Determination of Carbon Isotope Ratios ($\delta^{13}C$) of Dissolved Inorganic Carbon (DIC) in Marine Sediment Pore Water Using the Delta Ray IRIS with URI Connect

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Key Words
Dissolved inorganic carbon (DIC), isotope ratio infrared spectroscopy (IRIS), marine sediments

Goal

To demonstrate the performance of Delta Ray IRIS with URI Connect for the isotopic analysis of Dissolved Inorganic Carbon (DIC)

Introduction

The isotopic composition of carbon dioxide contains information about its sources and biogeochemical turnover processes in natural environments. Atmospheric CO_2 has a $\delta^{13}C$ value of about -8‰ (between -7.5 and -9.5‰ VPDB (Tans and Zellweger, 2013), depending on location and season), whereas corresponding $\delta^{13}C$ values of dissolved inorganic carbon (DIC) in ocean water are about +1.5‰ in the surface and around +0.5‰ in the deep on a global average. In marine sediments, processes such as the decomposition of organic matter and dissolution of $CaCO_3$ lead to modifications of the carbon isotope composition of DIC, spanning a wide range from more positive than +10‰ to more negative than -40‰ VPDB, with endmembers being produced during intense methanogenesis and methanotrophy, respectively.

The established method to analyze $\delta^{13}C$ of DIC in water samples is based on acidification and isotope determination of the released CO_2 in the gas phase (Torres et al., 2005). However, instead of employing a Thermo Scientific™ GasBench™ Isotope Ratio Mass Spectrometer (IRMS), a Thermo Scientific™ Delta Ray™ Isotope Ratio Infrared Spectrometer (IRIS) with Universal Reference Interface (URI) Connect was utilized.

Sample Collection and Preparation

The system was tested for sediment pore water DIC analysis from Eckernförde Bay. Eckernförde Bay is a shallow coastal system in the Baltic Sea of glacial origin where methane-rich Holocene sediment fillings are interacting spatially with low-salinity groundwater seepage in pockmark like structures (Whiticar, 2002). Several pockmark areas are distributed along the shores of the bay and around Mittelgrund, a relict submarine morain. In order to identify biogeochemical turnover processes depending on varying groundwater discharge intensities, sediment cores (up to 55 cm in length) were taken inside and outside of a pockmark at water depths of 23 and 21 m, respectively. Sediment pore water was extracted from the closed cores in several depth intervals by 0.7 µm rhizon samplers and transferred into glass vials. In addition to $\delta^{13}C$ analysis via the Delta Ray IRIS with URI Connect an aliquot of the samples was used for chloride analysis using ion chromatography as a geochemical parameter for freshwater fluid discharge.

Analytical Procedure

Carbon isotope ratios of pore water DIC samples were analyzed using a Delta Ray IRIS with URI Connect and autosampler unit (Figure 1).

Figure 1. Delta Ray IRIS with URI Connect and autosampler.

The analytical procedure is using acidification of the water sample followed by CO2 isotope determination of the released headspace gas, e.g. Torres et al. (2005). First, 20 mL headspace vials with crimp seal and butyl rubber stopper are prepared with 100 µL 43‰ H_3PO_4 per 1 mL of pore water sample, closed with a septum cap, and positioned in the autosampler. Using 1 mL of pore water sample is generally sufficient to provide at least 1.7 µmol CO_2, which has been determined to be the lower concentration limit in order to reach optimal external precision of 0.16‰ (Stoltmann, 2014). Second, headspace atmosphere in the vial is replaced by "Synthetic Air" (CO_2 free air) running the Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software in the autosampler-purging mode for 5 minutes followed by manual pore water sample injection via syringe. After equilibration at room temperature for at least 10 hours, the Qtegra ISDS workflow Software is run in the autosampler-measuring mode using "Synthetic Air" as carrier gas and a "CO_2 lab standard" as reference. The measurement method is implemented as follows:

1. Flush of the crimp vial headspace with synthetic air into the variable volume to a total volume of 100 mL.
2. Automatic determination of the concentration and, if necessary, additional dilution to reach the desired analysis concentration (typically 380 ppm).
3. Continuous transfer of the diluted sample gas into the laser cell at the targeted CO_2 concentration of 380 ppm during the measurement.
4. Depending on the amount of CO_2 per sample, up to three measurements at intervals of three minutes are performed, acquiring data points each second.
5. Reference gas analysis for processing of the raw sample data is done by bracketing calibration.

Results

Pore Water $\delta^{13}C_{DIC}$ Determination: Performance

Based on the strong salinity gradient inside the pockmark (Figure 2), selected samples are listed in Table 1 to demonstrate the internal precision that can be achieved on actual samples.

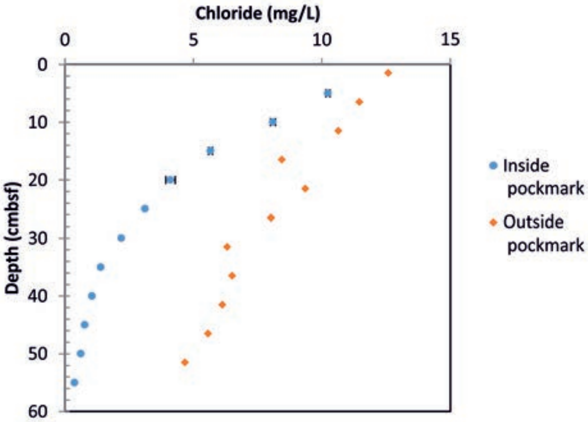

Figure 2. Chloride concentration in sediment pore water inside and outside a pockmark in Eckernförde Bay.

Table 1. Determination of pore water $\delta^{13}C_{DIC}$ in Eckernförde Bay sediments using IRIS. Average values and standard deviation SD are given in ‰.

Inside Pockmark	Delta Ray IRIS	
Sample Depth	$\delta^{13}C_{DIC}$ (‰)	SD (‰)
5 cm	-12.6	0.08
15 cm	-2.3	0.08
20 cm	4.6	0.18

$\delta^{13}C_{DIC}$ data provide evidence of a very strong gradient of $\delta^{13}C_{DIC}$ in Eckernförde Bay sediments, ranging from -12.6‰ at 5 cm depth to +4.9‰ at 20 cm depth. Small standard deviations of $\delta^{13}C_{DIC}$ measurements between 0.04 and 0.18‰ are achieved. Delta Ray IRIS with URI Connect offers a robust method for pore water $\delta^{13}C_{DIC}$ determination in marine sediments.

Biogeochemical Application

The influence of low salinity groundwater discharge in Eckernförde Bay is stronger inside the pockmark than outside as recognized by a much steeper chloride gradient of the former (Figure 2).

$\delta^{13}C$ values of pore water DIC at both sites are plotted against sediment depth in Figure 3, showing a comparable pattern. A minimum of $\delta^{13}C_{DIC}$ down to ~-12‰ is observed in intermediate depths and a maximum of $\delta^{13}C_{DIC}$ up to ~+1 and +5‰ at the deepest samples outside and inside the pockmark, respectively.

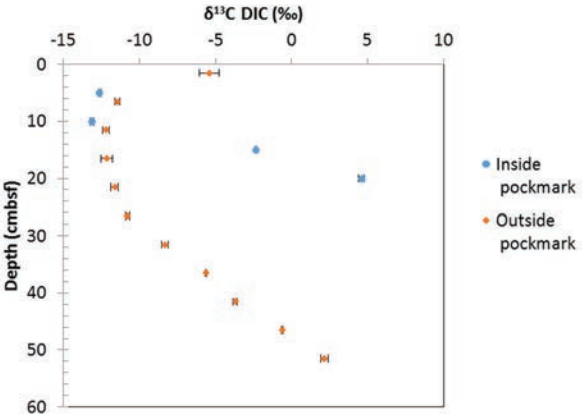

Figure 3. Pore water $\delta^{13}C_{DIC}$ values inside and outside pockmark in Eckernförde Bay. Bars indicate standard deviations in ‰.

Most positive $\delta^{13}C_{DIC}$ values at depth are associated with active methanogenesis by CO_2-reduction, leading to a ^{13}C-enrichment in the remaining CO_2 (DIC) pool and ^{13}C-depletion in the formed methane pool (Whiticar, 2002). Closer to the sediment surface, on the contrary, most negative $\delta^{13}C_{DIC}$ values result from sulfate-dependent anaerobic oxidation of methane (AOM). Methane transport and the depth of the AOM zone are controlled by the intensity of pore water advection due to groundwater discharge, resulting in an AOM zone being closer to the sediment surface where stronger groundwater discharge is observed, i.e. inside pockmarks of Eckernförde Bay. At the sediment surface of sites with reduced groundwater discharge, i.e. outside pockmarks, $\delta^{13}C_{DIC}$ values of -5‰ indicate that sediment pore water mixes with overlying seawater DIC.

Conclusions

The Thermo Scientific Delta Ray IRIS with URI Connect enables precise determination of pore water $\delta^{13}C_{DIC}$ in marine sediments. Its data quality is comparable to established isotope techniques as reported in the literature (Torres et al, 2005). Application of the system for $\delta^{13}C_{DIC}$ determination in pore water of Eckernförde Bay sediments accurately identified zones of methanogenesis, anaerobic oxidation of methane and pore water mixing with overlying seawater. The robust system could be directly applied in the field, for example, on a research vessel guiding dedicated sampling of other environmental parameters dependent on first-hand $\delta^{13}C_{DIC}$ profiles.

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