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Walter S. Borowski

Eastern Kentucky University, w.borowski@eku.edu

Charles K. Paull

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17. DATA REPORT: NITROGEN ISOTOPIC COMPOSITION OF PORE-WATER AMMONIUM, BLAKE RIDGE, SITE 997¹

Walter S. Borowski^{2,3} and Charles K. Paull^{2,4}

Ammonium (NH₄⁺) concentration profiles in piston-core sediments of the Carolina Rise and Blake Ridge generally have linear concentration profiles within the sulfate reduction zone (Borowski, 1998). Deep Sea Drilling Project (DSDP) Site 533, located on the Blake Ridge, also displayed a linear ammonium concentration profile through the sulfate reduction zone and the profile linearity continues into the upper methanogenic zone to a depth of ~200 meters below seafloor (mbsf), where the first methane gas hydrates probably occur (Jenden and Gieskes, 1983; Kvenvolden and Barnard, 1983). Sediments from the Ocean Drilling Program (ODP) Leg 164 deep holes (Sites 994, 995, and 997) also exhibit linear ammonium profiles above the top of the gas hydrate zone (~200 mbsf) (Paull, Matsumoto, Wallace, et al., 1996).

We hypothesized that a possible cause of linear ammonium profiles was diffusion of ammonium from a concentrated ammonium source at depth. We further reasoned that if this ammonium were produced by microbial fermentation reactions at depth, that a comparison of the nitrogen isotopic composition of sedimentary organic nitrogen and the nitrogen with pore-water ammonium would test this hypothesis. Convergence with depth of $\delta^{15}\text{N}$ values of the nitrogen source (sedimentary organic matter) and the nitrogen product (dissolved NH₄⁺) would strongly suggest that ammonium was produced within a particular depth zone by microbial fermentation reactions.

Here, we report $\delta^{15}\text{N}$ values of pore-water ammonium from selected interstitial water (IW) samples from Site 997, sampled during ODP Leg 164.

METHODS

Interstitial waters were collected from ODP cores using standard ODP methods with a hydraulic sediment press (Manheim, 1966) and collected in air-tight syringes (Manheim and Sayles, 1974). Ammonium concentration values were measured using the colorimetric method of Solorzano (1969) and the procedure outlined in Gieskes et al. (1991) (see Paull, Matsumoto, Wallace et al., 1996). Nitrate and nitrite were not measured but are assumed to be at near-zero concentration within pore waters. Filtered pore-water aliquots were stored immediately after squeezing in flame-sealed, air-tight ampoules for onshore measurement of nitrogen isotopes.

Ammonium extraction and nitrogen isotopic measurements of pore-water ammonium were made by Coastal Science Labs (Austin, Texas), using a modified procedure of Velinsky et al. (1989) (R.

Anderson, pers. comm., 1998). Ammonium was extracted from pore waters by distillation into an HCl acid trap. Care was taken to ensure that the acid trap did not become saturated, to avoid increased alkalinity, loss of NH₃, and isotopic fractionation. Ammonia was then captured onto an artificial zeolite molecular sieve. The zeolite (with absorbed ammonia) was loaded into borosilicate tubes with CuO and Cu, which were then evacuated, sealed, and heated to 590°C. The resultant N₂ is directed into a VG SIRA II model mass spectrometer. Measurement precision is at least $\pm 0.5\%$ (Air) and refers to reproducibility of the entire extraction and measurement process (R. Anderson, pers. comm., 1998).

Isotopic measurements of nitrogen contained within sedimentary organic matter are reported in Olsen (1997) and Paull et al. (Chap. 7, this volume). These measurements were performed using a GC-CIR-MS at the University of North Carolina, Chapel Hill. Measurement uncertainty for the entire procedure is $\pm 0.3\%$ (H. Mendlovitz, pers. comm., 1998).

RESULTS AND DISCUSSION

Measured pore-water ammonium concentrations and $\delta^{15}\text{N}$ values are tabulated in Table 1. Figure 1 shows the stratigraphic relationship between these measurements and the nitrogen isotopic values of sedimentary organic matter (Olsen, 1997; Paull et al., Chap. 7, this volume).

The uncertainty in the measured $\delta^{15}\text{N}$ values of pore-water ammonium ($\pm 0.5\%$) and sedimentary organic nitrogen ($\pm 0.3\%$) precludes recognition of an isotopic gradient in pore-water ammonium within the upper 200 m of the sedimentary section. Moreover, no convergence of the nitrogen isotopic composition of sedimentary organic matter and pore-water ammonium occurs with increasing depth. Below 200 mbsf, there is a clear disparity between the $\delta^{15}\text{N}$ values of nitrogen contained in sedimentary organic and nitrogen composing pore-water ammonium.

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²Geology Department, The University of North Carolina at Chapel Hill, Chapel Hill, NC 27599-3315, U.S.A.

³Present address: Exxon Exploration Company, P.O. Box 4778, Houston, TX 77210-4778, U.S.A. borowski@lcc.net

⁴Present address: Monterey Bay Aquarium Research Institute, 7700 Sandholdt Road, Moss Landing, CA 95039-0628, U.S.A.

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Table 1. Interstitial data from selected samples from Site 997.

IW sample	Depth (mbsf)	Ammonium (mM)	$\delta^{15}\text{N-NH}_4^+$ (‰ Air)
164-997A-			
3H-3	16.80	1.5	4.1
6H-2	43.80	4.1	4.1
12H-2	92.80	8.4	4.3
17H-5	144.70	13.2	4.8
21X-2	169.75	15.6	
30X-1	233.60	17.5	3.6
37X-5	296.15	20.4	4.5
164-997B-			
14X-2	493.56	22.2	4.9
29X-4	612.25	18.2	4.2
39X-3	687.65	10.6	3.9

Notes: IW = interstitial water. Ammonium concentrations are in millimolar (mM) units (from Paull, Matsumoto, Wallace, et al., 1996). Nitrogen isotopic data for pore-water ammonium are expressed in per mil units (‰) relative to the nitrogen isotopic standard, Air.

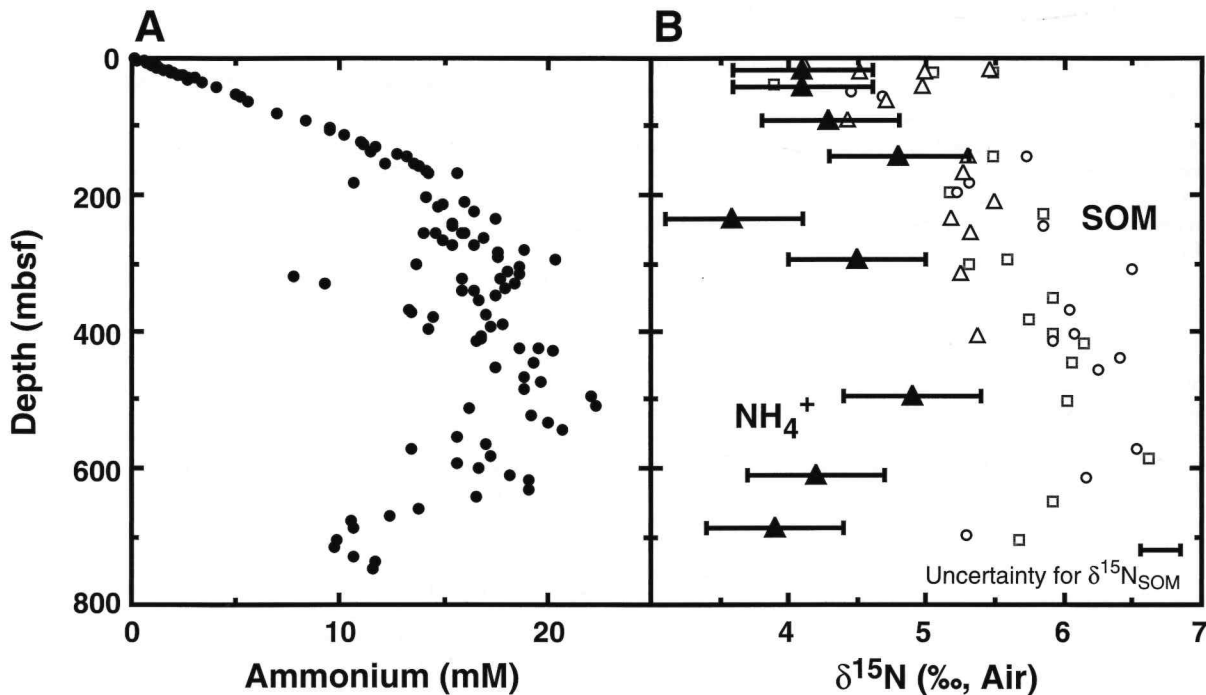


Figure 1. A. Plot of interstitial ammonium concentration values vs. depth from Paull, Matsumoto, Wallace, et al. (1996). Note linear profile above 200 mbsf. B. Interstitial ammonium $\delta^{15}\text{N}$ values in per mil units relative to the nitrogen Air standard (solid triangles) and nitrogen isotopic values of sedimentary organic matter (SOM) at Sites 994 (open circles), 995 (open squares), and 997 (open triangles) from Olsen (1997) and Paull et al. (Chap. 7, this volume). Measurement uncertainty in $\delta^{15}\text{N}_{\text{NH}_4^+}$ is shown by error bars; the error bar in the lower right corner refers to the general measurement uncertainty in $\delta^{15}\text{N}_{\text{SOM}}$ (H. Mendlovitz, pers. comm., 1998).