

Data report: carbon isotope composition of total dissolved inorganic carbon in interstitial water, Sites U1316, U1317, and U1318, Porcupine Seabight¹

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Abstract

The carbon isotope composition of total dissolved inorganic carbon (DIC) was measured on 111 samples of interstitial water from Sites U1316–U1318 drilled during Integrated Ocean Drilling Program Expedition 307 to the Porcupine Seabight, southwest of Ireland. The analyses were performed to aid in understanding processes involved in the origin and development of Challenger Mound, a deepwater coral mound that was the focus of the expedition. Site U1317 was drilled into the northwest shoulder of Challenger Mound, whereas Sites U1316 and U1318 penetrated siliciclastic slope facies that accumulated downslope and upslope of the mound, respectively. The $\delta^{13}\text{C}_{\text{DIC}}$ values in interstitial water range from -18.3‰ to $+3.9\text{‰}$ Vienna Pee Dee belemnite. Maximum and minimum values occur in juxtaposition in the two deepest samples recovered from Site U1317 and correspond to a maximum in dissolved methane. At all three sites, downhole profiles of $\delta^{13}\text{C}_{\text{DIC}}$ values show a marked change in slope across a major unconformity between the middle Miocene and upper Pliocene series. At Site U1317, $\delta^{13}\text{C}_{\text{DIC}}$ values decrease from -2.5‰ to -8.5‰ from the top of the core to the unconformity at ~ 122 meters below seafloor (mbsf). Below this depth, values increase overall to a maximum value of $+3.9\text{‰}$. At Sites U1316 and U1318, the $\delta^{13}\text{C}_{\text{DIC}}$ values decrease markedly over the uppermost 10 m to values lower than -15‰ before increasing with depth to approximately -6‰ at the middle Miocene/upper Pliocene unconformity. Below the unconformity, $\delta^{13}\text{C}_{\text{DIC}}$ values increase with depth toward maxima ranging between 0‰ and $+1.5\text{‰}$.

Introduction

This report provides the results of carbon isotopic analyses performed on total dissolved inorganic carbon (DIC) on 111 samples of interstitial water recovered from Integrated Ocean Drilling Program (IODP) Sites U1316–U1318 during Expedition 307 to the Porcupine Seabight. The seabight, located southwest of Ireland, is known for extensive development of deepwater coral mounds up to 160 m high that occur in water depths of 600–1000 m (Freiwald and Roberts, 2005). A major objective of IODP Expedition 307 was to investigate two competing hypotheses regarding the initiation and development of deepwater coral mounds: that mound development is (1) controlled by changes in ocean circulation and cli-

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mate (Mullins et al., 1981; Dorschel et al., 2005) and (2) related to the presence of light hydrocarbon seeps (Hovland et al., 1994, 1998). In this regard, the expedition focused on the origin and development of Challenger Mound (52°23'N, 11°43'W), which lies at a water depth of ~800 m in the Belgica mound province on the southwest-facing slope of Porcupine Seabight (see the “[Expedition 307 summary](#)” chapter).

Challenger Mound was penetrated five times during Expedition 307 (Holes U1317A–U1317E). Examinations of the resulting cores indicate that the mound developed atop a major unconformity between the middle Miocene and upper Pliocene that is also developed at nearby Sites U1316 and U1318 (see the “[Expedition 307 summary](#)” chapter; Kano et al., 2007). The stratigraphic section was divided into two distinct units on the basis of changes in lithology. The upper lithostratigraphic Unit 1, which records the initiation and growth of Challenger Mound, consists of silty coral floatstone and rudstone. These mound-related lithologies lie atop a sharp erosional contact with sandy, sometimes glauconitic, siltstone of Unit 2, which continues to the bottom of Holes U1317A–U1317E. Sr isotopic, biostratigraphic, and magnetostratigraphic data indicate that Unit 1 formed during the last 2.6 m.y., whereas the underlying sandy siltstone (Unit 2) dates to the middle Miocene (Kano et al., 2007).

To better understand the context of mound development, two additional sites, Sites U1316 and U1318, were drilled through slope sediments that enclose Challenger Mound. Site U1316 was located upslope and Site U1318 downslope of Site U1317. The stratigraphic section at both sites was divided into three lithostratigraphic units (see the “[Expedition 307 summary](#)” chapter). At both sites, the uppermost lithostratigraphic Unit 1 consists of grayish brown silty clay with scattered pebbles interpreted by shipboard scientists as ice-rafted debris. At Site U1318, the underlying Unit 2 consists of interbedded silty clay and fine- to medium-grained sandstone with scattered pebbles. At Site U1316, Unit 2 consists of a thin (2–4 m thick) interval of silty coral floatstone interpreted on the basis of seismic data to reflect penetration of the upslope basal edge of a coral mound (see the “[Site U1316](#)” chapter). At both sites, Unit 2 unconformably overlies variably sandy and glauconitic siltstone defined as Unit 3. Seismic, stratigraphic, and biostratigraphic data show that Unit 3 at Sites U1316 and U1318 corresponds to Unit 2 at Site U1317. Units 1 and 2 at Sites U1316 and U1318 correspond to the timing of coral mound development at Site U1317 (see the “[Expedition 307 summary](#)” chapter).

Because of distinct differences in the carbon isotope compositions of skeletal carbonate, sedimentary or-

ganic matter, and microbially or thermally derived methane (Arthur et al., 1983), the $\delta^{13}\text{C}$ data provided in the present study will help to constrain the major diagenetic processes affecting Challenger Mound and surrounding sediments and thereby contribute to understanding controls on the genesis of these unique ecosystems. Results are summarized in Table T1 and Figure F1.

Methods and materials

Interstitial water samples were collected from whole-round sections ranging from 5 to 20 cm in length, which were cut on the catwalk, capped, and taken to the laboratory for immediate processing. In the laboratory, samples were extruded from the core liner and the outside ~1 cm was removed to minimize the potential for contamination. Samples were cut in half to allow examination of the core interior, and any visible oversized clasts and fossil debris >1 cm in diameter were removed. The samples were then placed in a titanium squeezer, which was modified after the standard stainless steel squeezer of Manheim and Sayles (1974). Interstitial water was passed through a prewashed Whatman number 1 filter fitted above a titanium screen, filtered through a 0.45 μm Gelman polysulfone disposable filter, and subsequently extruded into a precleaned (10% HCl) 50 mL plastic syringe attached to the bottom of the squeezer assembly. Splits (1–2 mL) of samples were placed into clean glass vials with polyseal caps in preparation for analysis of $\delta^{13}\text{C}_{\text{DIC}}$. Approximately 10 mg of mercuric chloride (HgCl_2) was added to each sample to prevent microbial growth. Samples were stored at 4°–10°C until analysis. Isotopic analyses were performed at the Environmental Isotope Laboratory at the University of Arizona in Phoenix, Arizona (USA). Samples were analyzed using an automated headspace sampler (Finnigan GasBench) connected to a continuous-flow gas-ratio mass spectrometer (Finnigan Delta PlusXL). Samples were acidified with concentrated phosphoric acid, and a minimum of 30 min was allowed for degassing of the water sample. Carbon isotope ratios are reported in parts per thousand (‰) relative to the Vienna Peedee belemnite (VPDB) standard. Precision is $\pm 0.2\text{‰}$, as monitored through multiple analyses of an in-house sodium bicarbonate standard solution that was calibrated against National Bureau of Standards (NBS)-18 and NBS-19.

Results

The $\delta^{13}\text{C}_{\text{DIC}}$ values range from -18.3‰ to $+3.9\text{‰}$ VPDB (Table T1). At all three sites, the middle Miocene/upper Pliocene unconformity corresponds to

an inflection in the slope of downcore profiles in $\delta^{13}\text{C}_{\text{DIC}}$ values (Fig. F1). At Site U1317, $\delta^{13}\text{C}_{\text{DIC}}$ values decrease from -2.5‰ near the top of the core to -8.5‰ to the unconformity at ~ 148 meters below seafloor (mbsf) (base of lithostratigraphic Unit 1). Below this depth, values increase gradually downcore through Unit 2 to a maximum of $+3.9\text{‰}$ at 257.80 mbsf. The overall trend through Unit 2 is interrupted by two outliers to lower values of -13.8‰ at 207.80 mbsf and -18.5‰ at 266.01 mbsf. The maximum and minimum $\delta^{13}\text{C}_{\text{DIC}}$ values at this site occur in adjacent samples that represent the two deepest samples recovered from Site U1317. These extremes correspond to a dissolved methane concentration of $\sim 6500\ \mu\text{M}$, the highest concentration encountered during Expedition 307 (see the “Site U1317” chapter).

Downcore trends in $\delta^{13}\text{C}_{\text{DIC}}$ values are very similar at Sites U1316 and U1318 (Fig. F1). Within the upper ~ 10 m of Unit 1, $\delta^{13}\text{C}_{\text{DIC}}$ values decrease by $\sim 8\text{‰}$ to reach minimum values for these sites of -15‰ or lower. Below this depth, $\delta^{13}\text{C}_{\text{DIC}}$ values increase to approximately -6‰ at the middle Miocene/upper Pliocene unconformity (base of Unit 2), with the rate of change increasing with depth. In Unit 3, $\delta^{13}\text{C}_{\text{DIC}}$ values increase with depth toward maxima of $+0.4\text{‰}$ at Site U1316 and $+1.6\text{‰}$ at Site U1318.

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Figure F1. Downcore trends in the carbon isotope composition of total dissolved inorganic carbon ($\delta^{13}\text{C}_{\text{DIC}}$) in interstitial water, Sites U1316, U1317, and U1318. Also indicated are boundaries of major lithostratigraphic units and the depth of the middle Miocene/upper Pliocene unconformity (wavy unit boundaries). VPDB = Vienna Pee Dee belemnite.

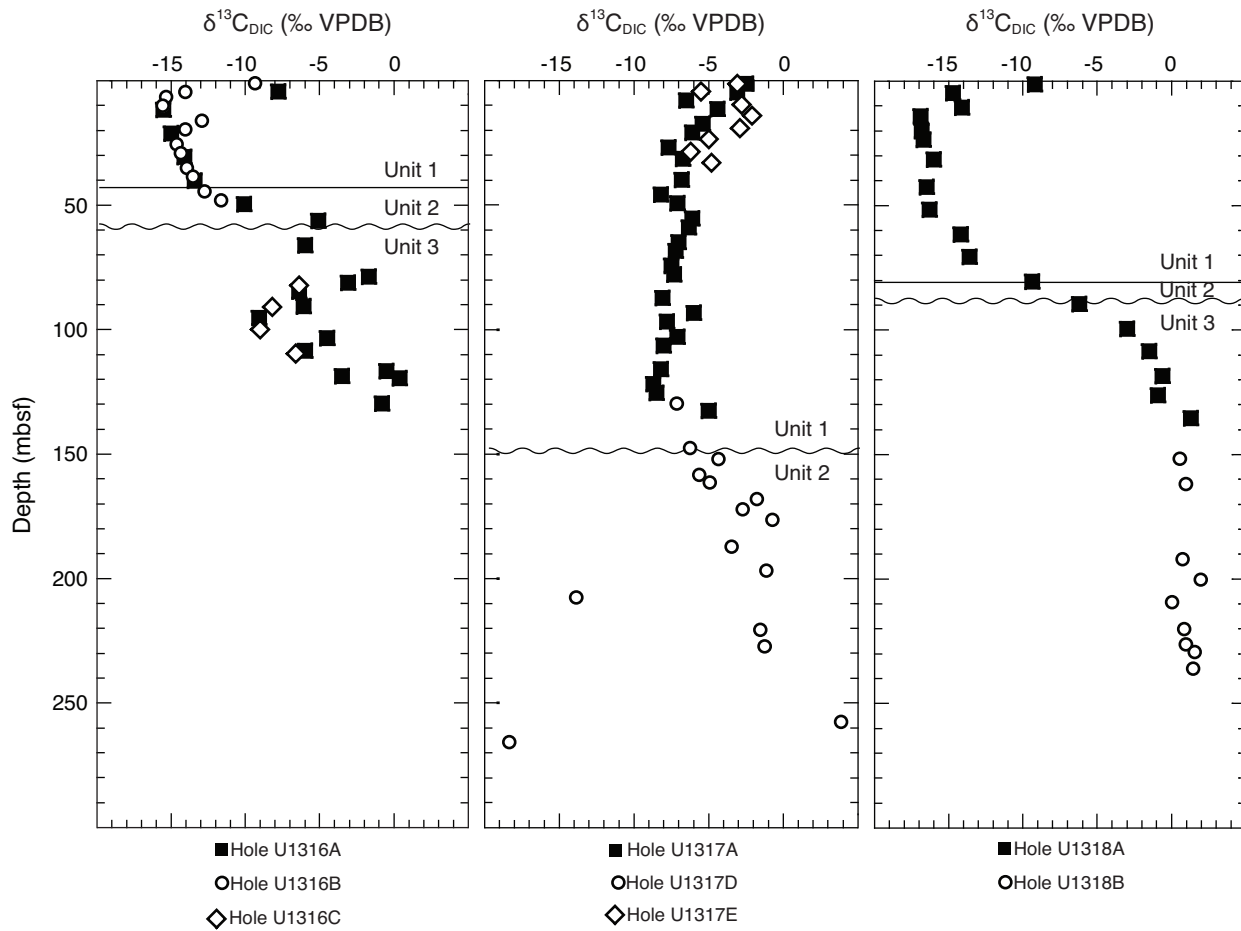


Table T1. Carbon isotope composition of total DIC in interstitial water, Sites U1316, U1317, and U1318. (See table note.)

Core, section, interval (cm)	Depth (mbsf)	$\delta^{13}\text{C}_{\text{DIC}}$ (‰, VPDB)	Core, section, interval (cm)	Depth (mbsf)	$\delta^{13}\text{C}_{\text{DIC}}$ (‰, VPDB)
307-U1316A-			14H-1, 140–150	121.90	-8.7
1H-3, 145–150	4.45	-7.8	14H-3, 190–200	125.40	-8.5
2H-3, 140–150	11.70	-15.5	17X-1, 190–200	132.70	-5
3H-3, 140–150	21.20	-15	307-U1317D-		
4H-3, 140–150	30.70	-14.1	3R-2, 185–200	129.95	-7.1
5H-3, 140–150	40.20	-13.4	5R-1, 198–213	147.78	-6.2
6H-3, 140–150	49.70	-10.1	6R-1, 185–200	152.25	-4.3
7H-1, 140–150	56.20	-5.1	7R-2, 185–200	158.75	-5.6
8H-2, 140–150	66.29	-6	7R-4, 135–150	161.75	-4.9
10X-2, 140–150	78.70	-1.7	8R-2, 182–197	168.42	-1.7
11X-2, 140–150	81.20	-3.1	8R-5, 91–115	172.48	-2.7
12X-1, 140–150	84.70	-6.4	9R-1, 185–200	176.55	-0.7
13X-2, 140–150	90.70	-6.1	10R-2, 124–145	187.54	-3.4
15X-1, 112–117	95.42	-9.1	11R-2, 180–200	197.20	-1.1
16X-3, 140–150	103.40	-4.5	12R-3, 180–200	207.80	-13.8
17X-1, 7–17	108.67	-6	13R-5, 180–200	220.90	-1.5
18X-3, 140–150	116.70	-0.5	14R-3, 180–200	227.50	-1.2
19X-1, 39–49	118.69	-3.5	17R-4, 130–150	257.80	3.9
20X-1, 75–85	119.55	0.4	18R-3, 180–200	266.01	-18.3
21X-3, 140–150	129.70	-0.8	307-U1317E-		
307-U1316B-			1H-1, 140–150	1.40	-3.1
1H-1, 140–150	1.40	-9.3	1H-3, 140–150	4.40	-5.5
1H-3, 190–200	4.90	-14	2H-2, 140–150	9.60	-2.8
2H-1, 140–150	6.90	-15.3	2H-5, 140–150	14.10	-2.1
2H-3, 190–200	10.40	-15.5	3H-2, 140–150	19.10	-2.9
3H-1, 140–150	16.40	-12.9	3H-5, 140–150	23.60	-5
3H-3, 190–200	19.90	-14	4H-2, 140–150	28.60	-6.2
4H-1, 140–150	25.90	-14.6	4H-5, 140–150	33.10	-4.8
4H-3, 190–200	29.40	-14.3	307-U1318A-		
5H-1, 140–150	35.40	-13.9	1H-1, 140–150	1.40	-9.2
5H-3, 190–200	38.90	-13.5	1H-3, 190–200	4.90	-14.7
6H-1, 140–150	44.90	-12.7	2H-1, 140–150	10.60	-14.1
6H-3, 190–200	48.40	-11.6	2H-3, 190–200	14.10	-16.9
307-U1316H-C-			3H-1, 140–150	20.10	-16.8
5H-3, 135–150	82.35	-6.4	3H-3, 190–200	23.60	-16.7
6H-3, 74–94	90.90	-8.2	4H-3, 140–150	31.45	-16
7H-2, 130–150	100.00	-9	5H-3, 190–200	42.60	-16.5
8H-2, 130–150	109.70	-6.6	6H-3, 140–150	51.60	-16.3
307-U1317A-			7H-3, 190–200	61.60	-14.2
1H-1, 140–150	1.40	-2.5	8H-3, 140–150	70.57	-13.6
1H-3, 190–200	4.90	-3.1	9H-3, 190–200	80.60	-9.4
2H-1, 140–150	7.90	-6.5	10H-3, 140–150	89.60	-6.2
2H-3, 190–200	11.40	-4.4	11H-3, 190–200	99.60	-3
3H-1, 140–150	17.40	-5.4	12H-3, 140–150	108.60	-1.5
3H-3, 190–200	20.90	-6.1	13H-3, 190–200	118.60	-0.6
4H-1, 140–150	26.90	-7.7	14H-2, 140–150	126.10	-0.9
4H-4, 140–150	31.40	-6.7	15H-2, 135–150	135.55	1.3
5H-3, 190–200	39.90	-6.8	307-U1318B-		
6H-1, 140–150	45.90	-8.2	17X-3, 130–150	152.00	0.6
6H-3, 190–200	49.40	-7.1	18X-3, 180–200	162.10	1.0
7H-1, 140–150	55.40	-6.1	21X-5, 80–100	192.40	0.8
7H-3, 190–200	58.90	-6.3	22X-4, 80–100	200.50	2.0
8H-1, 140–150	64.90	-7	23X-3, 140–150	209.60	0.1
8H-3, 190–200	68.40	-7.2	24X-4, 130–150	220.50	0.9
9H-1, 140–150	74.40	-7.5	25X-2, 130–150	226.50	1.0
9H-3, 190–200	77.90	-7.3	26X-2, 0–15	229.81	1.6
10H-3, 190–200	87.40	-8.1	27X-1, 135–150	236.35	1.5
11H-1, 140–150	93.40	-6			
11H-3, 190–200	96.90	-7.8			
12H-1, 140–150	102.90	-7.1			
12H-3, 190–200	106.40	-8			
13H-3, 190–200	115.90	-8.2			

Note: DIC = dissolved inorganic carbon, VPDB = Vienna Pee Dee belemnite.