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15. AUTHIGENIC CARBONATES, METHANE GENERATION, AND OXIDATION IN CONTINENTAL RISE AND SHELF SEDIMENTS, ODP LEG 188 SITES 1165 AND 1166, OFFSHORE ANTARCTICA (PRYDZ BAY)[1]

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ABSTRACT

Carbon and oxygen isotopic compositions of authigenic carbonate nodules or layers reflect the diagenetic conditions at the time of nodule growth. The shallowest samples of carbonate nodules and dissolved inorganic carbon of pore water samples beneath the sulfate reduction zone (0–160 meters below seafloor [mbsf]) at Site 1165 have extremely negative $\delta^{13}C$ values (–50‰ and –62‰, respectively). These negative $\delta^{13}C$ values indicate nodule formation in association with anaerobic methane oxidation coupled with sulfate reduction. The $\delta^{34}S$ of residual sulfate at Site 1165 shows only minor ^{34}S enrichment (+6‰), even with complete sulfate reduction. This small degree of apparent ^{34}S enrichment is due to extreme "open-system" sulfate reduction, with sulfate abundantly resupplied by diffusion from overlying seawater.

Ten calcite nodules from Site 1165 contain minor quartz and feldspar and have $\delta^{13}C$ values ranging from –49.7‰ to –8.2‰. The nodules with the most negative $\delta^{13}C$ values currently are at depths of 273 to 350 mbsf and must have precipitated from carbonate largely derived from subsurface anaerobic methane oxidation. The processes of sulfate reduction coupled with methane oxidation in sediments of Hole 1165B

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are indicated by characteristic concentration and isotopic ($\delta^{34}S$ and $\delta^{13}C$) profiles of dissolved sulfate and bicarbonate.

Three siderite nodules from Site 1166 contain feldspar and mica and one has significant carbonate-apatite. The siderite has $\delta^{13}C$ values ranging from –15.3‰ to –7.6‰ These siderite nodules probably represent early diagenetic carbonate precipitation during microbial methanogenesis.

INTRODUCTION

Authigenic carbonates record some of the physical, chemical, and stable isotopic conditions existing in sediments at the time of carbonate precipitation. Carbonates persist in the rock record after nascent fluids are gone, and authigenic carbonate composition can be used to reconstruct diagenetic environments. Observations of environments in which carbonates are currently forming provide the necessary interpretive analogs. Sediment and pore fluids collected during coring operations of the Deep Sea Drilling Project (DSDP) and Ocean Drilling Program (ODP) have been a useful source of observations of various stages of diagenesis and associated mineral precipitates (Malone et al., 2002; Rodriguez et al., 2000; Hicks et al., 1996; Kelts and MacKenzie, 1982; Pisciotto and Mahoney, 1981).

During Leg 188 of the Ocean Drilling Program, we cored sediments offshore Antarctica, on the continental rise, slope, and shelf north of Prydz Bay during the months of January, February, and March 2000 (O'Brien, Cooper, Richter, et al., 2001). At Site 1165 on the continental rise (3537 m water depth), the expedition cored Miocene and younger pelagic and hemipelagic drift sediments. At Site 1166 on the continental shelf (475 m water depth), the cored sediments included organic carbon–rich rocks of Cretaceous (Turonian) age deposited during temperate climate conditions that supported onshore swamp vegetation. Thirteen carbonate nodules were collected and analyzed, ten from Site 1165 and three from Site 1166. The objective of this study is to relate the chemical and isotopic composition of carbonate nodules to diagenetic conditions at the time of carbonate precipitation and to show how sedimentologic conditions (primarily sedimentation rate) have influenced the diagenetic history of the cored sediments in this region.

Methane-containing cores and bottom-simulating seismic reflectors have been observed in drift sediments deposited off Antarctica (Hayes, Frakes, et al., 1975; Barker, Camerlenghi, Acton, et al., 1999). Possible occurrence of gas hydrate was anticipated for Leg 188. Although elevated methane contents were observed in Hole 1165B and pressure and temperature conditions were such that the methane hydrate would have been stable to a depth of ~470 mbsf, no positive evidence of methane hydrate presence was found. Dissolved methane concentrations in Hole 1165B apparently were insufficient to saturate the pore water and stabilize the hydrate phase. A principal result of this study is evidence that anaerobic methane oxidation processes may have operated to erode and deplete a once robust methanogenic zone, thus destroying any gas hydrates that may have been present.

GEOLOGIC SETTING

Site 1165 is located in 3537 m of water on the continental rise offshore from Prydz Bay over sediments of the central Wild Drift (fig. F3 in Shipboard Scientific Party, 2001). The drift is an elongate sediment body formed by the interaction of sediment supplied from the shelf and westward-flowing currents on the continental rise of Antarctica. The main objective at Site 1165 was to obtain a proximal continental rise record of Antarctic glacial and interglacial periods for comparison with other sites around Antarctica and with those of Northern Hemisphere ice sheets.

Site 1166 is situated on the Prydz Bay continental shelf of Antarctica. Prydz Bay is at the downstream end of a drainage system that originates in the Gamburtsev Mountains of central East Antarctica. The early development and growth of the Cenozoic Antarctic Ice Sheet is believed to have started in middle Eocene to early Oligocene time, but to date, drilling on the continent and the continental margin has not sampled a stratigraphic section that clearly spans and includes the transition period from preglacial to glacial conditions. Site 1166 was chosen to recover core from the Cenozoic sediments and to provide an age for the arrival of glaciers in Prydz Bay and a record of changes in paleoenvironments and biota with the onset of glaciation.

SAMPLES AND METHODS

Samples of obvious carbonate nodules or layers in cores were collected at the sampling table on the *JOIDES Resolution* during Leg 188. After the cruise, the nodules were sectioned perpendicular to bedding and about one-fourth of each nodule was powdered for X-ray diffraction and carbon and oxygen isotope analysis. Semiquantitative determination of mineralogy by X-ray diffraction analysis was performed at the U.S. Geological Survey in Lakewood, Colorado. Samples were analyzed for stable carbon and oxygen isotopic compositions at Mountain Mass Spectrometry in Evergreen, Colorado. The samples were reacted with phosphoric acid containing excess P_2O_5 at 90°C in an automated preparation system, and the resulting was CO_2 gas was analyzed on a VG Isogas Sira Series II mass spectrometer.

Interstitial water was extracted from sediments by squeezing and was analyzed for the usual pore water ionic constituents by standard procedures aboard the *JOIDES Resolution* (Geiskes et al., 1991; O'Brien, Cooper, Richter, et al., 2001). Methane in cores was measured by the headspace method (Pimmel and Claypool, 2001) and converted to an estimated dissolved methane concentration (O'Brien, Cooper, Richter, et al., 2001). After Leg 188, pore water samples were analyzed for $\delta^{34}S$ of dissolved sulfate at the U.S. Geological Survey, Lakewood, Colorado. Barium sulfate was precipitated from acidified pore water with excess barium chloride and then was decomposed to sulfur dioxide for measurement of $\delta^{34}S$ in an online sample preparation–stable isotope ratio mass spectrometer. Pore water samples were also analyzed in shore-based laboratories for various properties, including carbon isotopic composition of dissolved inorganic carbon, at Boston and Harvard Universities.

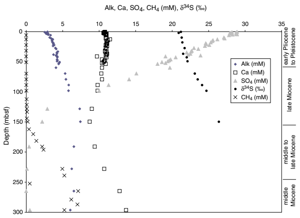
RESULTS

Interstitial Waters

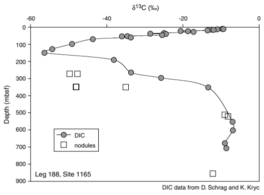
Concentrations and stable isotope ratios of selected pore water constituents in Holes 1165A–1165C are given in Table T1. A plot of the concentrations vs. depth of dissolved sulfate, methane, alkalinity, and the $\delta^{34}S$ of dissolved sulfate in Holes 1165A–1165C are shown in Figure F1. The $\delta^{13}C$ vs. depth of dissolved inorganic carbon and calcite nodules in Holes 1165A–1165C is shown in Figure F2.

T1. Dissolved sulfate, Hole 1165, p. 14.

F1. Interstitial water composition, Site 1165, p. 10.



F2. $\delta^{13}C$ of authigenic carbonate, p. 11.



Analyses of pore water samples from Site 1165 (Shipboard Scientific Party, 2001) showed that dissolved sulfate concentrations in Hole 1165B decreases linearly, approaching zero at a depth of ~150 mbsf. Alkalinities are low and reach a maximum of 7.4 mM at a depth of 150 mbsf. The alkalinity maximum is matched by a minimum in calcium concentrations, also at 150 mbsf, with a steep calcium gradient (0.05 mM/m) continuing to greater depths. In the depth interval from 30 to 150 mbsf, methane concentrations are low but above background levels (10–400 ppmv in headspace or 2–90 µM in pore water). At depths greater than 150 mbsf, the residual methane content of the pore water increases rapidly, reaching residual (after core outgassing) values of 6–7 mM at a depth of ~300 mbsf.

The $\delta^{34}S$ of sulfate increases from 21‰ to 26‰ over the 0- to 150-mbsf interval. The dissolved inorganic carbon (DIC) in Holes 1165A–1165C is characterized by extreme negative $\delta^{13}C$ values, reaching a minimum of –56‰ at a depth of 150 mbsf. Below 150 mbsf, $\delta^{13}C$ of DIC rapidly shifts to more positive values, reaching a maximum of about –7‰ at ~550 mbsf (D. Schrag and K. Kryc, pers. comm., 2001).

Authigenic Carbonates

The carbon and oxygen isotopic and mineralogical compositions of carbonate nodules are given in Table T2. Photographs of the nodules and layers are shown in core photographs in the Leg 188 *Initial Reports* volume (see "Core Descriptions" in O'Brien, Cooper, Richter, et al., 2001). The sampled calcite nodules or layers in Holes 1165B and 1165C occur over the depth range of 273 to 961 mbsf and have $\delta^{13}C$ values ranging from –48.1‰ to –8.2‰, generally subparallel with the DIC $\delta^{13}C$ curve. The $\delta^{18}O$ values of the authigenic carbonates in Holes 1165B and 1165C ranged from –1.5‰ to +4.6‰. Siderite nodules collected from Hole 1166A span a 1-m interval (296.5–297.6 mbsf) in Upper Cretaceous (Turonian) carbonaceous shales (organic carbon contents up to 5 wt%) near the base of the cored section on the Antarctic continental shelf in Prydz Bay. The nodules have $\delta^{13}C$ values ranging from –7.6‰ to –15.3‰ and $\delta^{18}O$ values of –0.7‰ to 3.2‰. There are no data on Cretaceous pore water to use to evaluate these nodules.

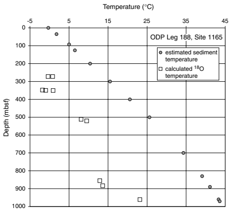
T2. Compositions of carbonate nodules, p. 15.

DISCUSSION

Authigenic carbonates from the two sites represent contrasting depositional environments. Siderite nodules from Site 1166 are present in carbonaceous shales deposited in a restricted marine or lagoonal environment. The carbon and oxygen isotopic compositions of the siderites are consistent with growth during early stages of methanogenesis but are not necessarily definitive in this regard. The siderite-bearing shale is interbedded with sandy silt and organic-rich laminae with common authigenic sulfides. The Fe^{2+} required for siderite precipitation probably did not become available until after sulfate removal from pore water enabled the onset of methane generation (Claypool and Kaplan, 1974).

The calcite layers or nodules in cores from Site 1165 apparently grew in or just below the sulfate reduction zone, with carbonates shallower than 400 mbsf likely incorporating carbon derived from the anaerobic oxidation of microbial methane. The $\delta^{13}C$ depth trends of the authigenic carbonate layers and the dissolved inorganic carbon (Fig. **F3**) are a record of diagenetic activity and provide important clues to the fate of methane in marine sediments.

F3. Estimated and calculated temperatures, p. 12.



Sediment accumulation rates at Site 1165 decrease monotonically from 130 m/m.y. in the early Miocene to 15 m/m.y. during the late Miocene to 5–7 m/m.y. during the Pliocene–Pleistocene. This long-term decrease in sedimentation rate should have resulted in subsidence of the sulfate/methane interface from depths on the order of 10–20 mbsf during the early Miocene to a present depth of 150 mbsf. In addition, it is likely that the minimum in the $\delta^{13}C$–DIC vs. depth curve has shifted from values on the order of –20‰ during the early Miocene to the present-day minimum of –56‰. The remainder of this discussion primarily focuses on Site 1165 and the evidence for these interpretations.

Pore Water $\delta^{34}S$ Profile

The $\delta^{34}S$ of dissolved sulfate at Site 1165 increases from near-seawater values of +21‰ just below the sediment/water interface to +26‰ at a depth of ~150 mbsf. Over this same interval, the dissolved sulfate concentration decreases from 28.9 to 2.2 mM. This small increase in $\delta^{34}S$ is associated with nearly complete sulfate reduction. More commonly, the residual sulfate $\delta^{34}S$ values would approach +100‰ with this degree of sulfate reduction (Rudniki et al., 2001). The increase in $\delta^{34}S$ in the residual sulfate for Site 1165 is small because slow sedimentation allows continuous replenishment with isotopically light sulfate by diffusion from overlying seawater (Claypool, 2002).

$\delta^{13}C$ of Authigenic Carbonate and Dissolved Inorganic Carbon

There is a remarkable parallelism between the $\delta^{13}C$ vs. depth trends of the authigenic calcite samples and the pore water DIC (Fig. **F2**) below ~250 mbsf. An obvious suggestion is that the carbonates have recently formed at current (or slightly shallower) burial depths from pore water DIC with the $\delta^{13}C$ being controlled by methane oxidation or generation at depths less or greater than ~200 mbsf. The preferred alternative interpretation is that all of the carbonates were formed at shallower depths (20–200 mbsf) near or just below the sulfate/methane interface and that pore water $\delta^{13}C$ of DIC has evolved with time such that authigenic carbonates formed were heavy during the early Miocene and became much lighter during the late Miocene to the present. This latter explanation is preferred based on analogy with pore water $\delta^{13}C$–DIC profiles at other DSDP/ODP sites (Borowski et al., 2001). Linear sedimentation rates on the order of 40–50 m/m.y. are generally required to exclude alternate electron acceptors and bring about microbial methane generation (Claypool and Kaplan, 1974; Stein et al., 1995). Under these conditions, methane oxidation at the sulfate/methane interface can cause pore water δ^{13}C–DIC to be as light as –40‰ (Claypool and Threlkeld, 1983; Paull et al., 2000). However, it is unusual to have δ^{13}C–DIC profiles with values as light as –60‰ at anything other than seafloor methane vent localities. The slowing sedimentation rate at Site 1165, beginning during the Pliocene, is probably responsible for the present conditions. During the early Miocene, when sediments in the present depth range of 500–1000 mbsf were being deposited and sedimentation rates were 130 m/m.y., the sulfate/methane interface was probably at a depth of 20–50 mbsf, just as it is at other DSDP/ODP sites with comparable sedimentation rates. The current slow sedimentation rate of 5–7 m/m.y. has only recently enabled deep diffusive penetration of sulfate and more intense anaerobic methane oxidation at the sulfate/methane interface presently at a depth of ~150 mbsf.

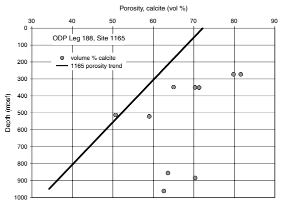
δ^{18}O of Authigenic Carbonate

The δ^{18}O of authigenic carbonate layers can be interpreted with respect to the temperature at the time of precipitation. As shown in Figure **F3**, the temperatures calculated from the δ^{18}O of the authigenic carbonate (assuming pore water has δ^{18}O = 0‰) are roughly parallel with the estimated temperatures based on extrapolated temperature probe measurements (table T16 in Shipboard Scientific Party, 2001). The ^{18}O temperatures are somewhat consistent with the interpretation that carbonate layers were deposited when present depths were some 300–500 m shallower but are not consistent with the preferred interpretation that the calcite nodules were precipitated in the zone of sulfate reduction and that the base of the sulfate reduction zone has gotten deeper since the Pliocene. If pore waters at Site 1165 were heavier than δ^{18}O = 0‰, the calculated ^{18}O temperatures (especially for the carbonates in the depth range of 273–351 mbsf) would more closely agree with the sediment temperatures in the range of 5°–15°C, the expected temperature for carbonate precipitation near the base of the sulfate reduction zone. Authigenic carbonates precipitated in methane-rich sediments commonly have anomalously heavy δ^{18}O values (Malone et al., 2002; Hicks et al., 1996; Matsumoto, 1989; Rodriguez et al., 2000). One explanation proposed is that pore waters are isotopically heavier due to ^{18}O–fractionated water derived from decomposition of methane hydrate (Hesse and Harrison, 1981; Matsumoto, 1989).

Porosity and Percent Calcite vs. Depth

The volume percent of carbonate in the nodule or layer provides an estimate of the depth in the sediment at the time of authigenic carbonate precipitation, assuming that carbonate cement filled the available pore space at the time of precipitation (Gautier and Claypool, 1984; Curtis et al., 1986). The volume percent calcite and the Site 1165 porosity trend (Shipboard Scientific Party, 2001) are plotted vs. depth in Figure **F4**. Most of the carbonate layers are 50%–80% calcite, consistent with formation in the upper 300 m of the sediment column at Site 1165. The linear porosity trend at Site 1165 is somewhat anomalous. Most ODP holes show an exponential decrease in porosity with increasing depth of burial. The shallow sediments at Site 1165 may be more compacted because of slower sedimentation rate. It is likely that deeper,

F4. Site 1165 porosity and calcite in authigenic carbonates, p. 13.



more rapidly deposited sediments may have had greater initial porosity than shown by the shallowest samples at Site 1165.

CONCLUSIONS

Calcite layers and siderite nodules were recovered from Miocene and Upper Cretaceous sediments on the East Antarctic continental rise (Site 1165) and shelf (Site 1166). The siderite nodules formed during the early stages of methanogenesis in preglacial marginal marine to lagoonal sediments of Late Cretaceous (Turonian) age. The calcite layers or concretions formed in the upper part of a methane-charged sediment drift near the base of the sulfate reduction zone from dissolved carbonate derived in part from anaerobic methane oxidation. The sediment drift at Site 1165 accumulated at sedimentation rates gradually slowing from 130 to 5 m/m.y. during the last 20 m.y. This slow rate of sedimentation has led to increased influx of dissolved sulfate by diffusion from overlying seawater. This sulfate is being reduced with small apparent ^{34}S fractionation (due to continuing influx of isotopically light sulfate) in conjunction with the oxidation of methane. This has led to expansion of the sulfate reduction zone, erosion of the upper zone of methanogenesis, and possible destabilization of methane hydrate because of a lowered concentration of dissolved methane.

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Erinn McCarty and the Leg 188 scientific and technical parties collected the samples during ODP Leg 188. We thank Keith Kvenvolden and Ronald Oremland for helpful reviews. This research used samples and/or data provided by the Ocean Drilling Program (ODP). The ODP is sponsored by the U.S. National Science Foundation (NSF) and participating countries under management of Joint Oceanographic Institutions (JOI), Inc. Participation on Leg 188 by G.E. Claypool was supported by JOI/U.S. Science Support Program.

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Figure F1. Interstitial water sulfate, alkalinity (Alk), headspace methane, and sulfur isotopic composition of dissolved sulfate at Site 1165.

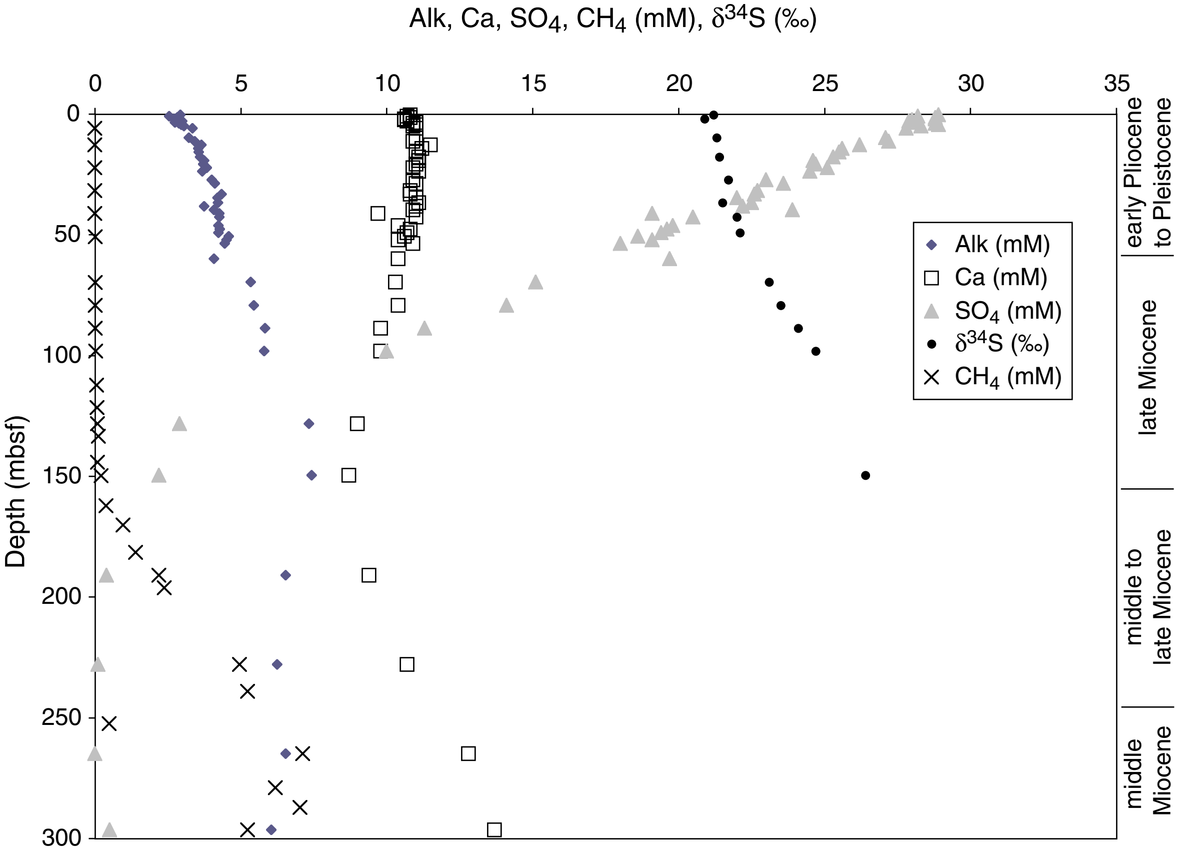
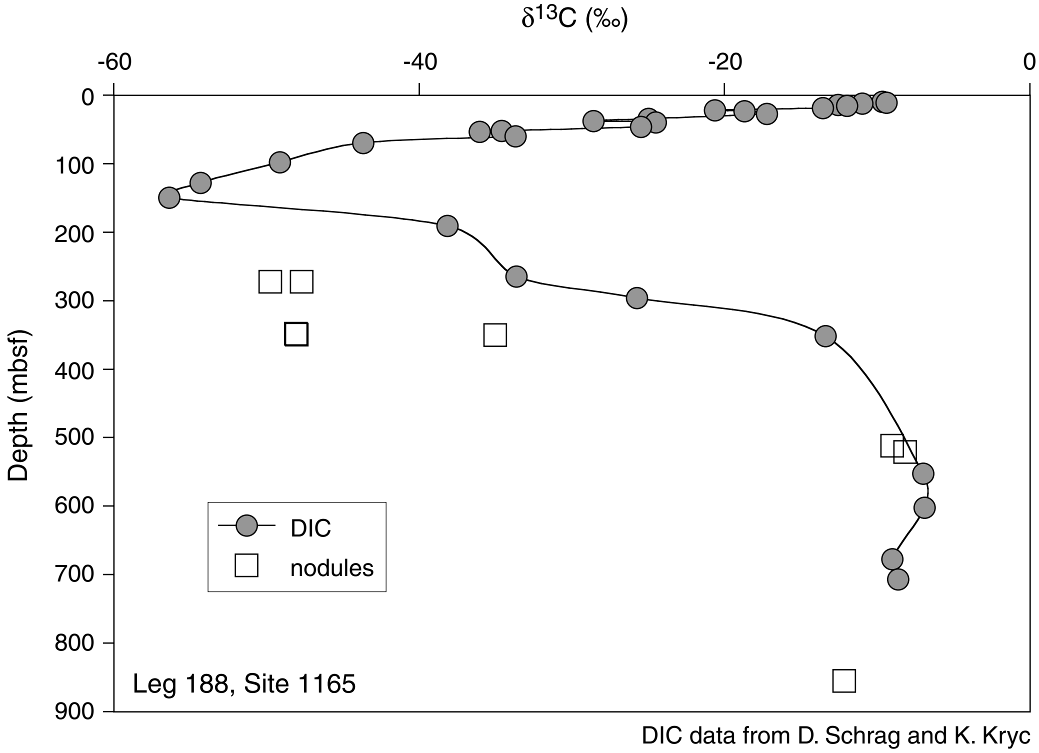


Figure F2. Plot of $\delta^{13}C$ vs. depth of authigenic carbonate layers recovered from Site 1165. Also shown is $\delta^{13}C$ of dissolved inorganic carbon (DIC) in interstitial water from Site 1165 (D. Schrag and K. Kryc, pers. comm., 2001).



DIC data from D. Schrag and K. Kryc

Figure F3. Plot of estimated temperatures from downhole temperature probes (Shipboard Scientific Party, 2001) and calculated temperatures from $\delta^{18}O$ of authigenic carbonates, assuming oxygen isotopic equilibrium with interstitial water having $\delta^{18}O$ = 0‰.

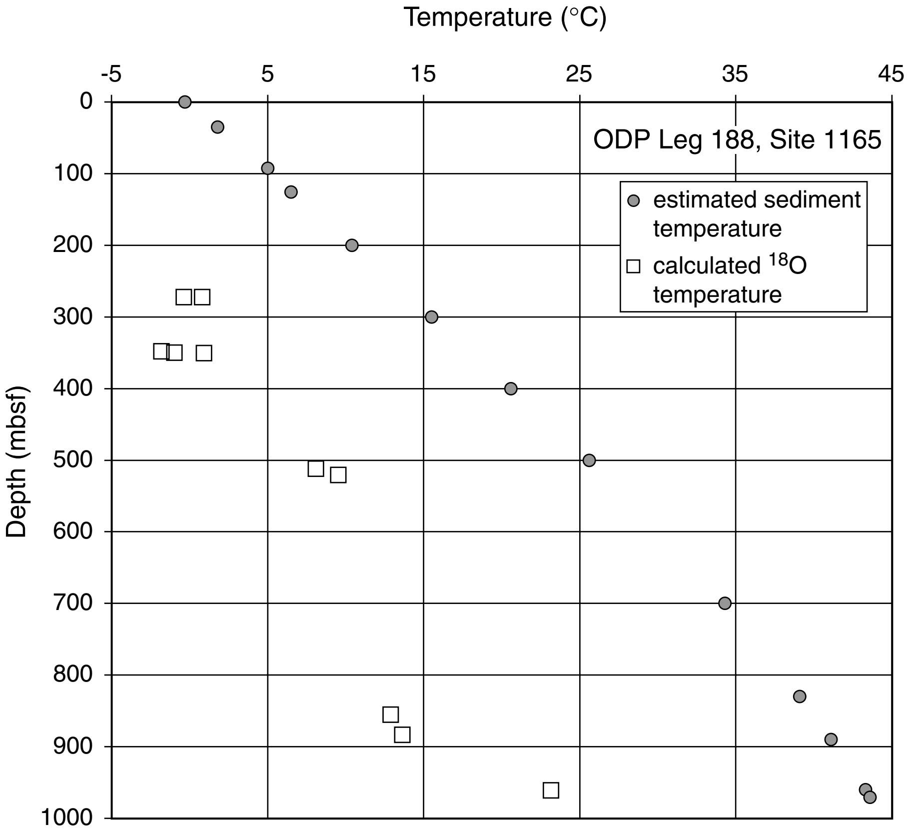


Figure F4. Plot of Site 1165 porosity trend (Shipboard Scientific Party, 2001) and percent calcite in authigenic carbonates vs. depth.

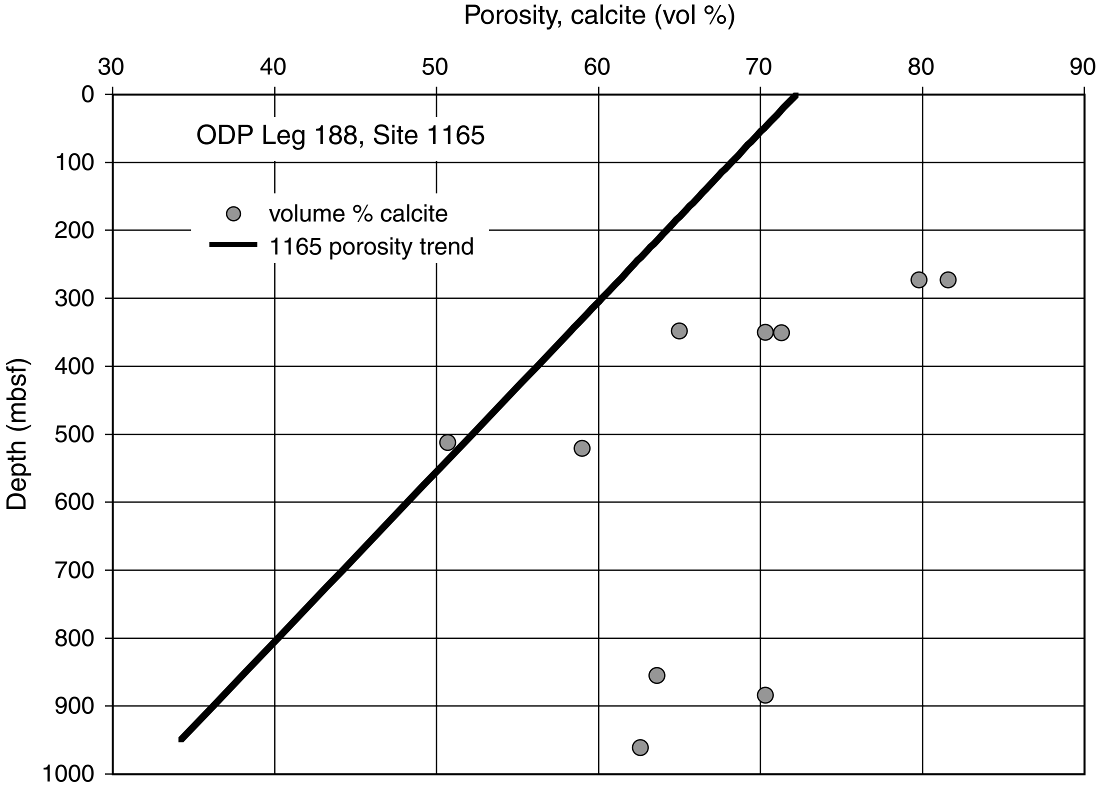


Table T1. Concentration and $\delta^{34}S$ of dissolved sulfate for analyzed pore water samples, Site 1165.

Core, section	Depth (mbsf)	SO_4^{2-} (mM)	$\delta^{34}S$ (‰)
188-1165A-			
1H-1	0.45	28.9	21.2
1H-4	1.95	28.8	20.9
188-1165B-			
1H-4	5.95	27.8	22.1
2H-2	9.75	27.1	21.3
2H-3	11.25	27.2	
2H-4	12.75	26.2	
2H-5	14.25	25.6	
2H-6	15.75	25.5	
3H-1	17.75	25.3	21.4
3H-2	19.25	24.6	
3H-3	20.75	24.7	
3H-4	22.25	25.1	
3H-5	23.75	24.5	
4H-1	27.20	23.0	21.7
4H-6	34.70	22.0	
5H-1	36.70	22.5	21.5
5H-2	38.20	22.2	
5H-3	39.70	23.9	
5H-5	42.70	20.5	22.0
6H-1	46.20	19.8	
6H-3	49.20	19.4	22.1
6H-5	52.20	19.1	
6H-6	53.70	18.0	
188-1165C-			
1R-4	59.90	19.7	
188-1165B-			
8H-4	69.70	15.1	23.1
9H-4	79.20	14.1	23.5
10H-4	88.70	11.3	24.1
11H-4	98.15	10.0	24.7
19X-1	149.70	2.2	26.4

Table T2. Isotopic ($\delta^{13}C$, $\delta^{18}O$) and mineralogic (by semiquantitative X-ray diffraction) compositions of carbonate nodules.

Core, section, interval (cm)	Depth (mbsf)	$\delta^{13}C_{PDB}$ (‰)	$\delta^{18}O_{PDB}$ (‰)	Calcite (%)	Siderite (%)	Quartz (%)	Feldspar (%)	Muscovite (%)	Kaolinite (%)	Carb-apatite (%)	Total
188-1165B- and 1165C-											
33X-1, 122–124	272.8	–49.73	4.24	79.8		11.4	8.7				99.9
33X-1, 129–131	272.9	–47.67	3.95	81.6		10.1	8.2				99.9
41X-1, 97–98	348.3	–48.05	4.59	65.0		13.2	11.5	10.2			99.9
41X-2, 106–107	350.2	–48.01	4.39	70.3		19.3	10.4				100.0
44X-3, 35–37	350.9	–35	3.92	71.3		15.1	13.6				100.0
58X-1, 96–98	511.9	–9.01	2.16	50.7		16.7	32.6				100.0
59X-1, 35–39	521.0	–8.17	1.81	59.0		13.7	11.2	16.2			100.1
8R-1, 42–43	855.3	–12.14	0.98	63.6		12.2	6.1	18.0			99.9
21R-1, 30–32	883.8	–12.26	0.8	70.3		20.9	8.8				100.0
23R-6, 91–93	961.4	–12.58	–1.54	62.6		11.7	6.0	19.6			99.9
188-1066A-											
32R-1, 115–117	296.2	–14.88	0		51.2		10.5	14.3	24.0		100.0
32R-1, 87–88	296.5	–15.25	3.24		51.4		7.1	7.6	9.7	19.4	95.2
32R-2, 42–43	297.1	–7.64	0.36		73.2		9.6				82.8
32R-2, 95–98	297.6	–13.65	–0.72		82.7		6.1				88.8

Note: PDB = Peedee belemnite standard.