Tiedemann, R., Mix, A.C., Richter, C., and Ruddiman, W.F. (Eds.)
*Proceedings of the Ocean Drilling Program, Scientific Results* Volume 202

# 9. LACK OF ISOTOPIC FRACTIONATION OF $\delta^{15}$N OF ORGANIC MATTER DURING LONG-TERM DIAGENESIS IN MARINE SEDIMENTS, ODP LEG 202, SITES 1234 AND 1235[1]

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## ABSTRACT

The isotopic composition of nitrogen in pore water ammonium and in sedimentary organic matter ($N_{org}$) was measured at Sites 1234 and 1235 in order to evaluate the impact of long-term (>100 k.y.) diagenesis on $\delta^{15}$N of preserved organic matter. At both sites, the average $\delta^{15}$N of pore water ammonium and $N_{org}$ are within 0.2‰ to 0.4‰. The small difference is less than the analytical uncertainty, indicating that no significant isotopic fractionation is associated with decomposition of organic matter in these sediments. A mass balance for nitrogen was also computed, indicating that ~20% of the organic matter flux buried below 1.45 meters composite depth (mcd) is degraded between this depth and 40 mcd (Site 1235) to 60 mcd (Site 1234) depth. Two factors determine the absence of isotopic fractionation in these sediments:

1. A high degree of organic matter preservation due to rapid sediment accumulation rates at both sites.
2. The dominance of a marine component in the sedimentary organic matter (with only a small fraction contributed by a terrestrial component).

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[1] Prokopenko, M.G., Hammond, D.E., and Stott, L., 2006. Lack of isotopic fractionation of $\delta^{15}$N of organic matter during long-term diagenesis in marine sediments, ODP Leg 202, Sites 1234 and 1235. *In* Tiedemann, R., Mix, A.C., Richter, C., and Ruddiman, W.F. (Eds.), *Proc. ODP, Sci. Results,* 202: College Station, TX (Ocean Drilling Program), 1–22. doi:10.2973/odp.proc.sr.202.207.2006

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Initial receipt: 15 October 2004
Acceptance: 28 April 2006
Web publication: 24 October 2006
Ms 202SR-207

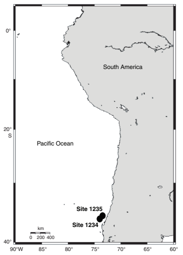
# INTRODUCTION

The $\delta^{15}N$ of sedimentary organic nitrogen ($N_{org}$) has been used over the last decade as a paleoceanographic proxy (Altabet and Francois, 1994; Altabet et al., 1999b, 1999a; Emmer and Thunell, 2000; Ganeshram et al., 1995; Pride et al., 1999; Sachs and Repeta, 1999; Sigman et al., 1999). However, bacterial decomposition of some fraction of organic matter deposited on the ocean floor may lead to alteration of the original $\delta^{15}N$ in the residual fraction by 2‰–5‰, as was found in laboratory studies of Macko and Estep (1984) and incubation experiments by Lehmann et al. (2002). Several field observations confirmed changes in $\delta^{15}N$ during organic matter diagenesis. Sigman et al. (1999), working with the sediments from the Southern Ocean, and Sachs (1997) and Sachs and Rapeta (1999), in the sapropels from Mediterranean Sea, found a 2‰–5‰ positive shift in $\delta^{15}N$ of bulk sediments relative to unaltered organic matter. On the other hand, Altabet et al. (1999a) and Pride et al. (1999) found no evidence of diagenetic alterations in $\delta^{15}N$ of preserved organic matter in California borderland basins and in the Gulf of California.

The observed disparity in the apparent diagenetic effects has been attributed to the differences in the degree of organic matter preservation (Altabet et al., 1999a; Sachs and Rapeta, 1999). Altabet et al. (1999a) suggested that diagenetic fractionation of nitrogen isotopes in the sedimentary organic matter occurs in regions with a low rate of organic input to the seafloor, whereas in regions of high organic supply rate and high sediment accumulation rates, the isotopic signal is preserved faithfully.

Previous field studies of diagenetic effects on sedimentary $\delta^{15}N$ preservation have focused on processes occurring in the upper few centimeters of sediments (Freudenthal et al., 2001; Sigman et al., 1999). The goal of this study is to evaluate the impact of diagenesis on the isotopic composition of preserved organic matter during timescales of $10^5$ yr. In this manuscript, we report results of a study that extends work on samples collected during the previous Ocean Drilling Program (ODP) expedition, Leg 201 at Sites 1227 and 1230 (Prokopenko et al., 2006b). Here, we discuss the results obtained from two sites: 1234 and 1235 (Fig. **F1**). Our approach is to construct mass balances for nitrogen and measure isotopic ratios of the $N_{org}$ and pore water ammonium, which is the major metabolic product of $N_{org}$ decomposition. The premise for this approach is that at steady state, in the absence of any other diagenetic reactions, ammonium released from decomposing organic matter should have $\delta^{15}N$ of the source plus any fractionation that takes place during diagenesis (Prokopenko et al., 2006a).

**F1.** Location map of Sites 1234 and 1235, p. 15.



# METHODS

Pore water ammonium concentrations, total nitrogen (TN), as well as the nitrogen isotope composition of solid-phase and pore water ammonium were determined through the sediment columns recovered from Sites 1234 and 1235. Pore water and sediment samples were stored frozen until analysis. The isotopic composition is reported in permil relative to atmospheric $N_2$ using the delta notation ($\delta^{15}N$). The procedure of sample processing and isotopic measurements is given in Prokopenko (2004) and Prokopenko et al. (2006b). Here, we discuss only the details specific for the samples collected during Leg 202. In order to evaluate the preservation of ammonium during storage, the ammonium concentrations for Sites 1234 and 1235 were determined colorimetrically (Bower and Holm-Hansen, 1980) at the University of Southern California (USC, USA). The USC results were compared to shipboard measurements (Shipboard Scientific Party, 2003a, 2003b) and are lower than shipboard measurements by 7%–10%. The USC colorimetric results agree within 2% with the amount of ammonium in each sample measured with a CN elemental analyzer. Loss of ammonium during storage of the samples is unlikely because a loss would have resulted in a positive correlation between $\delta^{15}N$ values and the magnitude of the difference, which was not observed. Therefore, we conclude that the 7%–10% difference between USC and shipboard analyses for Sites 1234 and 1235 stems from discrepancies in the ammonium calibrations. Ammonium isotopic composition was determined using the "passive diffusion" method of Sorensen and Jensen (1991), Sigman et al. (1997), and Holmes et al. (1998). In order to account for possible artifacts introduced by sample processing, several (between four and six) standards of known concentrations and isotopic composition were run with each set of samples through all the steps of the ammonium extraction procedure. The $\delta^{15}N$ of standards processed with Site 1235 samples were 0.65‰ ± 0.29‰ lighter than reported values, most likely due to a reagent blank. The samples and the standards were similar in their size and isotopic composition; therefore, the measured $\delta^{15}N$ values of samples were corrected by +0.65‰. The average precision of isotopic measurements, based on running duplicates and procedural standards, was 0.30‰ for the pore water ammonium and 0.15‰ for the sediments. Depths are reported in meters composite depth (mcd) (see explanation in Shipboard Scientific Party, 2003a, 2003b).

## SITE DESCRIPTIONS AND LITHOLOGY

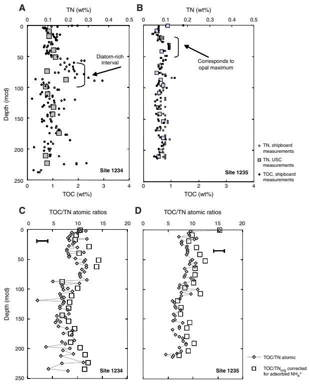
Both sites are located 60 km offshore. Characteristics of these sites are described by the Leg 202 Shipboard Scientific Party (2003a, 2003b). Here, we give brief summary of features relevant to the presented work. Site 1235 (36°9.594′S, 73°33.983′W) is 7 km northeast of Site 1234 (36°13.153′S, 73°40.902′W) (Fig. F1). Water depths are 1015 m at Site 1234 and 489 m at Site 1235. Sediments at both sites are characterized as a single lithologic unit, representing continuous hemipelagic sedimentation within the last <260 k.y. The location of the sites during the Quaternary within a strong upwelling system off Point Conceptión resulted in high contents of diatomaceous and calcareous nannofossils. Biogenic material is strongly diluted with high terrigenous input, mostly silty clays and clays. The degree of dilution is higher for shallower Site 1235. The biogenic component constitutes up to 30% of sediment material at Site 1234 but only 10%–15% at Site 1235. Sedimentation rates are estimated to be exceptionally high, 788 m/m.y. at Site 1234 and 696 m/m.y. at Site 1235. The lower concentration of biogenic material and lower sedimentation rate at the shallower Site 1235 suggests sedimentary winnowing at this location. Both sites also contain sedimentary sequences interpreted as distal turbidites.

# RESULTS

## Biogeochemistry of the Sediments and Pore Water at Sites 1234 and 1235

Both sites are characterized by moderate to low contents of organic carbon and nitrogen (Fig. F2), due to the high degree of dilution with siliciclastic terrestrial material. At Site 1234, total organic carbon (TOC) ranges between 0.6 and 2.5 wt%, TN is between <0.1 and 0.3 wt% (Fig. F2A), and the TOC/TN (atomic) ratios (Fig. F2C) vary between 4 and 11, with an average of 8.3 ± 0.3. Both TOC and TN concentrations exhibit a maximum between 60 and 80 mcd. There is a slight decrease in TOC/TN downcore.

**F2.** TOC and TN content of sediments, p. 16.

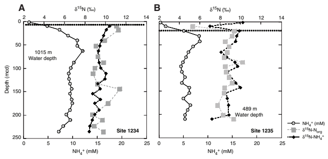


High pore water ammonium concentrations (~10 mM) and relatively low porosity (65%) may cause a significant amount of $NH_4^+$ to adsorb to clays. Assuming an ammonium partition coefficient between 1.8 and 2 ($cm^3/g$) for similar types of coastal sediments (Mackin and Aller, 1984), we calculated that as much as 20% of the total nitrogen in the bulk sediment may be the in the pool of the adsorbed ammonium. Figure F2C shows TOC/TN ratios and, for intervals where pore water ammonium concentrations were measured, TOC/TN$_{org}$ (total nitrogen $_{organic}$) ratios, which are corrected for nitrogen contributed by the adsorbed ammonium pool. At Site 1234, the average TOC/TN$_{org}$ ratio corrected for ammonium is ~10.3 ± 1.1. The uncertainty largely results from the possible nonlinearity of ammonium partition coefficients over a range of dissolved ammonium concentrations.

At Site 1235 (Fig. F2B), both TOC and TN concentrations are lower than at Site 1234, ranging between 0.5 and 1 wt% and 0.05 and 0.12 wt%, respectively; total atomic TOC/TN ratios vary between 4 and 11, with an average of 8.2 ± 0.3 (Fig. F2D). The contribution of adsorbed ammonium to the TN pool at Site 1235 is comparable to that at Site 1234, ~20%. The average value of TOC/TN$_{org}$ ratios corrected for adsorbed ammonium is 9.8 ± 1.1, identical to the TOC/TN$_{org}$ at Site 1234, when the uncertainty is taken into account. As at Site 1234, there are maxima in the TOC and TN concentrations, but at shallower depths, ~30–40 mcd. As at Site 1234, the TOC/TN$_{org}$ decreases slightly downcore.

The depth profiles of major metabolite concentrations are similar at the two sites as well (Fig. F3; Tables T1, T2) (dissolved inorganic carbon [DIC] data are not shown; see Shipboard Scientific Party, 2003a, 2003b). At Site 1234, DIC concentrations reach 71–72 mM at a depth of ~30 mcd. Ammonium concentrations reach the maximum of ~12 mM slightly deeper into the sediments, in the 40- to 50-mcd interval. Below 9 mcd, sulfate concentrations are less than the detection limit. At Site 1235, the DIC maximum of ~60 mM is located in the interval of 30–40 mcd, the zone where ammonium concentrations reach their highest values of ~8 mM. Sulfate concentrations are less than the detection limit below 19 mcd. At both sites, the ammonium maxima in pore water are roughly coincident with maxima in TN and TOC (Figs. F2, F3).

**F3.** Pore water ammonium profile and isotopic composition, p. 17.



**T1.** Site 1234, TN content, $\delta^{15}N$ of ammonium and N$_{org}$, p. 19.

**T2.** Site 1235, TN content, $\delta^{15}N$ of ammonium and N$_{org}$, p. 20.

## Isotopic Composition of Sedimentary Organic Matter and Pore Water Ammonium

The depth profiles of $\delta^{15}N$ of TN, assumed to represent mostly $N_{org}$, are similar at Sites 1234 and 1235, although the isotopic ratios at Site 1235 are ~1‰ lighter than those at Site 1234. At Site 1234, the uppermost interval measured (9.65 mcd) has $\delta^{15}N$ of 11‰ (Table T1; Fig. F3A). The values decrease to ~9‰ at 50 mcd and remain constant from 50 to 140 mcd. At 150 mcd, the $\delta^{15}N$ of $N_{org}$ increases to ~11‰ and then gradually returns to 9.5‰ downcore. The average isotopic composition of $N_{org}$ at Site 1234 is 9.8‰ ± 0.2‰ (Table T3).

**T3.** Average isotopic composition of pore water ammonium and $N_{org}$, p. 21.

At Site 1235 (Table T2; Fig. F3B), $\delta^{15}N$ changes gradually from ~10‰ at 1.45 mcd (the uppermost interval measured) to ~8‰ at a depth of ~70 mcd. A horizon at 9.5 mcd, a possible turbidite deposit, has anomalously low $\delta^{15}N$, where $N_{org}$ is ~6‰. With the exception of two horizons of small (up to ~9.5‰) enrichment, the $\delta^{15}N$ remains constant at 8‰ through the rest of the sediment column downcore. The average $\delta^{15}N$ of $N_{org}$ at Site 1235 is 9.0‰ ± 0.2‰.

The two sites exhibit similar trends in isotopic composition of pore water ammonium (Fig. F3) as well. At Site 1234 (Fig. F3A), $\delta^{15}N$ of ammonium decreases from 10.5‰ to ~9.5‰ within the upper 60–70 mcd then increases by ~0.5‰ from 70 to 120 mcd. Between 120 mcd and the bottom of the sediment column, $\delta^{15}N$ declines from 10‰ to 8.5‰. The average $\delta^{15}N$ of ammonium at Site 1234 is 9.4‰ ± 0.1‰, which is 0.4‰ ± 0.3‰ lighter than the solid-phase isotopic composition (Table T3).

The shallowest interval where $\delta^{15}N$ of ammonium was measured at Site 1235 (Fig. F3B) is 9.5 mcd (coincident with the possible turbidite deposit) (Shipboard Scientific Party, 2003a, 2003b). At this depth, $\delta^{15}N$ of ammonium is 5.3‰. Downhole, the ammonium $\delta^{15}N$ is 9.5‰ at 19.7 mcd, decreases to 8.5‰ at 70 mcd, increases by ~1‰ within the next 80 mcd, and oscillates between 9.3‰ and 7.8‰ between 150 and 210 mcd. At Site 1235, the average difference $\delta^{15}N$ of the pore water ammonium and $N_{org}$ is 0.2‰ ± 0.3‰ (Table T3), which is within the limits of the analytical precision.

# DISCUSSION

## Anaerobic Diagenesis of Organic Matter at Sites 1234 and 1235

Site 1235 is located at a shallower depth than Site 1234, which has led to a higher fraction of terrigenous siliciclastic component in the sediments at this site. However, the total sedimentation rate at Site 1235 is slightly lower than at the deeper neighboring site (696 m/m.y. vs. 788 m/m.y.) according to the preliminary age model presented in Shipboard Scientific Party (2003a, 2003b). A possible reason for this is sediment winnowing by benthic currents, as suggested by the presence of distal turbidite deposits in the sediment sequence at Site 1235. The combination of sediment winnowing and the higher degree of dilution by siliciclastic material resulted in lower concentrations of TOC and TN at Site 1235 compared to Site 1234. Consequently, the rate of organic matter decomposition (per volume of sediments) is lower for Site 1235 as well. This is consistent with the lower DIC and ammonium concentrations and deeper penetration of sulfate at this site. The average value of ~10 for the atomic TOC/TN ratios at both sites (Fig. F2C, F2D) is higher than the typical C/N Redfield ratio of marine organic matter of ~7 (Redfield et al., 1963) and might either reflect a small contribution from terrestrial organic matter, which typically has C/N >20, or represent a diagenetic effect. It is presently difficult to distinguish between these two possibilities without more specific information about the composition of organic matter in these sediments.

Ammonium profiles indicate that the net release of this metabolite appears to cease at depths below ~60 mcd at Site 1234 and ~40 mcd at Site 1235, where concentration maxima occur. Below these maxima, a modest decrease in ammonium occurs at both sites. If ammonium profiles are currently in steady state, a decrease could result from a sink for ammonium at depth. Alternatively, the decrease may represent temporal variation in the input of reactive organic matter in sediments that accumulate rapidly. At both sites, high sediment accumulation rates strongly influence solute transport through the sediment column. The Peclet number can be used to indicate the relative importance of diffusive and advective transport; values <1 indicate dominance of advection. The fast accumulation rates at these sites result in low (<1) Peclet numbers for both sites (Table T4), indicating that advection is more significant than diffusion for solute transport and in regulating the depth distribution of solutes. Consequently, it is most likely that the ammonium decreases at depth do not reflect a sink but rather are due to higher release rates near the depths of the apparent concentration maxima, in comparison to adjacent horizons. The elevated concentrations of TN near the depths of pore water ammonium maxima support this interpretation. Because of the strong influence of advection, diffusive transport is not able to homogenize the ammonium profiles at depth.

**T4.** Budgets for $N_{org}$ below the 1.45 mcd horizon, p. 22.

## Conversion of $N_{org}$ to Ammonium during Diagenesis

A fraction of the $N_{org}$ has been converted to ammonium by diagenesis during burial. We can estimate this fraction of $N_{org}$ by considering the fate of the time-averaged flux of $N_{org}$ buried below 1.45 mcd (the uppermost interval where data are available). The calculation can be done by comparing $N_{org}$ at 1.45 mcd to that at the depth of the ammonium maxima. At Site 1235, the decrease from 0.11% to 0.08% (Table T2) indicates ~27% is converted to ammonium during diagenesis. At Site 1234, there is not a TN measurement at 1.45 mcd, so such a calculation cannot be carried out.

Alternatively, the diagenetic transformation of $N_{org}$ can be calculated from pore water ammonium profiles. The advantage of this approach is that it provides a more sensitive assessment of the $N_{org}$ degradation. Both approaches rely on the assumption of steady state; their comparison helps to assess the validity of the steady-state approach. The maxima in ammonium profiles indicate the steady-state assumption is not strictly correct; however, it provides a useful approximation.

Using the pore water ammonium profile, the total $N_{org}$ decomposition in a specified layer should be the sum of ammonium lost via diffusion plus advection from this layer due to burial of pore water (Berner, 1980). The net ammonium production between two horizons ($P_N$) can be calculated based on mass conservation:

$$P_N = (J_{D2} - J_{D1}) + (J_{A2} - J_{A1}), \quad (1)$$

where

$J_{D1}$ = diffusive fluxes across the upper boundaries of the interval,
$J_{D2}$ = diffusive fluxes across the lower boundaries of the interval,
$J_{A1}$ = advective transport across the upper boundaries (Table T4), and
$J_{A2}$ = advective transport across the lower boundaries (Table T4).

Diffusive fluxes at the upper and lower boundaries were calculated by applying Fick's first law. Concentration gradients were determined as tangents to the ammonium profile at the boundaries of the considered interval, calculated from the derivative of a model curve fit to the profile (details are in Prokopenko, 2004). Advective fluxes were calculated as

$$J_A = C_{pw}\left(1 + K\frac{w_s}{w_{pw}}\right)w_{pw}\phi\,, \qquad (2)$$

where

$C_{pw}$ = concentrations at the boundaries,
$K$ = ammonium partition coefficient,
$\phi$ = porosity,
$w_{pw}$ = advection rate of pore fluid relative to the sediment/water interface, and
$w_s$ = sediment accumulation rate (Table T4).

In the absence of compaction, $w_s = w_{pw}$.

The calculated $P_N$ (Table T4) represents the total amount of $N_{org}$ degraded within the specified sediment interval. The intervals considered for Site 1234 and Site 1235 were 1.45–62 mcd and 1.45–42 mcd, respectively (the depth of our uppermost data point is 1.45 mcd). The total flux of $N_{org}$ delivered to the 1.45-m horizon from above is calculated as a sum of the $N_{org}$ burial flux at the bottom of the zone of active diagenesis (at 62 mcd for Site 1234 and at 42 mcd for Site 1235) and the depth-integrated ammonium production within the specified intervals. The $N_{org}$ fluxes at lower boundaries at both sites were estimated based on average sedimentation rates of 788 and 696 m/m.y. (for Sites 1234 and 1235, respectively), the $TN_{org}$ concentrations (measured TN concentrations corrected for adsorbed ammonium), and a porosity value of 0.65. We calculated (Table T4) that at Site 1234 the total flux of ammonium produced between 1.45 and 62 mcd is 0.025 $mmol/m^2d$. This constitutes 19% of the 0.106 $mmol/m^2d$ time average $N_{org}$ flux exported below 1.45 mcd. At Site 1235, the ammonium flux produced within the upper 42 mcd is slightly lower, 0.017 $mmol/m^2d$. This represents 18% of the $N_{org}$ burial flux at 1.45 mcd, and ~82% ± 10% remains as $N_{org}$. This is in reasonable agreement with the earlier estimates of 73% based on the measured decrease in $N_{org}$ at this site. To summarize, ~20% of $N_{org}$ is converted to ammonium at both of these sites during diagenesis of organic matter below 1.45 mcd.

Ammonium production fluxes in the interval of active diagenesis indicate that 70%–90% (when uncertainties associated with porosity estimates and possible nonsteady-state conditions are taken into account) of the organic matter buried below 1.45 mcd at Sites 1234 and 1235 escapes further degradation downcore. It is important to point out that these calculations do not reflect the total burial efficiency of the organic matter flux delivered to the ocean floor. Therefore, it cannot be directly compared to previously published burial efficiencies in the coastal marine sediments, though burial efficiency close to 80% has been reported for some coastal marine sediments (e.g., summary by Burdige [2005]). As a detailed discussion of factors contributing to the high degree of organic matter preservation is beyond the scope of this paper, we would like to simply point out that rapid sediment accumulation rates have been previously proposed as one of the possible mechanisms contributing to the enhanced preservation of sedimentary organic matter (Hartnett and Devol, 2003; Hartnett et al., 1998). These authors argued that one of the key factors influencing the burial efficiency is the time of organic matter exposure to aerobic degradation; therefore, in rapidly accumulating sediments, organic matter is removed from the oxic zone before it is substantially degraded.

## Effect of Compaction on $\delta^{15}$N Profiles of Pore Water Ammonium

The most prominent feature of the isotopic profiles at both sites is a noticeable similarity between the $\delta^{15}$N of ammonium and $\delta^{15}$N of $N_{org}$ (Fig. F3). Peclet numbers <1 indicate that the high rates of advection substantially decrease the degree of openness of the diagenetic system at both sites. Thus, only a modest fraction of the ammonium released at a particular horizon is able to diffuse away (because the sink location at the sediment/water interface is moving rapidly upward due to sediment accumulation).

At Site 1235, $\delta^{15}$N of ammonium very closely follows the $\delta^{15}$N of $N_{org}$ (Fig. F3B). The averages for both isotopic ratios are very similar at this site as well, suggesting that no isotopic fractionation occurs either during ammonium release in the upper 40–50 mcd or below, where net ammonium release ceases.

At Site 1234, the shape of the $\delta^{15}$N of ammonium profile bears strong resemblance to that of $\delta^{15}$N of $N_{org}$, but below ~60 mcd it appears to be offset upward relative to $\delta^{15}$N of $N_{org}$. The offset interval thickness increases with depth, suggesting that the observed offset is depth and/or time dependent. From this, we conclude that the observed offset is probably due to the difference between the burial velocities of fluids and solids. Such differences arise from sediment compaction, which extrudes pore fluids upward as sediments are buried.

Sediment compaction results in a decrease of porosity downcore within a certain interval of compaction, below which compaction ceases and sediment porosity becomes constant. We can adjust the vertical profile of ammonium $\delta^{15}$N values for the effect of compaction by computing the offset ($\chi_z$) between pore water and solids at each depth horizon. $\chi_z$ can be calculated at each depth horizon ($z$) using

$$\chi_z = \int_0^t (v_s - v_w)\,dt, \qquad (3)$$

where

$v_s$ = burial velocity of solids,
$v_w$ = burial velocity of pore water relative to the sediment/water interface, and
$t$ = time.

Next, the $v_s$ can be recast as

$$\left.\frac{dz}{dt}\right)_s = v_s$$

so that Equation 3 becomes Equation 4:

$$\chi_z = \int_0^z \left(1 - \frac{v_w}{v_s}\right) dz, \quad (4)$$

where

$z$ = depth.

We assume a linear decrease in porosity through an interval of thickness *b*, so that porosity changes downcore according to Equation 5:

$$\phi_z = \phi_0 - m(z), \quad (5)$$

where

$$m = \frac{\phi_0 - \phi_b}{b},$$

$\phi_z$ = porosity at depth z,
$\phi_0$ = porosity at the sediment/water interface,
$\phi_b$ = porosity at the base of the compaction zone, and
$b$ = depth of the base of the compaction zone.

As shown by Berner (1980), steady-state compaction requires the following equation to be true:

$$\phi_z v_w = \phi_b V_b, \quad (6)$$

where

$V_b$ = velocity of pore water = velocity of solids below the compaction zone, where further compaction does not occur.

For pore water, Equation 6 can be written as

$$(1 - \phi)v_w = (1 - \phi_b)V_b. \quad (7)$$

Substituting Equation 7 into Equation 4, we obtain the following:

$$\chi_z = \int_0^z \left(1 - \frac{\phi_b}{\phi_z}\left(\frac{1-\phi_z}{1-\phi_b}\right)\right) dz = \int_0^z \left(1 + a - \frac{a}{\phi_z}\right) dz, \quad (8)$$

where

$$a = \frac{\phi_b}{1 - \phi_b}.$$

Evaluating the integral in Equation 8 over the interval from 0 to *z*, we obtain

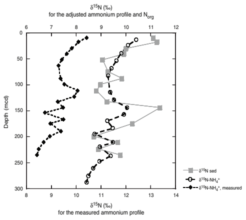
$$\int_0^z \frac{a\,dz}{\phi_0 - mz} = -\frac{a}{m}\ln(\phi_0 - mz). \quad (9)$$

Then $\chi_z$ can be found:

$$\chi_z = (1 + a)z + \frac{a}{m}\ln\left(\frac{\phi_0 - mz}{\phi_0}\right). \quad (10)$$

Porosity measurements at Site 1234 indicate a systematic decrease from 0.65 near the surface to 0.55 at 250 mcd. Assuming that 250 mcd was depth *b*, the base of the compaction zone, we can calculate the offset between solids and fluids at each depth horizon. Figure **F4** shows the adjusted and measured profiles of $\delta^{15}$N ammonium to illustrate the effect of compaction.

**F4.** Effect of compaction on the depth profile, Site 1234, p. 18.



At Site 1235, the ammonium $\delta^{15}$N follows the sedimentary $\delta^{15}$N more closely, and the effect of compaction seems to be missing. At this site, no porosity gradient was observed. It is possible that higher input of siliciclastic material and lower content of organic matter makes the sediments at Site 1235 less compactable than those at Site 1234.

## No Evidence for Isotopic Fractionation during Diagenesis

Figure **F4** demonstrates that once the impact of compaction is accounted for, $\delta^{15}$N of ammonium reflects the isotopic composition of organic matter at Site 1234. One implication of such close similarity between $\delta^{15}$N of ammonium and $N_{org}$ is that no isotopic fractionation is associated with the diagenesis of marine organic matter at this site, similar to Site 1235. The slight difference between $\delta^{15}$N of ammonium and $N_{org}$ is probably due to the partial diffusive mixing between the horizons with variable isotopic composition of organic matter (Fig. **F4**) wherever local isotopic gradients are formed. Diffusion is not fast enough to homogenize the $\delta^{15}$N of ammonium between these horizons. It is important to note also that no fractionation is observed through the part of the profile where ammonium is being presently released within the upper 50–60 mcd.

The close similarity between the ammonium and $N_{org}$ $\delta^{15}$N profiles indicate that little or no fractionation is associated with the long-term decomposition of organic matter at Sites 1234 and 1235. We reached similar conclusions based on our results from Site 1230 (ODP Leg 201) (Table **T3**), where despite the loss of more than 30% of the original organic matter, we found no evidence of changes in $\delta^{15}$N of residual $N_{org}$ (Prokopenko et al., 2006b). Our findings are consistent with the inference of Altabet et al. (1999a, 1999b) and Pride et al. (1999), who suggested the absence of diagenetic fractionation of nitrogen isotopes in rapidly accumulating organic-rich coastal sediments where organic matter is well preserved. As factors controlling the extent of organic matter diagenesis, these authors considered poor oxygenation of bottom water, high concentrations of organic matter, and rapid sediment accumulation rates. The $O_2$ concentration of the bottom water does not affect diagenesis in the sediments in the depth ranges considered in this study. These sediments do not have particularly high organic matter concentrations, and consequently, the concentration of organic matter is not as important for the high degree of preservation as are sediment accumulation rates. Sediments at Sites 1234 and 1235 contain low to moderate concentrations of organic matter (due to high degree of dilution with siliciclastic component) but accumulate at very high rates (788 m/m.y. and 696 m/m.y., respectively).

Moreover, when the results from Site 1230 are taken into consideration, it appears that the degree of organic matter preservation may not be the dominant factor behind the absence of diagenetic alteration of sedimentary $\delta^{15}$N. Perhaps another important factor, shared by the three sites, determines the absence of any significant isotopic fractionation in $N_{org}$. The sediments of all three sites (Table T3) are characterized by relatively low atomic C/N ratios (~10). This value indicates that the sedimentary organic matter is predominantly of marine origin. Apparently, the large input of terrigenous siliciclastic component is not associated with a transport of organic matter from land at these sites. We have shown previously (Prokopenko et al., 2006a) that preferential degradation of an isotopically distinct, more labile organic fraction (such as marine vs. terrestrial organic matter) may lead to a change in the residual bulk $\delta^{15}N$ of the sediments. The difference of 2‰–3‰ was observed between $\delta^{15}N$ of pore water ammonium and $N_{org}$ in the sediments of Site 1227 collected during the Leg 201. Sediments from Site 1227 (Prokopenko et al., 2006b), may contain a significant fraction of terrestrial organic matter as suggested by their high C/N ratios ranging from 12 to 18, with the average of 15, which appears to be resistant to degradation. Lithology of the sediments at Site 1227 (D'Hondt, Jørgensen, Miller, et al., 2003) also presents strong evidence for significant input of terrestrial material. Terrigenous organic matter may differ isotopically from the more labile marine $N_{org}$; in this case, the preferential degradation of the isotopically distinct marine fraction may leave the $\delta^{15}N$ of remaining bulk nitrogen diagenetically altered.

The observed absence of fractionation between ammonium and $N_{org}$ at Sites 1234 and 1235 is consistent with a dominance of the marine component in the organic matter at these sites. From the discussion above, we can state that the long-term diagenesis of marine organic matter in rapidly accumulating sediments does not affect the isotopic composition of preserved $N_{org}$, as long as the terrestrial component is minor. If both of these conditions occur, then the depth-dependent variations in preserved $\delta^{15}N$ should reflect changes in input composition.

# SUMMARY

Nitrogen isotopic composition of pore water ammonium and $N_{org}$ were examined at Sites 1234 and 1235. Mass balance calculations suggest that ~10%–30% of organic matter buried below the 1.45-mcd horizon is degraded between this interval and 42 mcd (Site 1235) to 62 mcd (Site 1234). The $\delta^{15}N$ of ammonium released in the processes of degradation closely resembles the isotopic composition of $N_{org}$ at these sites. The similarity between the pore water ammonium and $N_{org}$ $\delta^{15}N$ observed through the sediment column at Sites 1234 and 1235 implies that no significant isotopic fractionation is associated with decomposition of organic matter in these sediments on the timescale of hundreds of thousands of years. Two factors may have determined the absence of isotopic fractionation:

1. A high degree of organic matter preservation due to rapid sediment accumulation rates at both sites.
2. The predominantly marine nature of sedimentary organic matter at both sites, with only a small fraction of terrestrial organic material.

# ACKNOWLEDGMENTS

This study has been supported by National Science Foundation (NSF) grant OCE-0136500 to Douglas Hammond and an ODP Schlanger fellowship to Maria G. Prokopenko. The authors gratefully acknowledge members of the Scientific Party of Leg 202, who collected samples for us. We are also thankful to the Co-Chief Scientists of Leg 202, Drs. A. Mix and R. Tiedemann, for being very helpful in obtaining the samples, thus making this study possible. The technical assistance of M. Rincon and T. Gunderson at USC is greatly appreciated. This research used samples and/or data supplied by the Ocean Drilling Program (ODP). ODP is sponsored by U.S. National Science Foundation (NSF) and participating countries under management of Joint Oceanographic Institutions (JOI), Inc. Thoughtful suggestions by J. Brandes and the anonymous reviewer significantly improved this manuscript.

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**Figure F1.** Location map of Sites 1234 and 1235, ODP Leg 202 (www.aquarius.geomar.de/omc).

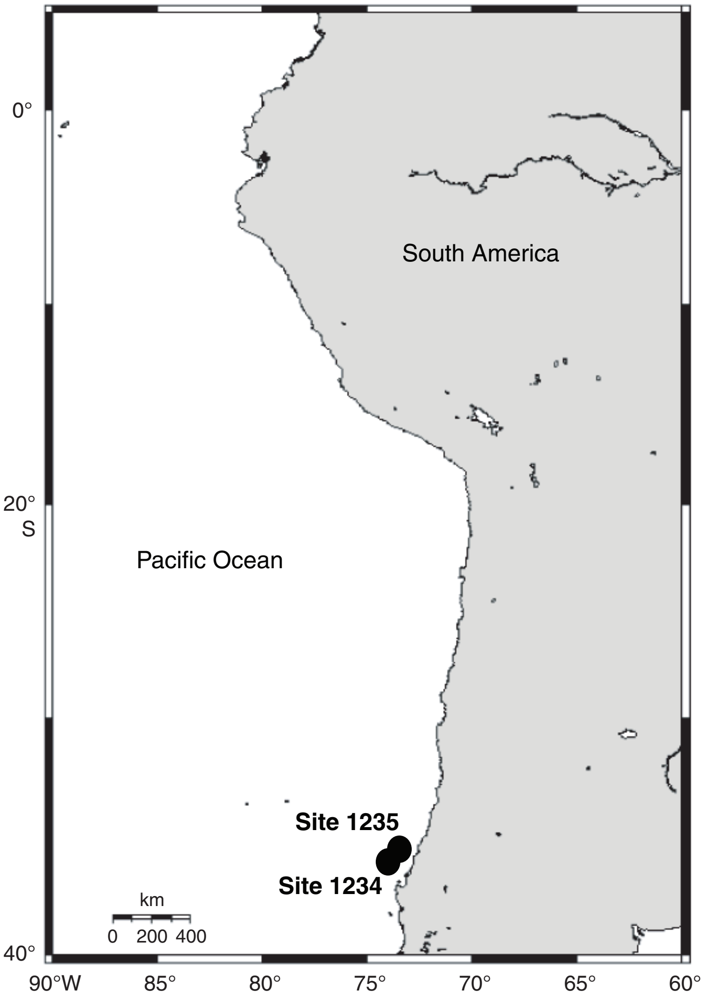

**Figure F2.** Total organic carbon (TOC) and total nitrogen (TN) content of sediments collected at Sites (**A**) 1234 and (**B**) 1235. TOC/TN ratios total and corrected for adsorbed ammonium for sediments from Sites (**C**) 1234 and (**D**) 1235. Error bar represents uncertainty associated with nonlinearity in ammonium partition coefficient for variable pore water ammonium concentrations. USC = University of Southern California. $TN_{org}$ = total nitrogen $_{organic}$.

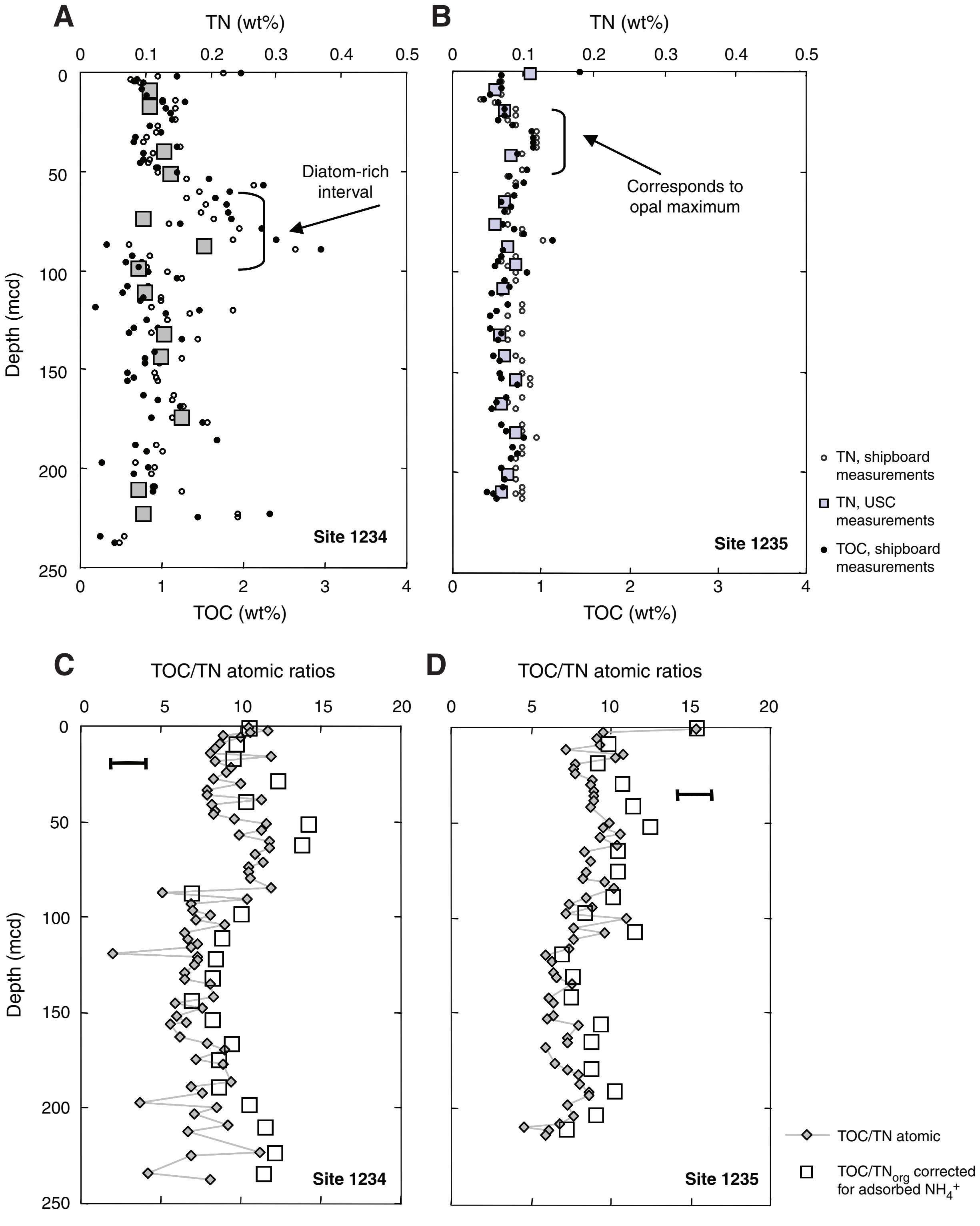

**Figure F3.** (**A**) Site 1234 and (**B**) Site 1235 pore water ammonium concentrations profile (USC measurements are plotted) and isotopic composition of pore water ammonium and $N_{org}$. Dotted lines indicate depths where sulfate is depleted below detection limit.

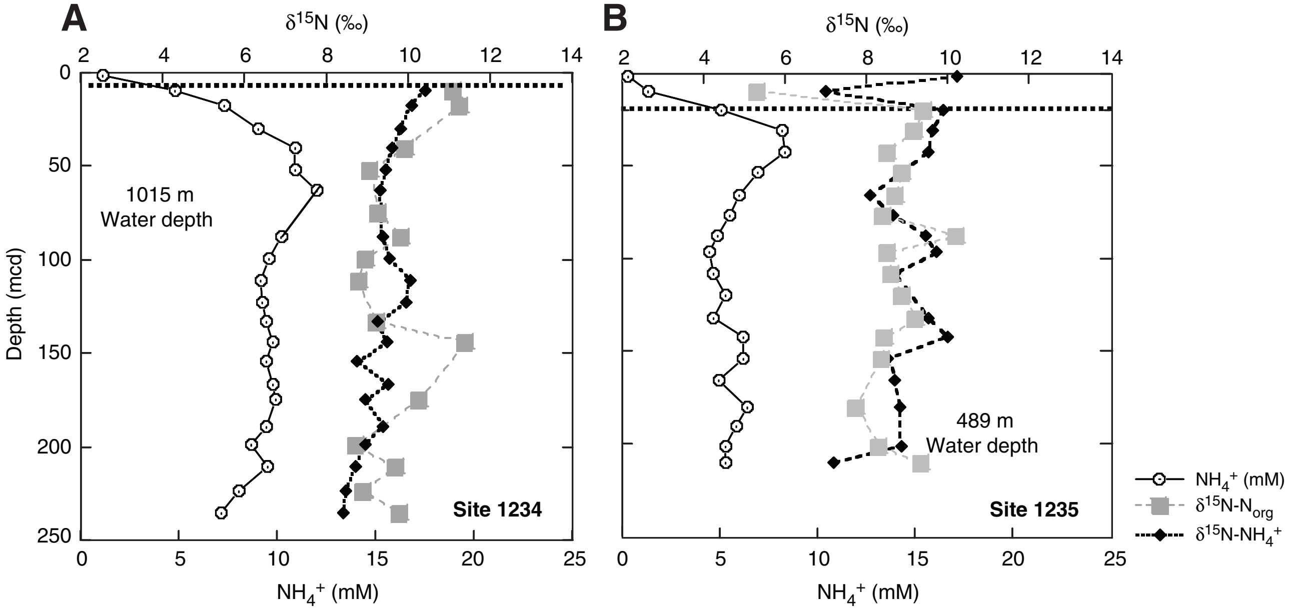

**Figure F4.** The effect of compaction on the depth profile of $\delta^{15}$N of pore water ammonium at Site 1234. Note that the scale for $\delta^{15}$N measured profile is offset by 2‰ relative to the adjusted profile for illustrative purposes. $\delta^{15}$N-$NH_4^+$ has been adjusted for calculated compaction.

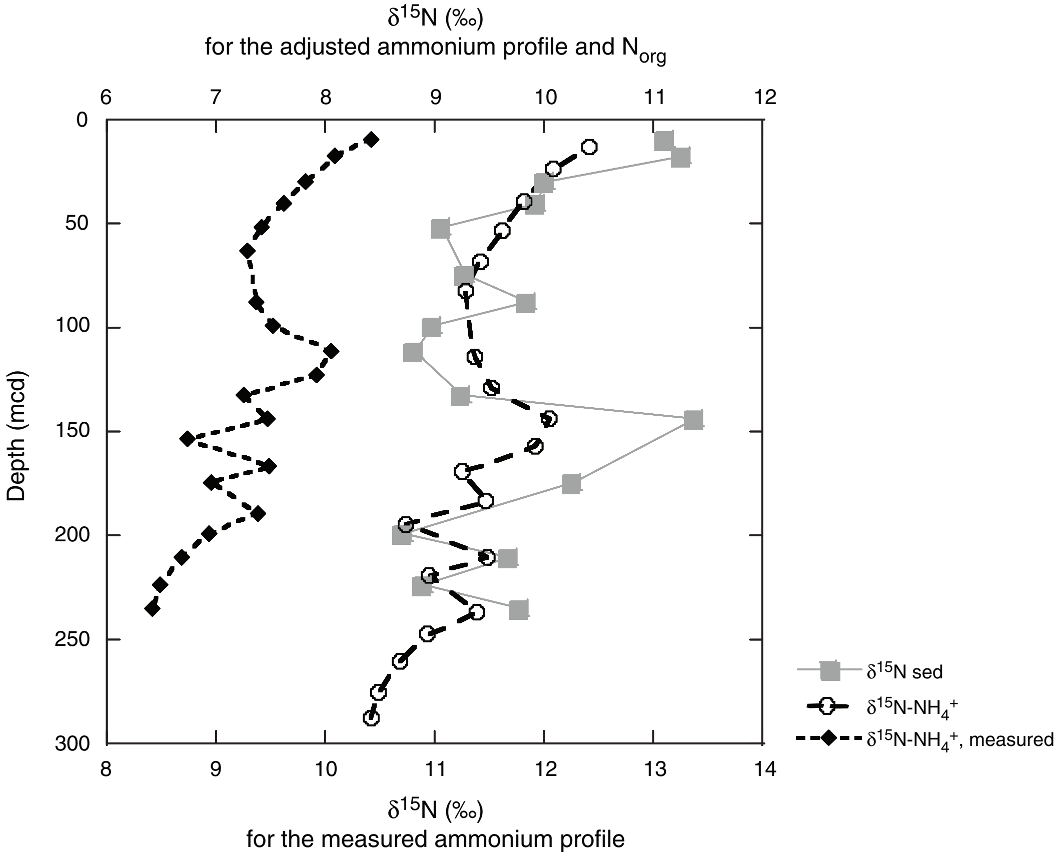

**Table T1.** Site 1234, TN concentrations, $\delta^{15}$N of ammonium and $N_{org}$.

| Core, section, interval (cm) | Depth (mcd) | Sediment TN (wt%) | Sediment $\delta^{15}$N (‰) | $NH_4^+$ (mM)* | Pore water ammonium $\delta^{15}$N (‰) |
|---|---|---|---|---|---|
| 202-1234A- | | | | | |
| 1H-1, 145–150 | 1.45 | NA | NA | 1.13 | NA |
| 2H-3, 145–150 | 9.65 | 0.11 | 11.11 | 4.78 | 10.41 |
| 3H-3, 145–150 | 17.89 | 0.11 | 11.27 | 7.27 | 10.08 |
| 4H-3, 145–150 | 29.67 | | 10.01 | 9.05 | 9.81 |
| 5H-3, 145–150 | 40.37 | 0.13 | 9.94 | 10.94 | 9.61 |
| 6H-3, 145–150 | 51.77 | 0.14 | 9.07 | 10.94 | 9.42 |
| 7H-3, 145–150 | 62.87 | NA | NA | 12.00 | 9.29 |
| 8H-3, 145–150 | 74.74 | 0.10 | 9.28 | NA | NA |
| 9H-3, 138–148 | 87.93 | 0.19 | 9.85 | 10.23 | 9.36 |
| 10H-3, 133–143 | 99.32 | 0.09 | 8.98 | 9.56 | 9.52 |
| 11H-3, 136–146 | 111.48 | 0.10 | 8.81 | 9.17 | 10.05 |
| 12X-3, 140–150 | 122.75 | NA | NA | 9.27 | 9.92 |
| 13X-3, 140–150 | 132.80 | 0.13 | 9.25 | 9.46 | 9.25 |
| 14X-3, 140–150 | 144.11 | 0.12 | 11.39 | 9.78 | 9.47 |
| 15X-2, 140–150 | 153.95 | NA | NA | 9.47 | 8.74 |
| 16X-3, 140–150 | 166.79 | NA | NA | 9.78 | 9.49 |
| 17X-1, 125–135 | 174.95 | 0.16 | 10.26 | 9.91 | 8.95 |
| 18X-3, 140–150 | 189.56 | NA | NA | 9.43 | 9.38 |
| 19X-2, 115–125 | 199.13 | NA | 8.72 | 8.65 | 8.94 |
| 20X-2, 140–150 | 210.82 | 0.09 | 9.69 | 9.53 | 8.69 |
| 21X-3, 140–150 | 223.66 | 0.10 | 8.90 | 8.06 | 8.48 |
| 22X-3, 140–150 | 235.12 | | 9.79 | 7.16 | 8.41 |
| Average† | | 0.12 ± 0.01 | 9.8 ± 0.2 | | 9.4 ± 0.2 |

Notes: * = measured at USC. NA = not available. † = uncertainties shown are standard deviation of the means.

**Table T2.** Site 1235, TN concentrations, $\delta^{15}N$ of ammonium and $N_{org}$.

| Core, section, interval (cm) | Depth (mcd) | Sediment TN (wt%) | Sediment $\delta^{15}N$ (‰) | $NH_4^+$ (mM)* | Pore water ammonium $\delta^{15}N$ (‰) |
|---|---|---|---|---|---|
| 202-1235A- | | | | | |
| 1H-1, 145–150 | 1.45 | 0.11 | 10.24 | 0.26 | NA |
| 2H-3, 145–150 | 9.49 | 0.06 | 6.99 | 1.34 | NA |
| 3H-3, 145–150 | 19.65 | 0.07 | 9.89 | 5.07 | 9.44 |
| 4H-3, 145–150 | 31.04 | NA | 9.63 | 8.18 | 9.20 |
| 5H-3, 145–150 | 42.12 | 0.08 | 9.53 | 8.36 | 8.55 |
| 6H-3, 143–148 | 53.55 | NA | NA | 6.93 | 8.91 |
| 7H-3, 145–150 | 65.81 | 0.07 | 8.10 | 6.01 | 8.72 |
| 8H-3, 134–139 | 76.96 | 0.06 | 8.66 | 5.48 | 8.45 |
| 9H-3, 124–134 | 88.03 | 0.08 | 9.48 | 4.86 | 10.22 |
| 10H-2, 140–150 | 96.86 | 0.09 | 9.73 | 4.46 | 8.52 |
| 11H-3, 130–140 | 108.49 | 0.07 | 8.69 | 4.69 | 8.63 |
| 12H-3, 140–150 | 120.19 | NA | NA | 5.30 | 8.89 |
| 13H-3, 140–150 | 132.04 | 0.07 | 9.54 | 4.65 | 9.25 |
| 14H-3, 150–160 | 142.56 | 0.07 | 10.01 | 6.17 | 8.46 |
| 15H-3, 140–150 | 154.13 | 0.09 | 8.54 | 6.17 | 8.40 |
| 16H-3, 140–150 | 166.12 | 0.07 | 8.71 | 4.95 | NA |
| 17H-3, 150–160 | 180.42 | 0.09 | 8.82 | 6.37 | 7.77 |
| 18H-2, 140–150 | 191.18 | NA | NA | 5.84 | NA |
| 19H-3, 140–150 | 201.60 | 0.08 | 8.86 | 5.26 | 8.35 |
| 20H-4, 140–150 | 210.32 | 0.07 | 7.21 | 5.25 | 9.38 |
| Average† | | 0.077 ± 0.003 | 8.9 ± 0.2 | | 8.8 ± 0.1 |

Notes: * = measured at USC. NA = not available. † = uncertainties shown are standard deviation of the means.

**Table T3.** Summary of average isotopic composition of pore water ammonium and $N_{org}$ for Sites 1234, 1235 (ODP Leg 202), and 1230 (ODP Leg 201).

| | Site* 1230 | Site 1234 | Site 1235 |
|---|---|---|---|
| Average C/N (atomic) | 9.5 ± 0.4 | 9.8 ± 1.1† | 10.09 ± 1.1† |
| Average $\delta^{15}$N of $N_{org}$ | 5.7 ± 0.9 | 9.8 ± 0.2 | 9.0 ± 0.2 |
| Average $\delta^{15}$N of ammonium | 5.0 ± 0.1 | 9.4 ± 0.1 | 8.8 ± 0.1 |
| Apparent fractionation factor, ε | –0.7 ± 0.2 | –0.4 ± 0.3 | –0.2 ± 0.3 |

Notes: * = data for Site 1230 (ODP Leg 201) are from Prokopenko et al. (2006b). † = corrected for adsorbed ammonium.

**Table T4.** Budgets for $N_{org}$ below 1.45 mcd horizon based on pore water ammonium.

| Parameters used in calculations | Site 1234 | Site 1235 |
|---|---|---|
| Average porosity, $\phi$ | 0.65 | 0.65 |
| Diffusivity, $D_s$, ($m^2$/day)* | $5.0 \times 10^{-5}$ | $5.0 \times 10^{-5}$ |
| Sediment accumulation rate, $w_s$, m/day | $2.15 \times 10^{-6}$ | $1.9 \times 10^{-6}$ |
| Pore fluid burial rate, $w_{pw}$, m/day | $1.33 \times 10^{-6}$ | $1.9 \times 10^{-6}$ |
| Peclet number = $D_s \times \beta/[(1 + K) \times w]$†, ‡ | 0.42 | 0.23 |
| $\beta$ (found by fitting the profiles) | 0.065 | 0.02 |
| Calculated fluxes | | |
| $J_{A2} - J_{A1}$ | 0.019 | 0.015 |
| $J_{D2} - J_{D1}$ | 0.006 | 0.003 |
| Total ammonium production flux, $P_N$ | 0.025 | 0.018 |
| Total $N_{org}$ flux at 1.45 mcd** | 0.131 | 0.097 |
| Fraction buried below zone of active diagenesis†† | 81% ± 10% | 82% ± 10% |

Notes: Fluxes are in mmol/$m^2 \times$ d. * = $D_s = D_m/[1 - \ln(\phi^2)]$ (Boudreau, 1997; Li and Gregory, 1974); $D_m$ = molecular diffusivity. † = $K = 1.3$, ammonium partition coefficient (Berner, 1980), dimensionless. ‡ = $\beta$ = 1/e-folding distance for ammonium profiles. ** = $TN_{org}$ flux = $P_N + TN_{org}$ at the bottom of active diagenesis zone; $TN_{org} = TN \times 0.8$, since adsorbed ammonium is 20% of TN. †† = The uncertainty is based on assumed porosity uncertainty of 5%.