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# Rapid sample preparation of dissolved inorganic carbon in natural waters using a headspace-extraction approach for radiocarbon analysis by accelerator mass spectrometry

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## Abstract

We have established a high-throughput headspace-extraction method for the preparation of dissolved inorganic carbon (DIC) from water samples for radiocarbon ($^{14}$C) analysis by accelerator mass spectrometry (AMS). Readily available septum-sealed screw cap vials were used for sample processing. Headspace-equilibrated gases with sample $CO_2$ were transferred using a syringe and cryogenically purified on a vacuum line for graphitization and $^{14}$C-AMS measurements in the Keck Carbon Cycle AMS facility at the University of California, Irvine (KCCAMS/UCI). Systematic investigations have shown that the extraction process does not introduce contaminants that could bias the $^{14}$C measurements and that the $^{14}$C results for standards are consistent with their consensus values. Large numbers of duplicate measurements have established a precision of 1.7‰ for modern samples with an average background of ~43,400 radiocarbon year for graphite target samples > 0.3 mg carbon. Seawater samples collected from Newport Beach, California, and processed using the headspace-extraction method yielded $^{14}$C results in excellent agreement with published values obtained with conventional DIC stripping (≤ ± 2σ). The simplicity of our headspace-extraction approach allows its easy adaptation/implementation to any isotope lab, as we demonstrate here by a series of tests carried out at Peking University, China (PKU). With this innovative method, just 30 mL seawater per sample is needed. Coupled with the sealed tube zinc reduction method, 15 water samples can be prepared and graphitized in 1 day.

The oceans play an important role in the global climate system because of their large heat and carbon storage capacities. A significant amount of carbon in the ocean is stored as dissolved inorganic carbon (DIC) (36,000 Pg carbon; Druffel et al. 2008), which is also the most active part of the marine carbon pool. Measurements of natural radiocarbon ($^{14}$C) in seawater DIC can help us understand oceanic carbon cycling, air-sea exchange, and global-regional ocean circulation (Stuiver et al.

1983; Broecker et al. 1985; Key et al. 1996, 2002, 2004; Matsumoto 2007). Bomb-produced $^{14}$C has also been studied to quantify air–sea gas exchange rates, to evaluate the oceanic uptake of anthropogenic carbon dioxide ($CO_2$), to constrain the residence times of ocean carbon pools, as well as to reveal water mass-mixing processes such as seasonal upwelling (Peng et al. 1998; Kumamoto et al. 2002; Sweeney et al. 2007; Druffel and Griffin 2008; Hinger et al. 2010; Santos et al. 2011; Graven et al. 2012). To obtain high-resolution DI$^{14}$C records in such studies, small sample volumes and rapid preparation of DIC samples for $^{14}$C measurements would be very helpful.

The amount of seawater needed for DI$^{14}$C measurements has decreased from 250-300 L (for liquid scintillation counting; Bhushan et al. 1994) to about 250 mL (recommended for conventional $^{14}$C-AMS; McNichol et al. 1994; Kwong et al. 2004) with the development of accelerator mass spectrometry (AMS). In the conventional method for preparing water sam-

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ples for DIC $^{14}$C-AMS measurements (McNichol et al. 1994) the DIC in acidified water samples is stripped out as $CO_2$ using an inert nitrogen ($N_2$) carrier gas on a vacuum line and then converted to graphite. This method can fully extract (> 98%) the DIC from water samples and provides an excellent precision of 2.0‰ and 0.2‰ (± 1σ standard deviation [stdev]) for $\Delta^{14}$C (as defined in Stuiver and Polach 1977) and δ$^{13}$C analyses, respectively (Santos et al. 2011). However, the technique requires substantial effort, and on average, 45 min is needed for extracting one sample. As a significant amount of water is frozen down in the cold traps during stripping, the stripping probe and cold traps must be changed for each sample, which limits throughput to 5-6 samples per day, not including sample $CO_2$ graphitization. Furthermore, the size of the stripping probe itself (McNichol et al. 1994) is optimized for water samples of about 250 mL, which limits the application of the conventional method in small water samples such as pore water. Pack et al. (2011) developed a compact stripping probe with good efficiency (99.1 ± 2.2%, *n* = 8) that requires only 60 mL water, but the extraction procedure still involves cleaning and flushing between samples, that limits sample processing throughput.

The headspace-extraction method is widely used for DIC δ$^{13}$C analyses. Torres et al. (2005) reported an online method using a Finnigan GasBench-II headspace autosampler coupled with a Finnigan DELTA plus XL isotope-ratio mass spectrometer (IRMS) for precise δ$^{13}$C measurements of DIC. Molnár et al. (2013) developed a similar headspace-extraction technique for DI$^{14}$C analysis of groundwater. In the method of Molnár et al. (2013), after acidifying the water sample, $CO_2$ in the headspace is carried out using a helium (He) flow through a double-hole needle on a GasBench autosampler, and then transferred to either an Automated Graphitization Equipment (AGE) or a gas ion source AMS (Mini Radiocarbon Dating System MICADAS) directly for $^{14}$C analysis. For AGE $^{14}$C analyses, 10 mL groundwater is needed and 80% to 85% of the DIC from acidified water samples can be extracted with a precision of 3.4‰ (± 1σ) for modern water samples. The gas ion source $^{14}$C-AMS analysis only requires 1 mL water and can extract > 90% of the DIC within 20 min, but the precision is only 10‰ (± 1σ) for modern samples. This lower precision is mainly due to the reduced sample sizes (10–100 μg C) that yield lower currents in the AMS, rather than the extraction method itself.

In this study, a high-throughput method for preparing DIC samples for high-precision $^{14}$C-AMS analysis was developed on the basis of the headspace-extraction approach of Molnár et al. (2013). The new method uses a syringe to transfer headspace-equilibrated gases containing the sample $CO_2$ to a vacuum line. This isolates the acidified sample water from the vacuum line during $CO_2$ purification, and minimizes the time and effort involved in sample extraction and subsequent cleaning. Although the extraction efficiency is low (46.6 ± 3.9%; *n* = 10), 0.33–0.37 milligram carbon (mg C) can be extracted from as little as 30 mL surface seawater (or 0.44–0.50 mg C from 45 mL

surface seawater) using one 60 mL syringe extraction, which is sufficient for high-precision $^{14}$C-AMS measurements. The isotopic fractionation associated with the partial extraction of DIC is small (≤ 0.6‰) and is fully corrected by simultaneous measurements of $^{13}$C/$^{12}$C and $^{14}$C/$^{12}$C in the AMS system (Beverly et al. 2010). The online $^{13}$C/$^{12}$C measurement also corrects for other isotopic fractionations that can occur during graphitization and inside the AMS ion source (Santos et al. 2007), which is the key for obtaining high-precision DI$^{14}$C measurements (Liu et al. 2007; Xu et al. 2007).

## Materials and procedures

### Standards and seawater samples

DIC standards were prepared by dissolving $^{14}$C free calcite, an in-house coral standard (CSTD coral from Ellen Druffel), or IAEA-C2 travertine in acidified and stripped seawater following an established protocol (Hinger et al. 2010). They were used to optimize the procedure and test the precision and accuracy of the new method. Calcite is also used as a $^{14}$C-blank for DIC processing and graphitization background corrections. The average fraction modern (Fm; as defined in Stuiver and Polach. 1977) value for 262 $^{14}$C measurements of the conventionally processed DIC coral standard at the Keck Carbon Cycle AMS facility at the University of California, Irvine (KCCAMS/UCI) from January 2006 to September 2011 is 0.9445 ± 0.0018 (1σ stdev). The IAEA consensus Fm value for IAEA-C2 is 0.4114 ± 0.0003 (*n* = 64) (Rozanski et al. 1992), whereas the average value for 100 $^{14}$C measurements of the conventionally processed (Santos et al. 2004) DIC IAEA-C2 at KCCAMS from August 2008 to September 2010 is 0.4118 ± 0.0035 (1σ stdev).

Six surface seawater samples collected in 2011 were analyzed for this study using both the conventional stripping and headspace methods. These seawater samples were used to verify our procedure's reproducibility and accuracy. In addition, 12 stored seawater samples collected during 2008-2009, which were previously measured by the conventional method (Santos et al. 2011) as part of a project to monitor coastal upwelling and local seawater geochemistry, were analyzed using the new headspace technique. All seawater samples were collected from the Newport Beach Pier (NBP) within the Southern California Bight (SCB; 33°36′21″N, 117°55′52″W), using methods described in Hinger et al. (2010).

### Procedure

The procedure of the new headspace-extraction method can be divided into two steps. During the first step, the water sample is acidified under an ultra-high purity (UHP) He or $N_2$ atmosphere and heated to 75°C for rapid equilibration and high $CO_2$ distribution toward the headspace. In step 2, the $CO_2$ produced is extracted using a syringe, purified on a vacuum line, and reduced to graphite.

#### *Water preparation and acidification*

Readily available 60 mL I-Chem septum-sealed screw cap vials (Fisher #05-719-432; with an actual volume of 64 mL)

pre-cleaned with 10% hydrochloric acid (HCl) and baked at 550°C for 4 hours, with Teflon on silicone septa (Fisher #05-719-410), are used for sample processing. An additional black Viton septum (Sigma Aldrich #27355) is added inside the screw cap (Fig. 1, E + D setup in Table 1), as the original I-Chem septum is permeable to $CO_2$ gas. The vials are flushed upside down with UHP He gas in a He glove bag to remove air and then capped tight. A 30 mL BD Luer-Lock tip syringe (Fisher #14-829-48) with a BD 23 g, 2.5 cm needle (Fisher #14-826A) is flushed 3 times with UHP $N_2$ before removing a water sample from a storage bottle, and injecting it into the I-Chem vial through the septum. During the injection, an overpressure will gradually build up in the vial. To fully inject the 30 mL sample water into the sealed He filled 64 mL vial, one has to push hard on the syringe piston for about 30 seconds. This involves some effort, but the advantage of creating an overpressure is that during the subsequent headspace-extraction, gases in the over-pressured headspace will automatically expand into the extraction syringe. After water samples are prepared, a BD 1 mL syringe (Fisher #148232F) attached with a BD 23 g, 2.5 cm needle is used for adding 0.5 mL 85% phosphoric acid ($H_3PO_4$) to each sample. The samples are then gently shaken to mix the acid and placed on a 75°C heating block for 2 hours.

To prepare DIC standards, 4-8 mg carbonate material is ground in an agate motor, weighed out in a small flat-bottomed Pyrex tube, and placed inside the screw cap of an I-Chem vial. After being flushed with He together with the I-Chem vial in a UHP He glove bag, the screw cap is attached to the vial sealing the small Pyrex tube with standard inside the vial. The vial is then upended to spill out the carbonate, 30 mL stripped seawater (made by bubbling $N_2$ gas through previously acidified seawater for > 15 min in a $N_2$ glove bag) is injected and the prepared DIC standards are put through the same acidification and preparation procedures as the water samples.

### $CO_2$ extraction and graphitization

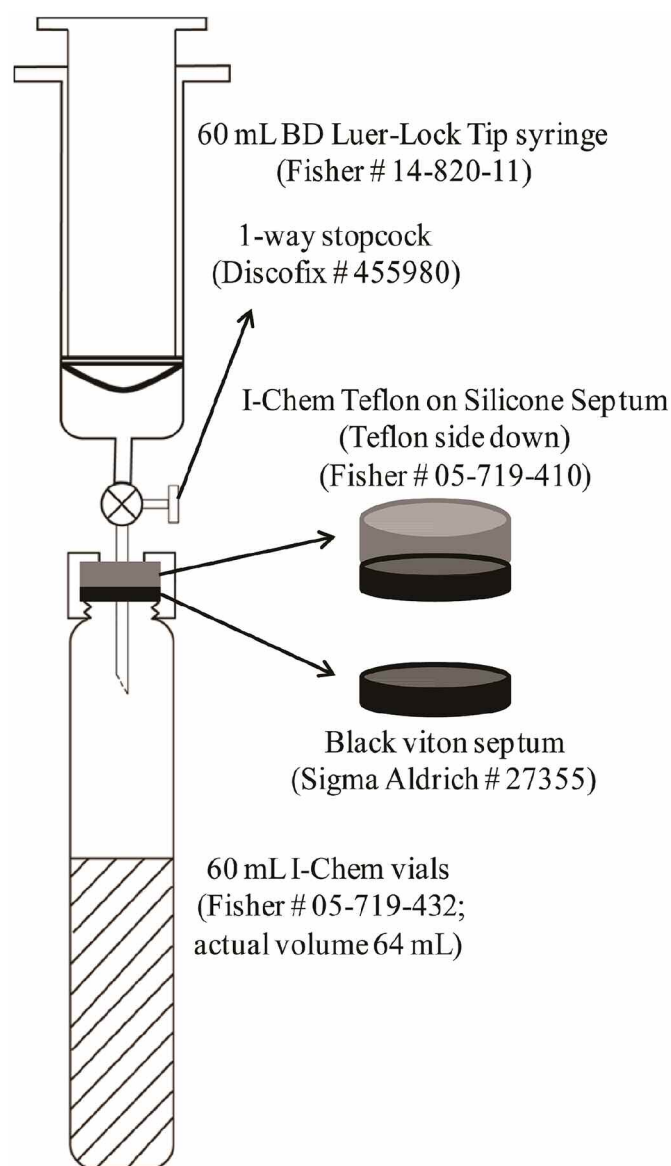The gases (including $CO_2$) in the vial headspace are extracted using a syringe, injected into a vacuum line and



**Fig. 1.** Schematic diagram of the headspace-extraction I-Chem vial setup.

**Table 1.** Stopper/septum combinations used in this study and their associated problems and test results. For septum combinations, such as "E + D," the first "E" was in contact with the water and the second "D" was above "E" as shown in Fig. 1. The Teflon side of the Teflon on silicone septum was placed facedown. *$^{14}$C results obtained using septum indicated with asterisks are discussed in the text.

| Septum[†] | Result | | Problems | |
|---|---|---|---|---|
| | Yield | $^{14}$C result | Leakage | Dead carbon contamination |
| A | Good | Lower | No | Yes |
| B* | Lower | Good | Yes | No |
| B + C* | Good | Good | No | No |
| D + C | Good | Lower | No | Yes |
| E + D* | Good | Good | No | No |

[†]A: Blue butyl rubber stopper (Bellco Glass #2048-11800); B: White Teflon on silicone septum (Fisher #05-719-432, came with I-Chem vials); C: PTFE rubber septum (Thermo Scientific #PI-12422); D: Blue Teflon on silicone septum (Fisher #05-719-410, replacement for septum B that was no longer available during the later stage of this study); E: Black Viton septum (Sigma Aldrich #27355).

cryogenically purified before graphitization. The headspace-extraction schematic diagram is shown in Fig. 1. First, a 1-way stopcock (Discofix #455980) and a BD 23 g, 2.5 cm needle are attached to a 60 mL BD Luer-Lock tip syringe (Fisher #14-820-11). Then, the entire volume of the syringe is flushed three times and filled with 60 mL of UHP $N_2$, which is fully expelled just before the needle penetrates the septum of the I-Chem vial. The over-pressured gases in the vial headspace automatically expand into the syringe. To extract as much headspace gases as possible, the syringe piston is pulled back to the 60 mL scale mark and held for about 20 seconds before the stopcock is closed. For a low DIC concentration (ie, 500 µmol L$^{-1}$ DIC) sample, a second or third extraction can be performed if more $CO_2$ is required.

The extraction syringe is attached to a cryogenic purification vacuum line (Xu et al. 2007) through a septum (Alltech #AT6518) in an Ultra-Torr fitting (Swaglok #SS-4-UT-3) and sample gases are released into the vacuum line after opening the stopcock. Sample $CO_2$ is cryogenically purified through a dry ice/ethanol trap and collected in a liquid nitrogen trap, and the purified $CO_2$ is converted to graphite using the sealed tube zinc reduction method described by Xu et al. (2007). The graphite/iron mixture is pressed into an aluminum target holder and analyzed for $^{14}$C at the KCCAMS facility (Southon et al. 2004; Beverly et al. 2010) or at the Peking University Accelerator Mass Spectrometry facility (PKUAMS) (Liu et al. 2007).

## Assessment

A series of experiments were conducted to optimize the new method, including tests of different types of septum, heating temperature, heating time, water volume (water/headspace ratio), number of headspace-extractions, and headspace pressure. Then the efficiency, background, accuracy, and precision were evaluated by comparing the DI$^{14}$C results of the standards and seawater samples to their consensus values or to DI$^{14}$C results previously obtained by the conventional method. Finally, the utility of the new method was demonstrated at a second AMS laboratory at Peking University, China (PKU).

### Septum contamination prevention

The choice of septa for the I-Chem vials is crucial for this technique. Septa must be impermeable to $CO_2$ and must also be resistant to acid vapor under elevated temperatures. Corrosion of a septum may release trace amounts of carbonaceous material and typically leads to lower $^{14}$C/$^{12}$C ratios, since most septa are made from $^{14}$C-free materials. The resulting bias may be significant, particularly for high-precision measurements on near-modern $^{14}$C samples such as seawater. Five types of stopper/septum combinations were tested, and the results are summarized in Table 1.

Some septa did release old carbon during sample processing: septum A for the 120 mL serum bottles that we used initially in these experiments showed the presence of contami-

nants (Table 1; Fig. 2). The Fm difference between the headspace-extraction method with septum A and the conventional stripping method (headspace minus conventional) ranged from 0.0046 to –0.0230, with most of the headspace Fm values lower than the conventional method values (Fig. 2). The mean Fm differences for the CSTD coral and NBP_12May_11 seawater sample are –0.0040 ± 0.0059 ($n$ = 17) and –0.0075 ± 0.0078 ($n$ = 13), respectively; equivalent to releases of 4.2 ± 5.8 and 7.4 ± 7.6 µg dead carbon (Fm = 0) per mg C sample, respectively. The Fm differences become larger and more erratic for samples subjected to higher heating temperatures and longer heating times (Fig. 2). The contamination introduced by this type of septum cannot be corrected for precisely, because the amount of old carbon incorporated into the sample is highly variable even under constant heating conditions.

Septum B used for the 64 mL I-Chem vials does not introduce any contamination, but unfortunately it is permeable to $CO_2$ gas. The efficiency for the first extraction with septum B for samples maintained at 75°C for 24 hours was 43.9 ± 2.3% ($n$ = 6), slightly lower than for samples maintained for just 2 hours (46.4 ± 4.5%, $n$ = 6), suggesting that $CO_2$ gas was escaping from the over-pressured headspace overnight.

Septum D shows minor contamination problems: the headspace Fm values for CSTD coral averaged 0.0025 ± 0.0023 ($n$ = 18) lower than the conventional method. Based on our tests, we choose septum E (black viton), which can resist acid vapor at elevated temperatures (75°C) and does not bias the $^{14}$C results. However, septum B or D is still needed because septum E is too thin to make a good seal with the vial screw cap. All
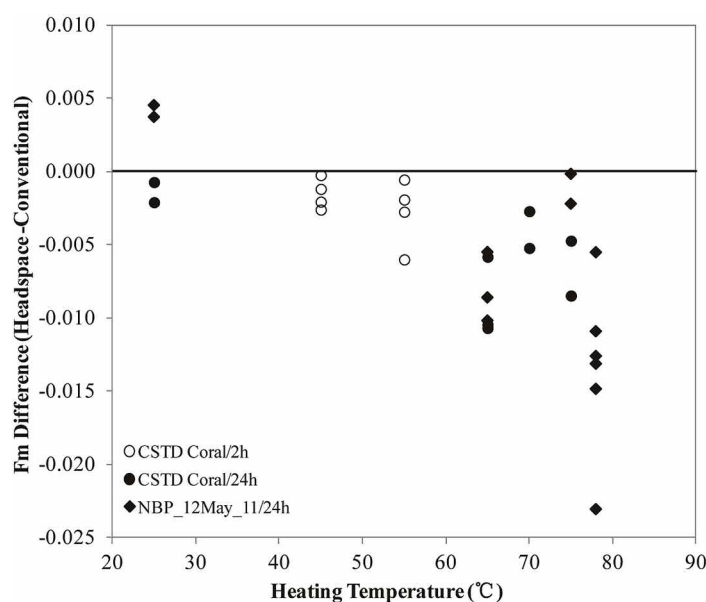


**Fig. 2.** Differences between $^{14}$C Fm values of CSTD coral and NBP_12May_11 seawater samples obtained using the headspace-extraction and conventional stripping methods. Headspace samples were prepared with Septum A (shown in Table 1) under different extraction temperatures and durations.

seawater results presented in this study were obtained using septum E facing the water sample plus septum D on top (Teflon side down; Fig. 1), although the septum combination of E + B would be equivalent.

**Temperature and time**

In a tightly capped 64 mL vial with a fixed water volume, temperature and time are the two key factors that control the sample $CO_2$ distribution between the water and headspace. Elevated temperature and longer equilibration time will shift the carbonate equilibrium toward higher $CO_2$ concentrations in the headspace, and thus affect the final extraction efficiency. We tested different temperatures (room temperature

and 75°C) and heating times (1, 2, and 24 h) to optimize extraction efficiencies (Fig. 3a and 3b). Extraction efficiency is calculated by comparing the amount of $CO_2$ extracted to the amount of standard added (i.e., extraction efficiency [%] = 100 × $C_{extracted}$ [mg]/[Carbonate weight (mg) × 12%]; where 12% is the average carbon content in carbonate standards).

After 24 hours of heating at 75°C, more headspace $CO_2$ can be extracted than at 25°C (Fig. 3a; 54.6 ± 0.7%; $n$ = 2 versus 26.5 ± 1.8%; $n$ = 11). This is expected because the solubility of $CO_2$ in water decreases with higher temperature and thus more $CO_2$ is distributed in the vial headspace. The extraction efficiency reached 46.6 ± 3.9% ($n$ = 10) after just 2 hours at
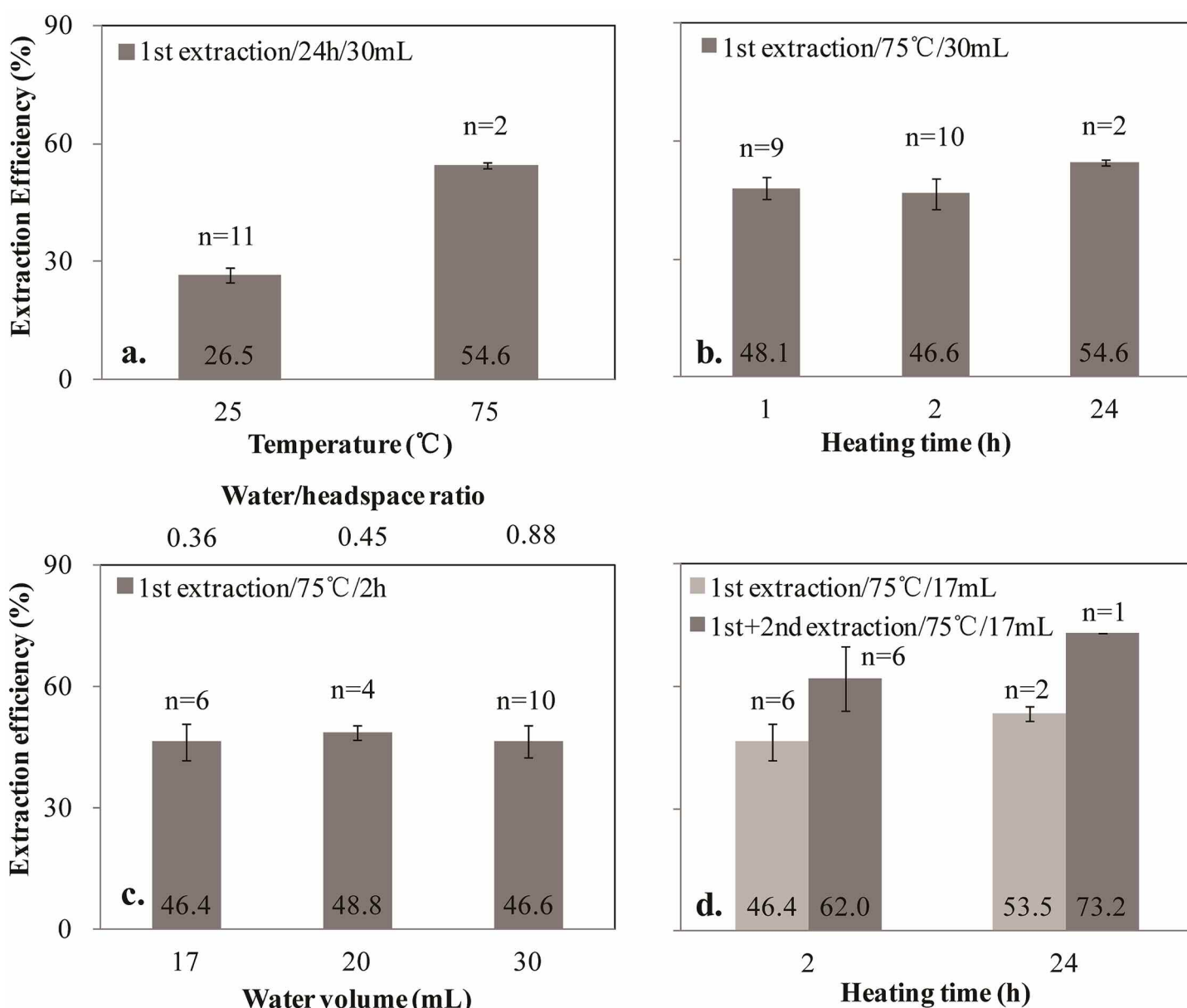


**Fig. 3.** Comparison of extraction efficiency (under an overpressured headspace) with a. temperature, b. heating time, c. water volume, and d. number of extraction. Values listed in columns are the average extraction efficiencies obtained under specified acidification/extraction conditions.

75°C (Fig. 3b), and we used these conditions for all of the remaining tests.

### Water/headspace ratio

The theoretical distribution of $CO_2$ between water and headspace versus different water volumes (mL) in a 64 mL over-pressured I-Chem vial was calculated based on Henry's Law (Fig. 4a). The calculations assume 1980 μmol DIC L$^{-1}$ (DIC concentration of surface seawater sample NBP_12May_11) and use the solubility of $CO_2$ in pure water (ranging from 0.0204% to 0.1049% mol $CO_2$ per mol pure water) at 75°C from Diamond and Akinfiev (2003) under different headspace over-pressures of 0.1201-0.4632 MPa that correspond to water volumes from 10-50 mL in a 64 mL vial. The salinity effect on $CO_2$ solubility is small based on carbonate standards prepared by stripped seawater and Milli-Q water, and thus is ignored. The theoretical percentage of DIC released as $CO_2$ from a water sample to the vial headspace decreases from 95% to 43% as headspace volumes decreases from 54 to 14 mL (Fig. 4a, thin dashed line). However, the theoretical total carbon mass of

$CO_2$ in the vial headspace follows a different pattern (Fig. 4a, thin solid line). It increases with water volume until 40 mL. For example, there is 0.23 mg C in the headspace with 10 mL water, whereas there is 0.61 mg C with 40 mL water. This is because larger volumes of water contain more DIC-carbon and thus releases more $CO_2$ to the vial headspace. Once the water volume passes 40 mL the total carbon mass of $CO_2$ in the vial headspace starts to decrease, as the vial headspace volume now becomes the limiting factor (Fig. 4a).

The theoretical yield (mg C) extracted with a 60 mL syringe extraction is also related to the fraction of headspace gases recovered. During the first extraction of a 30 mL water sample (34 mL headspace), the syringe can isolate and extract 63.8% of the headspace gases; while only 57.7% of the headspace gases can be recovered for a 20 mL water sample (44 mL headspace). Thus, after correcting for the fraction of headspace extractable in a 60 mL syringe, we get a ~50% theoretical yield for DIC from water samples ranging from 10 to 30 mL (Fig. 4a, thick dashed line). Accordingly, the corrected theoretical car-
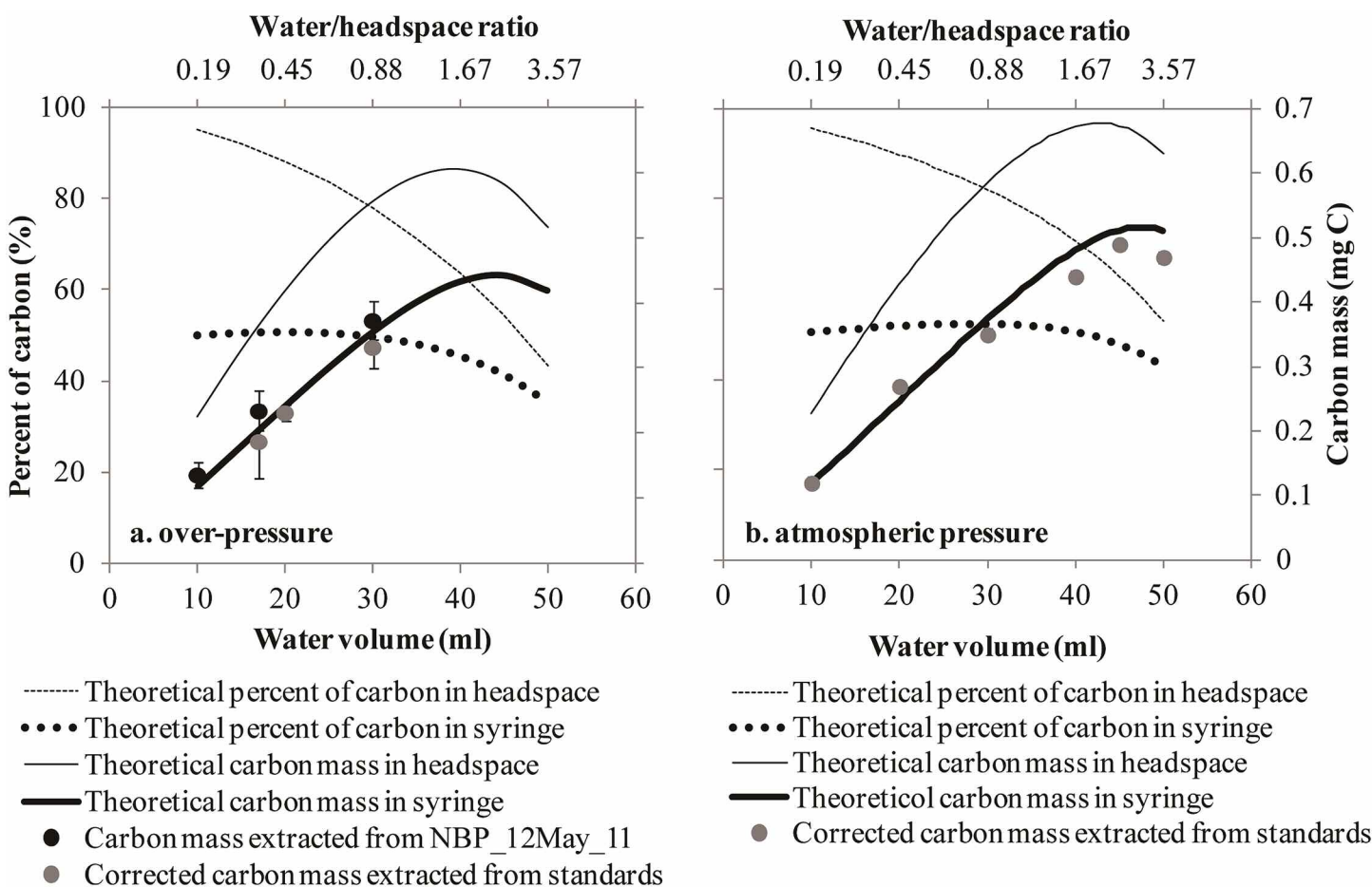


**Fig. 4.** The theoretical percent of carbon and carbon mass (mg C) distribution in the headspace of a 64 mL vial and extracted with a 60 mL syringe under different water volumes (water/headspace ratios): a, overpressured headspace created by injecting water into a septum capped 64 mL I-Chem vial; b, atmospheric pressure (0.1013 MPa) headspace created by pouring water into a 64 mL I-Chem vial inside a N2 glove bag. The mg C extracted from seawater samples (closed black circles) and standards (closed gray circles) are plotted also to compare with the theoretical curves. A DIC concentration of 1980 μmol DIC L-1 is assumed for the theoretical estimates, and standard samples have been corrected to this DIC concentration.

bon mass extractable in a 60 mL syringe would increase from 0.12 to 0.36 mg C (Fig. 4a, thick solid line) as the water volume increases from 10 to 30 mL.

The optimum water/headspace ratio was tested using standards and samples with water volumes of 17, 20, and 30 mL (water: headspace ratios ranging from 0.36 to 0.88, with an over-pressured headspace). Water volumes in the 30-40 mL range were not investigated because the additional carbon mass in the headspace is not significant (0.61 mg C for 40 mL water versus 0.56 mg C for 30 mL), and it becomes too difficult to inject > 30 mL water against the overpressure of the sealed 64 mL I-Chem vial. Water volumes > 40 mL were not investigated because the total mass of $CO_2$ in the headspace starts to decrease at this point (Fig. 4a). Yields of 46.4 ± 4.5% (*n* = 6) for 17 mL water and 46.6 ± 3.9% (*n* = 10) for 30 mL water were obtained (Fig. 3c), which are slightly lower (due to only 2 hours of equilibration), but comparable to the calculated percent of carbon (~ 50%) extractable in the 60 mL syringe. The total mg C extracted from the headspace of replicate surface seawater samples (closed black circles in Fig. 4a; NBP_12May_11 seawater, 1980 μmol DIC L$^{-1}$) increased from 0.14 to 0.37 mg C as water volume increased from 10 to 30 mL. Similarly, the total mg C extracted from standard samples corrected to a DIC concentration of 1980 μmol L$^{-1}$ increased from 0.19 to 0.33 mg C as water volumes increased from 17 to 30 mL (Fig. 4a; closed gray circles). Both sample and standard masses of C extracted are consistent with the Henry's Law calculations. These experiments show that a water/headspace ratio of 0.88 (i.e., 30 mL water and 34 mL headspace, with an overpressured headspace) provides a sufficient amount of $CO_2$ for graphitization.

**Second and third extraction**

After the first extraction, of a 30-mL water sample, which removes about 63.8% of the headspace gases from the I-Chem vial, the pressure in the headspace is < 0.1013 MPa and some of the $CO_2$ left in the water will move to the headspace under this lower pressure condition. Thus, the $CO_2$ left in the vial will redistribute between the water and headspace until it reaches a new equilibrium state. This enables us to perform a second or third headspace-extraction on the same sample if necessary. For this, the I-Chem vial is placed back in the heating block for 5 min before the next extraction. During the waiting time, another 60 mL BD syringe is flushed and filled with 60 mL of UHP N$_2$ gas. A portion of the N$_2$ gas (20 mL) is expelled from the syringe just before the needle penetrates the septum of the I-Chem vial, and the remaining 40 mL of N$_2$ gas is injected into the vial to serve as a carrier gas for the leftover headspace gases/$CO_2$. As before, the resulting overpressure in the headspace reduces the effort involved in the second extraction. A third extraction can be applied in a similar manner if more C is needed.

As expected, the extraction efficiency changes with the number of extractions (Fig. 3d). Note that we have not included the results for septa B (white Teflon on silicone sep-

tum) associated with the 24 hours heating time in Fig. 3d because this septum is prone to leakage. The average extraction efficiency for the first plus second extraction after 2 hours heating is 62.0 ± 7.8% (*n* = 6), about 15% higher than the first extraction (46.4 ± 4.5%; *n* = 6) alone. The average calcite blank values for the first plus second extraction and the first extraction are 45,600 ± 1400 radiocarbon year (*n* = 3) and 41,900 ± 1600 radiocarbon year (*n* = 3), respectively. We believe that the slightly better background from the first plus second extraction is due to a mass balance effect (Santos et al. 2007), as the total carbon mass for the combined extraction is larger, so that the modern carbon contamination involved in the whole procedure is diluted. The average CSTD coral Fm value is 0.9435 ± 0.0008 (*n* = 3) for the first extraction and 0.9436 ± 0.0020 (*n* = 3) for the first plus second extraction (Table 2) after 2 hours heating, indicating that the second extraction introduces no noticeable modern or old carbon. Considering that the second extraction is relatively time consuming (an additional 10 minutes for each sample), only the first extraction was used for seawater samples in this study. Nonetheless, we feel that this exercise was important, as a second extraction can also be used as a backup or duplicate for the sample if needed.

**Headspace pressure**

As described in the sample preparation above, injecting water into a sealed 64 mL I-Chem vial results in an overpressured headspace. We initially chose this procedure because we were handling water samples stored in septum crimp capped bottles, and it was easier to transfer water using a syringe and inject the water directly into the I-Chem vial. Further, this procedure does not require a glove bag and the overpressure makes the subsequent syringe extraction easier. Alternatively, for a near atmospheric headspace pressure (0.1013 MPa), we can remove some of the He gas to compensate for the volume of water that we intend to add, or pour water directly into the I-Chem vial in a N$_2$ glove bag. The advantages of a near atmospheric pressure headspace are (1) it reduces the chance of $CO_2$ leakage through septa compared to overpressured conditions; (2) it increases $CO_2$ distribution in headspace (Fig. 4b).

Similar to the overpressured headspace, the theoretical percentage of carbon in the atmospheric pressure headspace decreases when water volume increases (Fig. 4b, thin dashed line), but the carbon mass in the headspace (Fig. 4b, thin solid line) increases and reaches its maximum value (0.68 mg C) under 43 mL water volume. The theoretical carbon mass extractable by a 60 mL syringe would increase from 0.12 to 0.51 mg C (Fig. 4b, thick solid line) as the water volume increases from 10 to 45 mL. This is proven by our test results: the corrected carbon masses (mg C) of standards extracted in the 60 mL syringe (Fig. 4b, closed gray circles) increased from 0.12 to 0.49 mg C for water ranging from 10 to 45 mL, and dropped to 0.47 mg C under 50 mL.

Two CSTD coral and 3 calcite samples with released pressure (i.e., approximately 0.1013 MPa, noted by asterisks in Table 2) were processed and analyzed for $^{14}$C. For these sam-

**Table 2.** Measured ${}^{14}$C values of CSTD coral, IAEA-C2, and calcite standards prepared with the headspace method at the KCCAMS facility under different experimental conditions.

| Lab Nr UCIAMS | Standard ID | Weight (mg) | Septa type | Heating T (°C) | Heating time (h) | Water V (mL) | Extraction nr | Yield (mg C) | Fm | ± | ${}^{14}$C Age (yr) | ± |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 94555 | CSTD | 6.9 | B | 75 | 2 | 17 | first | 0.42 | 0.9445 | 0.0017 | 460 | 15 |
| 94556 | CSTD | 6.0 | B | 75 | 2 | 17 | first + second | 0.49 | 0.9456 | 0.0016 | 450 | 15 |
| 94862 | CSTD | 7.5 | B | 25 | 24 | 17 | first | 0.23 | 0.9459 | 0.0013 | 445 | 15 |
| 94863 | CSTD | 6.0 | B | 25 | 24 | 17 | first + second | 0.28 | 0.9462 | 0.0012 | 445 | 15 |
| 94864 | CSTD | 7.8 | B | 75 | 24 | 17 | first | 0.42 | 0.9420 | 0.0015 | 480 | 15 |
| 94865 | CSTD | 6.7 | B | 75 | 24 | 17 | first + second | 0.49 | 0.9427 | 0.0012 | 475 | 15 |
| 94870 | CSTD | 7.3 | B | 75 | 24 | 17 | first | 0.41 | 0.9453 | 0.0012 | 450 | 15 |
| 94872 | CSTD | 8.1 | B | 75 | 24 | 17 | first + second | 0.57 | 0.9427 | 0.0012 | 475 | 15 |
| 94873 | CSTD | 7.1 | B | 75 | 24 | 17 | first | 0.34 | 0.9423 | 0.0012 | 480 | 15 |
| 94874 | CSTD | 7.3 | B | 75 | 24 | 17 | first + second | 0.51 | 0.9453 | 0.0012 | 450 | 15 |
| 94879 | CSTD | 6.8 | B | 75 | 2 | 17 | first | 0.34 | 0.9431 | 0.0012 | 470 | 15 |
| 94880 | CSTD | 7.8 | B | 75 | 2 | 17 | first + second | 0.46 | 0.9416 | 0.0012 | 485 | 15 |
| 94881 | CSTD | 8.0 | B | 75 | 2 | 17 | first | 0.46 | 0.9430 | 0.0012 | 470 | 15 |
| 94882 | CSTD | 7.8 | B | 75 | 2 | 17 | first + second | 0.60 | 0.9436 | 0.0012 | 465 | 15 |
| 95651 | CSTD | 6.7 | B + C | 75 | 24 | 17 | first | 0.42 | 0.9439 | 0.0019 | 465 | 20 |
| 95795 | CSTD | 6.1 | B + C | 75 | 2 | 20 | first | 0.37 | 0.9442 | 0.0016 | 460 | 15 |
| 95803 | CSTD | 4.6 | B + C | 25 | 24 | 30 | first | 0.15 | 0.9486 | 0.0017 | 425 | 15 |
| 95804 | CSTD | 4.7 | B + C | 25 | 24 | 30 | first | 0.15 | 0.9469 | 0.0018 | 440 | 20 |
| 95805 | CSTD | 7.7 | B + C | 25 | 24 | 30 | first | 0.25 | 0.9458 | 0.0021 | 445 | 20 |
| 95807 | CSTD* | 8.2 | B + C | 25 | 24 | 30 | first | 0.25 | 0.9421 | 0.0017 | 480 | 15 |
| 95808 | CSTD* | 7.8 | B + C | 25 | 24 | 30 | first | 0.25 | 0.9408 | 0.0015 | 490 | 15 |
| 96214 | CSTD | 6.0 | B + C | 75 | 1 | 30 | first | 0.36 | 0.9440 | 0.0016 | 465 | 15 |
| 96215 | CSTD | 6.9 | B + C | 75 | 1 | 30 | first | 0.35 | 0.9442 | 0.0016 | 460 | 15 |
| 96217 | CSTD | 8.0 | B + C | 75 | 1 | 30 | first | 0.43 | 0.9438 | 0.0015 | 465 | 15 |
| 97341 | CSTD | 6.6 | B + C | 75 | 2 | 20 | first | 0.37 | 0.9432 | 0.0019 | 470 | 20 |
| 99133 | CSTD | 6.7 | E + D | 75 | 2 | 30 | first | 0.36 | 0.9433 | 0.0013 | 470 | 15 |
| 99134 | CSTD | 7.0 | E + D | 75 | 24 | 30 | first | 0.46 | 0.9439 | 0.0013 | 465 | 15 |
| 99408 | CSTD | 6.0 | E + D | 75 | 2 | 30 | first | 0.33 | 0.9436 | 0.0019 | 465 | 20 |
| 99435 | CSTD | 6.7 | E + D | 75 | 2 | 30 | first | 0.40 | 0.9441 | 0.0019 | 460 | 20 |
| 99437 | CSTD† | 6.3 | E + D | 75 | 2 | 30 | first | 0.31 | 0.9466 | 0.0017 | 440 | 15 |
| 96218 | IAEA-C2 | 6.3 | B + C | 75 | 1 | 30 | first | 0.39 | 0.4143 | 0.0011 | 7080 | 25 |
| 96219 | IAEA-C2 | 6.7 | B + C | 75 | 1 | 30 | first | 0.40 | 0.4142 | 0.0011 | 7080 | 25 |
| 96220 | IAEA-C2 | 8.1 | B + C | 75 | 1 | 30 | first | 0.46 | 0.4125 | 0.0011 | 7115 | 25 |
| 99409 | IAEA-C2 | 6.2 | E + D | 75 | 2 | 30 | first | 0.35 | 0.4139 | 0.0011 | 7085 | 25 |
| 99436 | IAEA-C2 | 6.1 | E + D | 75 | 2 | 30 | first | 0.36 | 0.4141 | 0.0010 | 7085 | 20 |
| 99438 | IAEA-C2† | 6.5 | E + D | 75 | 2 | 30 | first | 0.31 | 0.4159 | 0.0012 | 7050 | 25 |
| 94553 | Calcite | 5.7 | B | 75 | 2 | 17 | first | 0.30 | 0.0065 | 0.0001 | 40400 | 170 |
| 94554 | Calcite | 5.0 | B | 75 | 2 | 17 | first + second | 0.41 | 0.0029 | 0.0001 | 46940 | 190 |
| 94858 | Calcite | 5.2 | B | 25 | 24 | 17 | first | 0.15 | 0.0079 | 0.0001 | 38940 | 150 |
| 94859 | Calcite | 5.5 | B | 25 | 24 | 17 | first + second | 0.26 | 0.0059 | 0.0001 | 41180 | 140 |
| 94860 | Calcite | 5.9 | B | 75 | 24 | 17 | first | 0.30 | 0.0052 | 0.0001 | 42310 | 190 |
| 94861 | Calcite | 7.7 | B | 75 | 24 | 17 | first + second | 0.57 | 0.0036 | 0.0001 | 45130 | 160 |
| 94866 | Calcite | 7.3 | B | 75 | 24 | 17 | first | 0.38 | 0.0055 | 0.0001 | 41810 | 140 |
| 94867 | Calcite | 7.0 | B | 75 | 24 | 17 | first + second | 0.50 | 0.0053 | 0.0001 | 42060 | 150 |
| 94868 | Calcite | 8.1 | B | 75 | 24 | 17 | first | 0.44 | 0.0068 | 0.0001 | 40060 | 170 |
| 94869 | Calcite | 8.4 | B | 75 | 24 | 17 | first + second | 0.60 | 0.0060 | 0.0001 | 41060 | 130 |
| 94875 | Calcite | 6.2 | B | 75 | 2 | 17 | first | 0.39 | 0.0044 | 0.0001 | 43510 | 150 |
| 94876 | Calcite | 6.1 | B | 75 | 2 | 17 | first + second | 0.49 | 0.0041 | 0.0001 | 44100 | 180 |

*continued…*

**Table 2.** *Continued*

| Lab Nr UCIAMS | Standard ID | Weight (mg) | Septa type | Heating T (°C) | Heating time (h) | Water V (mL) | Extraction nr | Yield (mg C) | Fm | ± | $^{14}$C Age (yr) | ± |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 94877 | Calcite | 7.0 | B | 75 | 2 | 17 | first | 0.36 | 0.0055 | 0.0001 | 41860 | 140 |
| 94878 | Calcite | 7.8 | B | 75 | 2 | 17 | first + second | 0.52 | 0.0034 | 0.0001 | 45770 | 220 |
| 95652 | Calcite | 6.4 | B + C | 75 | 24 | 17 | first | 0.42 | 0.0051 | 0.0001 | 42400 | 160 |
| 95796 | Calcite | 6.3 | B + C | 75 | 2 | 20 | first | 0.37 | 0.0045 | 0.0001 | 43480 | 180 |
| 95797 | Calcite | 4.3 | B + C | 25 | 24 | 30 | first | 0.15 | 0.0091 | 0.0002 | 37780 | 160 |
| 95798 | Calcite | 4.6 | B + C | 25 | 24 | 30 | first | 0.16 | 0.0084 | 0.0002 | 38390 | 150 |
| 95799 | Calcite | 7.8 | B + C | 25 | 24 | 30 | first | 0.25 | 0.0057 | 0.0001 | 41560 | 170 |
| 95800 | Calcite* | 4.1 | B + C | 25 | 24 | 30 | first | 0.13 | 0.0091 | 0.0002 | 37750 | 170 |
| 95801 | Calcite* | 7.8 | B + C | 25 | 24 | 30 | first | 0.21 | 0.0060 | 0.0002 | 41030 | 260 |
| 95802 | Calcite* | 7.3 | B + C | 25 | 24 | 30 | first | 0.24 | 0.0057 | 0.0001 | 41540 | 160 |
| 96211 | Calcite | 6.2 | B + C | 75 | 1 | 30 | first | 0.36 | 0.0047 | 0.0001 | 42980 | 130 |
| 96212 | Calcite | 6.8 | B + C | 75 | 1 | 30 | first | 0.40 | 0.0042 | 0.0001 | 43980 | 120 |
| 96213 | Calcite | 8.1 | B + C | 75 | 1 | 30 | first | 0.49 | 0.0041 | 0.0001 | 44250 | 130 |
| 96783 | Calcite | 5.8 | B + C | 75 | 2 | 20 | first | 0.35 | 0.0060 | 0.0001 | 41150 | 100 |
| 97332 | Calcite | 6.0 | B + C | 75 | 24 | 17 | first + second | 0.53 | 0.0045 | 0.0001 | 43320 | 130 |
| 99137 | Calcite | 5.6 | E + D | 75 | 2 | 30 | first | 0.32 | 0.0047 | 0.0001 | 43050 | 170 |
| 99138 | Calcite | 6.4 | E + D | 75 | 24 | 30 | first | 0.42 | 0.0034 | 0.0001 | 45700 | 170 |
| 99407 | Calcite | 6.3 | E + D | 75 | 2 | 30 | first | 0.38 | 0.0032 | 0.0001 | 46180 | 160 |
| 99434 | Calcite | 6.1 | E + D | 75 | 2 | 30 | first | 0.37 | 0.0032 | 0.0001 | 46160 | 180 |

*Sample was under 0.1013 MPa released headspace pressure; †Sample was under N$_2$ headspace.

ples, 30 mL of He in the headspace of the 64 mL I-Chem vials was removed via syringe before injecting the acid-stripped seawater. Under the released pressure, the calcite blank value is 40,100 ± 2100 (*n* = 3) radiocarbon year, slightly higher than the one with overpressured headspace (44,100 ± 1700 radiocarbon year, *n* = 28), most likely due to the relatively smaller sample sizes (0.13-0.24 mg C) of these 3 standards. The CSTD coral Fm value under the released pressure is 0.9414 ± 0.0015 (*n* = 2), which is slightly depleted compared to its KCCAMS average value of 0.9445 ± 0.0018 (*n* = 262), but not statistically different (*t* = -4.7, df = 1, *P* = 0.13).

Another two standard samples (noted by daggers in Table 2) were prepared by pouring water into the vial in a UHP N$_2$ glove bag to create a atmospheric headspace pressure (0.1013 MPa): an I-Chem vial was flushed 3 times with UHP N$_2$, 30 mL stripped seawater was poured into the vial inside a N$_2$ glove bag, then the Pyrex tube containing the carbonate standard was dropped into the stripped seawater and the vial was immediately capped tight. The Fm value of the CSTD coral and IAEA-C2 standards obtained (0.9466 ± 0.0017 and 0.4159 ± 0.0012, respectively) are both in good agreement with the KCCAMS average values. Thus, a N$_2$ headspace with 0.1013 MPa pressure can be used as an alternative procedure. Under certain circumstances, where seawater samples are collected in glass storage bottles capped with nonpenetrable glass stoppers or plastic screw caps, it is easier and preferable to pour water into the I-Chem vial inside a UHP N$_2$ glove bag, and sample size of ~0.5 mg C for surface seawater could be obtained with 45 mL water under atmospheric headspace pressure.

**Protocol summary**

The optimum procedure for the headspace method (with overpressure headspace) in this study is set as follows: injection of 30 mL water into a He pre-flushed 64 mL vial setup (Fig. 1), heating under 75°C for 2 h followed by one headspace gas extraction. All seawater samples were processed using these experimental conditions. Alternatively, the UHP He used in preflushing can be substituted by UHP N$_2$ that is less expensive. Either overpressured or atmospheric pressure headspace does not affect the $^{14}$C results of the tested standards and seawater samples.

**Beam current and mass dependent fractionation**

For all standard and seawater samples obtained using the new method, samples > 0.3 mg C yielded 60-100 $\mu$A$^{12}$C$^{+1}$ current at the high energy Faraday cup in the KCCAMS system, which is comparable to ~0.75 mg C samples graphitized using the sealed tube zinc reduction method and run through the KCCAMS system (Khosh et al. 2010). Thus, the smaller size of graphite associated with the lower headspace-extraction efficiency has little effect on the $^{14}$C-AMS measurements.

Due to the incomplete extraction of headspace CO$_2$, one would expect some carbon isotopic fractionation between the CO$_2$ dissolved in the water and the CO$_2$ extracted from the headspace. To evaluate the magnitude of this fractionation, we measured the headspace $\delta^{13}$C-CO$_2$ of standard samples including calcite, IAEA-C2, CSTD coral, NBS-18, and NBS-19 and compared them to either $\delta^{13}$C consensus values or conventional stripping values. The conventional stripping method should have negligible isotope fractionation because

the sample $CO_2$ is fully stripped out from the water (> 98%). For the headspace measurements, after a 24 hours equilibration at room temperature (~25°C), 3 mL of the headspace gas in a 64 mL I-Chem vial was extracted using a 10 mL gas-tight syringe and injected into a He pre-flushed septum capped Exetainer vial (Labco). One NBS-18 and one NBS-19 headspace gas sample were extracted from the 64 mL vials after an additional 2 hours heating at 75°C. $\delta^{13}$C values were then measured using a Finnigan Delta-Plus IRMS coupled with a Gasbench II autosampler at UCI. There is an excellent correlation ($R^2$ = 0.9991) between the $\delta^{13}$C values of the headspace-extracted $CO_2$ and their consensus value or the corresponding aliquots extracted by the conventional stripping method (Fig. 5). However, the $\delta^{13}$C values for the headspace-extracted $CO_2$ after equilibrium at 25°C for 24 hours are slightly heavier than the fully stripped conventional method values (by ~0.6‰; Fig. 5, closed gray circles), and the 2 standards extracted after an additional 2 hours heating under 75°C show a similar deviation (~0.4‰ heavier; Fig. 5, closed black circles). We also measured the $\delta^{13}$C of one CSTD coral $CO_2$ subsampled from the purified $CO_2$ of its headspace-extraction using our regular $^{14}$C sample protocol (75°/2 h, first extraction), and compare it to the $\delta^{13}$C value measured using DIC-$\delta^{13}$C method similar to Torres et al. (2005) (Fig. 5, black triangle). Similarly, the $\delta^{13}$C value of this headspace $^{14}$C split is slightly heavier (0.23‰) than its DIC-$\delta^{13}$C value.

As mentioned earlier, the small fractionation caused by the headspace-extraction (ca. ≤ 0.6‰) will not affect the $^{14}$C-AMS measurements because it is fully corrected by the online $^{13}$C/$^{12}$C measurements in our AMS system. In addition, assuming that $^{14}$C fractionation is twice that of $^{13}$C, this fractionation would only introduce ~1.2‰ uncertainty into our $^{14}$C results, which is still well within our typical $^{14}$C analytical error of ~2-3‰ for modern samples. This means that the headspace method can potentially be used for AMS systems without the online $^{13}$C/$^{12}$C capability. However, when the sealed tube Zn reduction graphitization method is used as in this study, it is preferable to have the online $^{13}$C/$^{12}$C measurement for obtaining high-precision DI$^{14}$C results, because there is a ~2-3‰ fractionation (lighter) involved in this graphitization method (Xu et al. 2007) and additional fractionation can occur inside the AMS ion source.

**Background**

The background of the headspace method was evaluated by measuring a set of 31 $^{14}$C-free calcite standards under different experiment conditions at KCCAMS (Table 2; Fig. 6c). The overall average background of our headspace method is better than 42,500 ± 2500 radiocarbon year ($n$ = 31) for sample sizes from 0.13 to 0.6 mg C. Since the blank is mass dependent and improves as the sample size increases (Fig. 7), the average background for samples > 0.3 mg C is better than 43,400 ± 1900 radiocarbon year ($n$ = 23). This is older than the background value of 40,500 ± 1000 radiocarbon year ($n$ = 12) reported by Hinger et al. (2010) for conventional stripping
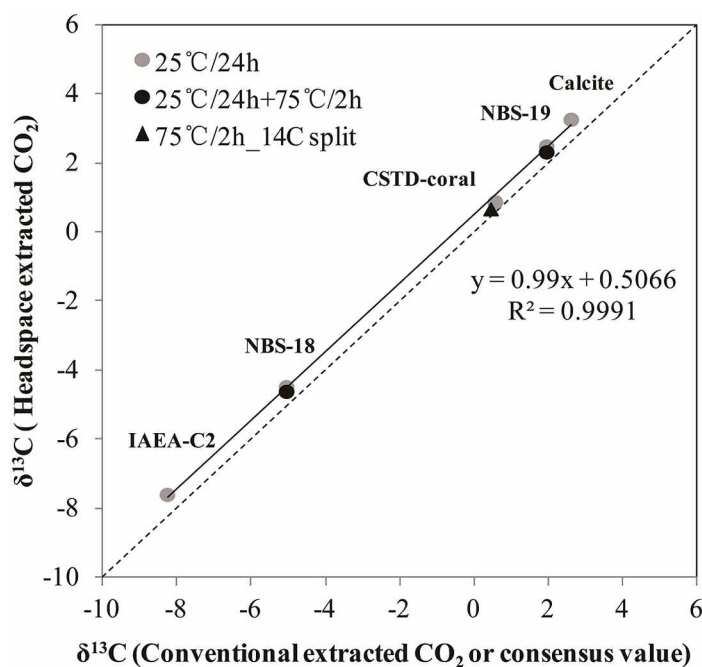


**Fig. 5.** Comparison of the IRMS measured $\delta^{13}$C value of headspace extracted $CO_2$ and conventional stripping extracted $CO_2$ sample ($\delta^{13}$C consensus values were used when available for standards IAEA-C2, NBS 18, and NBS 19). The dashed line is the 1:1 line, and the linear regression is shown as a solid line.

and graphitization of 1 mg C samples and thus will have very little influence on seawater DI$^{14}$C results, as the oldest seawater ages are around 2000 year (Matsumoto 2007).

**Precision and accuracy**

The average CSTD coral Fm value measured by the headspace-extraction method at KCCAMS is 0.9441 ± 0.0017 (1σ stdev, $n$ = 30) (Table 2; Fig. 6a), and one sample $t$ test shows that this is in good agreement with the average KCCAMS value for CSTD coral ($t$ = -1.3, df = 29, $P$ = 0.21). The stdev obtained from the headspace extracted CSTD coral yields a relative error of 1.7‰.

The average Fm value measured for IAEA-C2 is 0.4141 ± 0.0011 (1σ stdev, $n$ = 6) (Table 2; Fig. 6b). Although these results are consistent with the average value measured on leached IAEA-C2 at the KCCAMS (0.4118 ± 0.0035, $n$ = 100), the headspace average value is slightly higher compared with the IAEA consensus value (0.4114 ± 0.0003), perhaps because we did not leach the C2 powder before making up the six standards. Also, the C2 travertine material is not completely homogeneous: it contains small balls that have slightly older $^{14}$C ages (7148 ± 62 radiocarbon year, $n$ = 6) than the fine powder (7086 ± 17 radiocarbon year; $n$ = 6; unpublished data from John R. Southon), which may have contributed to the discrepancy. Moreover, fine powders of $CaCO_3$ tend to adsorb modern carbon from the atmosphere (Bush et al. 2013). In the later experiment at PKU (see below, also Fig. 6b), we pretreated the C2 by leaching it with 2 mL, 0.01 mol L$^{-1}$ HCl for every 11
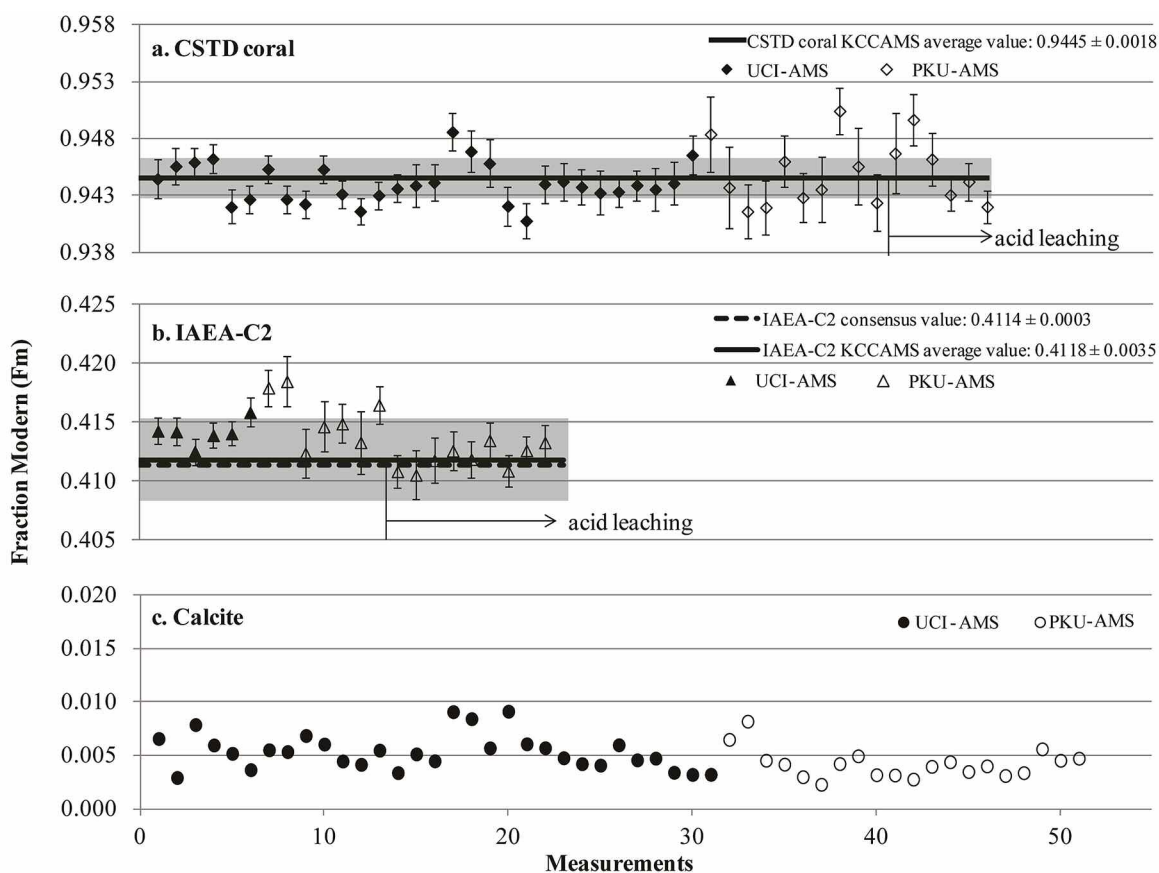
**Fig. 6.** Comparison of standard samples' $^{14}$C values obtained using the headspace method and their consensus values (solid black line): a. CSTD coral, b. IAEA-C2, and c. calcite. Gray area represents the ± 1σ stdev of the standards values from the KCCAMS. Closed symbols represent samples measured at the KCCAMS, and open symbols represent samples measured at the PKUAMS.
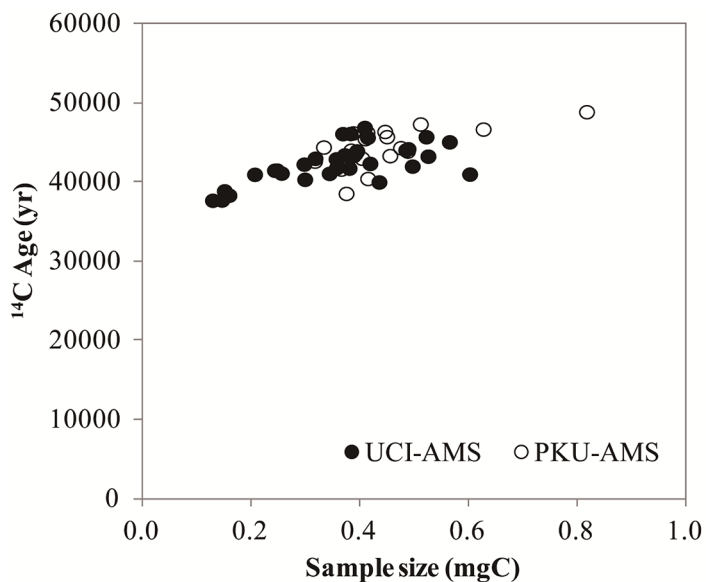


**Fig. 7.** Radiocarbon age of the procedural background using the headspace method vs. sample size. Closed symbols represent calcite samples measured in the KCCAMS, and open symbols represent samples measured in the PKUAMS.

mg C2 powder to remove absorbed modern $CO_2$ and obtained results in better agreement with the consensus value.

**Comparison to the conventional method**

The $^{14}$C results of 18 NBP surface seawater samples prepared using the headspace-extraction method and conventional stripping method show good agreement (Table 3; Fig. 8). The headspace-extraction method (with overpressured condition) was able to extract 0.33-0.37 mg C from surface seawater samples, which is consistent with the theoretical yield calculated in Fig. 4a. For the 6 samples collected in 2011, duplicates were prepared simultaneously by both the conventional and headspace-extraction methods (i.e., four aliquots per sample) to evaluate the reproducibility of the new method (Fig. 8a). The Fm stdev from 6 pairs of headspace duplicates is small (0.00004 to 0.0029), with a pooled stdev (McNaught and Wilkinson 1997) of 0.0015. Both the individual and average Fm values obtained with the headspace method are highly comparable with the conventional stripping data. *t* tests on paired samples all resulted in *P* values > 0.05 (Table 3), showing that the two methods are equivalent. For the 12 stored samples collected in 2008-2009, the headspace method $^{14}$C results are also comparable to the conventional stripping

**Table 3.** The DI$^{14}$C values of surface seawater samples collected at the NBP site during 2008-2009 and 2011. The $^{14}$C results for the 2008-2009 set obtained by the conventional DIC extraction method were published in Santos et al. (2011) and were reproduced in Fig. 8.

| Sample ID (day/month/year) | Lab Nr UCIAMS | Prep. method | Water weight (g) | Yield (mg C) | Fm | ± | T-test on paired samples |
|---|---|---|---|---|---|---|---|
| 13 Feb 11 | 99410 | Headspace | 30.5 | 0.36 | 1.0230 | 0.0019 | (t = 0.33, df = 1, P = 0.80) |
| | 99411 | Headspace | 29.6 | 0.37 | 1.0272 | 0.0019 | |
| | 98844 | Conventional | | | 1.0239 | 0.0017 | |
| | 98684 | Conventional | | | 1.0254 | 0.0013 | |
| 12 May 11 | 99412 | Headspace | 30.0 | 0.35 | 1.0246 | 0.0018 | (t = 5, df = 1, P = 0.13) |
| | 99413 | Headspace | 29.7 | 0.36 | 1.0234 | 0.0020 | |
| | 98845 | Conventional | | | 1.0237 | 0.0018 | |
| | 98685 | Conventional | | | 1.0228 | 0.0018 | |
| 13 Jun 11 | 99414 | Headspace | 29.7 | 0.35 | 1.0226 | 0.0018 | (t = 1, df = 1, P = 0.50) |
| | 99415 | Headspace | 30.0 | 0.37 | 1.0235 | 0.0021 | |
| | 98846 | Conventional | | | 1.0226 | 0.0017 | |
| | 98686 | Conventional | | | 1.0226 | 0.0014 | |
| 13 Jul 11 | 99416 | Headspace | 30.8 | 0.36 | 1.0234 | 0.0018 | (t = 0.49, df = 1, P = 0.71) |
| | 99417 | Headspace | 28.2 | 0.34 | 1.0244 | 0.0018 | |
| | 98847 | Conventional | | | 1.0244 | 0.0017 | |
| | 98687 | Conventional | | | 1.0215 | 0.0013 | |
| 11 Aug 11 | 99418 | Headspace | 30.0 | 0.37 | 1.0241 | 0.0019 | (t = 6, df = 1, P = 0.11) |
| | 99419 | Headspace | 29.9 | 0.36 | 1.0240 | 0.0022 | |
| | 98849 | Conventional | | | 1.0213 | 0.0016 | |
| | 98689 | Conventional | | | 1.0220 | 0.0013 | |
| 13 Sep 11 | 99420 | Headspace | 29.5 | 0.35 | 1.0212 | 0.0019 | (t = 0.46, df = 1, P = 0.73) |
| | 99421 | Headspace | 29.9 | 0.35 | 1.0238 | 0.0020 | |
| | 98850 | Conventional | | | 1.0225 | 0.0018 | |
| | 98690 | Conventional | | | 1.0203 | 0.0013 | |
| 15 Feb 08 | 99422 | Headspace | 30.1 | 0.33 | 1.0367 | 0.0022 | |
| 22 Apr 08 | 99423 | Headspace | 30.2 | 0.36 | 1.0322 | 0.0018 | |
| 7 May 08 | 99424 | Headspace | 30.5 | 0.37 | 1.0300 | 0.0019 | |
| 23 Jun 08 | 99425 | Headspace | 29.8 | 0.36 | 1.0318 | 0.0022 | |
| 18 Jul 08 | 99426 | Headspace | 30.2 | 0.37 | 1.0279 | 0.0022 | |
| 1 Aug 08 | 99427 | Headspace | 30.5 | 0.36 | 1.0308 | 0.0020 | |
| 29 Aug 08 | 99428 | Headspace | 30.2 | 0.36 | 1.0305 | 0.0020 | |
| 26 Sep 08 | 99429 | Headspace | 30.1 | 0.36 | 1.0331 | 0.0022 | |
| 24 Oct 08 | 99430 | Headspace | 30.7 | 0.37 | 1.0326 | 0.0022 | |
| 5 Dec 08 | 99431 | Headspace | 30.4 | 0.36 | 1.0320 | 0.0020 | |
| 16 Jan 09 | 99432 | Headspace | 30.3 | 0.36 | 1.0334 | 0.0021 | |
| 13 Feb 09 | 99433 | Headspace | 30.3 | 0.37 | 1.0354 | 0.0022 | |

results. It is notable that the headspace results show the most negative $^{14}$C values during the strong summer upwelling in 2008 (Santos et al. 2011, see also Fig. 8b), thus illustrating the suitability of the headspace method for DI$^{14}$C investigations that require high-precision and high temporal resolution. We also compared the two methods by first calculating the mean Fm value (average of headspace and conventional measured values) of each seawater sample, and then subtracting this mean from the average Fm value of each method to get the residual Fm (Fig. 9). The residual Fm values are within ± 1σ stdev for 16 out of 18 samples and within ± 2σ stdev for all 18.

**PKUAMS experiments**

We applied the new headspace-extraction method in the Cosmogenic Nuclide Preparation Laboratory at Peking University to evaluate its utility. Several standard samples were processed using the optimized overpressure protocol (75°C/2h/first extraction), and the extracted headspace/$CO_2$ gas samples were purified and graphitized on a vacuum system similar to that of Xu et al. (2007). Graphite samples were analyzed for $^{14}$C with the PKUAMS as described in Liu et al. (2007). The Fm values of all samples measured in PKUAMS are listed in Table 4 and plotted in Figs. 6 and 7 for compari-
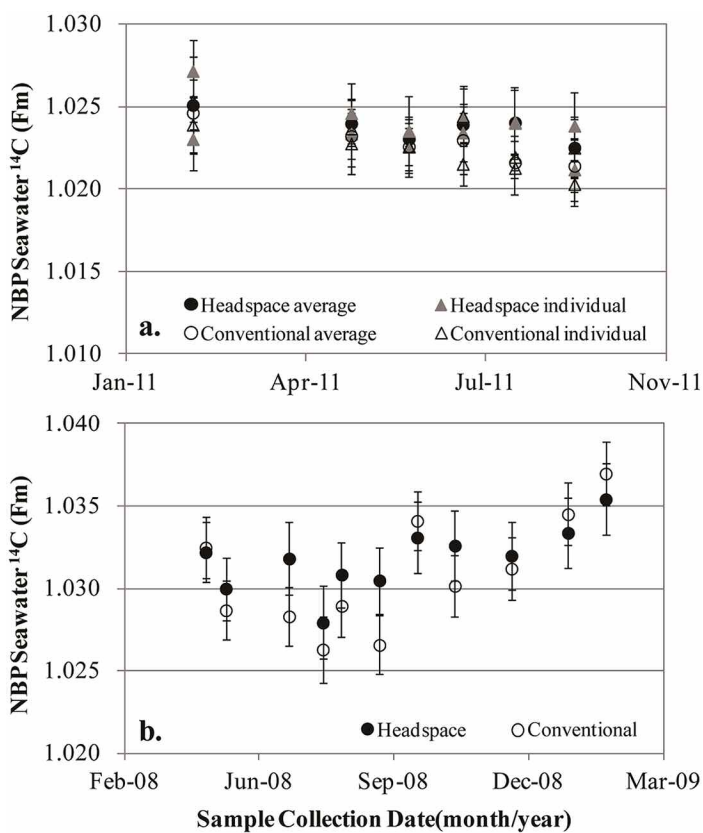
**Fig. 8.** Comparison of NBP surface seawater DI¹⁴C values obtained using the headspace method and conventional method: a. 6 NBP DIC samples collected during Feb-Sep 2011, for which two duplicates were measured by the headspace method and the conventional method at the same time (see also Table 3); b. 12 NBP DIC samples collected during Feb 2008 to Mar 2009, for which only one measurement was made by the headspace method for each sample; conventional method data are from Santos et al. (2011).
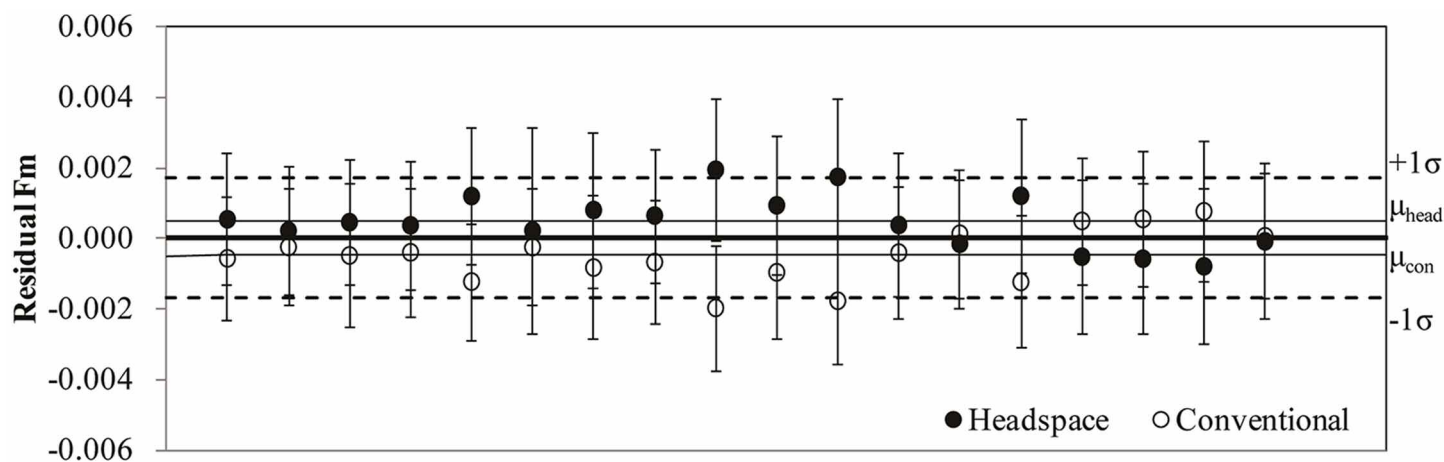
son with the KCCAMS data. The overall calcite background value measured with the PKUAMS is 44,000 ± 2000 radiocarbon year ($n = 20$), which is comparable with the KCCAMS background value (43,400 ± 1900 radiocarbon year; n = 23). The average Fm values of the CSTD coral standards obtained with PKUAMS is 0.9449 ± 0.0028 ($n = 16$), which is in good agreement with the headspace method results obtained at KCCAMS (0.9441 ± 0.0017; $n = 30$). Independent-samples $t$ test confirms the consistency ($t = –1.0$, df = 21, $P = 0.31$). The average PKUAMS Fm value for IAEA-C2 is 0.4135 ± 0.0024 ($n = 16$). For the last 9 samples where we applied acid leaching, the average value is 0.4119 ± 0.0011 ($n = 9$), and one sample $t$ test shows that these data are consistent with the IAEA-C2 consensus value of 0.4114 ± 0.0003 ($t = 1.7$, df = 8, $P = 0.14$). Thus, acid leaching to remove modern $CO_2$ adsorption from the C2 standard should be included as a routine procedure. The slightly larger analytical error in the PKUAMS Fm data are due to the general lower beam currents in the PKUAMS system (Liu et al. 2007) and correspondingly larger uncertainty from counting statistics.

## Discussion and recommendations

The DIC headspace-extraction method developed in this study is aimed at achieving high throughput sample preparation for high-precision ¹⁴C analysis by AMS. To minimize the time and effort involved in sample $CO_2$ stripping and cleaning between samples, the headspace $CO_2$ is isolated from the water using syringe extractions. The isotope fractionation of the sample $CO_2$ introduced by the incomplete extraction in this procedure is small (ca. ≤ 0.6‰). Moreover, this small fractionation can be fully corrected by an online ¹³C/¹²C measurement, which is standard on most AMS systems. The radiocarbon results obtained using this new method have accuracy and precision comparable with those obtained with conven-



**Fig. 9.** Residual Fm for 18 NBP seawater samples. Replicate samples from 2011 have been averaged. Error bars show the reported measurement uncertainty or the standard deviation of replicate measurements for samples collected in 2011, whichever is bigger. The average residuals of the headspace method ($\mu_{head}$) and conventional method ($\mu_{con}$) are shown by thin solid lines, whereas the thick solid line indicates 0 residual or no difference between the two methods. The ± 1σ relative error (± 1.7‰) is shown by dashed lines.

**Table 4.** Radiocarbon values of CSTD coral, IAEA-C2, and calcite standard samples prepared with the headspace method and analyzed at the PKUAMS facility.

| Lab Nr PKUAMS | Standard ID | Weight (mg) | Yield (mg C) | Fm | ± | ¹⁴C age (y) | ± |
|---|---|---|---|---|---|---|---|
| QAS0885 | CSTD | 7.4 | 0.48 | 0.9484 | 0.0033 | 425 | 30 |
| QAS0886 | CSTD | 6.6 | 0.47 | 0.9437 | 0.0036 | 465 | 35 |
| QAS0968 | CSTD | 6.0 | 0.43 | 0.9416 | 0.0023 | 485 | 20 |
| QAS1028 | CSTD | 6.9 | 0.47 | 0.9504 | 0.0021 | 410 | 20 |
| QAS1029 | CSTD | 6.6 | 0.43 | 0.9456 | 0.0033 | 450 | 30 |
| QAS1155 | CSTD | 3.9 | 0.25 | 0.9420 | 0.0024 | 480 | 25 |
| QAS1156 | CSTD | 5.8 | 0.37 | 0.9460 | 0.0023 | 445 | 20 |
| QAS1157 | CSTD | 6.7 | 0.40 | 0.9428 | 0.0022 | 475 | 20 |
| QAS1158 | CSTD | 8.0 | 0.47 | 0.9435 | 0.0028 | 465 | 25 |
| QAS1175 | CSTD | 7.2 | 0.44 | 0.9424 | 0.0025 | 475 | 25 |
| QAS1333 | CSTD | 6.9 | 0.43 | 0.9467 | 0.0035 | 440 | 30 |
| QAS1334 | CSTD | 6.9 | 0.43 | 0.9497 | 0.0023 | 415 | 20 |
| QAS1335 | CSTD | 6.6 | 0.39 | 0.9462 | 0.0023 | 445 | 20 |
| QAS1336 | CSTD | 6.7 | 0.41 | 0.9431 | 0.0014 | 470 | 15 |
| QAS1337 | CSTD | 7.1 | 0.35 | 0.9442 | 0.0016 | 460 | 15 |
| QAS1338 | CSTD | 6.7 | 0.37 | 0.9420 | 0.0015 | 480 | 15 |
| QAS0883 | IAEA-C2 | 7.0 | 0.46 | 0.4180 | 0.0016 | 7010 | 30 |
| QAS0884 | IAEA-C2 | 6.9 | 0.46 | 0.4185 | 0.0021 | 6995 | 45 |
| QAS0967 | IAEA-C2 | 6.0 | 0.44 | 0.4124 | 0.0021 | 7115 | 45 |
| QAS1151 | IAEA-C2 | 3.8 | 0.22 | 0.4147 | 0.0021 | 7070 | 45 |
| QAS1152 | IAEA-C2 | 6.0 | 0.36 | 0.4149 | 0.0017 | 7065 | 35 |
| QAS1153 | IAEA-C2 | 6.2 | 0.36 | 0.4133 | 0.0027 | 7100 | 60 |
| QAS1154 | IAEA-C2 | 8.9 | 0.53 | 0.4165 | 0.0016 | 7035 | 35 |
| QAS1252 | IAEA-C2 | 8.9 | 0.47 | 0.4109 | 0.0014 | 7145 | 30 |
| QAS1253 | IAEA-C2 | 8.9 | 0.67 | 0.4105 | 0.0021 | 7150 | 45 |
| QAS1254 | IAEA-C2 | 9.1 | 0.66 | 0.4118 | 0.0019 | 7125 | 40 |
| QAS1327 | IAEA-C2 | 6.8 | 0.36 | 0.4126 | 0.0016 | 7110 | 35 |
| QAS1328 | IAEA-C2 | 6.4 | 0.38 | 0.4119 | 0.0015 | 7125 | 30 |
| QAS1329 | IAEA-C2 | 6.6 | 0.37 | 0.4135 | 0.0015 | 7095 | 30 |
| QAS1330 | IAEA-C2 | 6.9 | 0.38 | 0.4109 | 0.0013 | 7145 | 30 |
| QAS1331 | IAEA-C2 | 7.5 | 0.44 | 0.4126 | 0.0012 | 7110 | 25 |
| QAS1332 | IAEA-C2 | 6.2 | 0.36 | 0.4133 | 0.0015 | 7100 | 30 |
| QAK0132 | Calcite | 6.6 | 0.42 | 0.0065 | 0.0001 | 40500 | 170 |
| QAK0133 | Calcite | 6.3 | 0.38 | 0.0082 | 0.0002 | 38620 | 160 |
| QAK0134 | Calcite | 6.8 | 0.39 | 0.0045 | 0.0001 | 43390 | 200 |
| QAK0135 | Calcite | 6.0 | 0.38 | 0.0041 | 0.0001 | 44070 | 210 |
| QAK0138 | Calcite | 8.5 | 0.63 | 0.0030 | 0.0002 | 46740 | 420 |
| QAK0139 | Calcite | 11.5 | 0.82 | 0.0023 | 0.0002 | 48930 | 630 |
| QAK0140 | Calcite | 8.3 | 0.49 | 0.0042 | 0.0002 | 43960 | 300 |
| QAK0141 | Calcite | 4.7 | 0.32 | 0.0049 | 0.0002 | 42690 | 300 |
| QAK0142 | Calcite | 6.1 | 0.39 | 0.0032 | 0.0001 | 46260 | 320 |
| QAK0143 | Calcite | 6.1 | 0.41 | 0.0031 | 0.0001 | 46320 | 320 |
| QAK0144 | Calcite | 8.2 | 0.51 | 0.0027 | 0.0002 | 47380 | 610 |
| QAK0145 | Calcite | 6.3 | 0.33 | 0.0039 | 0.0001 | 44470 | 300 |
| QAK0146 | Calcite | 6.2 | 0.39 | 0.0044 | 0.0001 | 43640 | 270 |
| QAK0147 | Calcite | 6.2 | 0.41 | 0.0035 | 0.0003 | 45530 | 650 |
| QAK0151 | Calcite | 6.9 | 0.48 | 0.0040 | 0.0003 | 44390 | 510 |
| QAK0152 | Calcite | 6.5 | 0.45 | 0.0031 | 0.0002 | 46440 | 470 |
| QAK0153 | Calcite | 6.6 | 0.45 | 0.0033 | 0.0003 | 45780 | 670 |
| QAK0154 | Calcite | 6.7 | 0.37 | 0.0056 | 0.0001 | 41680 | 190 |
| QAK0155 | Calcite | 7.4 | 0.46 | 0.0045 | 0.0001 | 43390 | 200 |
| QAK0156 | Calcite | 6.8 | 0.41 | 0.0047 | 0.0001 | 43060 | 180 |

**Table 5.** Preparation and sampling strategies for different storage conditions/needs, with check marks (√) indicating recommended approaches.

| | Stored sample bottle cap type | | Future sampling | |
| | | | < 1 month storage | > 1 month storage |
| Preparation choice | Penetrable septum crimp cap | Nonpenetrable screw cap/glass stopper | 64 mL I-Chem vials capped with septa (E + B or E + D) | Nonpenetrable screw cap/glass stopper capped bottles |
|---|---|---|---|---|
| Overpressured headspace[*] | √ | | √ (Inject 30 mL into vial) | |
| Atmospheric headspace[†] | | √ | √ (Fill 64 mL vial full,)[§] | √ |

[*]Overpressured headspace: Inject 30 mL water into $He/N_2$ pre-flushed septa (E + B or E + D) capped 64 mL I-Chem vial
[†]Atmospheric headspace: Pour 30-45 mL water into 64 mL vial in $N_2$ glove bag, with 45 mL water for maximum mg C extractable
[§]Split into two 30 mL for duplicates, or one 45 mL sample for maximum mg C extractable in $N_2$ glove bag

tional stripping. Therefore, the headspace method is suitable for DI[14]C investigations that require high-resolution analysis.

Compared with the conventional stripping methods, the headspace method is faster and involves less effort and expense. After acidification and heating, only 15 min is required for extracting and purifying $CO_2$ from one DIC sample, and no cleaning or flushing of the vacuum line is required between samples, since large amounts of water do not enter the vacuum line as they do with conventional stripping. The DIC sample preparation and acidification setup requires a UHP $N_2$ cylinder and 2 heating blocks, which would cost < US$500. The vacuum line for the headspace-extraction method is based on the system shown in Xu et al. (2007), and the vacuum pumping system (with a mechanical pump), vacuum and pressure gauges, hardware and glassware cost < $9,000. If one prefers an oil-free system with a turbo pump/diaphragm pump, the cost would be ~ $14,000. Consumables and labware such as septa, syringes, needles, and chemical reagents cost < $10 for each sample. Therefore, the main cost to fully implement this method is from the AMS measurement (US$120 per sample or more, depending on the facility price). A set of 15 DIC samples can be processed daily prior to AMS analysis. The skills required for these extraction and graphitization procedures include basic laboratory skills such as handling of compressed gas and common chemicals (acids, bases, and alcohols), and special skills such as vacuum line operation and simple gas torch/glass blowing that can be easily learned from an experienced technician.

It is also notable that the supplies needed, such as screw cap vials, plastic syringes, and needles are inexpensive and highly disposable. This would be particularly desirable when handling water samples involving ^{14}C tracer, such as labeled seawater samples or groundwater samples collected around radioactive waste dumping sites or nuclear power plants. However, we stress that for these applications, a dedicated vacuum line and rigorous cleaning between samples would be essential to avoid sample to sample memory and contamination; and for sufficiently "hot" samples, a completely disposable sample preparation system (Vogel et al. 1990; Ognibene et al. 2003) is recommended.

The method described here is based directly on the work of Molnár et al. (2013), but since this new version does not involve expensive apparatus such as a GasBench to control and extract the sample $CO_2$, it can be easily adapted in a radiocarbon graphite preparation laboratory and measured on almost any AMS system, not just those equipped with a gas ion source. This has been demonstrated by the satisfactory results on standards obtained with the PKUAMS.

An additional advantage of the new method is that the amount of water needed is reduced from the recommended amount of 250 mL seawater for conventional stripping to 30 mL, whereas the accuracy, precision, and background of the two methods are comparable. The new method is potentially very valuable for small and low DIC concentration samples, since extraction efficiencies of 80.2% and 58.5% can be obtained for the first + second extraction from 10 and 45 mL water under atmospheric pressure headspace. For example, 0.19 mg C could be extracted from just 10 mL water with a DIC concentration of 2000 μmol $L^{-1}$, and a 45 mL sample with 500 μmol $L^{-1}$ DIC would yield 0.16 mg C. In addition, larger volume I-Chem vial/bottle, which would hold more water may be used to accommodate low DIC concentration waters, such as fresh lake waters with a low pH. This could enable a substantial expansion of DI[14]C analysis in porewater, groundwater, and fresh water samples where only small or low DIC concentration water samples are available.

The overpressured headspace preparation is suitable for samples stored in penetrable septum/stopper capped storage bottles, as for water samples collected in bottles with nonpenetrable glass stoppers or screw caps, it is much easier to prepare the sample in a UHP $N_2$ glove bag, in which water is poured into the 64 mL I-Chem vial and capped quickly. Whether overpressure or not in the headspace, injecting or pouring water into I-Chem vials in a $N_2$ glove bag does not seem to affect ^{14}C results based on our investigation, indicating the headspace-extraction method is robust. Preparation choices for different sample storage conditions are summarized in Table 5.

Our storage test shows that the Fm value of a seawater sample drops ~ 0.003 Fm after 2 years of storage without head-

space in the 64 mL I-Chem vial with the E + B septum combination seal (Table 1). It seems that the $CO_2$ in the water sample leaked out very slowly over the 2 years of storage, but it is still possible to use this vial for short-term storage (i.e., within a month). For future sampling, if the sample can be measured in < 1 month, we can inject 30 mL water sample into $He/N_2$ pre-flushed vial in the field, and the vial would be ready for acidification and extraction immediately after it is brought back to the laboratory. Steps involving water transfer in a glove bag would be eliminated, making this method even more straightforward. Also, we can fill the 64 mL I-Chem vial with sample water (without headspace) in the field, and split the water into two 30 mL samples (with an option for duplicates) or make one 45 mL sample for maximum C mass in the lab when preparing the sample for ¹⁴C analysis. In this case, before splitting the sample for DI¹⁴C analysis, we can sample 1 mL water from the I-Chem vials and measure it for stable isotope $\delta^{13}C$ using the technique outlined in Torres et al. (2005). However, a systematic investigation of the maximum storage time for the I-Chem vials used in this study is still needed. For samples that need to be stored for more than 1 month before DI¹⁴C measurements, nonpenetrable screw caps or glass stopper sealed bottles filled with no headspace are recommended (Table 5), and they are appropriate for stable isotope $\delta^{13}C$ measurements as well.

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