



Nitrogen geochemistry of subducting sediments: New results from the Izu-Bonin-Mariana margin and insights regarding global nitrogen subduction

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[1] Toward understanding of the subduction mass balance in the Izu-Bonin-Mariana (IBM) convergent margin, we present an inventory of N and C concentrations and isotopic compositions in sediments obtained on Ocean Drilling Program (ODP) Legs 129 and 185. Samples from Sites 1149, 800, 801, and 802 contain 5 to 661 ppm total N (organic, inorganic combined) with $\delta^{15}\text{N}_{\text{Air}}$ of -0.2 to $+8.2\text{‰}$ (all $\delta^{15}\text{N}$ values $<+2.5\text{‰}$ from Site 800). At Site 1149, N content is higher in clay-rich layers and lower in chert and carbonate layers, and $\delta^{15}\text{N}$ shows a distinct down-section decrease from 0 to 120 mbsf (near $+8.0$ at shallow levels to near $+4.0\text{‰}$). Reduced-C concentration ranges from 0.02 to 0.5 wt.%, with $\delta^{13}\text{C}_{\text{VPDB}}$ of -28.1 to -21.7‰ . The down-section decreases in $\delta^{15}\text{N}$ and N concentration (and variations in concentrations and $\delta^{13}\text{C}$ of reduced C, and $C_{\text{reduced}}/\text{N}$) at Site 1149 could help reconcile differences between $\delta^{15}\text{N}$ values of modern deep-sea sediments from near the sediment-water interface and values for forearc metasedimentary rocks. At Site 1149, negative shifts in $\delta^{15}\text{N}$, from marine organic values (up to $\sim+8\text{‰}$) toward lower values approaching those for the metasedimentary rocks ($+1$ to $+3\text{‰}$), are most likely caused by complex diagenetic processes, conceivably with minor effects of changes in productivity and differing proportions of marine and terrestrial organic matter. However, the forearc metamorphic suites (e.g., Franciscan Complex) are known to have been deposited nearer continents, and their lower $\delta^{15}\text{N}$ at least partly reflects larger proportions of lower- $\delta^{15}\text{N}$ terrestrial organic matter. Subduction at the Izu-Bonin (IB) margin, of a sediment section like that at Site 1149, would deliver an approximate annual subduction flux of 2.5×10^6 g of N and 1.4×10^7 g of reduced C per linear kilometer of trench, with average $\delta^{15}\text{N}$ of $+5.0\text{‰}$ and $\delta^{13}\text{C}$ of -24‰ . Incorporating the larger C flux of 9.2×10^8 g/yr/linear-km in carbonate-rich layers of 1149B (average $\delta^{13}\text{C} = +2.3\text{‰}$) provides a total C flux of 9.3×10^8 g/yr/linear-km ($\delta^{13}\text{C} = +1.9\text{‰}$). Once subducted, sediments are shifted to higher $\delta^{15}\text{N}$ by N loss during devolatilization, with magnitudes of the shifts depending on the thermal evolution of the margin.

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Theme: Oceanic Inputs to the Subduction Factory

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1. Introduction

[2] Subduction of sedimentary rocks is an important factor in the global cycles of nitrogen (N) and carbon (C), as could be hydrothermally altered oceanic crust (AOC) [see *Javoy et al.*, 1986; *Zhang and Zindler*, 1993; *Bebout*, 1995; *Javoy*, 1998]. Despite much recent interest in cycling of volatile elements at convergent margins, there has been little previous study of the unmodified inputs of N and C (especially N) in subduction zones. Any previous attempts to determine the fluxes of these elements through convergent margins have required conjecture based on analyses of seafloor lithologies that may not be appropriate or estimates based on studies of low-grade metamorphic rocks. The quantification of true input fluxes of C and N into subduction zones, preferably on the scale of individual convergent margins, becomes all the more urgent in the context of recent attempts to mass balance inputs and outputs of the elements at individual convergent margins. Therefore, to better understand the role of subduction on the global chemical cycles of these elements, we attempt to produce an inventory of N and C contents and isotopic compositions in sediments recovered on Ocean Drilling Program Leg 185 (and Leg 129) outboard of the Izu-Bonin-Mariana (IBM) subduction zone. This inventory, combined with knowledge of devolatilization at greater depths in paleo-subduction zones (based on study of metamorphic suites [see *Bebout and Fogel*, 1992; *Sadofsky and Bebout*, 2003]), and outputs of volatiles in arc magmas [e.g., *Fischer et al.*, 2002; *Hilton et al.*, 2002; *Snyder et al.*, 2003], will help to better determine the magnitude and mass balance of N and C in convergent margins and elucidate the global cycling of these elements.

[3] The IBM arc system is formed through subduction of old (>170 Ma) oceanic crust of the Pacific plate beneath the Philippine plate (Figure 1). This section of the oceanic crust, along with the overlying sediment section, has been sampled outboard of the Izu-Bonin subduction zone, by Ocean Drilling Program (ODP) Site 1149, and by ODP Sites 800, 801, and 802 outboard of the Mariana Trench (see locations on the seafloor map in Figure 1). The IBM subduction system provides an ideal location for attempts to mass balance elements fluxes through the “subduction factory” because, unlike many other subduction zones, there appears to be no accumulation of sediments in an accretionary prism [see *von Huene and Scholl*, 1991]. The sedimentary section at site 1149 is 408m thick, and divided into 4 units by the Leg 185 Scientific party. Unit I (0–118 mbsf) is Pleistocene – late Miocene in age and composed of mixed volcanic ash, siliceous oozes, clay, and minor amounts of silt. Unit II (118–179 mbsf) is less well dated, and dominated by dark brown pelagic clay, with some volcanic ash and more minor radiolarians and diatoms. Unit III (179–282 mbsf) is composed of radiolarian chert and zeolitic clays, recovery in this section was relatively low, and these cherts are likely more minor reservoirs of N and C. Unit IV (282–408 mbsf) is composed of radiolarian chert, marl, and chalk overlying the oceanic crustal basement. Thus the section at site 1149 is a nearly classical sequence of oceanic sediment from the deeper parts of the ocean, with cherts and limestones near the bottom, more clayey layers above that and finally some input of volcanic ash. For our attempt to inventory the flux and isotopic compositions of C and N subducting in the modern Izu margin, we obtained samples from cores of the complete sediment section obtained at Site 1149 during

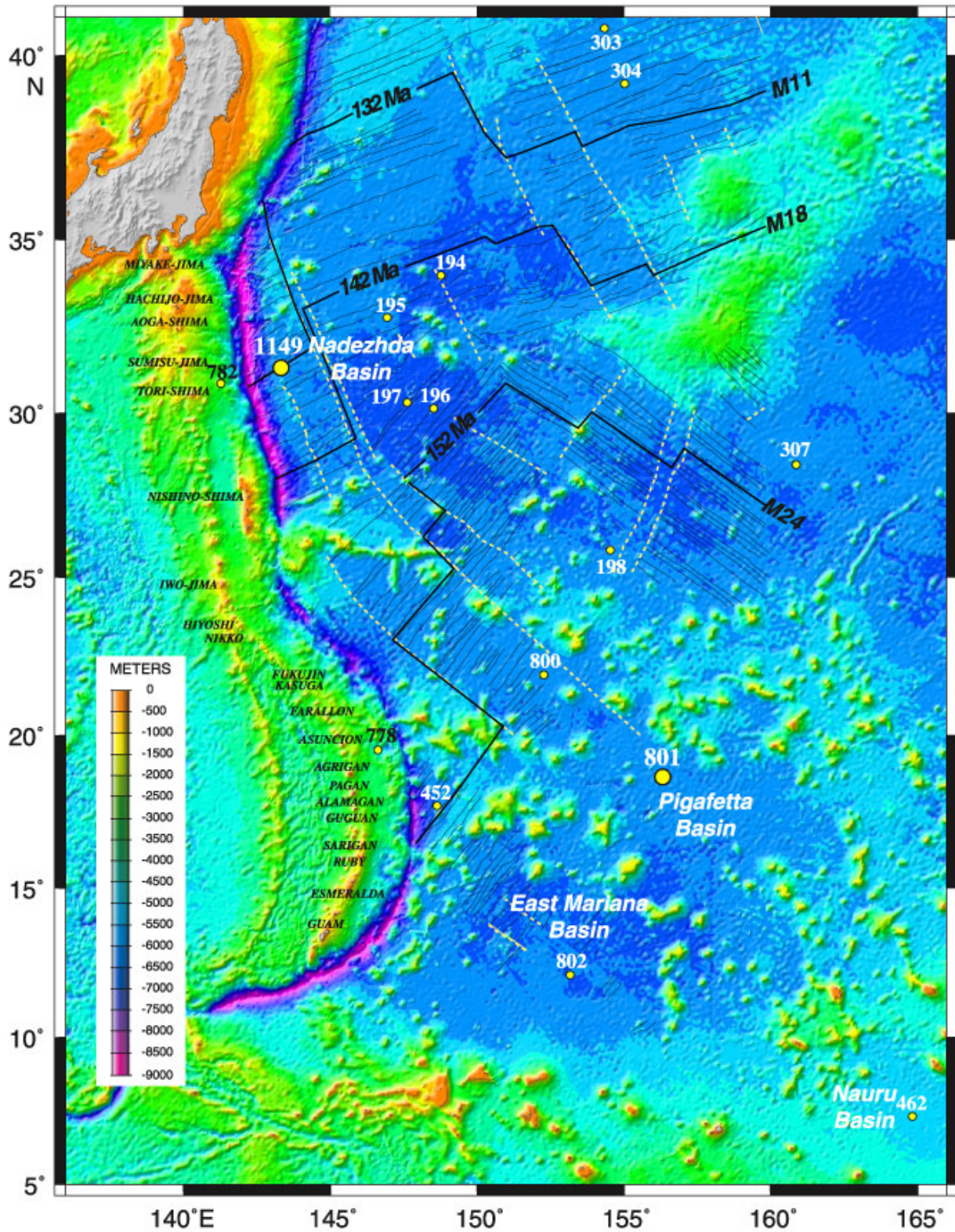


Figure 1. Map of IBM convergent margin and adjacent seafloor, showing bathymetry (see color-coded legend), structures and topography in the seafloor basement, the locations of the volcanic arc, and the locations of Sites 800, 801, 802, and 1149 (image used courtesy of the ODP; figure from *Plank et al.* [2000], where a detailed description of the data sources is provided).

ODP Leg 185 (see description of scientific goals and data obtained on this drilling leg by *Plank et al.* [2000]), and for comparison, a smaller number of samples of sediment at ODP Sites 800, 801, and 802 collected during Leg 129 and kept frozen since their collection.

[4] Nitrogen is bound into sediments primarily in organic detritus, but other complex ions, such as NO_3^- , can be adsorbed onto sedimentary particles. The primary $\delta^{15}\text{N}$ of sediments depends on the relative proportions of N from organic sediments, with different values depending on type of organism and food source, and N from other types of particles, such as marine nitrate bound onto clay minerals. Nitrogen fixation by cyanobacteria and atmospheric input of N into the ocean tends to initially create a reservoir with $\delta^{15}\text{N}$ near atmospheric values, denitrification of a marine reservoir tends to preferentially return ^{14}N to the atmosphere thereby increasing the $\delta^{15}\text{N}$ of the remaining reservoir, grazing increases $\delta^{15}\text{N}$ at each trophic level, and diagenetic alteration has been shown to either increase or decrease $\delta^{15}\text{N}$ depending on redox conditions (see summary by *Ettwein et al.* [2001, and references therein]). Variations in the proportions of marine and terrestrial organic inputs are also known to affect $\delta^{15}\text{N}$ in sediments [see *Peters et al.*, 1978; *Minoura et al.*, 1997; *Pride et al.*, 1999].

[5] Many previous studies have documented or considered sedimentary, including diagenetic, N-isotope behavior [*Peters et al.*, 1978; *Macko*, 1989; *Muzuka et al.*, 1991; *Williams et al.*, 1995; *Luther et al.*, 1997; *Minoura et al.*, 1997; *Wilson and Thomson*, 1998; *Thamdrup and Dalsgaard*, 2000; *Freudenthal et al.*, 2001]. However, most of these studies have not focused on the deep-sea lithologies most likely to be subducted, that is, in the sedimentary environments similar to those outboard of modern subduction zones (dominated by the circum-Pacific). This is the first study of its kind to examine N and $\delta^{15}\text{N}$ in sedimentary lithologies deposited outboard of a subduction zone and lacking a metamorphic overprint related to complex subduction and exhumation history (the latter experienced by the paleoaccretionary metamorphic suites). It is also the first to investi-

gate in detail the deep-sea sediment representative of an ocean-ocean subduction zone setting; most of the previous work, including the work to date on paleoaccretionary suites (e.g., work on the Catalina Schist, Franciscan Complex, both in California [*Bebout et al.*, 1999a; *Sadofsky and Bebout*, 2003]), has been conducted on sedimentary lithologies deposited near continents (in general, experiencing higher clastic sedimentation rates and with the greater potential for addition of terrestrial organic matter). The wide range in sedimentary $\delta^{15}\text{N}$ values from the literature (representative summary in Figure 2) illustrates the potential pitfall in using an averaged modern sedimentary N composition, based on sediment data for a wide variety of sedimentological environments, to estimate the fluxes of N through subduction zones. Also, the sedimentary $\delta^{15}\text{N}$ values from the literature are obviously different from (mostly higher than) values observed for low-grade metasedimentary rocks from subduction-zone settings for which deep-sea sediments are thought to be the protoliths [*Bebout and Fogel*, 1992; *Sadofsky and Bebout*, 2003]. Thus, as an additional goal of this study, we sought an explanation for the disparity in $\delta^{15}\text{N}$ illustrated in Figure 2, with possibilities including, (1) that the other studies were carried out on sediments not representative of sedimentological processes and organic deposition on the deep seafloor outboard of trenches, and perhaps were conducted on inappropriate sedimentary lithologies, and (2) that diagenetic and/or very low-grade metamorphic processes altered (decreased) the $\delta^{15}\text{N}$ of the seafloor sediment section during its initial transit into the trench and to depths of 5–40 km represented by the paleoaccretionary suites. In this paper, we present new C and N concentration and stable isotope data for deep-sea sedimentary sections obtained on ODP Legs 129 and 185 and discuss possible causes of variations observed in these sections in the context of the sedimentological and tectonic setting in which the sediments were deposited. We then use the concentrations and isotopic compositions to estimate the C-N fluxes into the Izu-Bonin convergent margin, based on the data for Site 1149 (obtained on Leg 185), and provide a synthesis of recent observations regarding the effects of forearc metamorphic

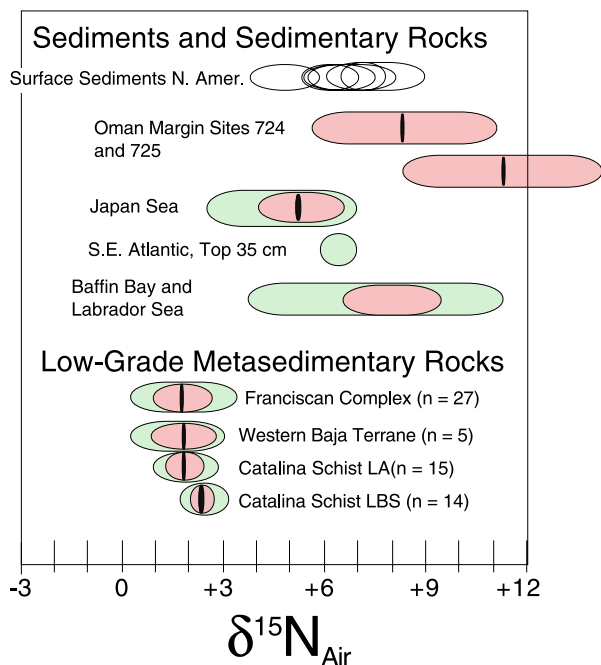


Figure 2. Nitrogen isotopic composition of marine sediments, compared with those for low-grade metamorphic rocks from subduction zone settings. Surface sediments off the shore of North America, ovals show mean and standard deviation for several basins off the western shore of North America [Peters *et al.*, 1978]. Oman Margin, mean (line) and standard deviation (field) are shown for each core. Data are from organic-rich sediments at depths of up to 200 m [Muzuka *et al.*, 1991]. Japan Sea, data are from the top 6 m of sediment [Minoura *et al.*, 1997]. S.E. Atlantic data are from cores between the Canary Islands and the Moroccan Coast [Freudenthal *et al.*, 2001]. Baffin Bay and Labrador Sea data are collected from depths of up to 60 m from ODP Leg 105 [Macko, 1989]. Franciscan Complex and Western Baja Terrane [Sadofsky and Bebout, 2003]. Catalina Schist, LA = lawsonite-albite facies, LBS = lawsonite-blueschist facies [Bebout and Fogel, 1992; Bebout, 1997].

processes on the deeper entrainment of N based on studies of metamorphic rocks exposed in paleoaccretionary complexes.

2. Analytical Methods

[6] Multiple samples of each sedimentary lithology were recovered from newly drilled core from site 1149 and from archived, frozen collections from sites 800, 801, and 802 (the latter obtained from the ODP Gulf Coast core repository, College Station, Texas, and from J. Alt; all samples had been kept

frozen since collection). In our laboratory, the frozen sediment samples were thawed and dried at 45°C for approximately 48 hours and then crushed finely enough to homogenize for stable isotope analyses.

[7] Nitrogen isotopic compositions of total N (combined organic and inorganic fractions) were obtained by sealed-tube combustions (910°C for 4 hours [see Bebout and Fogel, 1992; Sadofsky and Bebout, 2000; Bebout and Sadofsky, 2004]). Nitrogen yields were determined by measuring the signal at $m/z = 28$, for calibrated inlet volumes in the mass spectrometer. Combustions at higher temperatures (up to 1060°C), for one sediment sample, produced $\delta^{15}\text{N}$ values and N concentrations indistinguishable from those for the lower-temperature experiments; thus all other combustions for N were performed at the lower temperatures (910°C). For reduced-C analyses of $\delta^{13}\text{C}$, samples were first reacted overnight in 10 ml of 1N HCl to remove any carbonates. The samples were then centrifuged and rinsed three times to remove all HCl, then dried and prepared for isotopic analysis by sealed-tube combustion (850°C for 1.5 hours). Concentrations of C were determined by Hg manometry after cryogenic purification of the resulting CO_2 . CO_2 from carbonate-bearing samples was prepared by overnight dissolution in 100% phosphoric acid at 25°C, then purified and measured in the same manner as the CO_2 from the reduced-C experiments. All gases were analyzed for their isotopic compositions in dual-inlet mode on the Finnigan MAT 252 mass spectrometer at Lehigh University, and isotopic compositions are presented as $\delta^{15}\text{N}_{\text{Air}}$, $\delta^{13}\text{C}_{\text{VPDB}}$, and $\delta^{18}\text{O}_{\text{VSMOW}}$. Uncertainties, determined by replicates of internal and international standards, are $\leq 0.10\%$ (1σ) for all isotope analyses. For the concentration data, detection limits are, for C, < 0.1 wt.%, and for N, on the order of several ppm (depending somewhat on sediment type and preparation involved).

3. Results

[8] Forty bulk-sediment samples from sites 1149, 800, 801, and 802 contain 5 to 661 ppm total

N (organic and inorganic N fractions combined) with $\delta^{15}\text{N}$ ranging from -0.2 to $+8.2\text{‰}$ (Table 1, Figure 3a; the only two samples with $\delta^{15}\text{N} < +2.5\text{‰}$ are from Site 800). Various ash and clay units recovered from Site 1149A contain abundant N (>200 ppm) and show some variation in concentration as a function of depth within individual lithologies, particularly within ash in the upper 120 m of the section (see Figures 3a and 4a). Clastic (ash and clay) samples from Sites 800, 801, and 802 have highly variable N concentrations, whereas chert, carbonate, and some other pelagic clay samples are generally lower in N than samples from site 1149 (Table 1; Figures 3a and 4a). At Site 1149A, $\delta^{15}\text{N}$ varies with depth in Unit I (the upper 120 m of the section), with the sample closest to the sediment-water interface having $\delta^{15}\text{N}$ of $+8.2\text{‰}$, and showing decrease with depth toward values of $+4.7\text{‰}$ at ~ 120 meters (Figures 3a and 4b). At depths greater than ~ 120 mbsf, $\delta^{15}\text{N}$ ranges from $+3.7$ to $+4.9\text{‰}$ in clastic layers, and $\delta^{15}\text{N}$ values of chert and carbonate layers at greater depths are lower and more variable ($+2.5$ to $+4.6$; Figure 4b).

[9] Reduced C concentrations range from 0.02 to 0.5 wt.% (for 32 samples), with $\delta^{13}\text{C}$ ranging from -28.1 to -21.7‰ (Table 1, Figure 3b), and the concentrations show some decrease with depth in the ash and clay layers at Site 1149 (Figures 5a and 5b). The decrease in reduced C concentration with depth in Unit I at Site 1149 (Figure 5a) appears to be correlated with the slight decreases in N concentration (see Figures 3a, 3b, and 4a), and C_{reduced}/N shows subtle decrease over the upper 180 m of section (Figure 5c). Calcite from carbonate-rich layers (12–90 wt.%) of 1149B (all from >280 mbsf) has $\delta^{13}\text{C}$ of $+1.7$ to $+2.8\text{‰}$ and $\delta^{18}\text{O}$ of $+28.5$ to $+29.7\text{‰}$ (see Table 1).

4. Discussion

4.1. Downhole Variations in N and C Concentrations and Isotopic Compositions

[10] Sediments are highly variable in N concentration and isotopic composition and these variations have been used to trace a wide range of processes in organic-rich sediments, including diagenesis

[e.g., Sweeney *et al.*, 1978; Peters *et al.*, 1978; Rau *et al.*, 1987; Libes and Deuser, 1988; Altabet and Francois, 1994; Minoura *et al.*, 1997; Muller and Voss, 1999; Ettwein *et al.*, 2001]. Many of these studies were carried out in relatively organic-rich systems (compared with the section at Site 1149), very near the sediment-water interface [e.g., Peters *et al.*, 1978; Minoura *et al.*, 1997] or nearer continents, and relatively little attention has been paid to N behavior in deep-sea sediment sections such as that at Site 1149 (notable exceptions in the literature, but lacking N and C isotope data, are the studies by Muller [1977], Waples and Sloan [1980], and Waples [1985]). Here we will attempt to outline some of the possible reasons for the shifts in concentration and isotopic composition of N and C with depth at Site 1149.

4.1.1. Oceanographic Considerations

[11] The decrease in $\delta^{15}\text{N}$ with depth at Site 1149 could in part reflect change in $\delta^{15}\text{N}$ of the primary sediments being deposited at this site through time. An increase of $\delta^{15}\text{N}$ with time requires an increase in productivity or a decrease in nutrient supply that makes the preferential uptake of ^{14}N by organic matter less efficient [see Ettwein *et al.*, 2001]. Samples from 90 mbsf have $\delta^{15}\text{N}$ values similar to those at greater depths at Site 1149, and samples at around 50 mbsf are clearly higher in $\delta^{15}\text{N}$ than those below 90 mbsf. Therefore the shift in $\delta^{15}\text{N}$ (and less clear trends in N and C content and $\delta^{13}\text{C}$) would have begun within that period of deposition (Table 1, Figure 4), corresponding to ~ 2.5 to 3.5 Ma [Lozar and Mussa, 2003]. The most likely change in oceanographic factors around this time is the increase in the Kuroshio current (due to the closure of the seaway between North and South America) which is documented in the biostratigraphic record at Site 1149 by three events between 75.11 and 68.46 mbsf [Lozar and Mussa, 2003]. The general motion of the site toward the higher productivity waters of this current could help account for the gradual increases in $\delta^{15}\text{N}$, $\delta^{13}\text{C}$ -org, and N and C concentrations. However, the region known to have been strongly affected by the Kuroshio current is extremely high in productivity, with most samples containing 0.5 to 1.5 wt% C as documented during ODP Leg 186 [see Mora,

Table 1. Carbon and Nitrogen Concentration and Stable Isotope Compositions of Sediments From Sites 1149, 800, 801, and 802

Lithology ^a	Sample Identification				Depth, mbsf	Nitrogen ppm	Reduced Carbon		Carbonate			
	Leg	Site	Hole	Core			Section	Interval	Depth, mbsf	Section	Interval	Wt. %
Ash- and Biogenic Silica-Bearing Clay	185	1149	A	001H	01WR	140–150	1	330	8.2	-23.6	0.13	4.0
Ash- and Biogenic Silica-Bearing Clay	185	1149	A	001H	03W	30–32	3	371	6.1	-22.6	0.35	9.4
Ash- and Biogenic Silica-Bearing Clay	185	1149	A	002H	01WR	140–150	6	350	6.7	-22.1	0.29	8.3
Ash- and Biogenic Silica-Bearing Clay	185	1149	A	004H	02WR	140–150	26	462	6.1			
Ash- and Biogenic Silica-Bearing Clay	185	1149	A	004H	03WR	114–116	27	448	6.2	-22.2	0.35	7.8
Ash- and Biogenic Silica-Bearing Clay	185	1149	A	004H	03WR	140–150	28	508	6.1	-22.2	0.24	4.7
Ash- and Biogenic Silica-Bearing Clay	185	1149	A	005H	04WR	140–150	39	395	5.8	-22.5	0.21	5.4
Ash- and Biogenic Silica-Bearing Clay	185	1149	A	05H	05WR	140–150	40	366	5.7	-22.7	0.20	5.3
Ash- and Biogenic Silica-Bearing Clay	185	1149	A	006H	02WR	140–150	45	383	6.3	-21.7	0.35	9.0
Ash-Bearing Siliceous Clay	185	1149	A	007H	03WR	140–150	56	355	5.7	-23.2	0.16	4.5
Ash-Bearing Siliceous Clay	185	1149	A	007H	04WR	140–150	58	203	5.5			
Biogenic Silica- and Ash-Bearing Clay	185	1149	A	008H	03W	140–150	66	416	5.5	-23.1	0.17	4.0
Ash-Bearing Silica-Rich Clay	185	1149	A	009H	03W	140–150	75	383	5.3	-23.6	0.22	5.7
Ash-Bearing Siliceous Clay	185	1149	A	010H	03W	140–150	85	295	5.3	-22.0	0.25	8.4
Diatomaceous Clay	185	1149	A	011H	03W	140–150	93	365	4.8	-23.1	0.10	2.9
Ashley Clay	185	1149	A	012H	03W	140–150	104	400	5.0	-23.4	0.14	3.5
Silt-Bearing Clay	185	1149	A	013H	04W	18–20	113	281	4.7	-24.5	0.11	3.8
Ash-Bearing Clay	185	1149	A	014H	02W	140–150	121	240	4.7			
Clay (Bioturbated)	185	1149	A	015H	03W	104–106	135	281	3.9	-23.2	0.04	1.5
Clay (Bioturbated)	185	1149	A	016H	03W	140–150	142	214	3.7	-22.8	0.09	4.0
Clay (Bioturbated)	185	1149	A	017H	03W	110–112	151	329	4.6	-24.4	0.11	3.3
Clay (Bioturbated)	185	1149	A	018H	03W	123–125	160	340	4.7	-25.5	0.08	2.4
Clay (Bioturbated)	185	1149	A	018H	03W	140–150	161	335	4.9	-25.6	0.07	2.0
Silt-Bearing Clay	185	1149	A	019X	01W	58–60	165	285	4.5	-25.0	0.08	2.7
Silt-Bearing Clay	185	1149	A	020X	01W	140–150	171	259	4.9	-25.0	0.08	3.1
Zeolite-Rich Clay	185	1149	A	021X	01W	40–42	180	97	4.6	-28.1	0.16	16.7
Clay	185	1149	B	003R	04W	140–150	176	236	4.6	-24.6	0.09	4.0
Radiolarian Chert	185	1149	B	011R	01W	19–22	237	26	2.5			
Clay-, Ash- and Radiolarian-Bearing Nanofossil Marl	185	1149	B	016R	01W	93–98	283					
								15	2.7			29.7

Table 1. (continued)

Lithology ^a	Sample Identification			Section	Interval	Depth, mbsf	Nitrogen		Reduced Carbon		Carbonate		
	Leg	Site	Hole				Core	ppm	$\delta^{15}\text{N}_{\text{air}}$	$\delta^{13}\text{C}_{\text{VPDB}}$	Wt.%	$\text{C}_{\text{red}}/\text{N}$	$\delta^{13}\text{C}_{\text{VPDB}}$
Calcareous Radiolarian Marlstone	185	1149	B	020R	25–35	321					36	2.4	29.5
Nannofossil-Bearing Marlstone	185	1149	B	022R	20–25	340					12	2.8	28.5
Radiolarian Chert	185	1149	B	022R	106–110	341	18	3.0					
Clay-Bearing Nannofossil Chalk	185	1149	B	027R	49–55	388	23	4.0	–26.4	0.02	6.8	1.8	29.4
Radiolarian-Bearing nannofossil Marl	185	1149	B	028R	48–56	399					74	2.2	29.6
Nannofossil Marl	185	1149	B	029R	28–35	407					75	1.7	29.3
<i>Leg 129, Sites 800, 801, and 802</i>													
Pelagic Brown Clay	129	800	A	05R	14–20	32			–25.9	0.04			
Volcaniclastic Sandstone	129	800	A	26R	110	231			–26.2	0.54			
Volcaniclastic Siltstone	129	800	A	28R	80	248	661	–0.9					
Volcaniclastic Siltstone	129	800	A	30R	11–16	272	14						
Sandstone Breccia	129	800	A	41R	115	364	5						
Clay	129	800	A	53R	15	465	37	–0.2	–22.4	0.04	11.7		
Pelagic clay with Zeolites	129	801	A	03R	120–122	23	289	5.0	–24.7	0.06	2.1		
Pelagic Clay with Nannofossil Ooze	129	801	A	05R	120–122	44							
Volcaniclastic Sandstone/Claystone	129	801	A	16R	62–64	146	32		–26.7	0.07	21.4		
Volcaniclastic Sandstone/Claystone	129	801	B	01R	142–146	195	13		–26.0	0.0	38.4		
Volcaniclastic Claystone/Turbidite	129	801	B	05R	10–12	231							
Volcaniclastic Turbidite	129	801	B	06R	136–140	243	14					1.8	27.8
Volcaniclastic Turbidite	129	801	B	08R	125–127	262	22						
Red Radiolarite	129	801	B	33R	133–135	444	78	3.9			4.2		
Pelagic Claystone	129	802	ODP	38R	35	342	127	4.5					
Silty Claystone	129	802	ODP	47R	110	422	116	4.2					

^aLithological information from Lancelot et al. [1990] and Plank et al. [2000].

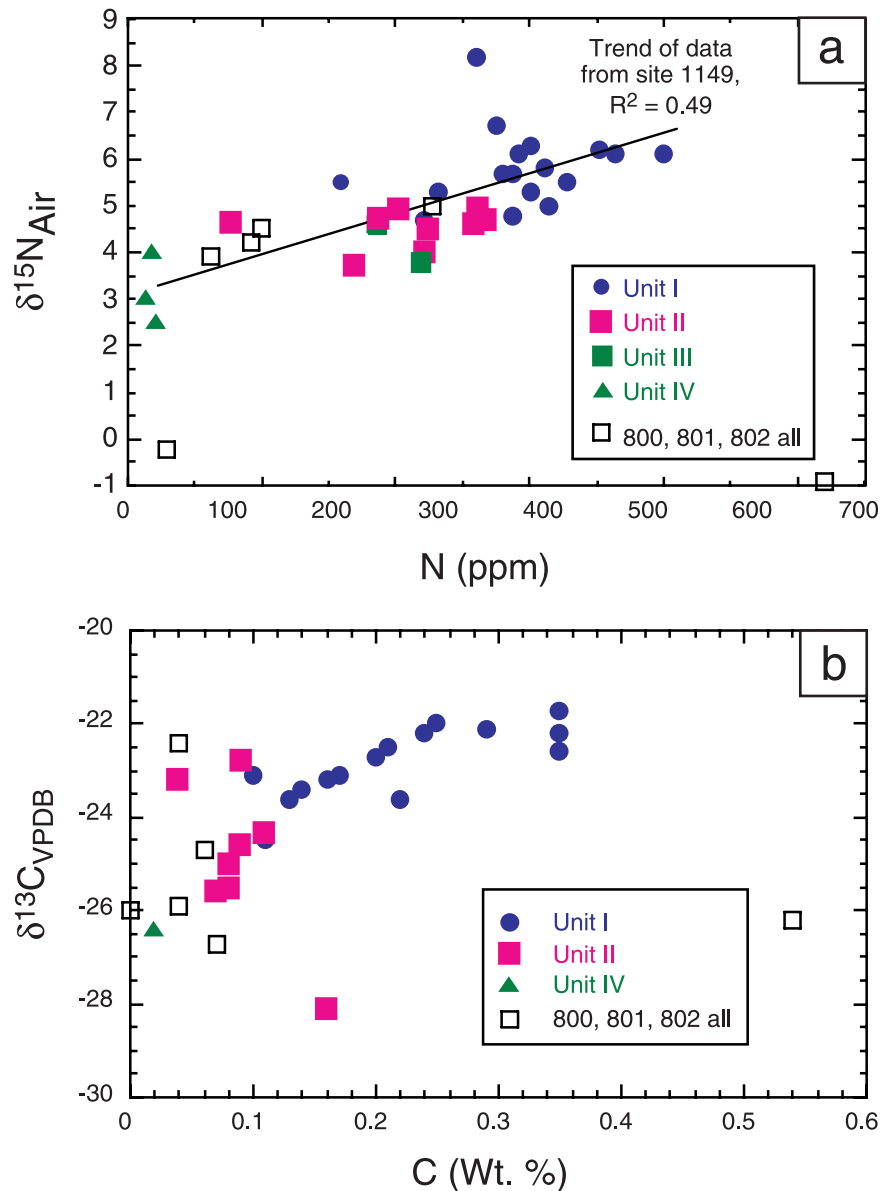


Figure 3. Whole-sediment N (a) and C (b) concentrations and corresponding isotopic compositions of all samples analyzed in this study (Sites 800, 801, 802, and mostly 1149), as a function of lithology (for lithologies of Sites 800, 801, and 802 samples, see Table 1).

2002]. Furthermore, although the waters affected by the Kuroshio current are higher in productivity, which could cause an increase in $\delta^{15}\text{N}$, they are also higher in nutrient supply, possibly mitigating the effects of productivity on marine $\delta^{15}\text{N}$ (see discussions by Farrell *et al.* [1995], Milder *et al.* [1999], Pride *et al.* [1999], and Ettwein *et al.* [2001]). Finally, it is unclear whether a change in productivity of this magnitude would produce a trend in C_{reduced}/N as seen in the data for Site

1149 (see discussions by Minoura *et al.* [1997], Milder *et al.* [1999], and Pride *et al.* [1999]).

[12] Variations in $\delta^{15}\text{N}$ similar to those at Site 1149 have been attributed in other studies to varying mixtures of terrestrial and marine organic matter [e.g., Peters *et al.*, 1978; Minoura *et al.*, 1997], with the marine component having $\delta^{15}\text{N}$ near +8‰, with $\delta^{13}\text{C}$ near -20.5‰, and the terrestrial component having $\delta^{15}\text{N}$ near +1.8‰,

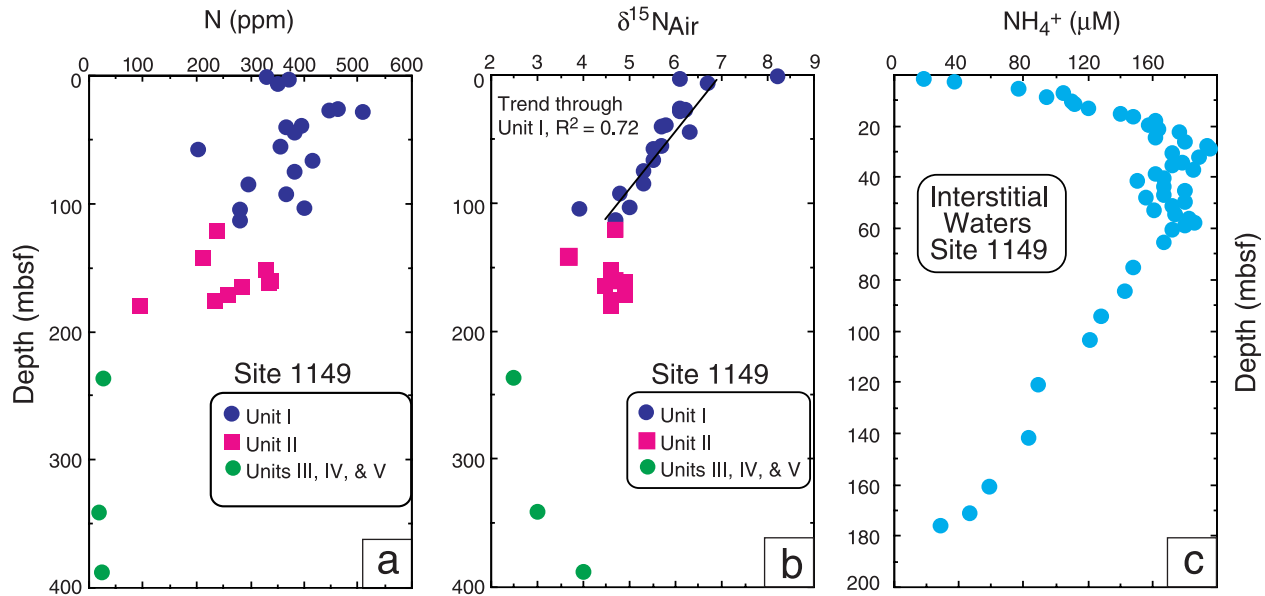


Figure 4. Nitrogen concentration and isotope data for the sediment section, and ammonium concentrations from the same depth interval, at Site 1149. (a) Sediment N concentration for Site 1149. Note slight trend toward lower N content as a function of depth. (b) Nitrogen isotopic composition of samples recovered from Site 1149. Note the shift in $\delta^{15}\text{N}$ in the upper ~ 100 mbsf, mostly within the ash- and biogenic-silica-bearing clay part of the section. Below 180 m depths, lithologies are radiolarian cherts and nannofossil chalk/marl, both containing low N concentrations with relatively low $\delta^{15}\text{N}$. (c) Ammonium concentrations in interstitial waters in the upper 200 m of the Site 1149 sediment section, demonstrating maximum concentrations near 50 m, resulting from organic breakdown, and decreased concentrations at greater depths related to sequestration by diagenetic clays (data from *Plank et al.* [2000]).

with $\delta^{13}\text{C}$ near -26.5% . The sediments analyzed in these two studies were deposited in settings more proximal to continental sources (for *Peters et al.* [1978], on the NE Pacific continental shelf; for *Minoura et al.* [1997], near Japan in the Japan Sea), and we consider the significant additions of terrestrial organic matter to the Site 1149 sediments (and certainly the sediments obtained on Leg 129) less likely. It is uncertain whether the volcanic ash-rich sediments deposited at Site 1149 contained appreciable terrestrial organic matter during their deposition (see discussion of sediment sources at Site 1149 by *Urbat and Pletsch* [2003]). However, this possible mixing warrants further study, and more detailed biogeochemical work could help elucidate the sources of the organic matter [e.g., *Madureira et al.*, 1997; *Meyers and Doose*, 1999; *Shipboard Scientific Party*, 2000]. In Figure 6, we compare the $\delta^{15}\text{N}$ - $\delta^{13}\text{C}$ data for the upper part of the Site 1149 section with the “Marine” and “Terrestrial” organic end-members proposed by *Minoura et al.*

[1997] (very similar to the end-members proposed by *Peters et al.* [1978]). From this comparison, in particular based on the relative scatter of the Site 1149 data about the mixing line for these two end-members, it is apparent that the Site 1149 sediments do not show a simple marine-terrestrial mixing behavior. The Site 1149 data do show some correlated variation, however (see Figure 6; noted above), and when three outliers are removed from consideration (indicated in boxes on Figure 6), the data show a linear relationship ($r^2 = 0.60$) with a slope quite different from that of the mixing line of *Minoura et al.* [1997]. The data in Figure 6 for Franciscan metasedimentary rocks are discussed in section 4.2. Finally, vascular land plants typically have C/N higher than that of algae [see *Meyers and Doose*, 1999, and references therein], and a down-section increase in the terrestrial organic component would thus have likely resulted in an *increase* in C/N rather than the observed *decrease* in C/N at Site 1149 (see Figure 5c). Furthermore, the $C_{\text{reduced}}/\text{N}$ values for

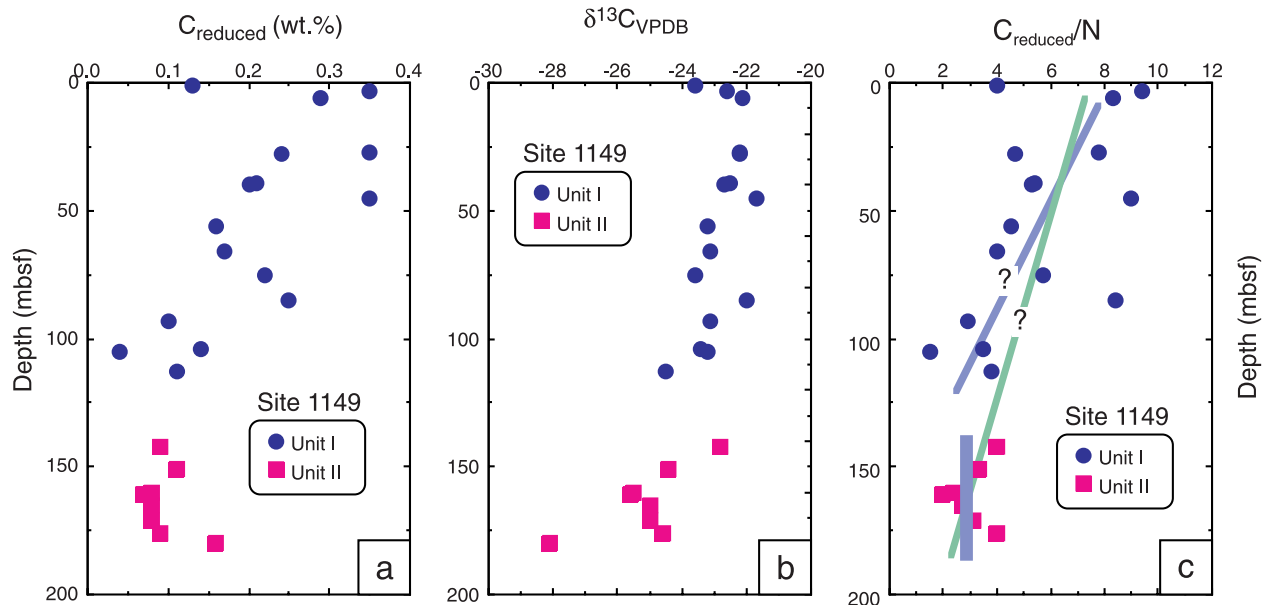


Figure 5. Carbon concentration and isotope data for the upper 180 m of the sediment section at Site 1149. (a) Sediment C concentration for Site 1149. Note slight trend toward lower C content as a function of depth. (b) Carbon isotopic composition of samples recovered from Site 1149. Note the shift in $\delta^{13}\text{C}$ in the upper ~100 mbsf, mostly within the ash- and biogenic-silica-bearing clay part of the section. Below 180 m depths, lithologies are radiolarian cherts and nanofossil chalk/marl. (c) C_{reduced}/N ratios (by weight) as a function of depth (mbsf) in the upper 180 m of the Site 1149 sediment section. Colored lines indicate two possible weak down-section trends, with either all of the variation occurring in the upper 120 m (the two separate blue lines), or a more continuous trend toward lower C_{reduced}/N over the depth interval shown in this figure (green line).

the Site 1149 sediments (2–9 on atomic basis) fall in the range for algae (4–10 on atomic basis) and not in the range of significantly higher C/N for vascular land plants (≥ 20 on atomic basis [Meyers, 1994; Meyers and Doose, 1999]).

4.1.2. Diagenetic Processes

[13] A third possibility is that the shift in $\delta^{15}\text{N}$ values in the sediments recovered from the upper part of the Site 1149 section (Site 1149A), with $\delta^{15}\text{N}$ decreasing steadily within the uppermost 120 m (Unit I) from +8.2‰ at 1.4 mbsf to +4.7 at 113 mbsf (Figure 4b), is due to complex diagenetic processes, conceivably with superimposed more minor effects of the two oceanographic alternatives presented above (changes in productivity related to ocean currents and/or deposition of differing proportions of marine and terrestrial organic fractions). The down-section change in $\delta^{15}\text{N}$ at Site 1149 is accompanied by a decrease in total N concentration (Figure 4a), which could reflect the loss of N with $\delta^{15}\text{N}$ significantly higher than

+8‰, perhaps a nitrate component. Reduced-C concentrations and $\delta^{13}\text{C}$ also decrease slightly with increasing depth in the upper 150 m of site 1149, contributing to a subtle down-section trend in C_{reduced}/N , and indicating some parallel behavior throughout the organic reservoir. Together, the shifts in reduced C, total N, and C_{reduced}/N with increasing depth at Site 1149 are compatible with the shifts in the same parameters over similar depth horizons reported for other Pacific Ocean deep-sea sediment cores and attributed to diagenesis [Muller, 1977; Waples and Sloan, 1980; Waples, 1985] (unfortunately, N and C isotope data were not obtained in these previous studies). A full explanation of these organic geochemical phenomena, and a more comprehensive reconstruction of diagenesis in this section, would require analyses of separated organic and inorganic N fractions (see studies by Muller [1977], Waples and Sloan [1980], and Williams *et al.* [1995]) and a more comprehensive consideration of the chemical compositions of the interstitial waters from the sediment cores.

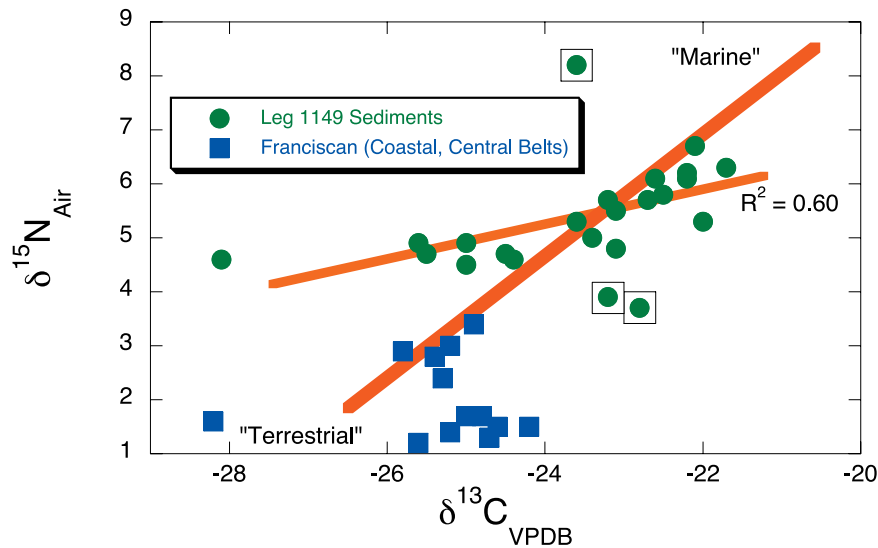


Figure 6. Plot of $\delta^{15}\text{N}$ vs. $\delta^{13}\text{C}$ of the upper part of the sediment section at Site 1149, compared with the mixing line (thicker, red line) between “Terrestrial” and “Marine” organic components proposed by *Minoura et al.* [1997; cf. *Peters et al.*, 1978]. When the three outliers indicated in the small boxes (the sediment sample from 1 mbsf, and two bioturbated clays from near 135–142 mbsf) are removed from consideration, an r^2 of ~ 0.60 is obtained for the Site 1149 data (see thinner, orange line), but the slope of this line differs significantly from that of the mixing line of *Minoura et al.* [1997]. The data for low-grade Franciscan Complex metasedimentary rocks plot near the “Terrestrial” organic component of *Minoura et al.* [1997], consistent with the known deposition of the Franciscan sediments near the continental margin in W. North America.

However, some reasonable speculation would be that the shift in $\delta^{15}\text{N}$, and the associated other variations in the C-N signature, are the result of diagenesis, perhaps a microbially mediated reprocessing of organic matter such as that suggested to occur in algal mats [*Lehmann et al.*, 2002].

[14] The results of *Lehmann et al.* [2002] deserve particular notice in this context for the similarity of results despite experimental conditions that differ significantly from the natural conditions in Site 1149. This study consisted of experimental simulations of early diagenesis of algae under varying redox conditions. These authors found minor shifts in concentration of C and N, during early diagenesis, and fairly significant changes in isotopic composition, including a shift in $\delta^{15}\text{N}$ of $\sim 3\text{‰}$ under anoxic conditions after 60 days. The similarity of the results of our study, showing shifts in $\delta^{15}\text{N}$ of $\sim 3\text{‰}$ in a 120 m sediment column and the *Lehmann et al.* [2002] study conducted at different pressures and temperatures, and at very different timescales, suggests that a shift in $\delta^{15}\text{N}$ could be a common feature of early diagenesis in

off-trench, deep-sea sediment sections, and that the magnitude of the negative shift (depending on a variety of conditions, notably the redox state) could conceivably be on the order of $\sim 1\text{--}3\text{‰}$. At Site 1149, the release of organic N, presumably related to the N and $\delta^{15}\text{N}$ shifts reported here, is recorded by the slight enrichments (up to $\sim 200\ \mu\text{M}$) in dissolved NH_4^+ in the interstitial waters, the overall chemistry of which has led to the conclusion that the Site 1149 diagenetic environment is slightly suboxic [*Plank et al.*, 2000]. Dissolved NH_4^+ in the waters (see Figure 4c) reaches a maximum through the upper 50 mbsf, reflecting N release during organic matter degradation, and the decreased dissolved NH_4^+ below this interval reflects enhanced uptake during clay diagenesis [*Plank et al.*, 2000].

4.2. Comparison of N Signature in Deep-Sea Sediments With That in Paleoaccretionary Rocks

[15] Although $\delta^{15}\text{N}$ is relatively high and highly variable in surface/near-surface oceanic sediments (with some values $>+10\text{‰}$; see Figure 2), the low grade, forearc metasedimentary rocks studied to

date appear to have a much narrower range of $\delta^{15}\text{N}$ values mostly lower and between +1 and +3‰ [Bebout and Fogel, 1992; Bebout, 1997; Bebout *et al.*, 1999a; Sadofsky and Bebout, 2003] (see comparisons in Figure 2). This “disconnect” between the $\delta^{15}\text{N}$ values of many oceanic sediments (see Figures 2–4), mostly from relatively near the sediment-water interface, and the values for low-grade metamorphosed deep-sea sediments in forearc metamorphic suites (representative data in Figure 2) could result from several factors. First, many of the deep-sea sediment sections analyzed previously and in the present study, are not representative of the near-continent, trench settings with high sedimentation rates resulting in the voluminous trench sediment and accretionary prisms sampled by the forearc metamorphic rocks (e.g., Catalina Schist, Franciscan Complex, Western Baja Terrane [see Sadofsky and Bebout, 2003]). Enhanced contributions of terrestrial organic matter (with lower $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ than marine organic matter) must be considered a factor when comparing the seafloor sediment data with the N and C isotope data for the circum-Pacific forearc metamorphic rocks as the metamorphosed voluminous clastic sediments in these metamorphic suites were deposited near a continental margin. Correspondingly, the $\delta^{15}\text{N}$ values of these low-grade forearc metamorphic rocks generally fall in the range of +1 to +3‰, and with low $\delta^{13}\text{C}$, quite near the “Terrestrial” organic component proposed by Peters *et al.* [1978] and Minoura *et al.* [1997] (see Figure 6). As another alternative, diagenesis (more pronounced with increasing depth), and conceivably also, incipient low-grade metamorphism during very early subduction history (perhaps in part accompanying mechanical fluid expulsion at shallow levels of accretionary prisms), shifts the $\delta^{15}\text{N}$ of the initially high- $\delta^{15}\text{N}$ seafloor sediments from their near-surface values ($\delta^{15}\text{N}$ near +8 per mil [see Libes and Deuser, 1988; this study] (Figure 4) toward values similar to those observed for the low-grade metamorphic equivalents, which represent subduction to depths of ~5–40 km. We propose (see section 4.1.2) that the variation in $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ (Figure 6) and C and N concentrations and C_{reduced}/N in the Site 1149 sediment section largely reflects diagenesis, possibly with

some lesser superimposed variation due to changes in primary productivity and marine-terrestrial organic sources. However, it appears extremely likely that the lower whole rock $\delta^{15}\text{N}$ (and the $\delta^{13}\text{C}$ of the reduced C) of the forearc metasedimentary rocks, relative to that for many marine sediments and most of the sediment section at Site 1149 (see comparison in Figure 2), is largely attributable to greater proportions of terrestrial organic matter in the forearc metamorphic suites deposited nearer a continental sediment source (perhaps with superimposed minor effects of diagenesis).

4.3. Mass Balance Calculations and Implications for Fluxes Into Subduction Zones

[16] Because there are significant variations in the concentrations and isotopic compositions of N and C throughout these sedimentary sections, the calculation of the fluxes of these elements into the IBM subduction zone is not straightforward. The approach that we favor is to use shipboard estimates of the lithologic units, including the thickness of these units (and average densities of the materials), and average all measured values for each lithological layer (see Table 2). We present only data from Site 1149 in these calculations. We will assume that a section like that at Site 1149 is subducted and not take the apparent shift in shift in $\delta^{15}\text{N}$ as a function of depth into account at this time, because of the difficulty of deciding the cutoff for which samples to include and which to leave out. We suspect that the actual $\delta^{15}\text{N}$ and N concentration could be slightly lower than the values used in the calculations we present below, but that the magnitudes of the differences produced by these small changes are at this point within error in any likely application of these data ($<\pm 0.5\%$ for $\delta^{15}\text{N}$, $<5\%$ relative for the mass of N subducted).

[17] To calculate the fluxes of C and N entering the subduction zone at the Izu trench, we begin by separating the materials into three general categories chosen to reflect the resolution of the sampling in this particular study. These categories are: Ash and diatomaceous clay (~120 m thick, Unit I at site 1149); Dark brown pelagic clay (~60 m, Unit

Table 2. Estimated Annual Sedimentary N-C Subduction Flux at the Izu Margin

	Thickness, m	N, ppm	$\delta^{15}\text{N}_{\text{Air}}$	$\text{C}_{\text{reduced}}$, wt. %	$\delta^{13}\text{C}_{\text{VPDB}}$	Average Density ^a
<i>Average</i>						
Ash and diatom/rad clay (1149 Unit I)	120	371	5.8	0.22	-22.8	0.641
Dark brown pelagic clay (1149 Unit II)	60	261	4.5	0.09	-25	0.695
Chert and marl layers (1149 Units III, IV, and V)	230	22	3.2	0.02	-24.8	2.04
		N, g	$\delta^{15}\text{N}_{\text{Air}}$	C, g	$\delta^{13}\text{C}_{\text{VPDB}}$	
<i>Fluxes (per Linear km)</i>						
Fluxes (for C only reduced C)		2.5E + 06	5.0	1.4E + 07	-24.0	
Calcite C flux, marl layers				9.2E + 08	2.3	
Total C flux (full section)				9.3E + 08	1.9	
<i>Total Fluxes (Over 1050 km Linear Trench Length)</i>						
This study		2.6E + 09	5.0	9.8E + 11	1.9	
Hilton <i>et al.</i> [2002]		5.8E + 09	7.0 subarc	6.2E + 11	0, -20 ^b	

^aThe average density, used in these calculations, is equal to bulk density minus the pore water content of a given depth interval. This takes into account the actual density of grains and the porosity. High porosity in the upper part of the section leads to low density of the actual sediment (solids).

^bHilton *et al.* [2002] use values of 0‰ and -20‰ for “carbonate” and “sedimentary/organic”, respectively (also see discussion by Van Soest *et al.* [1998]).

II, 1149); Radiolarian chert, zeolite-rich clay and marl layers (~230 m). Multiplying the thicknesses of these units by the orthogonal convergence rate of 5 cm/yr (see compilation of convergence rates by Plank and Langmuir [1998]), and the average dry densities for each unit (values from Plank *et al.* [2000]) allows a simple calculation of the mass of each lithology entering the subduction zone. Note that the volumes are multiplied by dry density to remove porosity (quite high in the upper 180 m) and pore water from the discussion, we assume for simplicity that all pore water is lost during the early stages of subduction. Average concentrations of C and N can then be combined with our knowledge of the mass of that lithology being subducted to determine the masses of C and N entering the subduction zone in solids. Simple averages of the $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values in each lithology are used to calculate an average isotopic composition for each unit. The mass of carbonate was calculated by averaging the shipboard analyses of carbonate content for the mixed carbonate/siliceous layers, combined with the isotopic compositions presented in Table 1.

[18] On the basis of these mass balance calculations, carried out using the orthogonal convergence

rate of 5 cm/yr [Plank *et al.*, 2000] (Table 2), we suggest that a sedimentary section like that at Site 1149 delivers an annual flux into the subduction zone of 2.5×10^6 g of N and 1.4×10^7 g of reduced C per linear km of trench, with average $\delta^{15}\text{N}$ of +5.0‰ and $\delta^{13}\text{C}$ of -24.0‰, respectively. In addition, 9.2×10^8 g/yr of C is subducted per linear km in carbonate-rich layers of 1149B with average $\delta^{13}\text{C}$ of +2.3‰. Because of the relatively low C content of the clastic units and the fairly thick carbonate section, the carbonate (oxidized C) budget overwhelms the reduced C budget at this site and 9.3×10^8 g/yr per linear km are input into the subduction zone with an average $\delta^{13}\text{C}$ of +1.9‰ near that of the carbonate-rich horizons. The overall $\text{C}_{\text{total}}/\text{N}$ of the subducting sediment is near 370:1 (including both reduced and oxidized C reservoirs), the $\text{C}_{\text{oxidized}}/\text{C}_{\text{reduced}}$ is ~65:1, and the $\text{C}_{\text{reduced}}/\text{N}$ (organic component) is ~5.6:1. The total N flux into the Izu-Bonin convergent margin, for a trench length of 1050 km [from Plank and Langmuir, 1998], is calculated at 2.62×10^9 g/yr, considerably smaller than the flux of 5.8×10^9 g/yr calculated by Hilton *et al.* [2002], who estimated concentrations for subducting sediments (using 100 ppm for the entire sediment section of 400 m) and used

a somewhat larger sediment flux into this margin (4.18×10^{13} g/yr compared with our use of 3.09×10^{13} g/yr).

[19] A more complete inventory of the incoming N and C budgets in the IBM convergent margin will require analyses of AOC from Sites 801 and 1149. $\delta^{15}\text{N}$ for MORB glass from the East Pacific Rise ranges from -1.0% to -6.5% (mean of $\sim -3.0\%$, $n = 7$ [Marty and Humbert, 1997]), with N_2 concentrations of $3\text{--}65 \times 10^{-10}$ moles/gram (<0.5 ppm) and concentrations of NH_4^+ in spilites (perhaps analogues to some seafloor basalts) from SW England are as high as 182 ppm (range of 1–182 ppm, with mean N concentration of 53 ppm [Hall, 1989, 1990]). These concentrations may represent the extremes for fresh seafloor basalt (with the baseline of 0.01–1.0 ppm N) and the most highly altered oceanic basalt (with up to ~ 200 ppm N), and the alteration in AOC at Sites 801c and 1149 is likely to be intermediate in extent. The high K_2O values reported for the crustal sections from ODP Site 801c (which experienced an increase of K_2O by 17% due to alteration) and 1149 (which is more heavily altered than 801c) provide an indication that AOC may contain appreciable N that could figure significantly in the subduction flux models. This may be especially true when one considers the large volume/mass of oceanic crust being subducted (~ 6 km section); any elevation in N concentration (due to hydrothermal alteration) above the maximum ~ 0.5 ppm levels observed in fresh basalt glass [Marty and Humbert, 1997] could result in the subduction of N in AOC rivaling that subducted in thin, shale-poor (e.g., carbonate or chert rich) sediment sections (see Bebout [1995, Table 2] and discussions below). However, these elevated N concentrations are likely to occur only within the uppermost, more hydrothermally altered 1 km of the subducting oceanic crust (see discussion below).

[20] Our study demonstrates the importance of evaluating subduction inputs through analyses of the materials outboard of individual trenches and thought to be subducting in any attempts to chemically mass balance individual convergent margins. As in the case of the considerations of

pre-subduction sediment $\delta^{15}\text{N}$, which can vary with a number of sedimentological and diagenetic factors (discussed above), the use of a single sediment N concentration as applicable in considerations of inputs and outputs at multiple convergent margins from quite different tectonic and sedimentological environments could easily yield flawed results. Our C and N input flux estimates, based on analyses of the Site 1149 section, differ significantly from recent estimates of C-N inputs based on generalized assumptions regarding C and N concentration made without the benefit of data for the sediment at this margin (latter estimates by Hilton *et al.* [2002]; see comparisons in Table 2). Attempts to deduce overall efficiencies of N and C return in arc volcanic gases are highly susceptible to uncertainties in the input (and output) estimates, as can be demonstrated for the Central American arc-trench system for which Fischer *et al.* [2002] recently claimed extremely efficient volcanic arc return of sedimentary N. Using N concentration data for only the upper 160 m of the section at Site 1039, Li *et al.* [2003] obtained a sedimentary N subduction rate of 9.9×10^9 g/yr (for the 1100 km of trench length). Use of even a quite low concentration for the lower, carbonate-rich section would significantly increase this flux estimate (work on the lower section is in progress). In comparison, Fischer *et al.* [2002] employed a smaller input rate of 2.4×10^9 g/yr, using an averaged N concentration of 100 ppm for the upper 175 m of the section (and assuming no N in the lower section) in their comparison with arc N outputs in Central America. Fischer *et al.* [2002] claimed similarity of their input of 2.4×10^9 g/yr with their estimate of arc output of 4.1×10^9 g/yr, and speculated that this similarity reflects extremely efficient return of subducted sedimentary N.

[21] It is worth noting that the $\delta^{15}\text{N}$ of $+7\%$ used by Fischer *et al.* [2002] and Snyder *et al.* [2003] for sediment contributing to arc magmatism is higher than those of both the aggregate sediment sections at Sites 1149 (IB) and 1039 (Central America; bulk $\delta^{15}\text{N}$ of $+5.0\%$ and $+5.6\%$, respectively for the two margins [see Li *et al.*, 2003]) and the shallowly subducted paleoaccre-

tionary rocks (+1 to +3‰; see Figure 2), a difference that could be related to increase in $\delta^{15}\text{N}$ during metamorphic N losses (see examples of this relationship by *Haendel et al.* [1986], *Bebout and Fogel* [1992], *Bebout et al.* [1999b], and *Mingram and Brauer* [2001]). These metamorphic N losses would affect the efficiency with which the seafloor sediment N inventory is conveyed to depths beneath arcs, and thus any mass balance employing seafloor sediment as input and arc gases as output. Regarding the input fluxes in subduction zones, it worth noting that all of the estimates of sediment geochemical inputs assume uniformity in the incoming sediment sections along-strike in active trenches, known not to be the case.

[22] We suggest that the apparent similarity in sediment N input with arc volcanic outputs reported by *Fischer et al.* [2002] for Central America could be partly coincidental, reflecting significant contributions from both sediments and devolatilizing AOC or significant errors in input or output estimates. Given the uncertainty of this N flux in AOC (see consideration by *Bebout* [1995]), the overall Central American mass balance of N inputs and arc outputs cannot be addressed in entirety; we estimate a N subduction rate of 1.7×10^{10} g/yr in AOC (four times the sedimentary flux for the same margin), using an estimated N concentration of 10 ppm for the crustal lithology. Use of the total sediment + AOC input (2.7×10^{10} g/yr), based on this 1.7×10^{10} g/yr flux in AOC and the sediment N input flux of 9.9×10^9 g/yr (see above), a ~15% arc return of subducted N would be indicated (incorporating the arc output rate of 4.1×10^9 g/yr from *Fischer et al.* [2002]). If the AOC N concentration is reduced to 5 ppm, a ~22% return in arcs would be indicated, and an ~36% N return in arcs is indicated if a concentration of 1 ppm N is assumed for the AOC. This crude set of comparisons highlights the dire need for any constraints on the total flux and isotopic composition (for both N and the noble gases) of the AOC volatiles component. Direct use of our information regarding N inputs into the Izu-Bonin convergent margin to mass balance with N outputs in the corresponding arc

awaits investigation of arc volcanic gases in this margin.

4.4. Fate of Subducted Sedimentary Nitrogen in the Izu-Bonin Margin (and Other Convergent Margins)

[23] Studies of low-grade metasedimentary suites in paleoaccretionary complexes in Western North America shed some light on the degrees of deep subduction of N in sediment and the stable isotope compositions of this N. Recent study of devolatilization in sedimentary lithologies subducted to 5–40 km depths in the Catalina Schist, California, the Franciscan Complex, California (Coast Ranges), and the Western Baja Terrane, Mexico [*Sadofsky and Bebout*, 2003] (see estimated peak P-T ranges in Figure 7), affords an assessment of the entrainment of N into forearc regions of a relatively “cool” subduction zone. Interestingly, samples from the Coastal Belt, the lowest-grade unit in the Coast Ranges subducted to only ~5 km depths, show correlated $\delta^{15}\text{N}$ and N concentration (see Figure 8a), conceivably reflecting differential loss of “heavy” N (as NO_3^- ?) during diagenesis and extremely low-grade metamorphism accompanying subduction to these extremely shallow levels [see *Sadofsky and Bebout*, 2003]. Moving up-grade in the Coast Ranges, the more uniform $\delta^{15}\text{N}$ of the somewhat higher-grade (more deeply subducted; see Figure 7) Central and Eastern Belt metasedimentary rocks (near +1.5‰) could reflect the more complete loss of this “heavy” component (see data for the three Coast Ranges units in Figure 8a).

[24] Carbon_{reduced}/nitrogen ratios are another useful indicator of the devolatilization of these elements, as both of these elements are provided to the sedimentary rocks largely by organic processes. Most deep-ocean sediments should have C_{reduced}/N ratios <20:1 [*Muller*, 1977; *Sweeney et al.*, 1978; *Waples and Sloan*, 1980], and the vast majority of the high-P/T metasedimentary suites fall into that range (see Figure 8b). The Coastal Belt samples have C_{reduced}/N more uniform than that of the higher-grade units (see the line for Coastal Belt samples on Figure 8b), fully within the range for

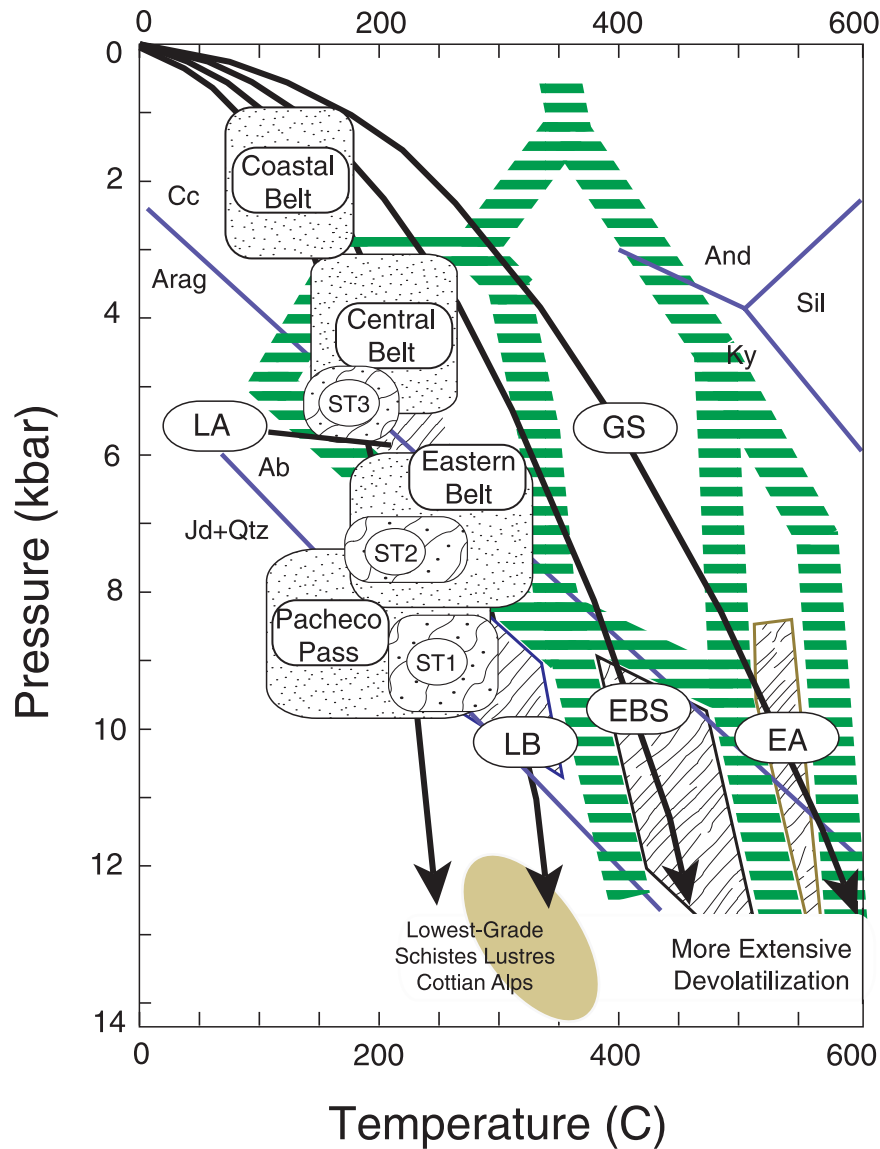


Figure 7. Pressure-temperature diagram showing estimates of peak metamorphism for low-grade paleoaccretionary prism rocks from California, USA, and Mexico (see *Grove and Bebout* [1995] for details regarding the generalized phase equilibria and stability fields compiled on this diagram). Arrows are schematic prograde P-T paths rocks take in subduction zones, reflecting a wide range in thermal structure; for the Catalina Schist, California, these paths are inferred to reflect rapid cooling in an incipiently formed subduction zone, with warmer conditions first producing the highest-temperature epidote-amphibolite-facies unit (labeled as “EA”) and latest-stage, cool subduction producing the lawsonite-blueschist and lawsonite-albite facies units (labeled in this figure as “LBS” and “LA”, respectively). Various units of the Coast Ranges Franciscan Complex are indicated (“Coastal Belt”, “Central Belt”, and “Eastern Belt”, in order of increasing peak metamorphic pressures thus depths of underthrusting [see *Sadofsky and Bebout*, 2003; *Blake et al.*, 1987]). Also indicated is the peak P-T for the Franciscan Complex metagreywackes at Pacheco Pass, California (estimates from *Ernst* [1993]). Fields labeled “ST1”, “ST2”, and “ST3” indicate peak conditions for tectonometamorphic units of the Western Baja Terrane [from *Sedlock*, 1988], with “ST3” representing the lower-P conditions in this suite.

modern seafloor sediments, and perhaps indicating that the loss of isotopically “heavy” N producing the decrease in whole rock $\delta^{15}\text{N}$ did not result in significant shifts in the $C_{\text{reduced}}/\text{N}$ of the same rocks

(i.e., the $\delta^{15}\text{N}$ of the N that was lost was significantly higher than that left behind in the sediments). The higher-grade units in the Coast Ranges show scatter in $C_{\text{reduced}}/\text{N}$ and shifts mostly

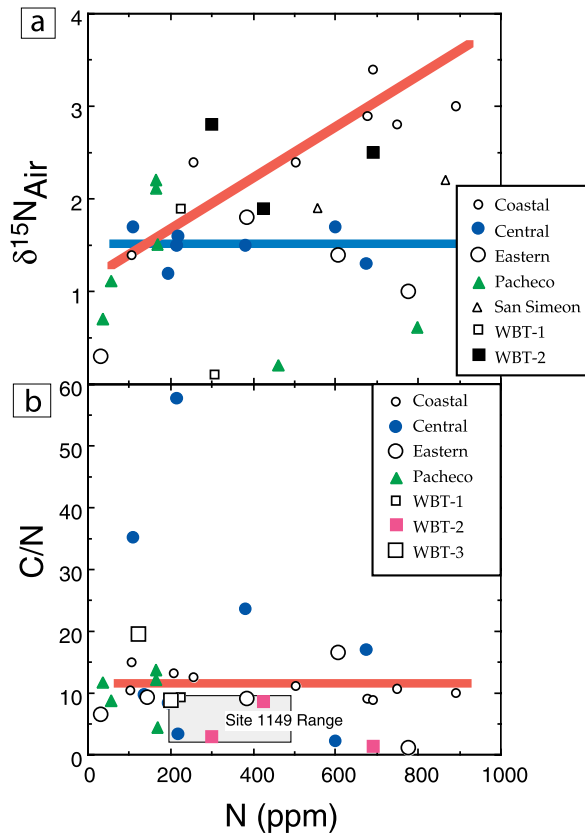


Figure 8. Nitrogen concentration and isotope compositions and C_{reduced}/N of subduction-zone metasedimentary rocks, and comparison with data for the Site 1149 sediments. (a) $\delta^{15}\text{N}_{\text{Air}}$ versus whole-sediment N concentration, illustrating differences among the tectonometamorphic units of the Franciscan Complex and Western Baja Terrane, Mexico [from *Sadofsky and Bebout, 2003*]. (b) C_{reduced}/N versus N concentration for metasedimentary rocks from the same units, demonstrating the extremely uniform C_{reduced}/N for the lowest grade rocks in the Coastal Belt, for which peak metamorphic temperatures are $<200^\circ\text{C}$ at approximately 5 km maximum depths of underthrusting. $\delta^{15}\text{N}$ values are similar to those expected in sediments with organic matter derived primarily from photosynthesizing organisms [see *Rau et al., 1987*]. Metamorphic devolatilization of N would be expected to produce a trend of increasing $\delta^{15}\text{N}$ with decreasing N content as N bearing fluids (likely with N_2 as the dominant N fluid species) preferentially fractionate the lighter isotope [see *Bebout et al., 1999a, 1999b*]. Also indicated in this figure is the range of C_{reduced}/N and N concentrations in the Site 1149 sediment section (data for the upper 180 m only).

to higher C_{reduced}/N relative to C_{reduced}/N of the lowest-grade Central Belt, perhaps reflecting the effects of deeper metamorphic devolatilization (i.e., at depths of 10–40 km).

[25] Yet unknown is the extent of N loss, and accompanying shift in $\delta^{15}\text{N}$, that occur during subduction of sedimentary lithologies to depths greater than those represented by the circum-Pacific paleoaccretionary suites we've examined (i.e., at depths >40 km). *Busigny et al. [2003]* reported whole rock and mica separate $\delta^{15}\text{N}$ values of +2.6 to +4.8‰ for metasedimentary samples of the Schistes Lustres (and metasedimentary rocks at Lago di Cignana, both exposed in NW Italy) subducted to depths corresponding to pressures of 1.5 to 2.5 GPa (approximately 60–90 km). Although the interpretation of the data for the Schistes Lustres and at Lago di Cignana is complicated by the variable, in some cases extreme, overprinting that occurred during exhumation of these rocks [*Reinecke, 1998; Agard et al., 2002; Bebout et al., 2003*], these somewhat higher values (relative to those for the lower-P suites studied by *Bebout and Fogel [1992]* and *Sadofsky and Bebout [2003]*) could conceivably reflect some increase due to small amounts of N loss during subduction to these greater depths. However, *Busigny et al. [2003]* also analyzed presumed non-metamorphic equivalents, and because the $\delta^{15}\text{N}$ values of these sediments are similar to those of the metamorphosed rocks, argued for no change in $\delta^{15}\text{N}$ in sediments subducted to depths approaching 90 km. Confirmation of whether these data for the Schistes Lustres do reflect deep subduction, without appreciable geochemical effects of exhumation-related overprinting, awaits a more detailed investigation of mineral chemistry (and single-grain $\delta^{15}\text{N}$ and trace element compositions) in these rocks. As briefly discussed above, recent studies of arc volcanic gases have employed $\delta^{15}\text{N}$ values of near +7‰ for the deeply subducted sedimentary N component [see *Fischer et al., 2002; Snyder et al., 2003*], and calculations of N isotope shifts due to metamorphic devolatilization at temperatures of less than 300°C (by Rayleigh or batch loss) can easily produce shifts of 3–4‰ (i.e., shifts in $\delta^{15}\text{N}$ from +3 to +7‰, perhaps with loss of $<25\%$ of the initially subducted N (see calculations by *Bebout and Fogel [1992]* and *Bebout et al. [1999a, 1999b]*; at $T < 300^\circ\text{C}$, $10^3 \ln \alpha_{\text{NH}_4^+ - \text{N}_2}$ is $>4\%$, based on the calculations of *Hanschmann [1981]*). These relatively small amounts of loss could be

difficult to identify in metamorphosed sediments, given the large degree of variability thought to represent variation in the isotopic composition of the seafloor sediment protoliths.

[26] It is appropriate to briefly discuss the extent to which our data, and recent work on subduction-zone metamorphic suites, can elucidate N cycling at the Izu-Bonin margin. For this margin (at 32°N), *Peacock* [2003] calculated temperatures at the slab-mantle interface of ~245°C at 50 km depths and ~540°C at sub-arc depths (~120 km). Thus, for reference, only the lowest-T paths shown in Figure 7 (resulting in temperatures of just over 200°C at depths approaching 40 km) mimic the prograde paths thought to be experienced in this relatively “cool” convergent margin. Even the P-T path experienced by the somewhat higher-grade lawsonite-blueschist-facies unit of the Catalina Schist (patterned field labeled as “LBS” on Figure 7) is somewhat higher-T than would be expected in this modern subduction zone. On the basis of the calculated P-T paths of *Peacock* [2003], nearly all of the Cottian Alps Schistes Lustres (peak conditions, 300–625°C, 50–70 km [*Agard et al.*, 2002]) and the rocks at Lago di Cignana (peak conditions, ~625°C, 90 km [see *Bebout and Nakamura*, 2003]), appear to have experienced peak metamorphic temperatures somewhat higher than those indicated for their respective maximum depths in the modern Izu-Bonin margin. However, the tectonometamorphic units in the Cottian Alps Schistes Lustres traverse studied by *Agard et al.* [2002], *Busigny et al.* [2003], and *Bebout et al.* [2003], combined with the Lago di Cignana rocks [studied by *Bebout and Nakamura* [2003] and *Busigny et al.* [2003]], certainly do cover a range of peak P-T broadly compatible with the P-T calculated for the slab-mantle interface in modern subduction zones (see the P-T field for only the lowest-grade unit of the Cottian Alps Schistes Lustres on Figure 7).

[27] In the Catalina Schist, even in the lawsonite-blueschist-facies metasedimentary unit (labeled “LBS” in Figures 2 and 7; peak conditions of 350°C at pressures corresponding to ~40 km), $\delta^{15}\text{N}$ values appear slightly higher than those in

lawsonite-albite-facies equivalents experiencing “cooler” prograde P-T paths and lower peak metamorphic temperatures of <250°C (see schematic prograde P-T paths in Figure 7). The Schistes Lustres rocks, metamorphosed at temperatures >300°C but at higher pressures, are similarly somewhat higher in $\delta^{15}\text{N}$ than the units of the Franciscan Complex and Western Baja Terrane, the latter for which peak temperatures are roughly consistent with peak recrystallization at shallower levels of 5–40 km in the modern Izu-Bonin subduction zone (again, 245°C at 50 km calculated by *Peacock* [2003]). However, *Busigny et al.* [2003] suggest that the protoliths for the Schistes Lustres had $\delta^{15}\text{N}$ higher than that of the protoliths for the metasedimentary rocks of the Catalina Schist, Franciscan Complex, and Western Baja Terrane. Together, the work on the circum-Pacific suites [*Bebout and Fogel*, 1992; *Sadofsky and Bebout*, 2003] and the work on the Schistes Lustres [*Busigny et al.*, 2003] appear to demonstrate the impressive compatibility of ammonium ions in micas (see discussion by *Boyd* [2001]), suggesting that efficient deep entrainment of N into convergent margins is facilitated by the extremely broad stability range of particularly the white micas (see experimental study of the stability relations of phengitic muscovite by *Domanik and Holloway* [2000]).

[28] Overall, given the likelihood that even small amounts of N loss can potentially result in significant shifts in sediment $\delta^{15}\text{N}$ (discussion above), and taking into account the systematics in circum-Pacific paleoaccretionary suites (Catalina Schist, Franciscan Complex, Western Baja Terrane; +1 to +3‰ in sediments subducted to 5–40 km) and the results presented by *Busigny et al.* [2003] (somewhat higher values of +2.6 to +4.8‰ in sediments subducted to 50–90 km), it appears that the use of a mean $\delta^{15}\text{N}$ value of +7‰ (perhaps $\pm 2\%$) is reasonable in the studies of volcanic gases (see recent studies by *Fischer et al.* [2002], *Hilton et al.* [2002], and *Snyder et al.* [2003]). However, as highlighted above, knowledge of the N concentrations and isotopic compositions of subducting AOC is critical in any further comparisons of the seafloor, metamorphic, and volcanic gas records of

convergent margin N cycling; also critical is the efficiency with which N and noble gases released from devolatilizing AOC (and sediment, for that matter) can be mobilized into the subarc mantle wedge. Integration of the N results with other data (trace element, isotopic) for individual arcs indicating relative slab contributions from AOC and sediment could potentially allow further delineation of AOC and sediment N (and C) sources.

5. Conclusions

[29] In this paper, we provide an inventory of the C and N concentrations and stable isotope compositions in the sediment sections obtained on ODP Legs 125 and 185, focusing primarily on Site 1149 drilled on Leg 185. The upper 120 m of the Site 1149 section shows correlated variation in the C and N concentrations and isotope compositions that we suggest are primarily related to diagenesis, but with possible superimposed lesser effects of changing productivity and relative contributions of terrigenous and marine sediment sources over the period of its deposition. More detailed biogeochemical study of the organic matter in this section would provide a more thorough assessment of organic matter sources in the section. With the data we obtained for the Site 1149 section, we estimate the C and N input fluxes (via subduction) into the Izu-Bonin convergent margin to be used in assessments of the input/output mass balance of these elements at this margin. We demonstrate the importance of using geochemical inputs constrained by drilling and geochemical analyses of the sedimentary section outboard of the margin being considered, rather than using estimates based on analyses of sediments from other tectonic and sedimentological settings, or “global” estimates of the concentrations and isotope compositions of subducting sedimentary lithologies. Further work on sediment sections outboard of the other major circum-Pacific (and other) modern subduction zones is warranted. It is worth noting that the majority of modern Earth subduction is circum-Pacific [see *Plank and Langmuir*, 1998; *Hilton et al.*, 2002] and the C and N budgets in other ocean basins do not contribute as significantly to the modern convergent margin flux of these elements.

On the basis of the existing observations regarding the effects of mechanical compaction, deformation, and diagenetic and metamorphic devolatilization in forearcs (from studies of forearc metamorphic complexes), we suggest that a significant fraction of the initially subducted N and C (reduced and oxidized) could be retained to great depths in subducting sediment sections to either return to the surface in arcs or enter the deeper mantle beyond sub-arc regions.

Acknowledgments

[30] We dedicate this paper to Stuart Boyd, who recently passed away quite prematurely. We acknowledge Stuart’s extremely creative contributions, including his ideas directed toward the understanding of (bio)geochemical N cycling that helped pave the way for more extensive use of the N isotope system in the growing field of geobiology. Funding for our study was provided by the Joint Oceanographic Institutions, United States Science Support Program (JOI-USSSP), and for the work on metamorphic suites, from the National Science Foundation (EAR-9805050). SJS acknowledges the DFG (SFB 574) for support during the completion of this study. We thank Leg 185 co-chief scientists Terry Plank and John Ludden for their support of our shorebased research. We would like to thank Jeff Alt for providing archived samples from Ocean Drilling Program Leg 129, David Velinsky for helpful discussions regarding sample preparation and sediment diagenesis, and Philippe Agard for discussions of the tectono-metamorphic and geochemical evolution of the Schistes Lustres exposed in the Cottian Alps, France and Italy. Finally, thanks to Terry Plank and Bill White for their editorial handling, and to Dave Hilton and an anonymous reviewer for their helpful reviews of our manuscript.

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