

DATA ARTICLE

High-resolution dataset of stable carbon isotope of dissolved inorganic carbon ($\delta^{13}\text{C}$ -DIC) from the North Atlantic Ocean

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Scientific Significance Statement

This work presents an unprecedented high spatial resolution dataset of stable carbon isotope of dissolved inorganic carbon ($\delta^{13}\text{C}$ -DIC) from the North Atlantic Ocean. Comprising over 3500 $\delta^{13}\text{C}$ -DIC measurements from the 2023 Global Ocean Ship-based Hydrographic Investigations Program (GO-SHIP) A16N cruise, this dataset represents a sevenfold increase in sampling density compared to typical Atlantic Ocean GO-SHIP cruises over the past three decades. Remarkably, 75% of the $\delta^{13}\text{C}$ -DIC measurements were conducted at sea using an innovative combination of CO_2 extraction technology and cavity ring-down spectroscopy. This approach enables high-resolution coverage, at-sea analysis, and reliable analytical precision, along with substantial improvements in operational flexibility and cost efficiency compared to conventional isotope ratio mass spectrometry methods. The resulting dataset is expected to advance the scientific community's ability to quantify, validate, and model the ocean's role in anthropogenic CO_2 uptake and storage, addressing a fundamental need in climate change research.

Abstract

The stable isotope ratio of dissolved inorganic carbon ($\delta^{13}\text{C}$ -DIC) is a valuable tracer for investigating carbon cycling in aquatic environments. However, its potential remains underutilized due to limited data availability. Fewer than 15% of cruise samples are analyzed for $\delta^{13}\text{C}$ -DIC, as isotope analysis using isotope ratio mass spectrometry is labor-intensive and restricted to onshore laboratories. We present over 3500 $\delta^{13}\text{C}$ -DIC measurements from the 2023 Global Ocean Ship-based Hydrographic Investigations Program A16N cruise in the North Atlantic. Notably, three-quarters of these measurements were conducted onboard using a CO_2 extraction device coupled with cavity ring-down spectroscopy, a more efficient and cost-effective method. This extensive dataset provides $\delta^{13}\text{C}$ -DIC values with spatial resolution comparable to other ocean carbonate chemistry and

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Data Availability Statement: The data are freely available from the Biological and Chemical Oceanography Data Management Office at <https://www.bco-dmo.org/dataset/942833> (DOI: [10.26008/1912/bco-dmo.942833.1](https://doi.org/10.26008/1912/bco-dmo.942833.1)). They are also accessible via the CLIVAR and Carbon Hydrographic Data Office at <https://cchdo.ucsd.edu/cruise/33RO20230306> (Leg 1) and <https://cchdo.ucsd.edu/cruise/33RO20230413> (Leg 2), where the $\delta^{13}\text{C}$ -DIC data have been integrated into the bottle files.

Zhentao Sun and Hui Gao contributed equally to this study.

biogeochemical parameters. This dataset supports improved quantification of anthropogenic CO_2 uptake and storage, and may facilitate the development of algorithms to estimate $\delta^{13}\text{C}$ -DIC in under sampled regions.

Background and motivation

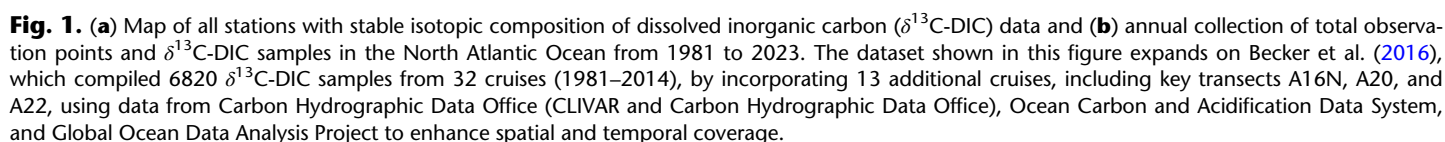
The ocean has absorbed 25–30% of anthropogenic CO_2 since the Industrial Revolution, helping mitigate global warming but also contributing to ocean acidification, which harms marine ecosystems (DeVries 2022; Doney et al. 2020; Friedlingstein et al. 2023; Le Quéré et al. 2009; Sabine et al. 2004). While the ocean's carbon uptake is steadily increasing, the subpolar North Atlantic is particularly important (Pérez et al. 2010; Sabine et al. 2004) because deep convection in this region enables the Atlantic to store twice as much anthropogenic carbon per unit area as the Pacific (DeVries et al. 2017; Gruber et al. 2019; Quay et al. 2007). However, decadal variations in carbon uptake have been observed, driven by changes in ocean circulation (DeVries et al. 2017), which can lead to differing findings depending on the study's period and methods (Wanninkhof et al. 2010; Woosley et al. 2016). A key challenge is detecting small decadal anthropogenic changes in dissolved inorganic carbon (DIC) against large natural background variations, even with long-term observations (Carter et al. 2019).

The $^{13}\text{C}/^{12}\text{C}$ isotope ratio of DIC, expressed as $\delta^{13}\text{C}$ -DIC, is an independent and potentially more effective tracer of carbon sources and biogeochemical processes than DIC. Fossil fuel combustion releases ^{13}C -depleted CO_2 into the atmosphere, lowering $\delta^{13}\text{C}$ -DIC as ocean absorbs this anthropogenic CO_2 —a phenomenon known as the Suess effect (Keeling 1979). $\delta^{13}\text{C}$ -DIC is a valuable tracer for regional ^{13}C -DIC inventory changes and air–sea $^{13}\text{CO}_2$ flux (Lynch-Stieglitz et al. 1995), providing insights into the net addition or removal of anthropogenic CO_2 via lateral transport (Quay et al. 2007). The $\delta^{13}\text{C}$ -DIC also offers an alternative method to compare contemporary air–sea CO_2 flux with anthropogenic CO_2 fluxes, helping reconcile differences between observations and carbon cycle models (Quay et al. 2017). Beyond air–sea exchange, anthropogenic $\delta^{13}\text{C}$ -DIC change and its ratio to anthropogenic CO_2 change are useful tracers for assessing the impact of water mass mixing on anthropogenic CO_2 distribution, particularly at mid- to high-latitudes (Humphreys et al. 2015; Ko and Quay 2020; Sonnerup and Quay 2012). In regions where deep-water, mode, and intermediate water formation drive the spatial distribution of anthropogenic CO_2 , as any proposed mixing scenario must account for both $\delta^{13}\text{C}$ -derived and the DIC-derived anthropogenic CO_2 changes, $\delta^{13}\text{C}$ -DIC data provide additional constraints to refine possible mixing pathways. Furthermore, the $\delta^{13}\text{C}$ -DIC can be a valuable metric for evaluating biological production (Quay 2023; Quay et al. 2020; Yang et al. 2019), which typically tends to elevate sea surface $\delta^{13}\text{C}$ -DIC levels, and for examining carbon cycling across the land–ocean interface (Alling et al. 2012; Samanta et al. 2015).

To fully utilize $\delta^{13}\text{C}$ -DIC as a powerful tool in ocean carbon research, expanded data coverage is desirable, particularly for improving spatial resolution and enabling regional-to-global syntheses. However, the application of $\delta^{13}\text{C}$ -DIC is limited by analytical constraints. Traditional $\delta^{13}\text{C}$ -DIC measurements require preserving water samples and analyzing them using isotope ratio mass spectrometry (IRMS) in shore-based laboratories. While highly precise and accurate, this method is labor-intensive and unsuitable for at-sea analysis, restricting sample processing capacity and limiting the ability to capture spatiotemporal variability and long-term trends. To overcome this challenge, we developed a precise, rapid, and field-deployable method for $\delta^{13}\text{C}$ -DIC analysis by integrating a CO_2 extraction device with a cavity ring-down spectroscopy (CRDS) CO_2 isotope analyzer (Deng et al. 2022; Su et al. 2019; Sun et al. 2024). The onboard CRDS system enables $\delta^{13}\text{C}$ -DIC measurements with minimal sample preparation and reduced logistical burden, offering a cost-effective alternative to conventional shore-based isotope ratio mass spectrometry analysis. Most recently, we improved the analytical uncertainty of the $\delta^{13}\text{C}$ -DIC to 0.03‰ by increasing sample injection volumes and implementing an extensive calibration and quality control protocol using in-house NaHCO_3 standards. This improvement enabled high-precision measurements during extended oceanic cruises along the North American eastern margin in summer 2022 (Sun et al. 2024).

The $\delta^{13}\text{C}$ -DIC is listed as an essential ocean variable (EOV) by the Global Ocean Observation System. To collect a high spatial resolution $\delta^{13}\text{C}$ -DIC dataset and assess the spatial and temporal changes of the anthropogenic CO_2 uptake and storage in the North Atlantic Ocean, we participated in the 2023 A16N cruise, part of the Global Ocean Ship-based Hydrographic Investigations Program (GO-SHIP). For this cruise effort, more than 3500 $\delta^{13}\text{C}$ -DIC samples were analyzed, achieving spatial coverage comparable to other GO-SHIP Level 1 parameters such as DIC concentration analyzed via coulometry at sea (Johnson 1992; Johnson et al. 1999; O'Sullivan and Millero 1998). This work marks the first large-scale effort to collect $\delta^{13}\text{C}$ -DIC data on board ships of any oceanographic expedition in open oceans. We compiled a record of the cruises with $\delta^{13}\text{C}$ -DIC observations in the North Atlantic Ocean from 1981 to 2023 (Fig. 1a). Prior to our measurements, only 8755 $\delta^{13}\text{C}$ -DIC samples had been collected across 79,287 observation points (Fig. 1b), accounting for just 11% of the total dataset. Our dataset significantly enhances the spatial resolution of $\delta^{13}\text{C}$ -DIC observations, providing a critical foundation for improving estimates of anthropogenic CO_2 uptake and evaluating ocean carbon cycle models.

This dataset is published as a standalone Data Article to promote its visibility, transparency, and reuse within the



Data description

Map of the North Atlantic Ocean showing bathymetry and two cruise tracks. The map covers 60°N to the Equator (EQ) and 40°W to 0°W. Bathymetry is color-coded from 250 m (lightest) to 6000 m (darkest). Leg 1 is a red dotted line starting at ~25°N, 25°W and ending at ~15°N, 25°W. Leg 2 is a blue dotted line starting at ~60°N, 25°W and ending at ~35°N, 25°W. A legend in the bottom right identifies the tracks.

Fig. 2. Map of the 150 sampling stations occupied during the GO-SHIP A16N cruise in 2023.

The dataset is in comma-separated value (csv) format and hosted by the Biological and Chemical Oceanography Data Management Office. Each entry includes the expedition code (EXPOCODE), section ID, sampling date and time (ISO_DateTime_UTC, ISO 8601 format) recorded in Coordinated Universal Time (UTC) following the ISO 8601 format, station and Niskin bottle numbers, sampling location (latitude and longitude, decimal degrees), water depth (meters), $\delta^{13}\text{C}$ -DIC values (DELC13, per mil) relative to the Vienna Pee Dee Belemnite standard, and quality flags (DELC13_FLAG) indicating measurement reliability (2 = acceptable; 3 = questionable; 6 = median of replicates; 9 = missing value) (Jiang et al. 2022). The dataset comprises 3539 data points, of which 3460 confirmed (flagged 2 or 6) through quality assurance/control procedures detailed in the following sections. This indicates that approximately 98% of the tripped Niskin bottles have a corresponding validated $\delta^{13}\text{C}$ -DIC value. The $\delta^{13}\text{C}$ -DIC values range from -0.14‰ to 1.36‰ , spanning depths from 0 to 6000 m and latitudes from 6° S to 63.3° N, offering extensive spatial and depth coverage for $\delta^{13}\text{C}$ -DIC analysis.

Sample collection

During the 56-d expedition, a total of 3825 discrete water samples were collected from 150 CTD casts for $\delta^{13}\text{C}$ -DIC analysis. Samples were drawn from all Niskin bottles at multiple depths, with two to three replicates typically collected from the surface, oxygen minimum zone, and bottom rosette bottles to evaluate measurement consistency. These replicates were analyzed at different times to assess reproducibility. Among all samples, 2875 (75%) were analyzed onboard using CRDS, while the remaining samples were preserved and analyzed ashore within 3 months.

The $\delta^{13}\text{C}$ -DIC analytical system comprises a Picarro G2131-i Isotope and Gas Concentration CRDS Analyzer and

We calibrated the system using multiple in-house NaHCO_3 standard solutions with pre-calibrated $\delta^{13}\text{C}\text{-DIC}$ values ranging from -4‰ to 2‰ . These in-house standards were prepared, and the $\delta^{13}\text{C}\text{-DIC}$ values were verified by the University of California Davis Stable Isotope Facility with the headspace equilibration technique (Atekwana and Krishnamurthy 1998). A detailed description of the in-house standards preparation and the analytical procedure can be found in Sun et al. (2024). Briefly, for sample analysis, seawater samples mixed with acid brine were injected at a controlled speed into the reactor to liberate all DIC. The generated CO_2 was carried by CO_2 -free air to the CRDS analyzer, which measured CO_2 concentration and $\delta^{13}\text{C}\text{-CO}_2$ values at 1 Hz for ~ 500 s. The cycle ended when CO_2 levels stabilized, with each measurement lasting ~ 13 min. Each sample underwent at least two and up to four consecutive measurements. A relative standard deviation threshold of 0.06 between replicate measurements was used onboard as a quality control criterion to determine whether a third or fourth measurement was required. This threshold ensures high reproducibility but is distinct from the absolute analytical precision established through repeated testing of the same sample. The final $\delta^{13}\text{C}\text{-DIC}$ value was reported as an average of two measurements meeting precision criteria.

Based on our previous evaluation (Sun et al. 2024), the analytical uncertainty of the $\delta^{13}\text{C}$ -DIC method was estimated to be 0.03‰ (1σ) during shipboard operation, based on repeated measurements and comprehensive uncertainty analysis including sampling, handling, instrument drift, and standard variability. In the present dataset, 320 pairs of duplicate samples were analyzed to evaluate the internal reproducibility, yielding $\delta^{13}\text{C}$ -DIC values ranging from -0.07‰ to 1.35‰ . The distribution of absolute differences between replicate measurements is shown in Fig. 3, where over 70% of replicate pairs differed by

Table 1. Summary of the measured stable isotopic composition of dissolved inorganic carbon ($\delta^{13}\text{C}$ -DIC) in certified reference materials (CRMs) from different batches.

CRM #	Period	Number of bottles	$\delta^{13}\text{C}$ -DIC (‰)
197	Legs 1 and 2	8	0.13 ± 0.06 ($n = 28$)
199	Legs 1 and 2	8	0.97 ± 0.05 ($n = 36$)
201	Leg 2	40	0.62 ± 0.06 ($n = 99$)
202	Leg 1	20	0.56 ± 0.07 ($n = 48$)
206	Onshore	14	0.89 ± 0.07 ($n = 68$)

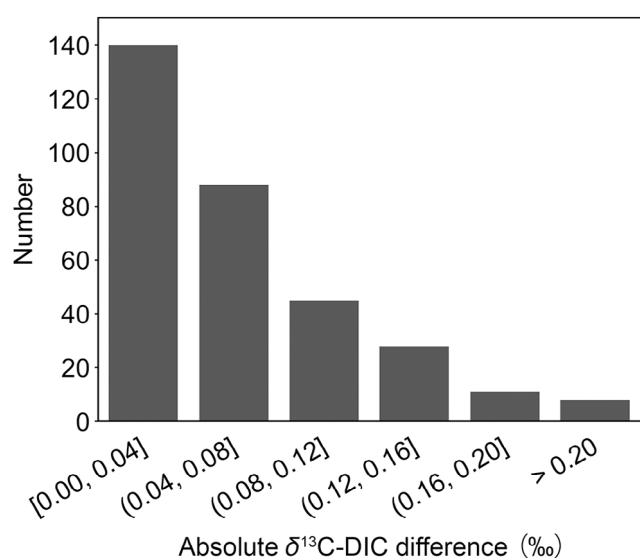


Fig. 3. Histogram of absolute stable isotopic composition of dissolved inorganic carbon ($\delta^{13}\text{C}$ -DIC) differences between pairs of duplicate samples.

less than 0.08‰, indicating good reproducibility under operational conditions. After excluding eight pairs with an absolute difference greater than 0.2‰ (likely due to sampling or handling artifacts), the remaining 312 pairs exhibited a mean absolute difference of 0.06‰ and a standard deviation of 0.07‰ for the pairwise differences. This corresponds to a single-measurement uncertainty of 0.05‰ (1σ), consistent with the method's reported precision under operational conditions. For samples measured only once (quality flag = 2), this uncertainty is assigned. For samples with multiple replicates (quality flag = 6), the propagated uncertainty of the average value is estimated to be approximately 0.04‰ (1σ).

Technical validation

The technical validation and quality assurance/control process involved two key steps. First, to minimize potential biases in $\delta^{13}\text{C}$ -DIC data at each station, measurements from deep-water samples (1800–4200 m) were selected. These samples

were chosen because they are less affected by air-sea gas exchange, anthropogenic carbon processes, and upper-layer interactions, making them relatively stable (Becker et al. 2016; Cheng et al. 2019; Lauvset and Tanhua 2015; Tanhua et al. 2010). To ensure consistency, the data were interpolated to fixed depths (2000, 2250, 2500, ..., 4000 m) and compared across adjacent stations to detect anomalies. Stations with $\delta^{13}\text{C}$ -DIC values deviating by more than 0.07‰ from neighboring stations were flagged for further manual inspection to determine if the differences were statistically significant. Cross-checks were conducted based on the analysis of reference standards, as outlined in “Methods” section, to determine if systematic bias corrections were necessary for any station. This process led to an offset adjustment of -0.07 ‰ to Sta. 81 to correct an identified discrepancy.

Next, a spatial consistency check was performed for each sampling point. This involved calculating the average $\delta^{13}\text{C}$ -DIC value of surrounding points and assessing whether any individual points deviated significantly. This approach helped identify and address outliers or anomalies in the dataset. A secondary manual inspection was conducted for points with large deviations. If the discrepancies remained unresolved, the sample was assigned a flag value of 3 (Jiang et al. 2022). Through this quality control process, 47 questionable measurements were flagged.

Comparison with existing datasets

The A16N repeat hydrographic section has been occupied multiple times since the 1980s, with expeditions conducted in 1988–1990, 1993, 2003, and 2013. Among these, $\delta^{13}\text{C}$ -DIC measurements were taken during the 1993 (EXPOCODE 33MW19930704), 2003 (EXPOCODE 33RO20030604), and 2013 (EXPOCODE 33RO20130803) cruises, though the 2003 cruise was limited to surface observations. The 1993 $\delta^{13}\text{C}$ -DIC data were analyzed by the University of Washington (Quay's lab) using isotope ratio mass spectrometry, while the 2003 and 2013 measurements were conducted using isotope ratio mass spectrometry by the National Ocean Sciences Accelerator Mass Spectrometry facility also at Woods Hole Oceanographic Institution. The number of valid $\delta^{13}\text{C}$ -DIC data points, identified by flags of 2 or 6, was 526 in 1993, 38 in 2003, and 498 in 2013. In comparison, our 2023 $\delta^{13}\text{C}$ -DIC dataset contains 3460 valid values, nearly 7 times the density of previous records (Fig. 4).

To assess data consistency, we compared the deep-water $\delta^{13}\text{C}$ -DIC values from 1993, 2013, and 2023 expeditions. The $\delta^{13}\text{C}$ -DIC measurements were interpolated onto a fixed depth grid ($0.5^\circ \times 50$ m), and mean differences were calculated for values below 2000 m. The average difference between the 2023 and 2013 datasets was 0.019‰, while the difference between 2013 and 1993 was -0.023 ‰. Comparatively, the mean difference between 2023 and 1993 was -0.004 ‰.

A crossover analysis was conducted with neighboring stations from the historical observations to further evaluate data

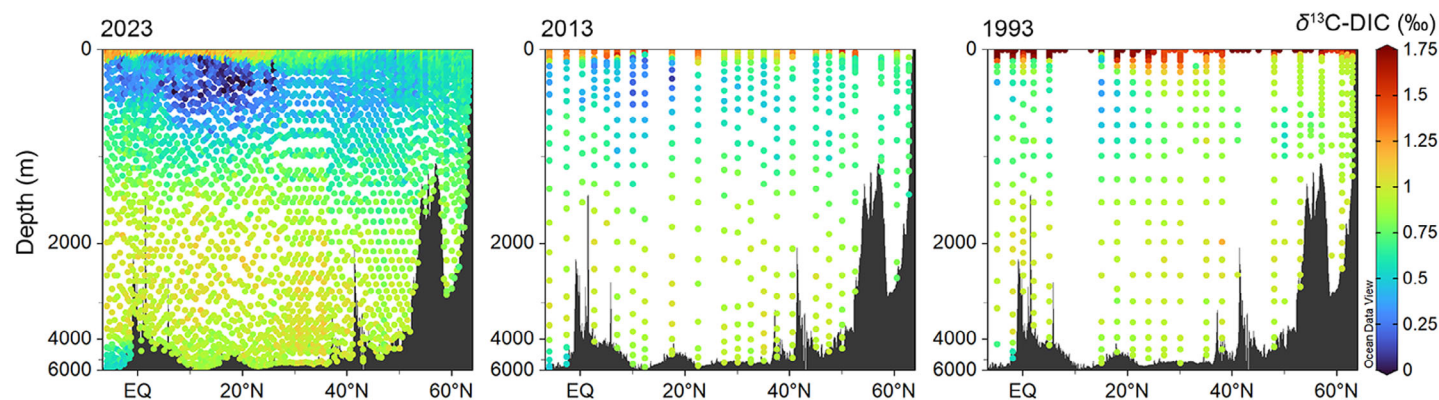


Fig. 4. The distribution of stable isotopic composition of dissolved inorganic carbon ($\delta^{13}\text{C}$ -DIC) along A16N in 2023, 2013, and 1993 (from left to right).

consistency and reliability. This process objectively compares deep-water data from different cruises within the same region (Becker et al. 2016; Lauvset and Tanhua 2015; Tanhua et al. 2010). For the 2023 A16N cruise, we combined Leg 1 (33RO20230306) and Leg 2 (33RO20230413) into a single dataset. Crossover analyses were then performed along A16N for the following cruise pairs: 1993 vs. 2023, and 2013 vs. 2023. To identify crossover points, a maximum station separation of 2° latitude was applied. At these locations, $\delta^{13}\text{C}$ -DIC data from depths greater than 2000 m were compared based on equal potential density. Overall, the cruise pairs showed crossover stations with small weighted offsets, indicating good agreement and consistent data across the years (Fig. 5). For A16N in 1993, 20 deep-water stations from cruise 33MW19930704 overlapped with 120 stations from A16N in 2023, with a weighted offset of $0.012\text{‰} \pm 0.06\text{‰}$ (Fig. 5a). Between the 2013 and 2023 cruises, 19 and 122 deep-water stations overlapped, resulting in a weighted offset of $-0.016\text{‰} \pm 0.05\text{‰}$ (Fig. 5b).

Using 33MW19930704 as the core reference cruise, as suggested by Becker et al. (2016), the offsets between cruises range from -0.02‰ to 0.02‰ , demonstrating good consistency in $\delta^{13}\text{C}$ -DIC measurements. Given these minimal offsets, no adjustments are required for the 2023 cruises (both 33RO20230306 and 33RO20230413). These findings confirm the overall reliability of $\delta^{13}\text{C}$ -DIC data across all analyzed samples. However, we suspect that the 2013 $\delta^{13}\text{C}$ -DIC data were systematically too low by 0.02‰ .

Data use and recommendations for reuse

The $\delta^{13}\text{C}$ -DIC serves as a sensitive indicator of carbonate system dynamics. Its distribution in the ocean reflects various processes, including air-sea CO_2 exchange, biological production and respiration, water mass mixing, and the formation or dissolution of calcium carbonate minerals (Alling et al. 2012; Körtzinger et al. 2003; Quay et al. 2017).

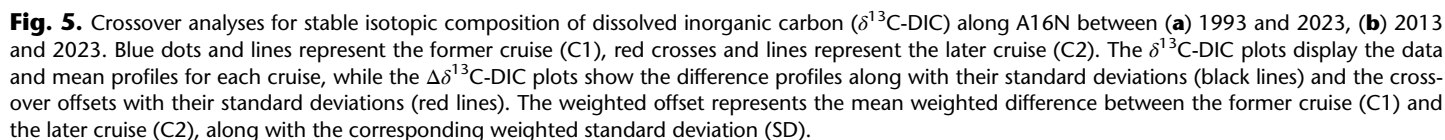
One key application of $\delta^{13}\text{C}$ -DIC dataset is investigating the disequilibrium between atmospheric CO_2 and the dissolved

carbon pool in seawater. The $\delta^{13}\text{C}$ -DIC helps quantify the air-sea $^{13}\text{C}\text{O}_2$ flux and explore the factors driving air-sea $\delta^{13}\text{C}$ disequilibrium (Quay et al. 2017, 2007; Tans et al. 1993). Additionally, $\delta^{13}\text{C}$ -DIC has been widely used to estimate the oceanic uptake of anthropogenic CO_2 through various approaches, including back-calculation (Körtzinger et al. 2003; Olsen and Ninnemann 2010; Sonnerup et al. 1999), regression-based methods (Ko and Quay 2020; Olsen et al. 2006; Quay et al. 2007, 2003; Sonnerup et al. 2000), and carbon budgeting (Heimann and Maier-Reimer 1996; Quay et al. 1992; Tans et al. 1993).

The $\delta^{13}\text{C}$ -DIC dataset functions as a useful resource for estimating net community production. This is driven by distinct isotopic patterns in biological processes—photosynthesis at the sea surface enriches the water with a more positive $\delta^{13}\text{C}$ signal, while sinking organic matter releases a highly negative $\delta^{13}\text{C}$ signal into subsurface waters. Unlike dissolved oxygen-based assessments, $\delta^{13}\text{C}$ -DIC provides a longer-term perspective on biological pump productivity, offering insights into carbon cycling over extended timescales (Quay 2023; Quay et al. 2020, 2009; Quay and Stutsman 2003; Yang et al. 2019).

Furthermore, incorporating $\delta^{13}\text{C}$ -DIC data provides observational benchmarks for evaluating and constraining ocean biogeochemical models. By integrating these measurements into biogeochemical models, researchers can better understand the processes that regulate carbon uptake, storage, and export in the ocean (Claret et al. 2021; Schmittner et al. 2013; Sonnerup and Quay 2012). Additionally, analyzing $\delta^{13}\text{C}$ -DIC variations alongside DIC changes provides a powerful approach for identifying carbon sources and distinguishing between biological and physical influences on carbon cycling in both the global open ocean (Eide et al. 2017a, 2017b; Gruber et al. 1999) and coastal systems (Alling et al. 2012; Chen et al. 2022; Deng et al. 2022; Quiñones-Rivera et al. 2022; Su et al. 2019).

For example, Ouyang et al. (2024) used $\delta^{13}\text{C}$ -DIC to differentiate marine and terrestrial carbon inputs in Pacific Winter Water in the western Arctic Ocean. Similarly, Su et al. (2020)



Our high-resolution $\delta^{13}\text{C}$ -DIC dataset allows for detailed analysis of fine-scale variations in carbon cycling and biological production. It is essential for improving global understanding of oceanic carbon cycling and refining estimates of oceanic biological production and terrestrial carbon export. Moreover, our $\delta^{13}\text{C}$ -DIC measurements exhibit a high precision and strong consistency with historical records, ensuring the reliability and comparability of the dataset. Given its accuracy, this dataset can serve as a valuable training set for machine learning applications, enabling the fitting, prediction, and reconstruction of $\delta^{13}\text{C}$ -DIC values for earlier cruises lacking direct measurements but containing other relevant variables. This approach has the potential to greatly expand the spatial and temporal coverage of $\delta^{13}\text{C}$ -DIC data, further improving our ability to assess oceanic carbon dynamics and anthropogenic CO_2 uptake in the future including the evaluation of the efficacy of marine carbon dioxide removal effort if it is scaled up in future decades.

Zhentao Sun and Hui Gao initiated the manuscript. Zhentao Sun and Hui Gao led data management and QA/QC efforts. Zhentao Sun, Bo Dong, and Najid Hussain participated in the cruise and performed sample analysis. Wei-Jun Cai and Eliot A. Atekwana secured funding and Wei-Jun Cai directed the overall project. All co-authors read and contributed to editing the paper.

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