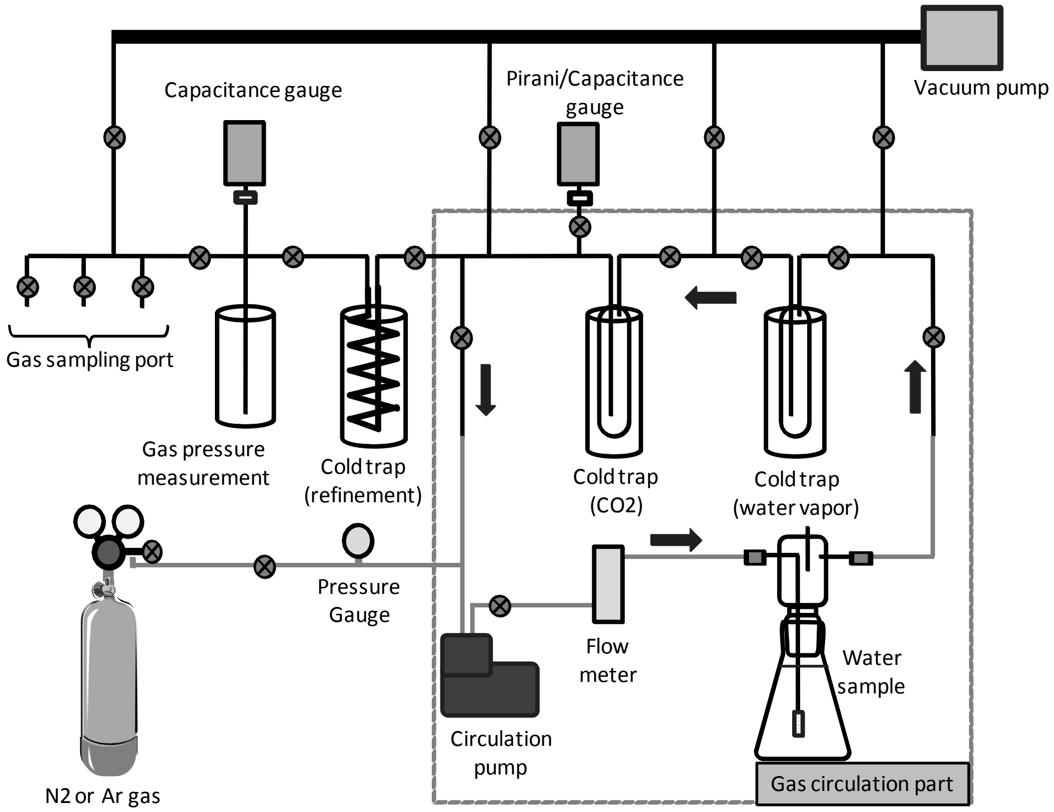

Figure 1 Gas-strip line to extract DIC from groundwater

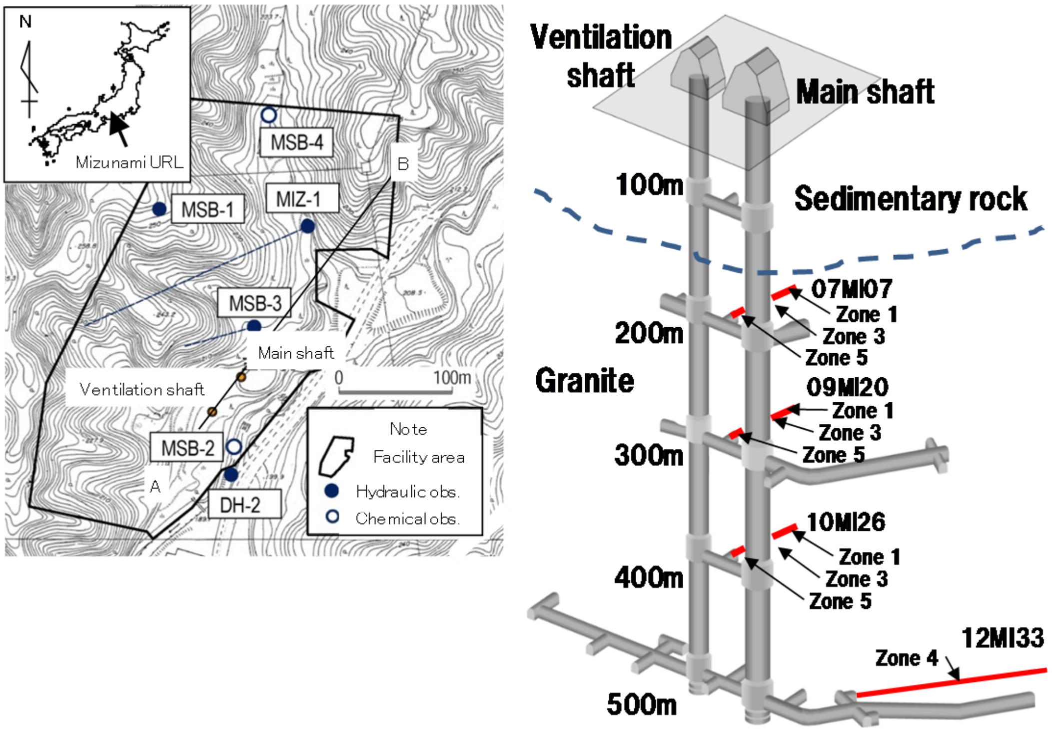

Figure 2 Groundwater sampling point at Mizunami underground research laboratory.

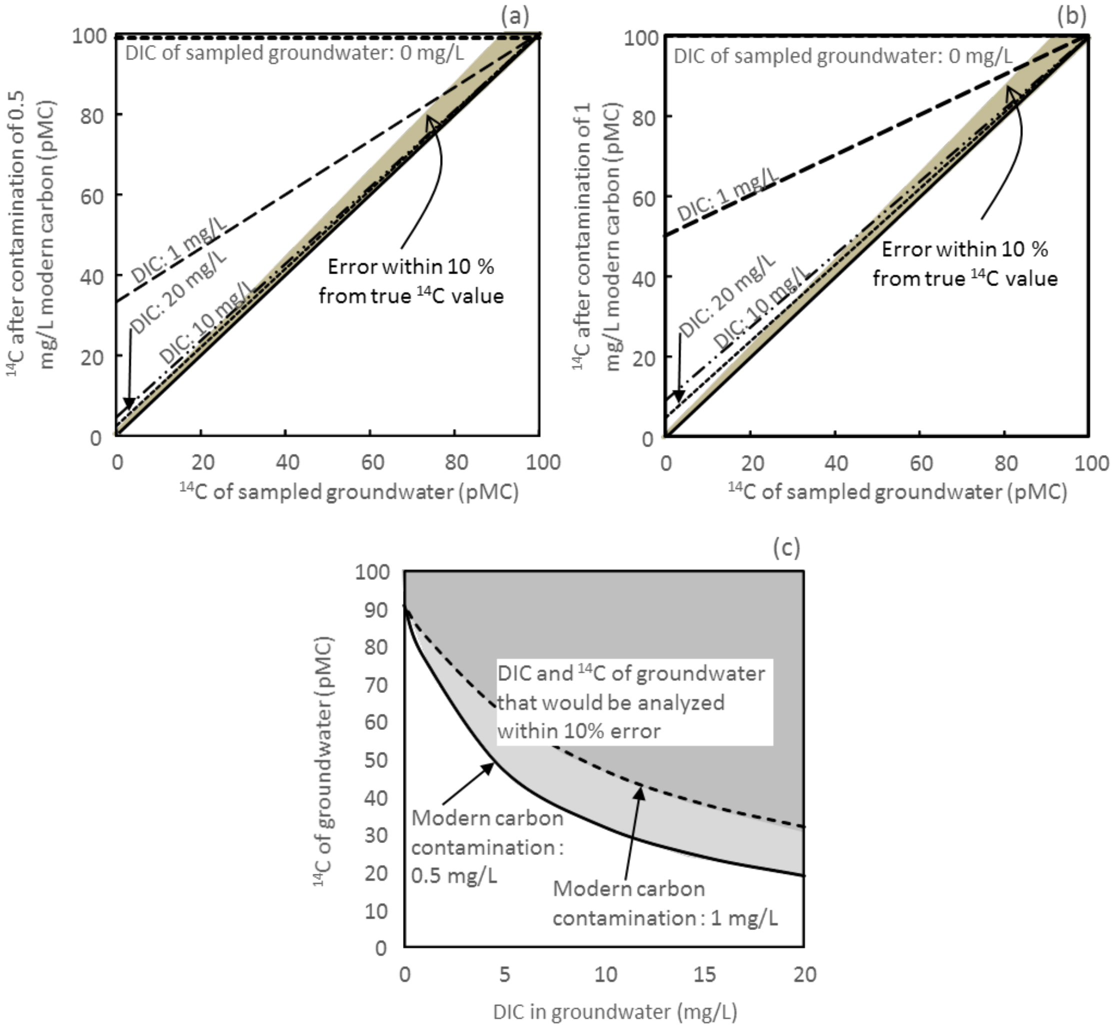

Figure 3 Error in ^{14}C analysis for contamination by modern carbon for groundwater with initial DIC concentrations of 0–20 mg/L. ^{14}C value of contaminated modern carbon is assumed to be 100 pMC. (a) Contamination by modern carbon is 0.5 mg/L. (b) Contamination by modern carbon is 1 mg/L. Shaded area shows error within 10% of true ^{14}C value. (c) Constraint for DIC and ^{14}C of groundwater that should be analyzed within 10% error in the case of modern carbon contamination with 0.5 and 1 mg/L.

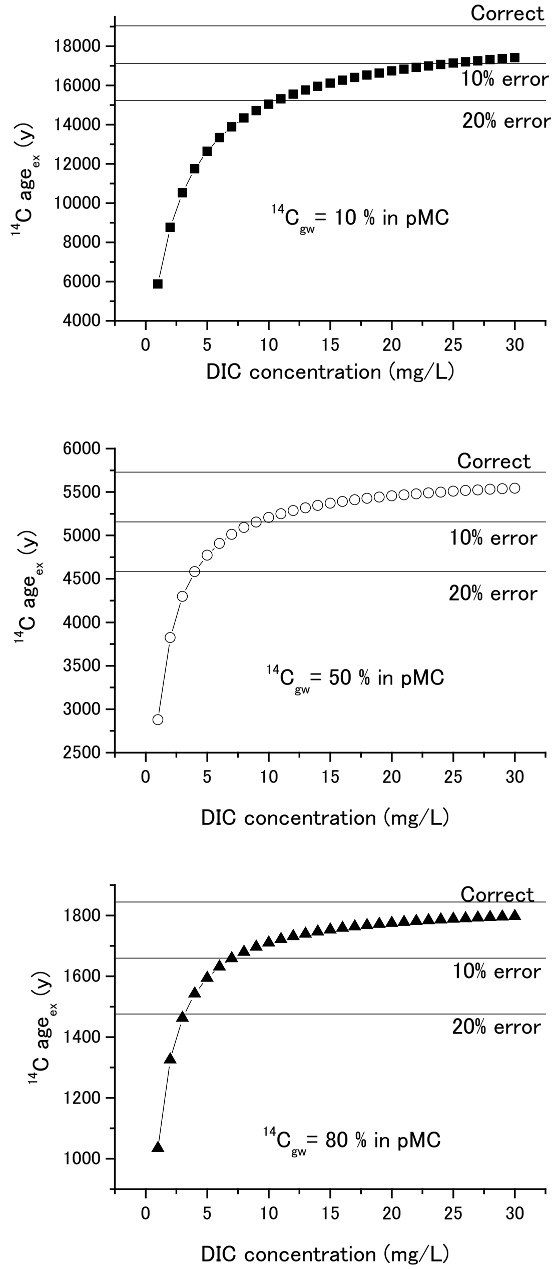

Figure 4 Relationships between concentration of DIC in groundwater sample and expected ^{14}C ages (^{14}C age$_{ex}$) of samples prepared by precipitation method where groundwater ^{14}C ($^{14}C_{gw}$) is 10, 50 and 80 pMC. ^{14}C age$_{ex}$ were calculated by equations (3) and (4).