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A SUITABLE PROCEDURE FOR PREPARING OF WATER SAMPLES USED IN RADIOCARBON INTERCOMPARISON

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ABSTRACT. We studied a suitable procedure for preparing of water samples used in radiocarbon intercomparisons involving dissolved inorganic carbon (DIC). The water samples must have inter-batch consistency and stable ^{14}C concentrations and no sterilizing agent (e.g., $HgCl_2$) should be added, in order to avoid the production of hazardous material. Six water samples, containing widely different amounts and types of salts, DIC, and ^{14}C concentrations (1–100 pMC), were prepared in order to assess the procedure. Sample consistency was investigated through $\delta^{13}C$ and chemical compositions; their low variabilities indicate that our procedure can be applied to radiocarbon intercomparison. A specific sample preparation protocol was developed for this kind of applications.

KEYWORDS: experiment, intercomparison, water.

INTRODUCTION

The isotopic composition of dissolved inorganic carbon (DIC) in natural waters is used in oceanography and hydrology to obtain clues about carbon behavior. Radiocarbon (^{14}C) concentrations provide information on water residence time, atmosphere-ocean carbon exchange, ocean water circulation, and anthropogenic or magmatic carbon supplies (Ostlund 1987; Rose and Davisson 1996; Elliot et al. 1999; Sikes et al. 2000; Matsumoto 2007; Takahashi et al. 2013). International programs on ocean water analysis, like WOCE, GLODAP, and GEOTRACES (McNichol et al. 1994; Key 1996; Ge et al. 2016; Olsen et al. 2016), provided an experimental protocol for the analysis of carbon isotopes and the analytical intercomparison using same seawater samples, in order to prevent biases between laboratories and obtain high accuracy dataset (McNichol et al. 1994; Dickson et al. 2007). The seawater samples collected during these programs were poisoned with a sterilizing agent (e.g. $HgCl_2$), to avoid any biogenic activity. However, the treatment of poisoned water is controlled by law and difficult to perform in comparison program due to the hazardous level of mercury present in the wastewater. Takahashi et al. (2019) reported that ^{14}C concentrations in unpoisoned natural waters (seawater, hot-spring water, and groundwater) changed over several days, while in $NaHCO_3$ solutions ^{14}C contents were stable over periods of years. The purpose of this study, therefore, is to prepare ^{14}C-stable and inter-batch homogeneous waters with a wide range of natural conditions (i.e. widely varying amounts and types of salts), DIC and ^{14}C concentrations in order to use ^{14}C intercomparison. Here, a procedure for preparing of comparison waters artificially without a sterilizing agent is described and we discussed the ^{14}C stability and inter-batch homogeneity of comparison waters.

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Table 1 Chemical reagents used in 22 L for water samples W09–W14. The artificial seawater powder was Marine Art SF-1 (Osakayakken Co., Ltd); * indicates an alternative to the $NaHCO_3$ reagent, because of a supply shortage. The nominal ^{14}C and DIC values were computed from the mixture ratio of the chemical reagents. The DIC concentrations of the hydroxide solutions were measured by acid titration, using bubbling solutions of NaOH and $Ca(OH)_3$ during the pre-test experiment.

	W09	W10	W11	W12	W13	W14
Chemical reagents						
Artificial seawater powder (g)	0	0	0	0	330	0
NaCl (g)	0	0	19.8	99.0	341	431
Na_2SO_4 (g)	0.11	15.4	3.30	1.10	55.0	0.66
$NaHCO_3$ (g)	0.11	0	17.6	79.2	0	75.7
$CaC1_2 \cdot 2H_2O$ (g)	0	2.33	0.87	39.3	16.0	9.03
$MgCl_2 \cdot 6H_2O$ (g)	0.66	3.08	2.88	57.2	47.0	38.5
KCl (g)	0.026	0.088	0.88	2.64	10.6	15.2
*NaOH (lM) + dead CO_2 (mL)	0	0	0	0	0	3000
NaOH (lM) + modern CO_2 (mL)	44.0	0	220	0	44.0	530
$Ca(OH)_2$ (0.0lM) + dead CO_2 (mL)	0	4400	0	4400	0	0
$Ca(OH)_2$ (0.0lM) + modern CO_2 (mL)	660	2200	0	0	0	0
Nominal ^{14}C content (pMC)	95.1	33.3	51.2	0	69.3	11.8
Nominal DIC concentration (mg/L)	14.5	114	235	591	34.6	2430

PROCEDURE FOR PREPARING COMPARISON WATERS

Six water samples (W09–W14) were prepared using purified water (Milli-Q Gradient A10, Elix water purification system, Merck-Millipore) and guaranteed chemical reagents; more details are provided in Table 1. The Milli-Q water was purified from organic matter using ultraviolet oxidation and ultrafiltration (total organic carbon <3 ppb). The prepared water samples were then stored in gamma-sterilized polyacrylonitrile (PAN) bottles (250 mL; Nikko Hansen & Co., Ltd.). PAN bottles provide an effective barrier against gas exchange (Takahashi et al. 2019).

The nominal ^{14}C content of the samples was targeted to be 0–95 pMC (Table 1), while chemical contents (Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, SO_4^{2-}, HCO_3^-, and CO_3^{2-}) were similar to those of natural waters (Table 2). The carbon sources included $NaHCO_3$, gas-bottle CO_2 (Taiyo Nippon Sanso Co.), and natural shell powder (Naitoh Shouten Co., Ltd.; employed as pigment in the Japanese painting industry). The former two sources were considered dead-carbon sources, while the latter was considered modern. Shell powder was reacted with H_3PO_4 or HCl in 1 L plastic bottles to produce CO_2. The CO_2 released from the shell powder and the gas-bottle CO_2 were collected in 20 L Tedlar® gas-sampling bags; then, the CO_2 gas was dissolved through bubbling in 1 M NaOH or 0.01 M $Ca(OH)_2$ solutions (360–500 mL). The NaOH and $Ca(OH)_2$ solutions acted as a control of the cation content and adjust it to natural water chemical compositions (Na and Ca types). The obtained CO_2 gas was pumped through both the hydroxide solutions at ~20 L hr^{-1} for 3–5 hr (gas bags were exchanged several times). The bubbling was stopped when the pH of hydroxide solution reached ~7.6. The $Ca(OH)_2$ solution was filtered under suction (with a 5 μm glass-fiber filter), in order to remove any precipitate generated during bubbling. The carbon contamination to the hydroxide solutions produced during bubbling cannot be eliminated,

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Table 2 Initial (n = 1) and final (n = 12) chemical features of samples W09–W14 at the elapsed days of ~15 and ~1000, respectively. The errors are given as standard deviations across 12 batches of storage bottles. The saturation index (SI) values, in parentheses, were calculated assuming a Ca^{2+} concentration of 0.1 mg L^{-1}. n.d. = not detected.

	W09		W10		W11	
	Initial	Final	Initial	Final	Initial	Final
pH	7.1	7.2±0.1	6.8	7.3±0.0	8.8	8.8±0.0
Na^+ (mg/L)	8.9	9.2±0.1	226.2	240.3±0.8	853.8	903.2±5.6
K^+ (mg/L)	0.5	0.5±0.0	1.9	1.8±0.0	21.0	21.0±0.2
Mg^{2+} (mg/L)	3.5	3.7±0.0	17.4	17.9±0.1	13.0	13.8±0.1
Ca^{2+} (mg/L)	10.9	11.9±0.0	140.0	153.4±0.7	3.0	n.d.
Cl^- (mg/L)	10.7	11.1±0.0	99.9	104.2±0.5	611.1	654.5±5.9
SO_4^{2-} (mg/L)	3.2	3.5±0.0	471.0	501.9±2.6	101.6	108.6±0.9
HCO_3^- (mg/L)	51.1	54.5±0.3	325.7	344.8±1.6	1017	1076±8
CO_3^{2-} (mg/L)	n.d.	n.d.	n.d.	n.d.	15.6	16.8±0.6
DIC (mg/L)	12.7	12.3±0.1	93.3	82.1±1.0	222.0	240.8±1.8
$\delta^{13}C$ (‰)	2.8	2.7±0.1	–13.4	–11.8±0.1	–5.0	–5.1±0.0
SI (calcite)	–1.6	–1.5	-0.4	0.2	0.5	(–1.9)
SI (aragonite)	–1.8	–1.6	-0.5	0.1	0.4	(–2.1)

	W12		W13		W14	
	Initial	Final	Initial	Final	Initial	Final
pH	7.0	7.1±0.0	8.2	8.1±0.0	8.1	8.2±0.0
Na^+ (mg/L)	2836	2984±26	11,680	12,100±70	12,900	13,450±140
K^+ (mg/L)	62.6	62.9±0.5	410.7	407.9±2.5	370.1	376.1±3.7
Mg^{2+} (mg/L)	311.5	318.0±3.1	694.4	720.5±4.2	177.2	196.3±2.1
Ca^{2+} (mg/L)	219.2	91.8±8.9	160.0	133.1±0.7	5.8	n.d.
Cl^- (mg/L)	4853	4870±40	18,160	19,130±140	13,350	14,010±110
SO_4^{2-} (mg/L)	30.0	31.5±0.3	2841	2980±23	17.7	17.6±0.3
HCO_3^- (mg/L)	1723	1396±26	183.1	192.4±1.4	11,630	12,230±140
CO_3^{2-} (mg/L)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
DIC (mg/L)	487.2	361.2±9.8	37.4	38.9±0.3	2340	2535±30
$\delta^{13}C$ (‰)	–13.0	–11.8±0.2	–0.8	–0.9±0.0	–20.0	–20.0±0.0
SI (calcite)	0.5	0.1	0.4	0.2	0.6	(–2.2)
SI (aragonite)	0.4	0.0	0.2	0.1	0.4	(–2.3)

but it does not really matter because a slight contamination does not influence to perform intercomparison using these waters. Additionally, we made sure that all batches of comparison water had identical ^{14}C concentrations and chemical compositions.

The reagents (Table 1) were dissolved and mixed in ~10 L of Milli-Q water, inside a 22 L plastic container, and then diluted with Milli-Q water reaching a total volume of 22 L. The solutions were homogenized using a magnetic stirrer for >3 hr, and then left to stand overnight. The precipitates which accumulated in sample W12 during this time were redissolved in the solution by further stirring. Each solution was dispensed by siphoning into a 250 mL PAN bottle (full filling amount = ~310 mL), leaving no headspace. We prepared 66 bottles for each comparison water. All of the bottles were stored in a dark room (~20°C) until use.

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INTER-BATCH HOMOGENEITY

Inter-batch homogeneity was assessed by determining the chemical compositions and $\delta^{13}C$ values for 12 samples chosen randomly from the PAN bottle batches. The samples were analyzed by ion chromatography (Dionex ICS-2100, Thermo Fisher Scientific) and an isotope-ratio mass spectrometer (IRMS) coupled with a gas chromatography system (GC–IRMS; Delta-V Advantage with GasBench II, Thermo Fisher Scientific), at the Geological Survey of Japan. Measurement errors were lower than ±10% for the chemical composition, ±2% for the DIC concentration, and ±0.1‰ for the $\delta^{13}C$.

Standard deviations for chemical compositions and $\delta^{13}C$ values after storage (~1000 days) were <1% and <0.1‰, respectively (Table 2). We concluded that the inter-batch homogeneity was high enough to allow an intercomparison.

MONITORING OF SAMPLE STABILITY

The stability of the intercomparison water samples was assessed by monitoring DIC, ^{14}C, and $\delta^{13}C$ values during storage. The $\delta^{13}C$ and DIC values were determined by GC–IRMS as described above. CO_2 was extracted from water samples by a headspace gas-purge procedure (Torres et al. 2005; Molnár et al. 2013) in order to measure ^{14}C. The sample water was injected into a pre-evacuated glass bottle containing H_3PO_4 sealed by a butyl rubber septum using syringe. The CO_2 released in the head-space of the glass bottle was purged and the carrier gas transferred the CO_2 to the vacuum line through a needle. Afterwards, the CO_2 gas was purified cryogenically and reduced to graphite with hydrogen gas (Kitagawa et al. 1993) to make ^{14}C measurement targets. We measured the ^{14}C contents at two accelerator mass spectrometry (AMS) facilities, Nagoya University and National Institute for Environmental Studies (NIES), relative to NIST oxalic acid (HOx-II) and corrected it for isotopic fractionation using the $^{13}C/^{12}C$ measurements in each of the AMS systems. Corresponding results are shown in Figure 1, while the chemical features are given in Table 2.

Takahashi et al. (2019) reported that, when DIC concentration was relatively high (~200 mM), the ^{14}C content of a $NaHCO_3$ solution stored in a PAN bottle was stable over periods of up to 900 days, even if the ^{14}C content was very low (approximating the ^{14}C-free level). However, when DIC concentration was low (~2 mM), the ^{14}C concentration increased from 0.6 to 1.8 pMC. Because of the low storage PAN bottle performance, it is difficult to prepare comparison water having very low DIC and ^{14}C concentrations.

During storage, samples W09 and W12 showed significant changes in their ^{14}C and DIC concentrations. The reasons for the decrease in ^{14}C concentration of W09 is uncertain; possibly, it was triggered by air-exchange between the storage room (low ^{14}C; atmospheric $^{14}CO_2$ was lower than global levels; Takahashi et al. 2002) and the sample. The change in ^{14}C concentration observed for W12 was almost identical to the increase seen during the performance test in a PAN bottle (Takahashi et al. 2019). The results suggested that W12 should not be used in the intercomparison.

The concentrations of most chemical species remained constant within the margin of error (error = ±10%) during storage (Table 2). Nevertheless, Ca^{2+} and DIC concentrations decreased in samples W10, W12, and W13, while Ca^{2+} was not detectable in samples W11 and W14 after storage. Moreover, a precipitate was found in sample W12 after storage. We measured

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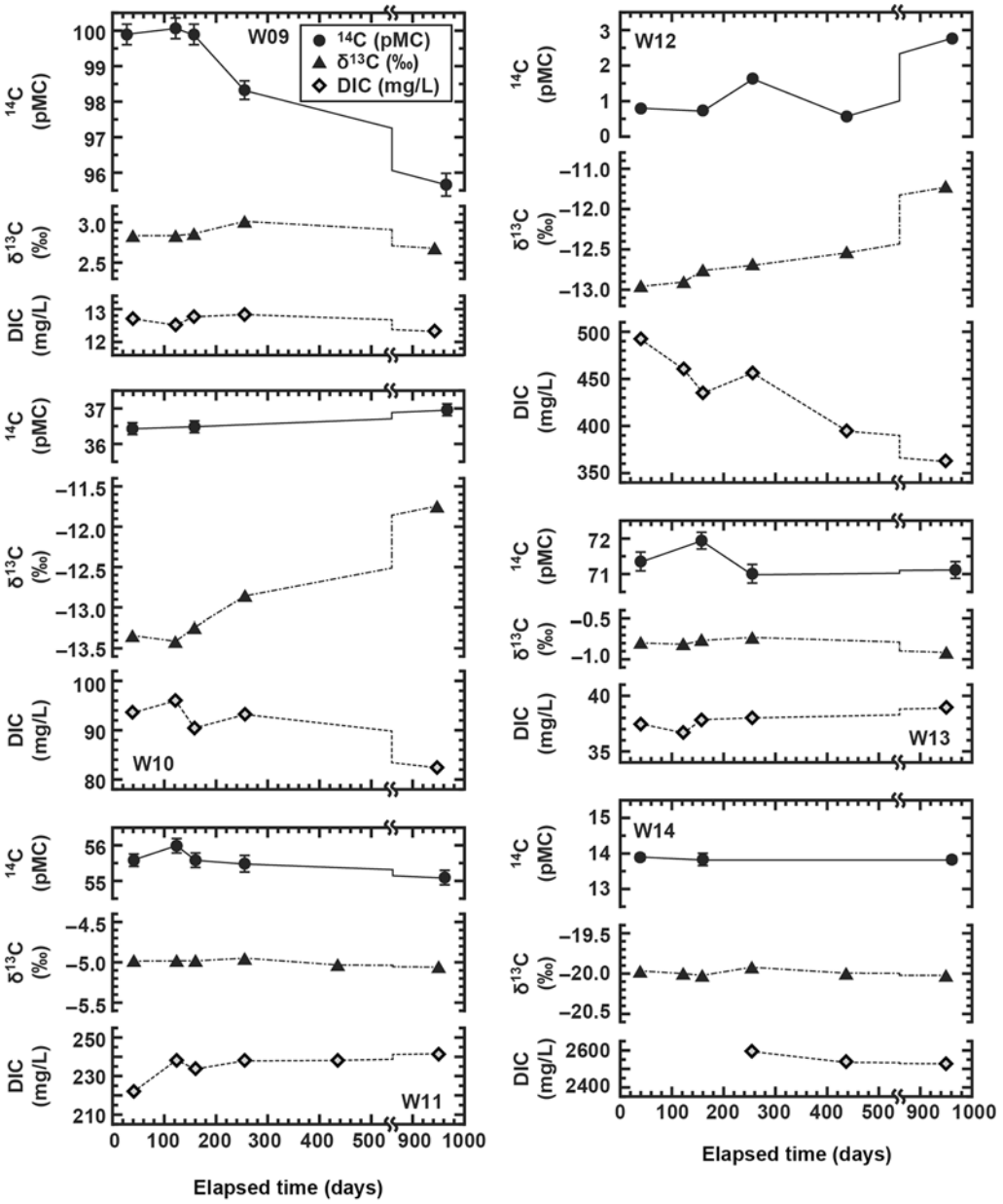


Figure 1 Results of the stability monitoring for ^{14}C (circles), $\delta^{13}C$ (triangles), and DIC concentration (diamonds).

^{14}C and $\delta^{13}C$ values of the precipitate by AMS and IRMS with dual inlet system (Delta-V advantage) to be 0.8 pMC and −8.5‰, respectively. The ^{14}C content of the precipitate was identical with that of DIC in W12 (Figures 1 and 2), indicating that the carbonate mineral was directly precipitated from DIC of W12. The x-ray diffraction analysis (CuKα; Rigaku MiniFlex) of the precipitate indicated the presence of $CaCO_3$ (aragonite) and MgO; perhaps, the relatively high concentration of Mg^{2+} in the sample induced the precipitation of aragonite (Burton and Walter 1987). No precipitates were found in the other samples, although W10 and

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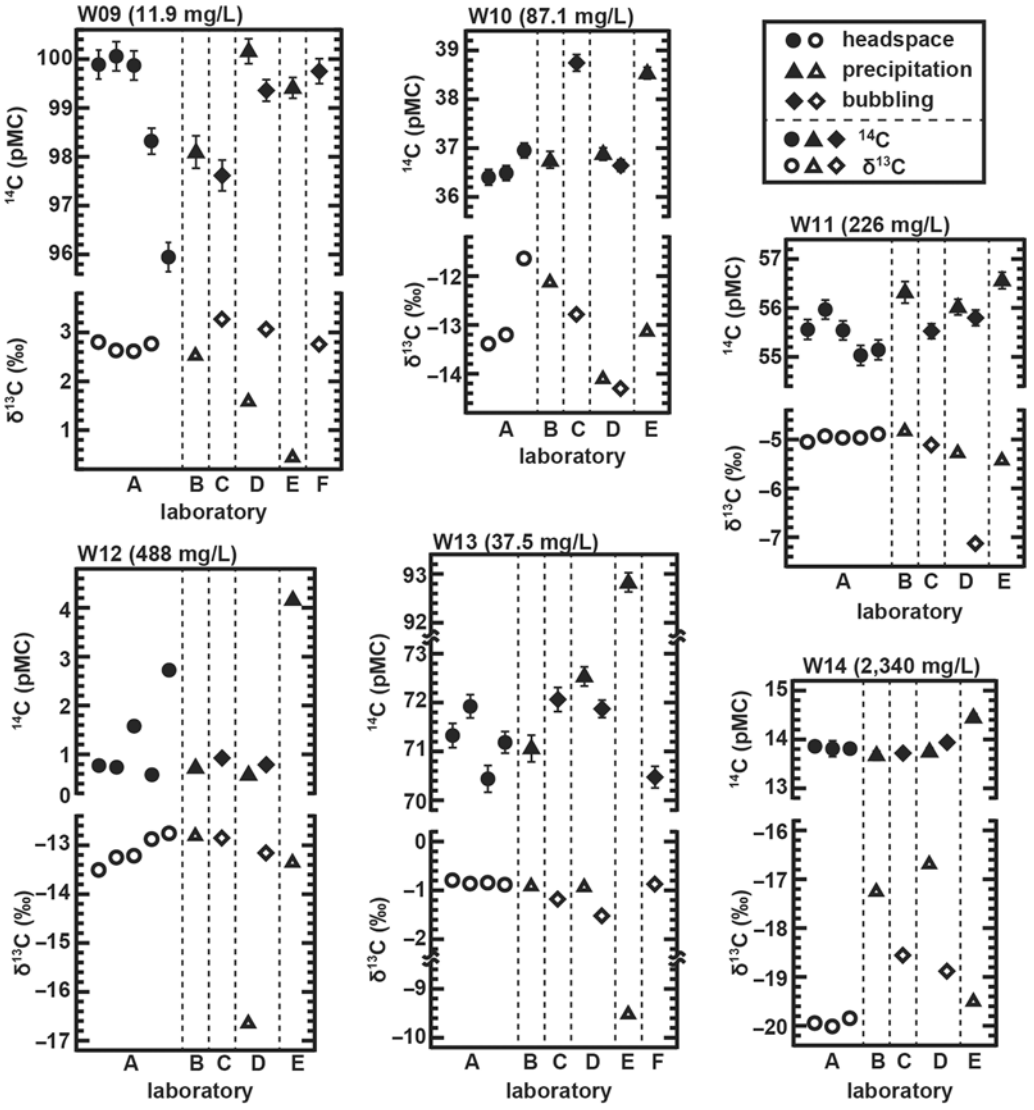


Figure 2 Results of the intercomparison exercise involving laboratories A–F: ^{14}C (solid symbols), $\delta^{13}C$ (open symbols). CO_2 extraction procedures: headspace-gas purging (circles), carbonate precipitation (triangles), gas bubbling (diamonds). The treatment periods were different between laboratory A (27–976 elapsed days; Figure 1) and the other laboratories (378–431 elapsed days). The ^{14}C concentrations of some samples from laboratory A indicated secular changes (Figure 1), and therefore, a notice is necessary for the comparison of results from laboratory A with those from the other laboratories.

W12 displayed significant chemical and $\delta^{13}C$ changes during storage (Table 2; Figure 1). Likely, some calcite precipitated at the invisible scale in low-Mg^{2+} solutions (e.g., W10, which showed an increase in the saturation index of carbonate minerals).

Samples W10 and W12 showed decreases in DIC concentration and increases in $\delta^{13}C$ values. The isotopic mass-balance estimations suggested that the $\delta^{13}C$ values, corresponding to the carbon removed from the W10 and W12 solutions, were −23‰ and −16‰, respectively.

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These values were much lower than that of precipitate (aragonite) found in sample W12. Therefore, the change in $\delta^{13}C$ for W12 is caused by not only precipitation but also by other processes. The pH values of samples W10 and W12 were lower than those of other samples with higher carbonate saturation index (SI) values (Table 2). The relatively high SI values and low pH condition likely caused DIC changes during storage; waters with higher pH were apparently more stable. In conclusion, in order to maintain maximum stability, the intercomparison samples should not have very low DIC and ^{14}C values, while pH should be >8.

TRIAL INTERCOMPARISON

The water samples prepared in this study had to be tested to determine whether they can be used in the intercomparison program. A trial intercomparison campaign was undertaken by six laboratories (laboratories A–F), in order to reveal possible problems. A set of six water samples was delivered to each laboratory. The CO_2 extraction, purification and graphitization processes were performed using usual procedures of respective laboratories. CO_2 extraction was done in three different procedures: by carbonate precipitation (laboratories B, D, and E), gas bubbling (laboratories C, D, and F), and headspace-gas purging (laboratory A). The precipitation method involved the addition of $BaCl_2$ or $SrCl_2$ to the water sample to trigger the precipitation of carbonates, and the addition of H_3PO_4 to release CO_2 (Haynes and Haas 1980; Drimmie et al. 1991; Aucour et al. 1999). The bubbling procedure followed the procedure in the WOCE program (Dickson et al. 2007): the CO_2 gas was extracted from acidified water by bubbling it with a carrier gas. The extracted CO_2 gas was then cryogenically purified in a vacuum line. The graphitization procedure of all participating laboratories followed that described in Kitagawa et al. (1993). The ^{14}C content was measured by five AMS facilities in Japan: Nagoya University, JAEA-Tono, NIES, Paleo Labo Co. Ltd., and Institute of Accelerator Analysis Ltd.; isotopic fractionation was corrected using the $^{13}C/^{12}C$ measurements in each of the AMS systems. The $\delta^{13}C$ values were determined by IRMS with a dual inlet system using purified CO_2.

Across all laboratories, most of the ^{14}C results were consistent, although there were large variations in ^{14}C and $\delta^{13}C$ at low DIC (sample W09) and ^{14}C (sample W12) concentrations. The results suggested that waters with low DIC content were probably susceptible to the carbon contamination during the CO_2 extraction process. Sample W14 presented a wide range of $\delta^{13}C$ values, whereas its ^{14}C contents were relatively similar across the laboratories. High DIC concentrations of W14 could cause carbon isotopic fractionation during the CO_2 extraction and purification processes, because of very small amount (less than 1 mL) of water used. The target range of DIC concentrations varied among laboratories: some of them could not treat such a small amount of water.

Samples W10 and W13 had the highest SO_4^{2-} concentrations. The effect of SO_4^{2-} on the $\delta^{13}C$ measurements became appreciable when the mole fraction of CO_3^{2-} in the precipitate $BaCO_3/(BaCO_3+BaSO_4)$ was <0.3, due to low carbon recovery (Kusakabe 2001). Conversely, at high SO_4^{2-} concentrations, there was a positive shift in $\delta^{13}C$ values; this was caused by the occurrence of isotopic fractionation during precipitation. The ^{14}C content was not expected to be affected in this case. However, the ^{14}C data results for W10 and W13 from laboratories C and E, obtained through precipitation, differed significantly from other samples (Figure 2). Possibly, the low carbon recovery accentuated the contamination of modern carbon. Across all laboratories, the ^{14}C results for W13 varied quite a lot, regardless of the technique used. Perhaps, high SO_4^{2-} concentrations impeded the CO_2

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extraction and graphitization processes. The $\delta^{13}C$ values obtained through precipitation procedure tended to deviate from other results, regardless of SO_4^{2-} concentrations (Figure 2).

CONCLUSION

The proposed procedure for preparing of intercomparison water samples was suitable for radiocarbon intercomparison, although care must be taken in the selection of chemical reagents type and amount. The pH and the carbonate saturation index of the solution can affect sample stability: for pH >8, ^{14}C and DIC contents remained stable, even with oversaturation of carbonate minerals. The variability of ^{14}C and $\delta^{13}C$ results was larger for waters with low DIC and/or high SO_4^{2-} concentrations.

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