





RESEARCH ARTICLE

Radiocarbon measurements of dissolved inorganic carbon (DIC) in sediment porewater and seawater at AWI MICADAS

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Abstract

Radiocarbon (^{14}C) measurements on dissolved inorganic carbon (DIC) are a powerful tool to trace water masses and carbon cycling in the ocean. Existing methodologies to determine the ^{14}C content of seawater DIC requires large volumes of sample (usually >100 mL) and specialized graphitization techniques to achieve the accuracy and precision needed for meaningful data interpretation. The advancement of the CO_2 gas ionization accelerator mass spectrometry (AMS) technique today allows routine ^{14}C measurements on small samples (<100 μgC) and may thus permit reducing the sample volumes needed to determine ^{14}C content of seawater DIC to ~2 mL. The proposed method utilizes the carbonate handling system (CHS), gas interface system (GIS) and MICADAS AMS, and provides good accuracy but reduced precision compared to established methods. Good accuracy is shown by comparing results for a marine in-house DIC standard and a DIC seawater profile from Antarctica between the proposed CHS-GIS-MICADAS approach and reference measurements conducted on the same material at established laboratories (ETH and NOSAMS). Further, two sedimentary porewater profiles from a fjord system in Svalbard are presented. Despite good agreement, the precision of the CHS-GIS-MICADAS approach is reduced, potentially limiting possible interpretations on seawater DIC. Nonetheless, the reduction of sample volumes proves particularly helpful to analyze porewater DIC from sediment cores, where sample material is notoriously limited, reduces the required amounts of toxic HgCl_2 and simplifies expedition logistics.

Introduction

The atmospheric $p\text{CO}_2$, and hence climate, is highly responsive to changes in surface ocean dissolved inorganic carbon (DIC) content due to the rapid exchange of CO_2 between the ocean's surface and the atmosphere. The processes that control distribution and fluxes of DIC are well understood and described by the “carbon pump model” (Sarmiento and Gruber 2006). CO_2 uptake is highest in high-latitude cold surface waters where deep-water forms. DIC rich, dense surface water sinks rapidly and the redistribution in the ocean causes efficient pumping of atmospheric carbon to the deep ocean. DIC is removed in surface waters by photosynthesis and is fixed as particulate organic carbon (POC) and dissolved organic carbon (DOC). Both POC and DOC are intensely recycled by microbes in the photic zone, but small amounts of POC escape surface waters by forming sinking particles. In the open ocean sinking POC is heterotrophically re-mineralized to DIC and this process is so efficient that only 1–6% of

the POC export production reaches the sea floor, where just 0.3% escapes benthic degradation and gets buried (Dunne et al. 2007). Nonetheless, large amounts of organic carbon accumulate at the seafloor, particularly in deltas or fjords, and its remineralization within the sediments represents a major source for marine DIC (Cai 2011). While the general carbon pump model is well understood, interactions between carbon phases in the water column on local scales are complex and differ temporally and regionally. The concentration of radiocarbon (^{14}C) within local oceanic carbon compartments can serve as an excellent tracer to better constrain such interaction. Given the complexity of the marine carbon system, reliable methods that allow for high sample throughput are required to grasp such interaction.

The usefulness of ^{14}C to trace oceanographic processes was shown by a series of global ocean surveys (GEOSECS, TTO, WOCE, CLIVAR, GO-SHIP) and led to significant technological advancements and the development of reliable and precise methodologies to routinely analyze radiocarbon signatures of seawater DIC. Today's established methods like the Rapid Extraction of Dissolved Inorganic Carbon System (REDICS, Gospodinova et al. [2016]) applied at the National Ocean Science Accelerator Mass Spectrometry Facility (NOSAMS) or the ETH-LIP method developed at the Laboratory of Ion Beam Physics of ETH Zürich (Casacuberta et al. 2019; Castrillejo et al. 2023) are capable of generating seawater DIC ^{14}C datasets with unprecedented accuracy and precision. High precision is achieved as both methods ultimately convert the CO_2 extracted from 50–100 mL of seawater to graphite for routine AMS dating.

The development of hybrid gas-ion source AMS systems (Fahrni et al. 2013; Synal et al. 2007; Wacker, Fahrni, et al. 2013) allows in combination with the Carbonate Handling System (CHS) and the Gas Interface System (GIS) the routine analysis of small-scale samples ($<100\text{ }\mu\text{gC}$, (as described by Wacker, Lippold, et al. [2013]; Bard et al. [2015] or Mollenhauer et al. [2021]). The system proved useful for applications in paleoclimatology/oceanography (Ausín et al. 2021; Gottschalk et al. 2020; Wollenburg et al. 2023) or carbon cycling (Ruben et al. 2023; Wu et al. 2022), however its use to trace ^{14}C distributions through marine carbon compartments remains under-explored and was only briefly described for solid phase extracted dissolved organic carbon (SPE-DOC, Hildebrand et al. [2022]) and particulate organic carbon (POC, Druffel et al. [2022]). Currently no seawater DIC ^{14}C method using a gas ion source is reported in the literature, which is surprising given that few mL of seawater (DIC concentration $\sim 2.4\text{ mmol/L}$) could be sufficient to generate reliable radiocarbon measurements using the CHS-GIS-MICADAS setup. Reduction of sample volume to a few mL minimizes the logistical burden to marine expeditions by significantly reducing the amounts of toxic and environmentally hazardous HgCl_2 needed to poison seawater samples, and by reducing the quantity of transported seawater required for the established methods analyzing DIC as graphite. Paired with rapid analytical throughput, analyzing seawater DIC ^{14}C samples directly as CO_2 has the potential to significantly increase the global dataset for seawater DIC ^{14}C . Further, while seawater for analysis may be available in abundance, sedimentary porewater extracted from gravity cores (GC) or multi collector cores (MUC) is not, and often only few mL can be extracted from the sediment, limiting our ability to extend the investigation of marine carbon fluxes to the sediment.

The first method to analyze DIC using the CHS-GIS-MICADAS approach was published by Molnár et al. (2013) for terrestrial groundwaters. Here we report on our modified approach to process marine seawater and sediment porewater DIC on sample volumes as little as 2 mL, where previously $\sim 10\text{ mL}$ was required (Aller and Blair 2004; Aller et al. 2008; Dumoulin et al. 2018, 2022). We evaluate our method using an in-house seawater standard and seawater from Antarctica which were processed for comparison following established protocols at ETH or NOSAMS. Further, we report on sediment porewater samples from a high-latitude fjord system. The data show good agreement between direct gas CO_2 measurements at AWI and graphite measurements at ETH or NOSAMS. Nonetheless, the current approach fails to provide the high precision achieved following established protocols.

Materials and method

In-house DIC standard

No internationally recognized standard material is available for ^{14}C analysis of DIC. To overcome this limitation and assure quality of reported radiocarbon values we have implemented an in-house reference material. The in-house reference material was collected during research cruise M165 (Zonneveld et al. 2020) on the research vessel FS Meteor in August 2020 to the Eastern Boundary Upwelling Ecosystem (EBUE) off Cape Blanc, Mauritania in the North Atlantic. Water was collected from the CTD-ROS cast GeoB24130-1 (25th of August 2020 at 20.84805°N; -18.72778°E, 2682 m bottom depth, close to the long-term monitoring station CBeu [Fischer et al. 2016]). Twenty replicates from the same Niskin bottle were collected in 330 mL brown-glass flip-top bottles. After sample collection replicates were poisoned with a saturated mercury chloride solution (HgCl_2) and stored without headspace at +4°C.

One replicate bottle was sent to the Laboratory of Ion Beam Physics, ETH Zürich and the radiocarbon value of DIC was analyzed in 4 sub-samples according to their established standard operation procedure for DIC (Casacuberta et al. 2019; Castrillejo et al. 2023). The reported $\text{F}^{14}\text{C}_{\text{ETH}}$ 0.915 ± 0.002 (mean \pm mean 1σ , $n = 4$) is regarded the true value of the in-house reference material and is used in the following to evaluate the method described. In our laboratory, one bottle was split into $\sim 60 \times 4.5$ mL replicates (4 mL exetainer vials [IVA948W, IVA Analysentechnik]) under N_2 atmosphere in a glovebox to prevent air CO_2 re-equilibration and serves as easy-to-handle reference material for daily use.

Seawater DIC from Antarctica

The DIC ^{14}C results of the methodology reported here were further compared to results obtained following the established protocol at NOSAMS, Woods Hole Oceanographic Institution (WHOI). For this comparison DIC samples were collected during research cruise PS128 (Tiedemann and Müller 2022) on the research vessel FS Polarstern in January 2022 to the Antarctic continental margin. Water was collected from CTD-ROS cast PS128_11-1 (19th of January 2022 at -70.04372°N; -8.61667°E, 2690 m bottom depth) from 10 depths. Water was transferred from the Niskin bottles directly into a) 500 mL glass bottles with 29 mm outer diameter glass stoppers (according to NOSAMS recommendations) and b) replicates of 2×5 mL glass vials with crimp cap. After sample collection all replicates were poisoned with a saturated solution of HgCl_2 , closed and stored refrigerated at +4°C. Upon return to the laboratory, 500 mL glass bottle samples were shipped to NOSAMS and analyzed following their standard operation procedure for DIC radiocarbon analysis (Gospodina et al. 2016; McNichol et al. 1994). The 5 mL samples were analyzed in replicates ($n = 3-4$) at AWI.

Porewater DIC from Svalbard

Porewater DIC samples were collected during research cruise HE627 on research vessel FS Heincke in August 2023 from the Bellsundet fjord system in the south of Svalbard. Sediment was retrieved by two multi collector core (MUC) deployments. The first station (HE627_2-8, 19th of August 2023 at 77.64166°N, 14.46951°E, 156 m bottom depth, 22 cm core length) was located at the confluence of Van Keulenfjord and Van Mijentfjord at a location distal from the glacier. The second station (HE627_4-10, 21st of August 2023, at 77.79009°N, 15.50026°E, 90 m bottom depth, 35 cm core length) was located within Van Mijentfjord proximal to the glacier. Immediately after core retrieval, the sediment was sliced every cm from the top to 10 cm and every 2 cm below and transferred to 50 mL Falcon tubes. Any potential headspace was exchanged with argon gas. Porewater was sampled with rhizon samplers (pore size 0.15 μm ; Rhizosphere Research Products) inserted through a drill hole in the lid of the falcon tube

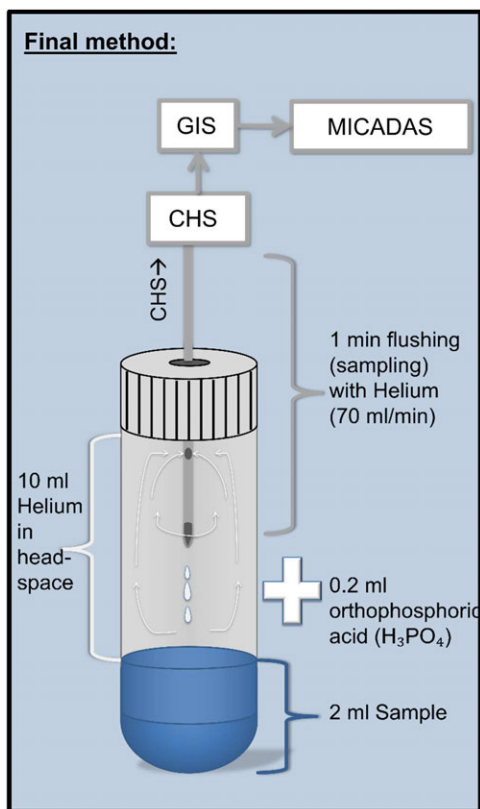


Figure 1. Schematic representation of the final CHS-GIS-MICADAS methodology to analyze sea- and porewater DIC samples.

forming an air-tight seal. The porewater was sucked out from the tubes by 10 mL plastic syringes and transferred to 4.5 mL exetainer vials (IVA948W, IVA Analysentechnik) for radiocarbon measurements, poisoned with HgCl_2 , properly closed without headspace and store refrigerated at $+4^\circ\text{C}$. The porewater sample approach was previously described in research cruise reports, for example in Kasten (2023).

Method

The radiocarbon analysis of DIC at AWI utilizes the standard CHS-GIS-MICADAS AMS, as described by Mollenhauer et al. (2021) and is an adaptation of the methodology described by Molnár et al. (2013) for marine samples. The final method is described in Figure 1. Immediately before the analysis 2 mL of seawater or porewater are transferred into sealed and flushed 12 mL exetainer vials (flushed for 10 min with He at 70 mL/min; IVA938W, IVA Analysentechnik) using a 2.5 mL gas-tight glass syringe which was flushed with MilliQ and sample seawater in-between samples. Subsequently, 200 μL of orthophosphoric acid ($\geq 85\%$ H_3PO_4 , Fluka 30417) are added by a 1 mL gas-tight glass syringe. The exetainer vials are vigorously shaken to ensure mixing, placed on the CHS heating-block at 40°C and let to rest for 30 min to ensure outgassing of CO_2 from the water phase.

The exetainer headspace containing the CO_2 -He mixture is sampled individually by a two-way needle for 1 min with He at 70 mL/min and dried over a Sicapent water trap before CO_2 is concentrated on the zeolite trap of the GIS (Wacker, Fahrni, et al. 2013). By heating the zeolite trap

to 450°C, CO₂ is desorbed and transferred by gas expansion into the GIS injection syringe, where CO₂ is manometrically quantified, and He is automatically added to obtain a gas mixture of ~3–5% CO₂ in He. The gas mixture is subsequently fed into the MICADAS AMS under constant pressure and flow.

Radiocarbon data are normalized against Oxalic Acid II standard gas (CO₂ produced from NIST Oxalic Acid II, NIST SRM4990C) and blank corrected against ¹⁴C-free CO₂ reference gas analyzed in the same sequence using the BATS software (Wacker et al. 2010). Instrument performance is assured by processing a minimum of 4 replicates of the DIC ¹⁴C in-house standard and 2 replicates of IAEA-C2 carbonate standard in each sequence. The radiocarbon results of IAEA-C2 carbonate standards measured alongside samples agree in 1σ analytical uncertainty ($F^{14}C_{\text{measured}} = 0.411 \pm 0.009$ (mean ± sd); $n = 64$) with the reference value ($F^{14}C_{\text{reference}} = 0.4114 \pm 0.0003$).

Results and discussion

Validation of the in-house DIC standard and method parameters

The in-house DIC standard (GeoB24130-1 1000 m) was analyzed 70 times (Figure 2) at AWI following the method described above. The $F^{14}C_{\text{AWI}}$ value ($F^{14}C_{\text{AWI}} = 0.912 \pm 0.009$ [mean ± sd, $n = 70$]) was comparable to results reported by the Laboratory of Ion Beam Physics, ETH Zürich ($F^{14}C_{\text{ETH}} = 0.915 \pm 0.002$ [mean ± mean 1σ, $n = 4$]). The mean analytical uncertainty ($1\sigma_{\text{AWI}} = 0.007$) is slightly lower than the observed sd of replicated analysis, suggesting that this approach underestimates the true uncertainty, and external uncertainties should be increased. The difference in mean values ($\Delta F^{14}C_{\text{ETH-AWI}} = 0.003$) is less than half of the mean analytical uncertainty of the CO₂ gas measurements at AWI. Considering the larger analytical uncertainty of CO₂ analysis (AWI) compared to graphite analysis (ETH) we conclude that measurements at AWI result in comparable $F^{14}C$ values for the in-house standard. However, the reduced precision of the reported method needs to be considered when unknown samples are being analyzed. We recommend performing replicate analysis for several samples within a measurement sequence and to carefully evaluate reported uncertainties during data evaluation and interpretation.

Variation of method parameters were tested on replicate analysis of the in-house DIC standard at AWI, but changes on the measured $F^{14}C$ values were insignificant. For example, changes in flushing time (1, 2, 3 min), acid volume (100, 200, 300 μL H₃PO₄), or sample volume (1, 3 mL) analyzed in replicates resulted in mean $F^{14}C$ values that agreed within mean analytical uncertainty (1σ; Figure 3). Further, extra additions of acid and/or resampling on replicates that were previously analyzed resulted in no quantifiable amounts of CO₂, suggesting that routine method parameters were efficient at quantitatively stripping DIC from the seawater.

Seawater DIC from Antarctica

DIC radiocarbon data (Figure 4A) from PS128_11-1 measured at NOSAMS shows a $\Delta^{14}C$ value of $-111 \pm 2\text{‰}$ ($\pm 1\sigma$) in surface waters followed by continuous depletion towards 1800 m water depth ($-146 \pm 2\text{‰}$). Deeper waters show a moderate relative ¹⁴C enrichment towards $-142 \pm 2\text{‰}$ in the deepest water sample (2690 m water depth). Results measured at AWI for the same water sample replicates follow the same trend with $-107 \pm 8\text{‰}$ (mean ± mean 1σ; $n = 4$) for surface waters, a depletion towards 1800 m water depth ($-155 \pm 8\text{‰}$; $n = 3$) and a continuous ¹⁴C enrichment towards the sea floor ($-142 \pm 7\text{‰}$; $n = 3$). The replicate at 300 m water depths, analyzed at AWI, does not follow the general pattern, and is considered an outlier. The 5 mL glass-vial was likely not properly sealed resulting in progressing isotopic equilibration between sample DIC and atmospheric CO₂ during storage. Data from this sample will not be further discussed.

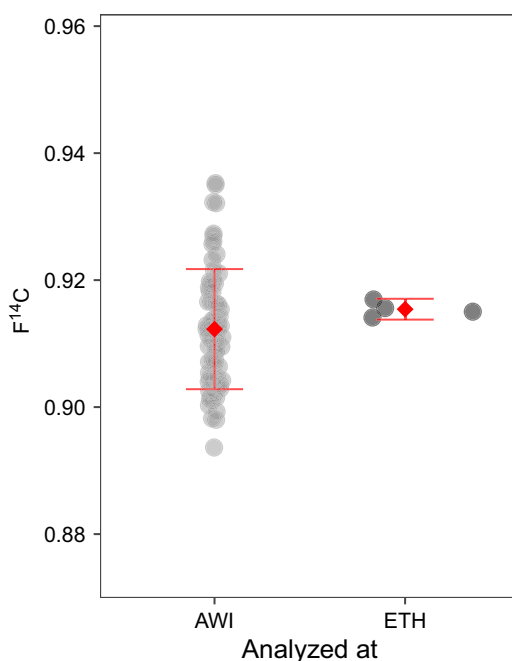


Figure 2. Comparison of measured $F^{14}C$ values for the AWI in-house seawater DIC standard (M165 GeoB24130-1 1000 m). Left results of replicate analysis at AWI, right results provided by ETH. Mean values are shown by red diamonds and error bars represent sd (AWI) and mean 1σ analytical uncertainty (ETH).

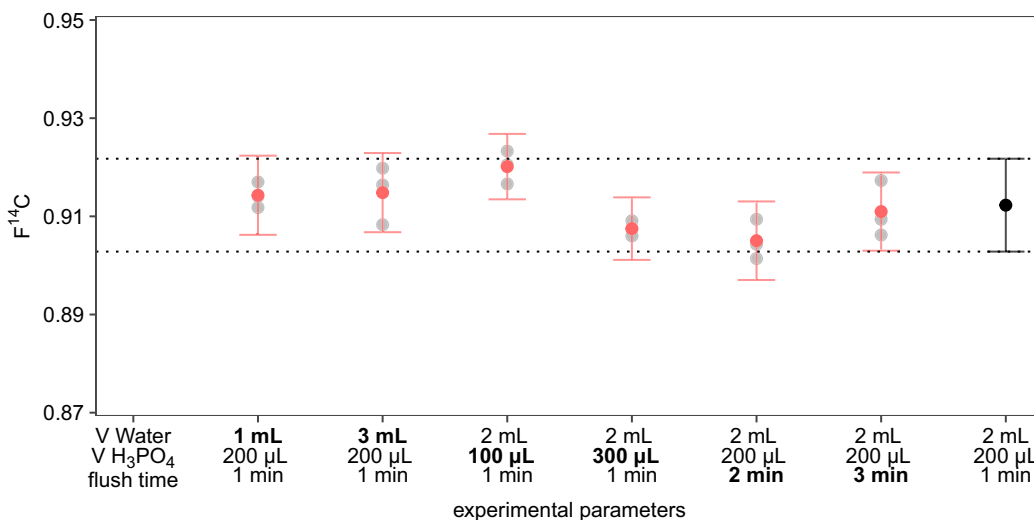


Figure 3. Compilation of method validation results based on replicate analysis of in-house seawater DIC standard. Tested/modified experimental parameter in bold and resulting average $F^{14}C$ results \pm mean 1σ in red circles. Black circle represents mean $F^{14}C \pm sd$ ($n = 70$) of the final method parameters.

The isotope cross-plot (Figure 4B) between $\Delta^{14}C$ values measured at AWI and NOSAMS shows good agreement within uncertainty range (1σ for single measurements at NOSAMS and mean 1σ for replicate measurements at AWI). Isotopic differences ($\Delta\Delta^{14}C_{\text{AWI-NOSAMS}}$) between samples of the same water depth ranged between -10 to $+5\text{‰}$ with a mean difference of -4‰ .

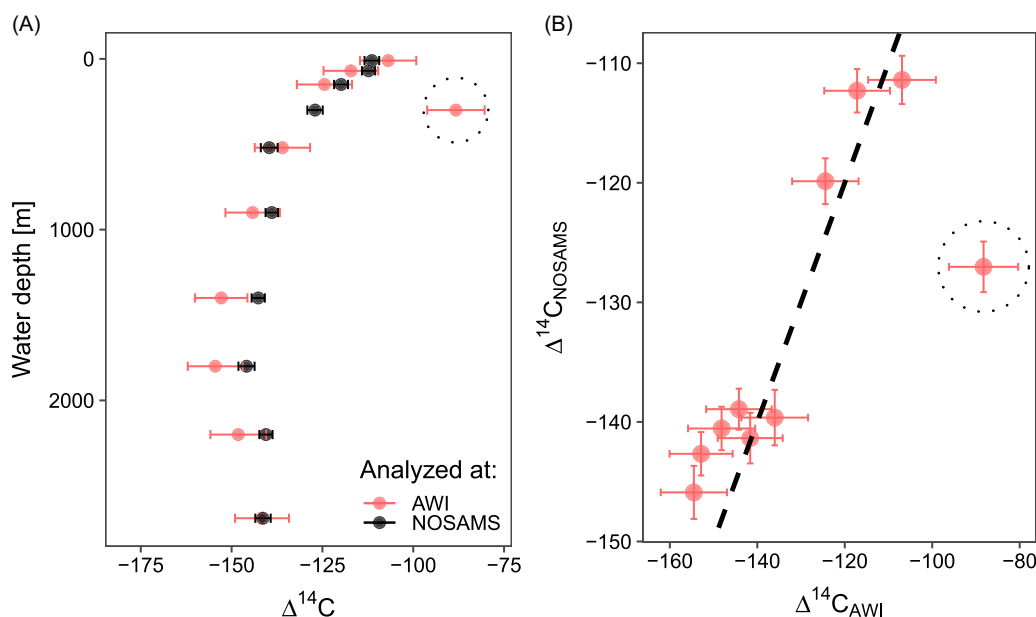


Figure 4. (A) Water column profile of seawater DIC $\Delta^{14}\text{C}$ collected at PS128_11-1, analyzed at NOSAMS (black circles, error bars represent 1σ) and at AWI (red circles represent mean values and error bars represent mean 1σ , $n = 3-4$). Data point at 300 m (dashed circle) considered outlier. (B) Cross-plot of $\Delta^{14}\text{C}$ values measured at NOSAMS and AWI, dashed line indicates 1:1 relationship. Data point at 300 m (dashed circle) considered outlier.

Porewater DIC from Svalbard

Porewaters (Figure 5) at both stations were depleted relative to the overlying bottom waters ($\Delta^{14}\text{C}_{\text{BW}} = 40 \pm 7\text{‰}$, mean $\pm 1\sigma$, $n = 2$) and porewater $\Delta^{14}\text{C}_{\text{PW}}$ values vary between the two investigated cores. Within core HE627_2-8, distal to the glacier, $\Delta^{14}\text{C}_{\text{PW}}$ was relatively homogenous ($\Delta^{14}\text{C}_{\text{PW}} = 20 \pm 7\text{‰}$, mean $\pm \text{sd}$, mean $1\sigma = 7\text{‰}$, $n = 20$, 0–22 cm sediment depth) with no apparent trends. DIC concentration increased from 2.48 mmol/L at the sediment-water interface to 2.98 mmol/L at 15 cm sediment depth. More proximal to the glacier, HE627_4-10 shows similar $\Delta^{14}\text{C}_{\text{PW}}$ values for the top part of the core ($\Delta^{14}\text{C}_{\text{PW}} = 19 \pm 8\text{‰}$, mean $\pm \text{sd}$, mean $1\sigma = 7\text{‰}$, $n = 11$, 0–12 cm sediment depth), but shows a clear depletion towards greater sediment depths (minimum $\Delta^{14}\text{C}_{\text{PW}} = -48 \pm 7\text{‰}$, $\pm 1\sigma$, at 30 cm). The $\Delta^{14}\text{C}$ depletion trend is paralleled by a distinct increase in DIC concentration from 2.59 mmol/L at the core surface to 3.2 mmol/L at 33 cm core depth.

Depleted $\Delta^{14}\text{C}_{\text{PW}}$ values and increased DIC concentration proximal to the glacier could indicate enhanced remineralization of aged organic matter deposited at the core site, derived from glacial erosion of the organic rich bedrocks on Svalbard. Ruben et al. (2023) suggested that marine bacteria utilize up to 55% petrogenic carbon for their biosynthesis in marine sediments in the Hornsund Fjord, Svalbard highlighting microbial remineralization of petrogenic carbon as natural source of greenhouse gas emissions. Porewater $\Delta^{14}\text{C}$ measurements, paired with DIC flux calculations and sediment accumulation rate estimations, will help in the future to investigate the influence sedimentary remineralization of organic matter might have on the global greenhouse gas emissions. The methodology presented here enables rapid ^{14}C analysis of porewater DIC in high sample resolution (1 cm) by reducing the necessary porewater volume to 2 mL. Previously, 10 mL of porewater were needed to enable robust ^{14}C DIC measurements which required pooling of porewater from multiple cm sections (Aller and Blair 2004; Aller et al. 2008; Dumoulin et al. 2018, 2022). The methodology presented here has the potential of becoming a routine analysis on porewaters allowing the community

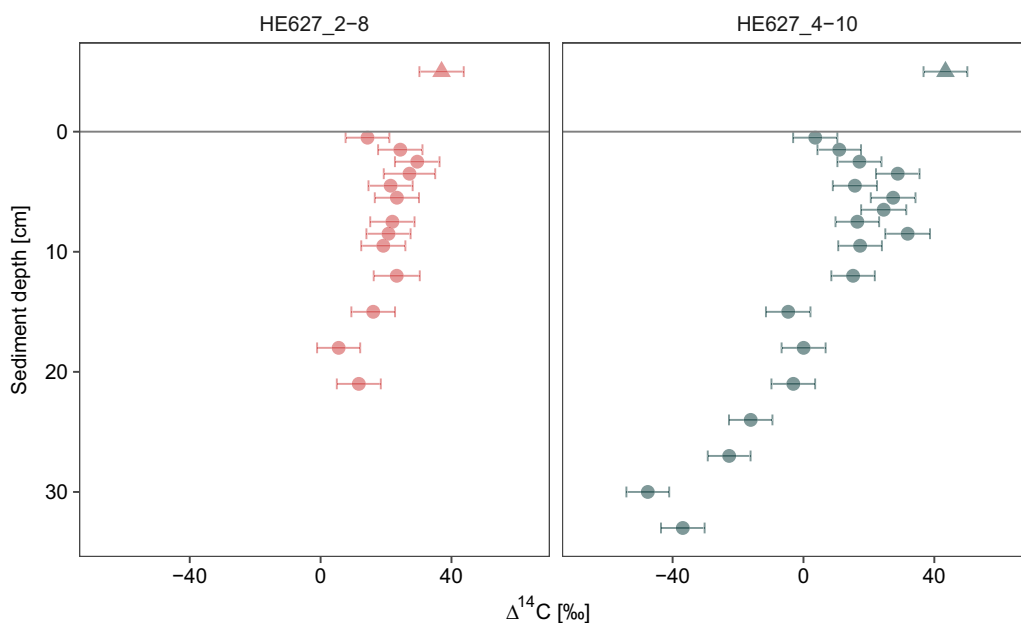


Figure 5. DIC $\Delta^{14}\text{C}$ results for two MUC cores retrieved from the Bellsundet Fjord system south Svalbard. Left: $\Delta^{14}\text{C}$ results for station HE627_2-8 distal to the glacier (red, error bars $\pm 1\sigma$); Right: $\Delta^{14}\text{C}$ results for station HE627_4-10 proximal to the glacier (green, error bars $\pm 1\sigma$). Results for bottom water DIC overlying the MUC core shown as triangles, porewater DIC as circles.

to build up on the initial works on early diagenetic organic carbon cycling by Aller and Blair (2004) or Dumoulin et al. (2022) at unprecedented resolution and detail.

Limitations

The results for the in-house DIC standard and PS124_11-1 seawater DIC show good agreement with results from established methodologies. However, while the AWI method allows processing of very low sample volumes and enables high sample-throughput the main caveat is the significantly reduced analytical precision of the CO_2 gas measurement compared to established methods analyzing DIC as graphite. The high analytical uncertainty ($1\sigma_{\text{AWI}} \sim 8\text{‰}$) of the CO_2 measurements at AWI is problematic given that the maximum $\Delta^{14}\text{C}$ difference of seawater DIC at PS128_11-1 is on the order of $\sim 40\text{‰}$ and adjacent samples may vary only by a few permille, as it is to be expected for seawater DIC $\Delta^{14}\text{C}$ profiles. Further, the reported uncertainties do not comply with the requirements of the World Ocean Circulation Experiment (WOCE) Hydrographic Program (WHP) established in 1988, which requires a precision of 5–10‰ for surface and 3–4‰ for deep water samples as summarized by McNichol et al. (1994). Reduced precision of CO_2 gas compared to graphite radiocarbon measurements is a known phenomenon and was described elsewhere (Bard et al. 2015; Mollenhauer et al. 2021; Grotheer and Mollenhauer 2023). The analytical precision is determined, among other factors, by the sample specific $\Delta^{14}\text{C}$ counting statistic (Wacker et al. 2010), and for the same sample is a direct result of analysis time. A typical CO_2 sample is analyzed for ~ 10 min until the target cathode becomes unstable, whereas graphitized samples can be analyzed for > 30 min each, resulting in significantly increased $\Delta^{14}\text{C}$ counts, better counting statistics and in turn a higher precision (lower 1σ). To improve analytical precision of CO_2 gas measurement while still enabling high sample throughput, one may consider increasing the duration of each analytical run, but this is limited by the durability of the gas cathode. Considering average marine DIC concentrations in the order of 2.4 mmol/L processing of 2 mL seawater results in

~58 µgC per sample, which is sufficient to be split into a minimum of 2 analytical runs and hence doubling the analytical time per sample. This approach led to a 1σ reduction for the in-house DIC standard from 7‰ to 5‰. This would reduce the sample throughput per day (15–25 instead of 30–50), but still enables the rapid generation of robust seawater DIC ¹⁴C datasets.

Nonetheless, the reported method allows accurate and high throughput measurements on seawater and sedimentary porewater DIC. While the reduced precision of this approach might be challenging to the interpretation of seawater DIC profiles, the reduction of sample volume requirements proves particularly helpful to allow high sample resolution measurements on sedimentary porewater.

Supplementary material. To view supplementary material for this article, please visit <https://doi.org/10.1017/RDC.2024.139>

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