

# Data report: isotopic and elemental analyses of pore fluids and carbonates from Sites U1378 and U1380 drilled during CRISP-A Expeditions 334 and 344 in the middle slope offshore Costa Rica<sup>1</sup>

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## Abstract

Integrated Ocean Drilling Program (IODP) Sites U1378 and U1380, located in the middle slope off Costa Rica, were drilled to characterize the nature, composition, and physical properties of the margin. Drilling results from IODP Expeditions 334 and 344 revealed the material in the margin framework to be well lithified with calcite cemented horizons, which precluded the collection of pore fluids below the slope cover. We report on the elemental and isotopic composition of carbonate leached from cemented sediments underlying the slope cover and on the dissolved inorganic carbon and water isotopic composition of pore fluids in the slope cover. Molar ratios of Sr/Ca (0.21–3.78 mmol/mol), Mn/Ca (2.3–13.8 mmol/mol), and Ba/Ca (0.04–0.84 mmol/mol) in the leached carbonate are shown relative to the pore water distribution of these elements. The <sup>87</sup>Sr/<sup>86</sup>Sr ratios in carbonate range from 0.70797 to 0.70899. Such nonradiogenic values are consistent with previously published dissolved strontium isotopes, which were attributed to a component of tephra alteration. Pore fluid  $\delta^{13}\text{C}$  values range from  $-22.35\text{‰}$  to  $10.88\text{‰}$  referenced to Pee Dee belemnite (PDB), with a marked depletion in <sup>13</sup>C in the upper sediment ( $\delta^{13}\text{C} = -22.35\text{‰}$  PDB at 11.2 meters below seafloor [mbsf]) and enrichment in <sup>13</sup>C in the sediment section from 20.7 to 425.0 mbsf. Most carbonate samples have  $\delta^{13}\text{C}$  values in the range of  $-2.62\text{‰}$  to  $0.24\text{‰}$  PDB, and only three samples have  $\delta^{13}\text{C}$  values higher than  $3.5\text{‰}$  PDB. The  $\delta^{18}\text{O}$  of the carbonate samples ranges from  $-6.35\text{‰}$  to  $2.31\text{‰}$  PDB, and the  $\delta^{18}\text{O}$  of the water ranges from  $-0.71\text{‰}$  to  $3.38\text{‰}$  referenced to standard mean ocean water (SMOW).

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## Introduction

A primary objective of Integrated Ocean Drilling Program (IODP) Expeditions 334 and 344 was to understand the processes that generate earthquakes along the subduction plate boundary at erosive margins. Fundamental to this objective is determining the nature of the upper plate seaward of the seismogenic zone. Current models suggest that at erosive margins, such as those proposed for Costa Rica, fluids migrate from the plate interface and react little with the framework wedge material as they ascend and



vent at the seafloor (e.g., Ranero and von Huene, 2000; Hensen et al., 2004; Sahling et al., 2008). Carbonate formation in the Costa Rica forearc was thus expected to result solely from anaerobic oxidation of the discharging methane-rich fluids, forming carbonate mounds that punctuate the margin. However, IODP drilling during the Costa Rica Seismogenesis Project (CRISP) revealed that significant fluid-rock reactions occur in the margin framework, including extensive carbonate cementation at depth.

Here, we report on the chemical and isotopic composition of the carbonates recovered from Site U1380 and on isotopic composition of the dissolved inorganic carbon and water at Site U1378, which may aid in unraveling fluid sources and the processes that led to formation of the carbonate cements in the wedge framework of the margin.

## Site description

Sites U1378 and U1380 are located on the middle slope of the Costa Rica margin (8°35.9980'N, 84°4.4037'W) (Figure F1). The upper 560 m of the sediment section was sampled at Site U1378, and deeper penetration was achieved by drilling Site U1380. The sites lie above the unlocked portion of the plate boundary, as indicated by interplate earthquake relocation and geodetic measurements (LaFemina et al., 2009). The primary goal in choosing these sites was to investigate the nature, composition, and physical properties of the upper plate framework.

The sediments at Site U1378, dominantly composed of a monotonous sequence of silty clay to clay that alternates with widely interspersed centimeter-scale sandy layers, were divided into two main lithostratigraphic units (Figure F1C). Unit I (0–128 meters below seafloor [mbsf]) is composed of terrigenous silty clay with interbedded fining-upward sequences consisting of lithic sands. Unit II (128–514 mbsf) is predominantly well-consolidated terrigenous clayey silt that remains unlithified to 560 mbsf. This site was abandoned during Expedition 334 because the thick slope sediment package (~750 m) prevented the drill from reaching the underlying basement rock of interest, whereas the thinner slope cover of Site U1380 provided easier access.

At Site U1380, the margin consists of a ~550 m thick section of slope sediment (Unit I) overlying upper plate framework rock (Figure F1). Drilling in Hole U1380A during Expedition 334 was terminated at 482.4 mbsf; this site was revisited during Expedition 344, and penetration in Hole U1380C reached 797.4 mbsf. In Unit I, three sandstone-rich horizons were

recovered with centimeter- to decimeter-thick sandy layers cemented with calcite. Unit II (553–772 mbsf) is visually defined by a relatively sharp lithologic change into greenish gray clayey siltstone with intercalated sandstone and conglomerate layers. In the upper 120 m of Unit II, occasional thin sandstone horizons are well lithified by calcite cement; however, most are poorly consolidated. Shells, shell fragments, and lithic fragments are abundant and conspicuous components in the sandstone. Below 564 mbsf, the sandstone layers are abundant and massive (as thick as 80 cm), normally graded, and become thicker and coarser with depth. The siltstone, sandstone, and conglomerate layers are moderately well lithified by calcite cement. Toward the bottom of the sequence, rip-up siltstone clasts and fragmented (as large as 8 cm) calcite-cemented breccia are more frequent. Siltstone and sandstone smear slides indicate that the dominant matrix composition is volcanogenic with sedimentary lithic fragments, along with common feldspar and glass. The tuff layers are highly altered. The biogenic components decline precipitously and are absent in the lowermost part of this unit. Unit III is a 29.44 m thick massive, well-lithified, very dark greenish gray silty claystone with intercalated sandstone layers. The silty claystone contains common calcite-cemented horizons (Figure F1D). The matrix contains mostly terrigenous material dominated by lithic fragments and feldspar but is nearly devoid of biogenic material.

A major finding of these expeditions was that the margin wedge is composed of well-indurated, cemented clastic sediment (Expedition 334 Scientists, 2012a; Harris et al., 2013a; Bangs et al., 2011). The anomalous porosity profiles and conspicuous seismic reflectors in the margin wedge have now been attributed to the lithologic changes associated with cementation, which is pervasive throughout the 800 m drilled at this site (Expedition 334 Scientists, 2012a; Harris et al., 2013a).

## Analytical methods

### Pore water analyses (carbon, oxygen, and hydrogen isotopes)

Pore water extraction was conducted on board the R/V *JOIDES Resolution* following the procedures described by Expedition 334 Scientists (2012b) and Harris et al. (2013b). The squeezed pore fluids were collected in precleaned, plastic syringes attached to the squeezing assembly and subsequently filtered through a 0.45  $\mu\text{m}$  Gelman polysulfone disposable filter. Samples collected for oxygen and hydrogen analyses were sealed in glass ampoules. Samples for

isotopic composition of dissolved inorganic carbon (DIC) were collected in 2 mL glass vials and preserved with 10  $\mu$ L of saturated HgCl<sub>2</sub>.

Pore water oxygen and hydrogen stable isotopic compositions were measured at the University of Washington (USA) on a Picarro Cavity Ring-Down Spectrometer water analyzer (Model L2130-i). The data are reported in standard delta notation relative to Vienna standard mean ocean water (VSMOW). The precision of the  $\delta^{18}\text{O}$  and  $\delta\text{D}$  measurements based on repeated analyses of VSMOW and several in-house standards is better than  $\pm 0.05\text{‰}$  and  $\pm 0.2\text{‰}$ , respectively.

The stable isotopic composition ( $\delta^{13}\text{C}$ ) of the DIC was measured at Oregon State University (USA) using a GasBench II automated sampler interfaced to a gas source stable isotope mass spectrometer as described by Torres et al. (2005). The precision of the  $\delta^{13}\text{C}$  measurements based on replicate analyses of a NaHCO<sub>3</sub> stock solution is better than  $\pm 0.1\text{‰}$ . Instrument calibration was accomplished by comparison to National Institute of Standards and Technology (NIST)-8544 limestone (also known as NBS-19) prepared using a Kiel-III online acid digestion device, which yields isotopic values of  $-2.19\text{‰} \pm 0.06\text{‰}$  for  $\delta^{18}\text{O}$  and  $1.94\text{‰} \pm 0.02\text{‰}$  for  $\delta^{13}\text{C}$  ( $N = 25$ ). These values compare well with certified values of  $-2.20\text{‰}$  and  $1.95\text{‰}$  for  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$ .

### Solid-phase analyses

Carbonate samples from Hole U1380C were selected from the lithified sediments in Units II and III. The total CaCO<sub>3</sub> content was measured on board the *JOIDES Resolution* using a UIC 5011 CO<sub>2</sub> coulometer, as described by Expedition 334 Scientists (2012b) and Harris et al. (2013b).

Two leaching procedures were compared in their effectiveness at maximizing carbonate leached (represented by fraction carbonate leached) while minimizing clay contamination (represented by a molar ratio of aluminum to calcium): a 4.4 M acetic acid leach (henceforth referred to as the “hard” leach) and a buffered acetic acid leach (referred to as the “soft” leach).

For the hard leach approach (method of Joseph et al., 2012), 8 mL of 4.4 M acetic acid was added to 10 mg of powdered sediment in Teflon vials (Savillex) and refluxed for 12 h at 70°C. Samples were then sonicated and centrifuged, dried down, and redissolved in 3% nitric acid (v/w) for analysis. The soft leach procedure uses a modified version of the buffered acetic acid leaching method outlined by Du et al. (2016). About 0.2 g of powdered sample was added to preleached 15 mL Falcon tubes to which

6.5 mL ultrapure (resistivity >18 M $\Omega$ ) water (Milli-Q water purification system; Millipore; USA) and 0.6 mL buffered acetic acid (0.5 M sodium acetate and 3.3 M acetic acid in ultrapure water buffered to pH 4) were added. The tubes were shaken on a rotary benchtop shaker for 3 h, centrifuged for 10 min at 4000 rpm, and the leachate was decanted and filtered using 0.45  $\mu$ m filters into clean Teflon vials. These leached fractions were then dried down, refluxed for 1 h with 1 mL concentrated HNO<sub>3</sub>, dried down a second time, and refluxed for 1 h with 2 mL of 6 M HNO<sub>3</sub>.

### Elemental analysis of carbonate samples

Major (Al, Ca, Fe, and Mg) and minor (Ba, Mn, and Sr) elements in carbonate were analyzed on an Ametek SPECTRO ARCOS inductively coupled plasma-optical emission spectrometer at the W.M. Keck Collaboratory for Plasma Spectrometry at Oregon State University. Element concentrations are reported as a molar ratio to calcium. Experimental uncertainties reported are  $2\sigma$  errors based on the three replicate analyses performed by the instrument per sample tube. Detection limits were calculated by multiplying the standard deviation of the three blank measurements for each element by the corresponding t-value for a 99% confidence interval ( $df = 2$ ;  $t = 6.965$ ). This value was then regressed on the standard curve to give the detection limit in parts per million.

### Isotopic analyses of carbonate samples

In preparation for strontium isotopic analysis, aliquots of the sediment leaches containing ~200 ng Sr were loaded onto in-house made microcolumns containing 50  $\mu$ L of Sr spec 100–150  $\mu$ m resin from Eichrom. The Sr fractions were subsequently diluted 50/50 with 3% HNO<sub>3</sub>, and the isotopic analysis was performed using a Nu Plasma multicollector inductively coupled plasma-mass spectrometer at the W.M. Keck Collaboratory for Plasma Spectrometry. The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios were doubly corrected: once by using the intraelemental correction for mass fractionation ( $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$ ) and again by internally normalizing the ratios to NIST standard NBS-987, with repeated measurements yielding a  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of  $0.701245 \pm 0.000027$  ( $2\sigma_{\text{mean}}$ ;  $N = 115$ ). Instrument precision was determined through replicate analysis of an in-house standard with a measured  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of  $0.708183 \pm 0.000028$  ( $2\sigma_{\text{mean}}$ ;  $N = 100$ ). These standards were run every six samples and in replicate at the beginning and end of every batch run.

Carbonate samples were isotopically characterized at Oregon State University using traditional phosphoric

acid digestion and isotope ratio mass spectrometry (IRMS). Carbonate powders were reacted with 100% phosphoric acid at 75°C; and isotopic composition was measured using the Kiel III device connected to a Thermo Fisher 252 gas source mass spectrometer. Isotopic analyses with this technique yield a precision better than  $\pm 0.1\text{‰}$  and  $0.2\text{‰}$  for  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ , respectively. Instrument calibration was accomplished by comparison to NBS-19.

## Results

Results from the pore water analyses are listed in Table T1, and data from carbonate extractions are listed in Table T2. We compare results from the two different leaching approaches to determine the method from which a minimum amount of clay is removed so as to minimize the influence of clays in the strontium isotopic composition attributed to the carbonate phase. The soft leaching method was shown to be the more favorable method in terms of both clay contamination and fraction of  $\text{CaCO}_3$  leached. Aluminum leached was far greater for all samples using the hard leach method, whereas  $\text{CaCO}_3$  leached was greater for all samples when the soft leach method was employed (Figure F2). In both cases, the amount of strontium leached remained relatively consistent. All subsequent carbonate elemental and Sr isotope data reported here for Hole U1380C samples were obtained using the soft leaching procedure.

The elemental (Sr/Ba, Ba/Ca, and Mn/Ca) and isotopic ( $^{87}\text{Sr}/^{86}\text{Sr}$ ,  $\delta^{13}\text{C}$ , and  $\delta^{18}\text{O}$ ) composition of carbonate samples is shown in Figure F3 (triangles); the downcore plots also include pore water data from Sites U1378 and U1380 (circles) for comparison; the oxygen and carbon isotope data are from this study, the cation data are from Harris et al. (2013c) and Torres et al. (2014), and dissolved strontium isotope data are from Ross et al. (2015).

Downhole  $^{87}\text{Sr}/^{86}\text{Sr}$  values for the Hole U1380C carbonates range from 0.70797 to 0.70899; these values are lower than seawater and are consistent with pore water data. Several samples from 707 to 796 mbsf exhibit  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios in a narrow range, from 0.70854 to 0.70872, departing from the decreasing trend of the other samples in that depth range. The strontium concentration in the leached carbonate ranges from 0.52 to 4.46  $\mu\text{mol/g}$ , corresponding to molar ratios with respect to calcium of 0.21–3.78 mmol/mol. Barium and manganese concentrations range from 0.06 to 0.69  $\mu\text{mol/g}$  and from 2.7 to 77.8  $\mu\text{mol/g}$ , respectively, which correspond to molar ratios to calcium that range from 0.04 to 0.84 mmol/mol and from 2.3

to 13.8 mmol/mol for barium and manganese, respectively. Although strontium concentrations generally show a slight decrease downcore, depth plots of Ba/Ca and Mn/Ca display no such trend.

DIC (Figure F3E) shows a strong depletion in  $^{13}\text{C}$  with depth, reaching a low value of  $-22.35\text{‰}$  Peedee belemnite (PDB) at 12 mbsf. This minimum corresponds to the depth of the sulfate depletion and methane increase (not shown), indicative of  $^{13}\text{C}$  depletion driven by anaerobic oxidation of methane, as documented by Expedition 334 Scientists (2012c). Below 12 mbsf, DIC is progressively enriched in  $^{13}\text{C}$ , reaching a  $\delta^{13}\text{C}$  highest value of 10.88‰ PDB at 84 mbsf. All values above seawater from 20 to 350 mbsf likely reflect residual DIC from methanogenesis. Most carbonate samples have  $\delta^{13}\text{C}$  values in the range of  $-2.62\text{‰}$  to  $0.24\text{‰}$  PDB, and only three samples (344-U1380C-41R-1, 50–52 cm; 42R-1, 30–31 cm; and 52R-2, 67–68, cm) have values exceeding 3.5‰ PDB, which sets them apart from the relatively consistent trend of the others. These three samples (open triangles) also exhibit slightly higher Mn/Ca ratios and a more radiogenic strontium signal but are unexceptional with respect to the other elemental and isotope data.

The  $\delta^{18}\text{O}$  composition of the carbonates shows a slight decreasing trend with depth, whereas pore water data show fairly constant values to 552 mbsf. The isotopic composition of pore water recovered from the squeezed sediment has oxygen values that range from  $-0.71\text{‰}$  to  $3.38\text{‰}$  standard mean ocean water (SMOW) in  $\delta^{18}\text{O}$  (Figure F3F), with only a few samples outside that range. The  $\delta^{18}\text{O}$  versus  $\delta^{13}\text{C}$  plot shown in Figure F4 illustrates the deviations in the isotopic composition of the carbonate relative to seawater (dashed lines) and the clear enrichment in  $^{13}\text{C}$  in three of the samples.

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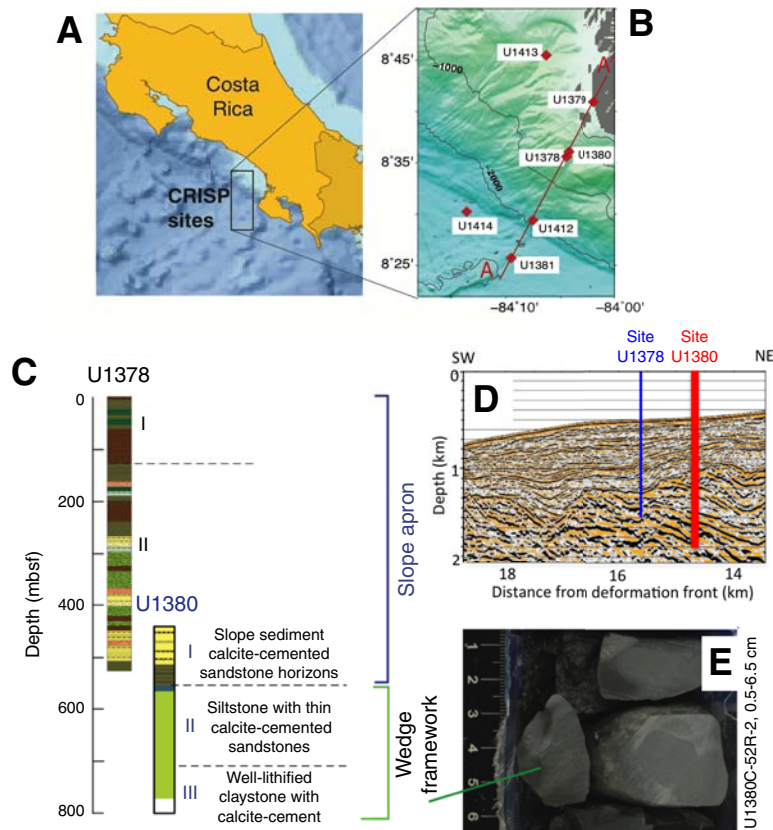
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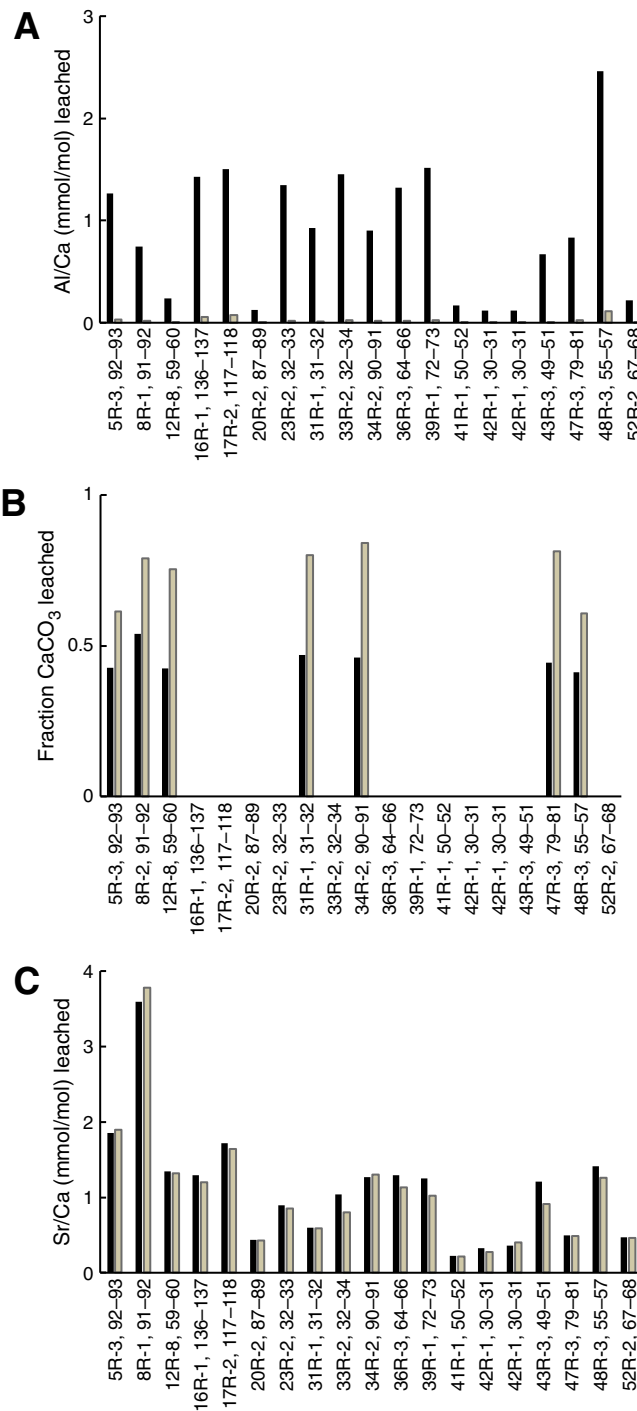
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**Figure F1.** A. Map of the region offshore Costa Rica targeted by the IODP CRISP program. B. Sites drilled during Expeditions 334 and 344, showing location of Sites U1378 and U1380 used in this study. C. Simplified lithologic column for Sites U1378 and U1380 drilled on the middle slope. D. Location of Sites U1378 and U1380 in seismic data. Both lithologic and seismic data revealed a discontinuity between the upper sequences that correspond to slope sediment deposits and the underlying margin framework. The slope cover is ~750 m thick at Site U1378, whereas the discontinuity between slope cover and underlying framework is at 550 mbsf at Site U1380. E. Hole U1380C rocks from below 550 mbsf, described by Expedition 344 sedimentologists as calcite-cemented clastic sediment (344-U1380C-52R-2, 0.5–6.5 cm). From Expedition 334 Scientists (2012a) and Harris et al. (2013a).

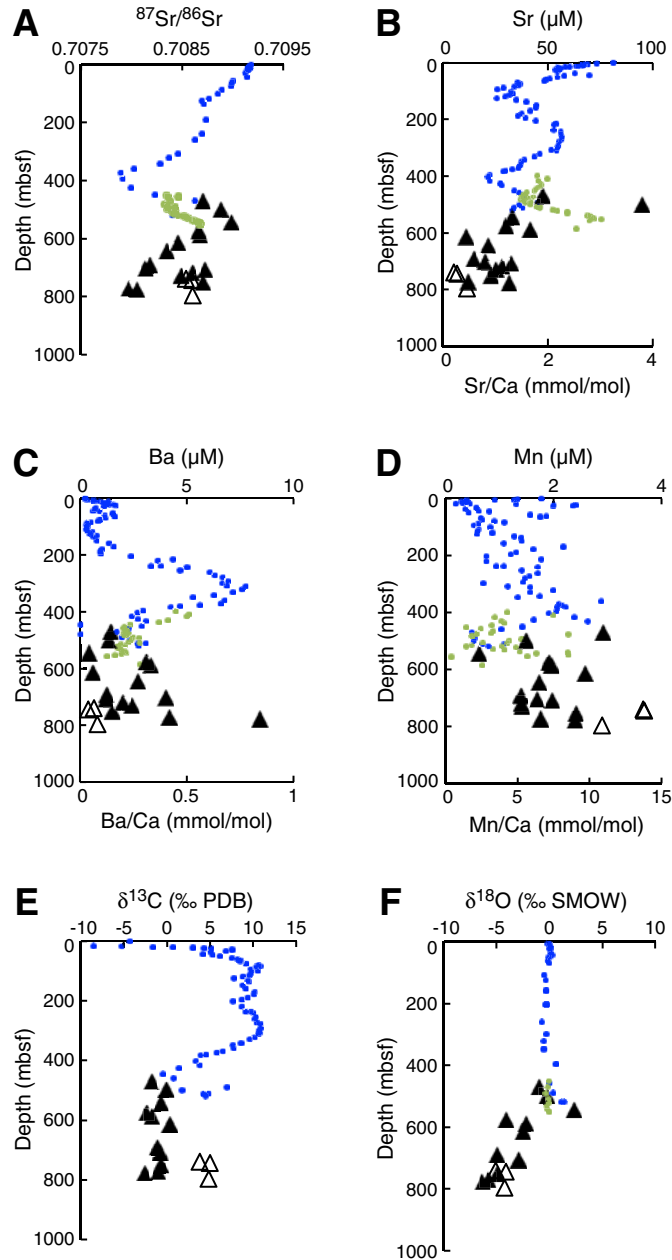


**Figure F2.** Results from hard (black) and soft (gray) sediment leaching procedures used to extract carbonate component from sediments, Hole U1380C. (A) Al/Ca, (B) fraction of  $\text{CaCO}_3$ , and (C) Sr/Ca leached.





**Figure F3.** A.  $^{87}\text{Sr}/^{86}\text{Sr}$  in Hole U1380C carbonates (triangles) compared with ratios in pore fluids reported by Ross et al. (2015) (blue circles = Hole U1378B, green circles = Hole U1380C). B–D. Elemental composition of Hole U1380C carbonate samples (triangles) from soft leaching procedure compared with published pore water composition of fluids from Hole U1378B (blue circles) and Holes U1380A and U1380C (green circles) (Harris et al., 2013c; Torres et al., 2014). E–F. Downcore profiles of  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  in Hole U1380C carbonates (triangles) and corresponding pore water isotopic data for DIC and water for Holes U1378B (blue circles) and U1380C (green circles). Open triangles represent samples with heavier carbon isotopic values relative to the other carbonates (344-U1380C-41R-1, 50–52 cm; 42R-1, 30–31 cm; and 52R-2, 67–68 cm).



**Figure F4.** Plot of  $\delta^{18}\text{O}$  vs.  $\delta^{13}\text{C}$  for Hole U1380C carbonates. Open triangles represent samples with heavier isotopic carbon signatures when compared with the other carbonates (344-U1380C-41R-1, 50–52 cm; 42R-1, 30–31 cm; and 52R-2, 67–68 cm).

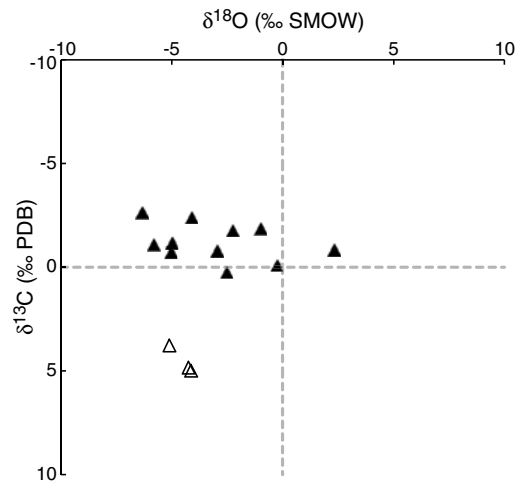


Table T1. Pore fluid geochemical data, Holes U1378B and U1380C. (Continued on next page.)

Core, section, interval (cm)	Depth (mbsf)	$\delta^{13}\text{C}$ (‰ PDB)	$\delta^{18}\text{O}$ (‰ SMOW)	$\delta\text{D}$ (‰ SMOW)	$^{87}\text{Sr}/^{86}\text{Sr}$
334-U1378B-					
1H-1, 138-168	1.38	-4.34			0.70918
1H-2, 138-168	2.88	-12.74			0.70917
1H-3, 138-168	4.38	-10.76			
1H-4, 46-58	4.96	-14.12			0.70916
2H-1, 138-168	6.68	-15.45	-0.03	0.98	
2H-1, 138-168*	6.68		-0.22	2.75	
2H-2, 138-150	8.18	-18.62			
2H-3, 138-168	9.68	-19.85			0.70915
2H-4, 138-168	11.18	-22.35			0.70916
2H-5, 138-150	12.68	-21.91			
2H-6, 138-150	14.18	-16.45			0.70917
2H-7, 54-66	14.84	-14.08			
3H-1, 138-150	16.18	-8.57			0.70916
3H-2, 138-150	17.68	-5.35	0.13	2.69	
3H-3, 138-148	19.18	-1.67			0.70914
3H-4, 138-148	20.68	0.65			
3H-5, 138-148	22.18	2.92			
3H-6, 133-143	23.63	4.17	0.06	2.52	
3H-6, 133-143*	23.63		-0.06	3.49	0.70914
3H-7, 58-68	24.38	5.08	0.06	2.81	
4H-3, 138-148	27.79	7.52			0.70912
4H-6, 138-148	32.29	6.77	0.05	3.42	
5H-2, 138-148	36.68	5.05			
5H-6, 138-148	42.68	4.11	0.22	3.83	0.70914
6H-2, 138-148	46.18	5.25			
6H-5, 138-148	50.68	6.13	0.06	4.45	
6H-5, 138-148*	50.68		-0.10	5.50	
7H-2, 138-148	55.68	7.56			0.709
7H-5, 138-148	60.18	8.12	-0.17	3.40	
8H-2, 138-148	63.82	8.6			0.70899
8H-5, 138-153	68.32	8.49	-0.09	3.73	
9H-2, 138-153	74.68	9.19			0.70898
9H-5, 130-145	79.10	10.54			
10H-2, 130-145	84.10	10.88			
10H-4, 138-153	87.10	10.27			0.70889
11H-3, 138-153	93.98	9.69			
12H-3, 138-153	99.83	10.47			0.70885
13H-4, 138-153	107.88	9.7	-0.46	2.99	
13H-4, 138-153*	107.88		-0.56	3.50	
14H-3, 138-153	114.09	9.53			
15H-2, 118-133	118.48	8.82			0.70876
16H-3, 133-148	124.78	7.77	-0.35	1.82	0.70869
17X-3, 133-148	132.13	9.32			
18X-3, 113-128	136.33	9.49			0.70871
19X-5, 71-86	148.55	8.73			
20X-5, 130-145	158.24		-0.36	2.20	
20X-5, 130-145*	158.24	9.11	-0.32	2.36	
21X-7, 68-83	169.64	10.12			
22X-5, 88-103	178.18	10.08			
23X-6, 109-124	188.79	9.33			0.70873
24X-4, 122-137	194.91	8.68			
25X-3, 74-89	202.69	7.59	-0.22	1.85	
25X-3, 74-89*	202.69		-0.43	1.98	
27X-2, 100-115	220.00	8.65			
28X-7, 33-63	236.43	9.07			
29X-3, 45-80	236.75	9.66			0.70869
30X-2, 110-145	240.90	9.97			
31X-4, 118-148	252.48	10.29			
32X-3, 73-103	259.83	10.11	-0.71	-0.36	0.70862
33X-5, 58-93	271.89	10.46			
34X-2, 86-121	277.96	10.79			
35X-5, 98-133	292.08	10.84			
36X-2, 93-128	297.63	10.65	-0.33	-0.39	
37X-2, 91-126	307.21	10.84			0.70846
38X-1, 118-153	310.48	10.58			
39X-5, 118-153	321.68	10.1	-0.55	-3.11	0.70836
40X-4, 80-115	329.10	9.57			
41X-5, 104-139	340.74	8.56			0.70828

Table T1 (continued).

Core, section, interval (cm)	Depth (mbsf)	$\delta^{13}\text{C}$ (‰ PDB)	$\delta^{18}\text{O}$ (‰ SMOW)	$\delta\text{D}$ (‰ SMOW)	$^{87}\text{Sr}/^{86}\text{Sr}$
42X-3, 64–94	347.04	7.63	-0.46	-2.91	
42X-3, 64–94*	347.04		-0.58	-2.50	
43X-5, 55–85	358.71	7.68			0.70802
45X-3, 55–85	369.65	6.44			
46X-2, 115–145	374.25	5.77			0.70789
47X-2, 95–125	379.35	4.45			
48X-1, 96–121	382.86	3.88			
49X-3, 106–136	394.66		0.59	-3.03	0.70791
49X-3, 106–136*	394.66		0.56	-1.97	
50X-2, 97–127	402.27	3.31			
51X-5, 85–115	415.96	3.72			
52X-5, 70–100	425.00	1.29			0.70799
54X-5, 104–140	444.24	-0.53			
55X-2, 81–116	448.81				0.70823
56X-2, 64–99	458.24	0.7	-0.02	-4.65	
57X-3, 63–98	469.33				0.70862
58X-2, 90–126	478.26				
59X-4, 93–128	489.66	6.83	0.30	-5.17	
60X-4, 60–95	499.72	1.76			
61X-4, 102–137	510.12	4.16			0.70844
62X-1, 54–79	510.24	4.8			0.7084
63X-4, 84–119	518.74	4.39	1.36	-5.37	
63X-4, 84–119*	518.74		1.07	-4.22	0.7084
344-U1380C-					
3R-3, 114–144	451.94		-0.06	-6.42	0.70834
3R-5, 112–150	454.70				0.70846
4R-1, 51–73	458.13				0.70836
5R-3, 107–137	470.67		-0.21	-6.57	0.70838
6R-3, 122–152	481.25				0.70833
7R-3, 120–150	491.00		-0.40	-6.05	0.70842
7R-5, 87–107	493.40				0.70837
8R-2, 116–146	499.12				0.70835
9R-1, 102–132	507.22		-0.11	-6.97	0.70844
9R-6, 79–109	513.28				0.70841
10R-4, 53–78	519.53				0.70846
10R-6, 64–90	521.93		-0.05	-7.67	0.70851
11R-2, 59–89	526.87				0.70854
11R-4, 87–117	529.54		-0.33	-8.18	0.70856
12R-2, 79–113	537.55				0.7086
12R-4, 78–108	539.58		-0.26	-7.81	0.70864
12R-8, 62–92	543.72				0.70867
13R-3, 50–80	548.02		-0.09	-6.81	0.70868
13R-6, 58–88	551.90		-0.06	-7.78	0.70868

\* = duplicate sample.  $^{87}\text{Sr}/^{86}\text{Sr}$  data normalized to NIST standard NBS-987 (Ross et al., 2015). PDB = Peedee belemnite, SMOW = standard mean ocean water.

Table T2. Carbonate geochemical data, Hole U1380C.

Core, section, interval (cm)	Depth (mbsf)	CaCO <sub>3</sub> (wt%)	Fraction CaCO <sub>3</sub> leached	δ <sup>13</sup> C (‰ PDB)	δ <sup>18</sup> O (‰ SMOW)	<sup>87</sup> Sr/ <sup>86</sup> Sr	Ba/Ca (mmol/mol)	Mn/Ca (mmol/mol)	Sr/Ca (mmol/mol)
344-U1380C-									
5R-3, 92–93	470.22	2.816	0.614	-1.84	-1.01	0.70870	0.14	10.9	1.89
8R-2, 91–92	498.61	5.298	0.790	-0.10	-0.26	0.70888	0.13	5.5	3.78
12R-8, 59–60	543.65	12.878	0.753	-0.82	2.31	0.70899	0.04	2.3	1.32
16R-1, 136–137	575.16			-2.41	-4.12	0.70866	0.31	7.1	1.20
17R-2, 117–118	587.20			-1.77	-2.25	0.70867	0.33	7.4	1.64
20R-2, 87–89	614.22			0.24	-2.53	0.70846	0.06	9.7	0.43
23R-2, 32–33	643.49					0.70834	0.27	6.5	0.85
31R-1, 31–32	690.61	7.589	0.801	-1.16	-5.00	0.70818	0.12	5.2	0.59
33R-2, 32–34	701.86					0.70814	0.40	6.4	0.80
34R-2, 90–91	707.03	5.598	0.841	-0.77	-2.97	0.70872	0.12	7.4	1.30
36R-3, 64–66	717.94					0.70859	0.20	5.2	1.13
39R-1, 72–73	729.72					0.70849	0.24	5.3	1.02
41R-1, 50–52	739.30			3.78	-5.11	0.70854	0.07	13.7	0.21
42R-1, 30–31	744.00			4.99	-4.13	0.70860	0.04	13.8	0.27
42R-1, 30–31*	744.00			4.75	-3.13	0.70863	0.05	10.7	0.40
43R-3, 49–51	751.84			-0.71	-5.04	0.70870	0.15	9.0	0.91
47R-3, 79–81	771.35	8.138	0.814	-1.10	-5.82	0.70797	0.42	6.6	0.48
48R-3, 55–57	776.24	2.99	0.607	-2.62	-6.35	0.70805	0.84	9.0	1.26
52R-2, 67–68	795.97			4.85	-4.25	0.70861	0.08	10.9	0.46

\* = duplicate sample. <sup>87</sup>Sr/<sup>86</sup>Sr data normalized to NIST standard NBS-987. Repeated measurements yielded a mean value of 0.701245 ± 0.000027 (2σ<sub>mean</sub>; N = 115). PDB = Peedee belemnite, SMOW = standard mean ocean water.