In situ measurements of $\delta^{13}C$ and $\delta^{18}O$ of dissolved CO_2 using an underwater mass spectrometer

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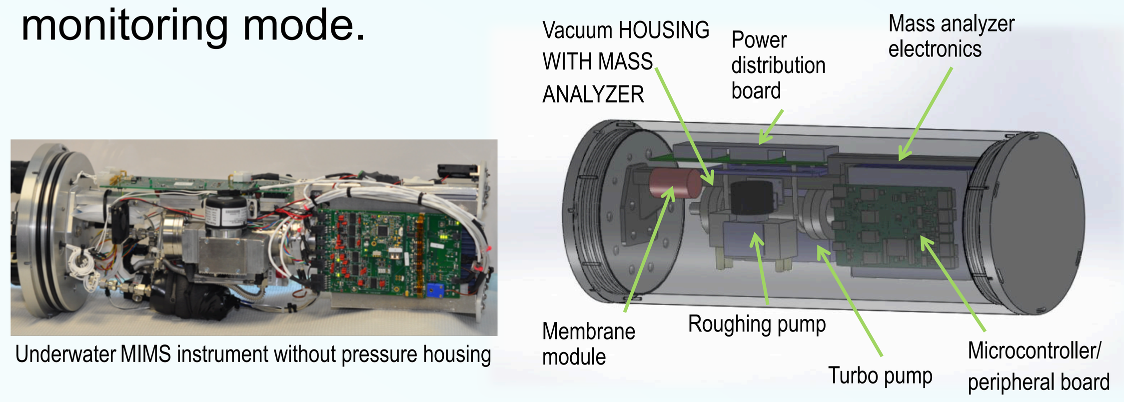
Abstract

We present here novel measurements of stable isotopic ratios of dissolved CO_2 ($\delta^{13}C$ and $\delta^{18}O$) calculated from an underwater mass spectrometer. The isotopic composition of dissolved CO_2 can be diagnostic of the gas source and may enable identification of leaks around oil and gas sites. The SRI underwater mass spectrometer we used to generate data utilizes a selective membrane to introduce relatively non-polar dissolved volatiles to a linear quadrupole mass analyzer. We show that this underwater mass spectrometer is able to measure masses 44, 45, and 46 in sufficiently high resolution to enable precise *in situ* measurements of CO_2 isotopes in deionized water. There are also possible interferences at masses 45 and 46 in seawater, and their effects on our stable isotope calculations are addressed. We present data from both laboratory studies of CO_2 dissolved in seawater and measurements taken in the Gulf of Mexico with very high depth resolution. A high-resolution record of dissolved CO_2 isotopes would further our understanding of the oceanic carbon cycle and pave the way for *in-situ* isotopic measurements of other species of interest such as methane and ethane.

SRI Underwater Mass Spectrometer

The SRI underwater mass spectrometer uses a polydimethyl siloxane membrane to introduce relatively non-polar dissolved volatile analytes into the vacuum housing of a 200 amu linear quadruple mass analyzer with an electron impact ionization source and Faraday cup detector. A small pressure compensated peristaltic pump is used to flow water over the membrane surface and the mass analyzer is typically operated in monitoring mode.



Underwater MIMS instrument without pressure housing

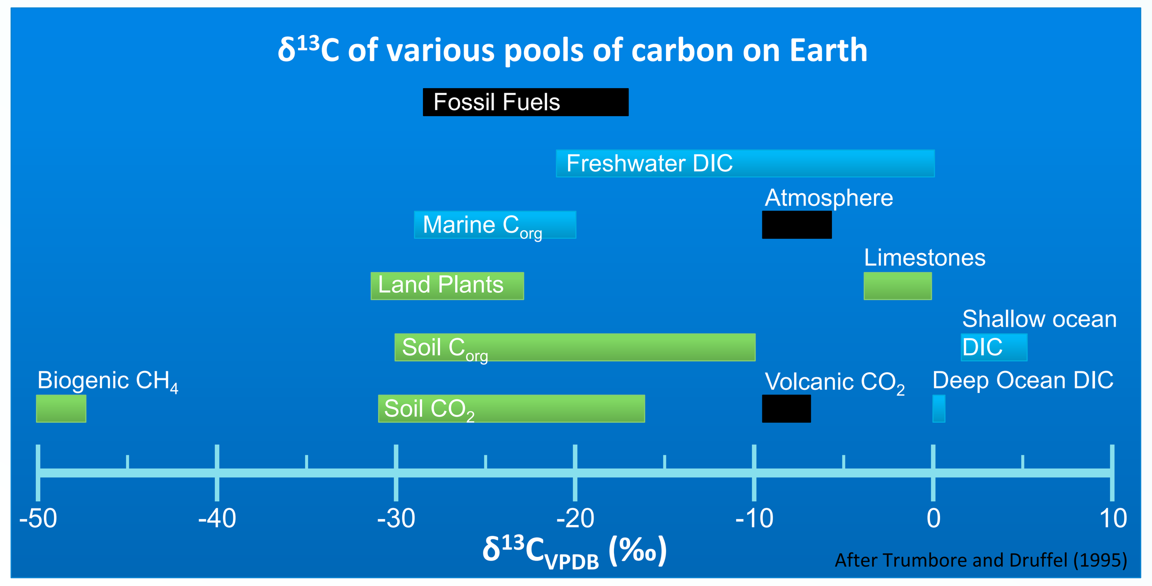
Isotopes!

Isotopes are useful tracers of Earth system processes. Every reaction and phase change happening in the natural world gives rise to fractionations, favoring one isotope of a given element over another. The water cycle is a good example: because of its slightly lighter mass, $H^{16}OH$ evaporates more easily than $H^{18}OH$, resulting in clouds that have ~2‰ less ^{18}O in them compared to the ocean. For the same reason, the $H^{18}OH$ condenses and rains out more readily, making clouds lighter near the poles. The fractionation of isotopes allows us to differentiate spatially or temporally disparate sources for an analyte.

Delta notation

$$\delta^{13}C = \frac{Ratio_{sam} - Ratio_{VPDB}}{Ratio_{VPDB}}$$

Ratio of rare isotope to common isotope

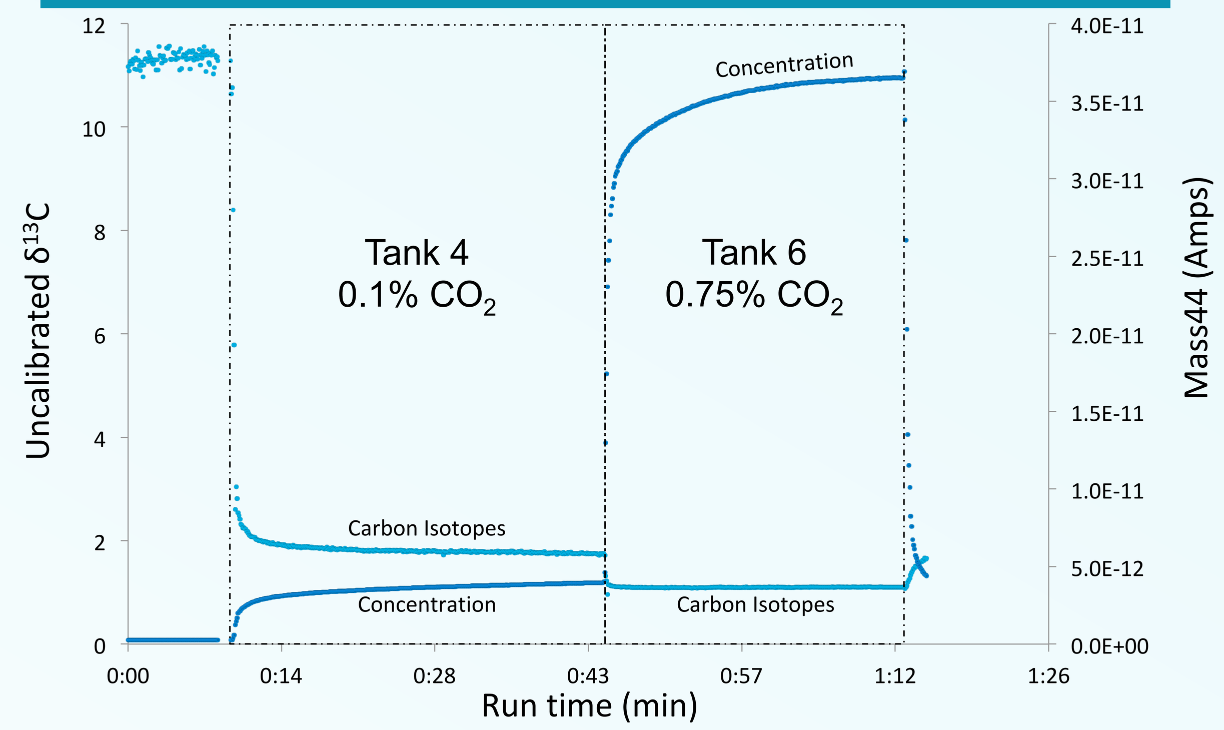


Standards

Gas mixtures

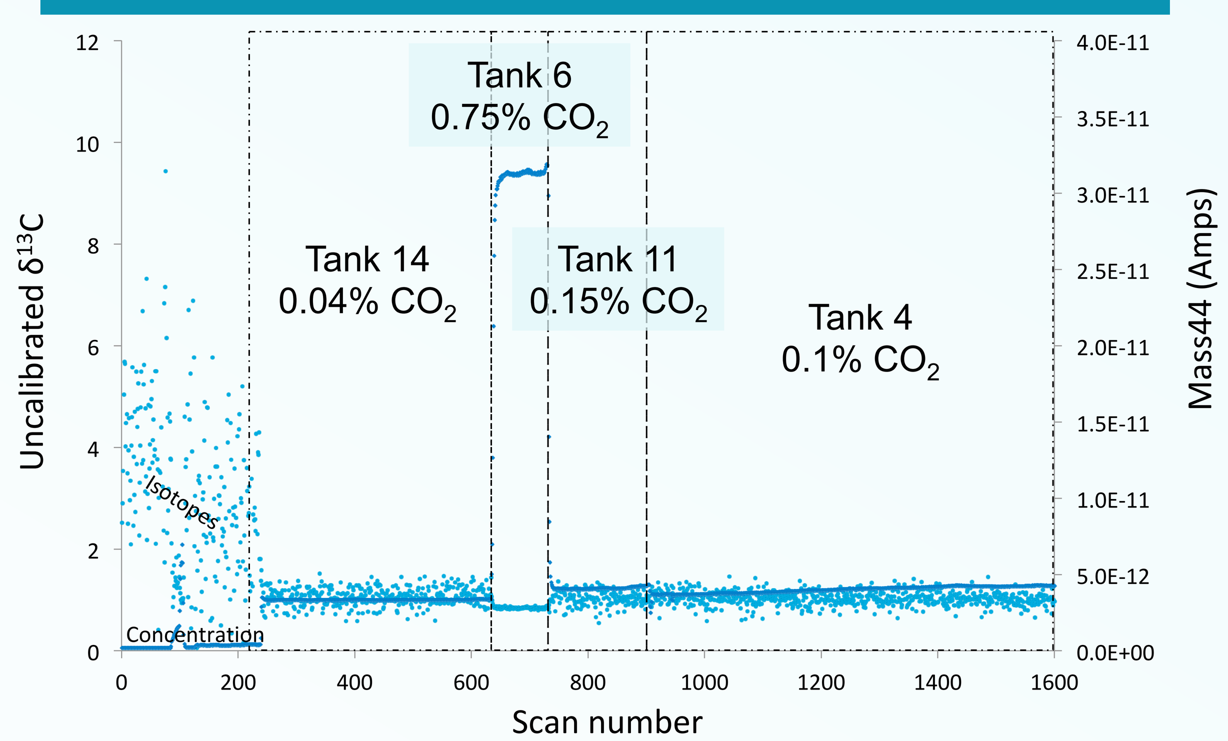
Gas	Tank 4	Tank 6	Tank 11	Tank 14
CO_2	**0.1%**	**0.75%**	**0.15%**	**0.04%**
O_2	20.9%	21%	17%	9.96%
Ar	1%	1.3%	1%	0.7%
CH_4	0.1%	0.25%	2.5%	3.35%
N_2	77.9%	76.7%	79.35%	75.59%

In Deionized Water



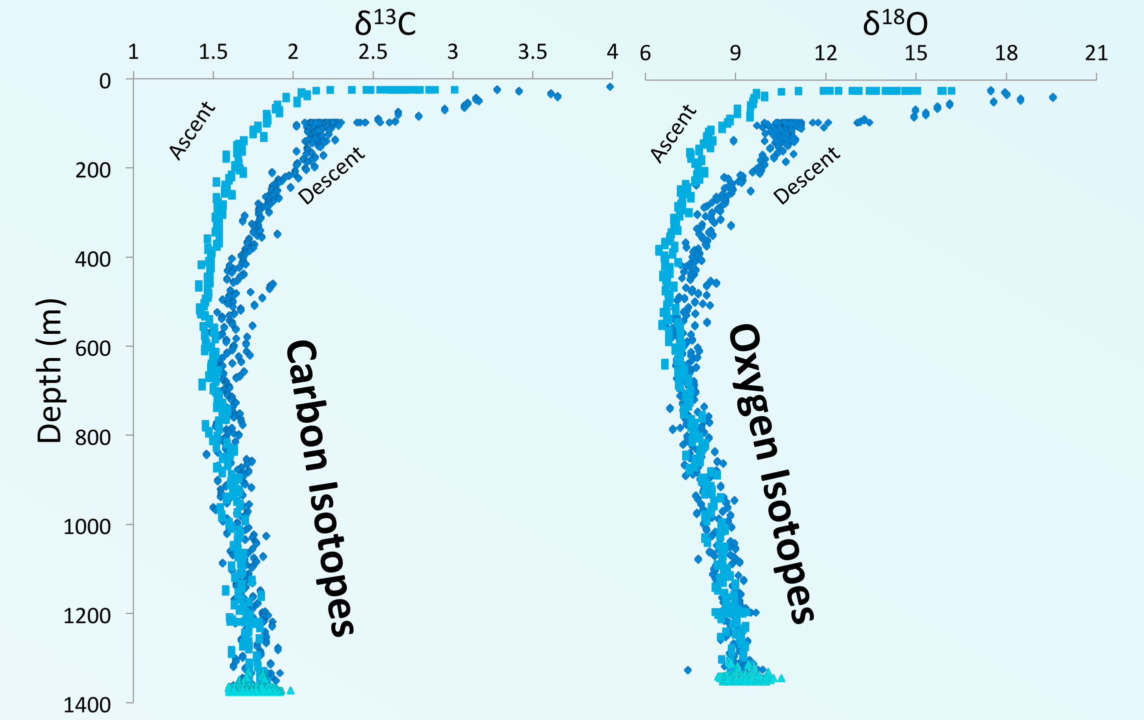
Graph 1: Two different gas mixtures run in deionized water. The light points are calculated carbon isotopes, the dark points are the mass 44 signal.

In Seawater

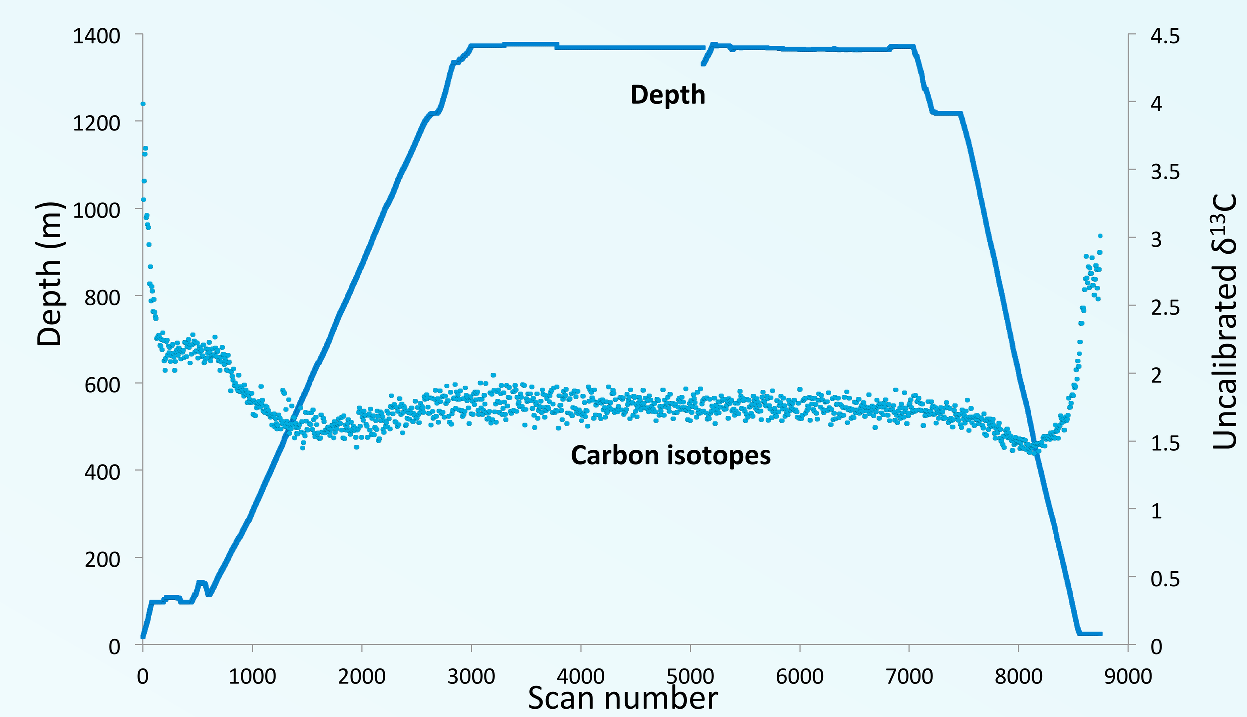


Graph 2: Four different gas mixtures run in seawater. The light points are calculated carbon isotopes, the dark points are the mass 44 signal.

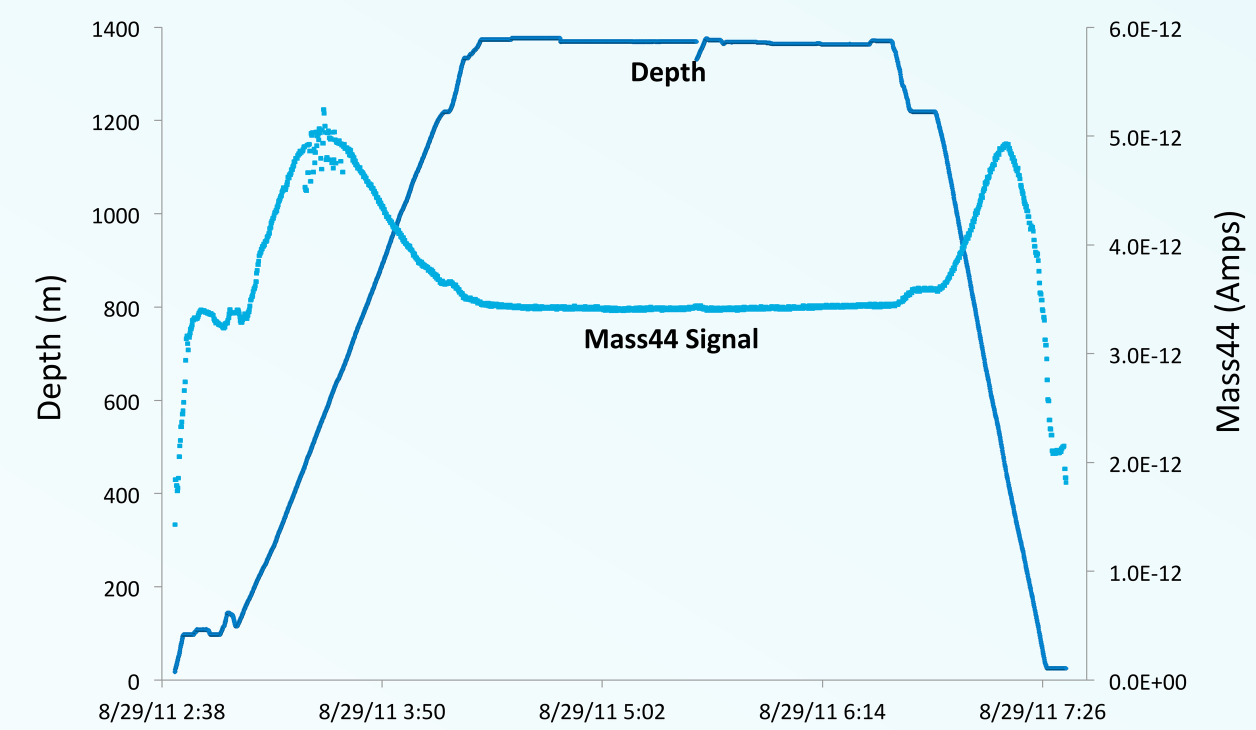
Gulf of Mexico: August 29, 2011



Graph 3: Carbon and oxygen isotopes calculated for the descending (dark blue), ascending (light blue), and steady (teal) legs of the transit in the Gulf.

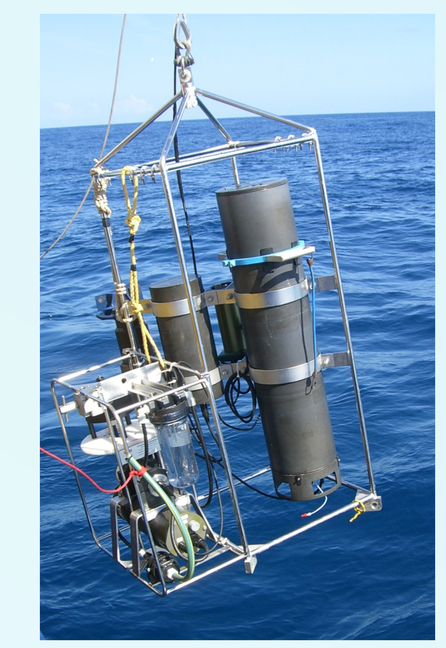


Graph 4: Depth (dark blue) and carbon isotope (light blue) profiles over the course of the Gulf of Mexico voyage.



Graph 5: Depth (dark blue) and mass 44 (light blue) profiles over the course of the Gulf of Mexico voyage.

Results



The underwater membrane inlet mass spectrometer from SRI is able to measure carbon and oxygen isotopes *in situ*. Standards have shown linearity issues with isotope measurements in deionized water. Deionized measurements are highly precise, and CO_2 concentrations of 0.6% (perhaps less) yield consistent isotopes. However, measurements in salt water are significantly less precise at low concentrations, likely due to mild isobaric interferences. Measurements conducted in the Gulf of Mexico show similar carbon and oxygen isotope profiles as have been observed and modeled in the oceans generally. These profiles have significantly higher depth resolution than has previously been achieved; this resolution would enable identification of different sources of CO_2 in the water column.

The Path Forward

There are three relatively clear next steps in this work: First, we need to measure the isotopic composition of the CO_2 in the different reference tanks at SRI. This will allow us to pin current calculations to a meaningful scale and correct for linearity effects. With the data standardized, we want to calculate carbon isotopes of dissolved CO_2 in data sets where methane and ethane plumes indicate oil and gas influences on the water column. Finally, we want to explore the possibility of calculating carbon isotopes from *in situ* measurements of methane and ethane to further fingerprint sources of carbon.

Possible implications

- Creation of high resolution *in situ* records of CO_2 carbon and oxygen isotopes in bodies of water
- Differentiation of various sources of dissolved CO_2 in the water column, particularly of oil and gas
- Better contextualization of local effects on incorporation of carbon and oxygen into foraminifera and the broader geologic record.

Trumbore, S. E., & Druffel, E. R. M. (1995). Carbon isotopes for characterizing sources and turnover of nonliving organic matter. In R. G. Zepp, & C. Sonntag (Eds.), Role of Nonliving Organic Matter in the Earth's Carbon Cycle (pp. 7-22). Chichester: John Wiley & Sons Ltd.