sphere, we have calculated the atmospheric residence time of $MeONO_2$ and $EtONO_2$. Use of the mean sea-to-air fluxes for 0° to 40°S (Table 1) and measured atmospheric concentrations results in a lifetime of between 4.5 and 25 days for $MeONO_2$ and between 5 and 10 days for $EtONO_2$ (*22*). Literature estimates of the atmospheric lifetime of $MeONO_2$, based on known atmospheric destruction processes, are poorly constrained, ranging from 6 to 29 days (*23, 24*). For $EtONO_2$, the atmospheric lifetime with respect to photodissociation at the equator and at 40°S has been estimated to be 7 and 12 days, respectively, for October (*25*). The reasonable agreement between the two methods implies that, for this region at least, the oceanic flux of these light alkyl nitrates is a significant source component of the light alkyl nitrate budget, thereby satisfying the requirements of the reported atmospheric measurements for a marine source.

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14. Water samples (40 ml) were typically analyzed within 4 hours of collection. During depth profiling, samples were unavoidably stored for up to 10 hours and were kept in the dark under running seawater. Air samples (600 ml) were analyzed within 2 hours of collection. Both sample types were injected into the same volatile extraction and preconcentration system. The volatile compounds were concentrated on an empty stainless steel sampling loop (30 cm length, 0.03" internal diameter) positioned above the temperature-controlled headspace of a liquid nitrogen–filled dewar. The analytes were injected onto the GC column (DB 624, 60 m length, 0.53 mm outer diameter, and 3 μm phase thickness) by heating the trap to ~100°C using boiling water. The column was temperature-programmed from 35° to 150°C. Tests for purging and trap efficiency, detector linearity, and storage artefacts were performed on board. Peak precision for $MeONO_2$ and $EtONO_2$ was better than 11%, based on the analysis of triplicate seawater samples.
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16. Air sampling was carried out less frequently than seawater sampling. A linear interpolation procedure was used to estimate atmospheric concentrations when no paired air and water concentrations were available. Chromatographic problems during ANT XVIII/1 resulted in very few measurements of $EtONO_2$, particularly in the Southern Hemisphere.
17. Temperature-dependent H_c's for the alkyl nitrates in seawater were determined experimentally in our laboratory using the McAuliffe technique (*26*). The temperature-dependent equations obtained were $\ln H_c = -4427/T + 11.48$ for $MeONO_2$ and $\ln H_c = -4137/T + 10.78$ for $EtONO_2$, where T is temperature.
18. The saturation anomaly (in percent) is defined as the departure of the observed dissolved amount from equilibrium saturation anomaly (%) =
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20. These estimates are sensitive to the value of the transfer velocity (k). The relationship of Nightingale *et al.* (*16*) was used in this work, because it was considered to be the most up-to-date parameterization. The fluxes would be lowered by approximately 30% had the relationship of Liss and Merlivat (1986) (*27*) been used in the calculations and increased by 15% had the parameterization of Wannikhof (1992) (*28*) been used. In a similar calculation, but using the temperature-dependent H_c's of Kames and Schurath (1992) (*29*) instead of our values, we find the mean flux calculated for the ocean area between the equator and 40°S to be 56 nmol m^{-2} day^{-1}; that is, approximately half of the ~119 nmol m^{-2} day^{-1} reported above. This highlights the importance of obtaining accurate data for the H_c's of these compounds in seawater over a range of water temperatures.
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Subduction and Recycling of Nitrogen Along the Central American Margin

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We report N and He isotopic and relative abundance characteristics of volatiles emitted from two segments of the Central American volcanic arc. In Guatemala, $\delta^{15}N$ values are positive (i.e., greater than air) and N_2/He ratios are high (up to 25,000). In contrast, Costa Rican N_2/He ratios are low (maximum 1483) and $\delta^{15}N$ values are negative (minimum –3.0 per mil). The results identify shallow hemipelagic sediments, subducted into the Guatemalan mantle, as the transport medium for the heavy N. Mass balance arguments indicate that the subducted N is efficiently cycled to the atmosphere by arc volcanism. Therefore, the subduction zone acts as a "barrier" to input of sedimentary N to the deeper mantle.

The present-day isotopic composition of N (*1*) is different in the various terrestrial reservoirs. For example, the mantle supplying mid-ocean ridge basalts (MORB) is depleted [$\delta^{15}N \sim -5$ per mil (‰)] compared with Earth's atmosphere (*2–7*). The isotopic difference between mantle and atmospheric N was probably established early in Earth's history, reflecting the integrated effects of partial outgassing of primordial N, possible late addition of asteroidal and/or cometary N, and/or hydrodynamic escape of a primary atmosphere (*8–11*). Subsequent modifications to the N isotope balance between the mantle and atmosphere may have occurred through subduction of biogenic and terrigenous sediments into the mantle (*12*). Sedimentary material also has a N isotopic composition ($\delta^{15}N \sim +6$ to $+7$‰) distinct from the atmosphere and upper mantle (*13, 14*) resulting from a kinetic isotope effect that has enriched (residual) nitrate in ^{15}N (*15–17*). This large isotopic contrast between mantle and crustal/atmospheric reservoirs gives N potential as a tracer of volatile recycling between the surface and Earth's interior. Here we focus on volatile exchange associated with the sub-

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duction process and specifically on the N isotope systematics of the volcanic arc of Central America.

Central America is the site of active subduction of the Cocos Plate beneath the Caribbean Plate. Resulting volcanism occurs along a linear front extending some 1100 km from the Guatemala-Mexico border to central Costa Rica. Volcanoes tend to occur as large composite volcanic centers, with an average spacing of ~25 km—which is less than the spacing at other subduction zones (*18, 19*). There is no geophysical evidence for sediment accretion along the Central American arc, implying that the bulk of the sediments on the downgoing Cocos Plate are subducted into the mantle (*20–23*). Deep sea drilling sites off Guatemala/El Salvador (site 495) and Costa Rica (site 1039) have revealed

Table 1. Nitrogen and helium isotope and relative abundance characteristics of Central American volcanic gases. Guatemala samples were taken in May 2001, Costa Rica samples in January, March, and July 2001. Type code: GF, gas from fumarole; GS, gas from (hot) spring; GW, gas from geothermal well; GM, gas from mudpot. Nitrogen source codes denote fraction of nitrogen derived from air (A), mantle (M), and sediment (S); see (*28*) for calculation of these fractions. nd, Not determined; stm, steam.

Volcano/location	Lat. (N)	Long. (W)	Temp. (°C)	Type	δ^{15}N (‰)	^{3}He/^{4}He (R_C/R_A)*	N$_2$ (mmol/mol)	N$_2$/He	Nitrogen source			%S†	δ^{15}N$_C$‡ (‰)
									A	S	M		
Guatemala													
Zunil													
Zunil	14° 46.693′	91° 30.542′	93.0	GF	1.9 ± 0.5	4.69 ± 0.05	0.006	5139 ± 524	0.69	0.29	0.02	92.3	6.07
San Marcos													
La Cimarron	nd	nd	94.7	GS	1.3 ± 0.4	2.23 ± 0.03	0.034	6691 ± 682	0.78	0.20	0.02	91.4	5.97
Volcan Fuego													
Summit	14° 28.590′	90° 52.816′	87.7	GF	5.7 ± 0.2	6.95 ± 0.06	0.090	2227 ± 227	0.09	0.85	0.05	94.0	6.28
Amatitlan-Pacaya													
Lake Shore	14° 28.395′	90° 36.140′	93.8	GS	−0.5 ± 0.4	6.72 ± 0.07	1.595	9748 ± 994	–	–	–	–	
Hot water dyke	14° 27.074′	90° 38.572′	76.4	GS	2.1 ± 0.2	6.22 ± 0.06	2.324	4385 ± 447	0.65	0.32	0.03	91.8	6.01
Laguna de caldera	14° 24.695′	90° 35.807′	stm	GW	1.0 ± 0.5	7.31 ± 0.07	0.001	1393 ± 142	0.68	0.22	0.10	67.7	3.12
Laguna de caldera (2nd well)	14° 24.695′	90° 35.807′	stm	GW	3.1 ± 0.4	7.60 ± 0.08	0.001	1870 ± 191	0.43	0.49	0.07	87.2	5.47
Tecuamburro													
Laguna Ixpacho	14° 11.577′	90° 25.394′	77.8	GS	6.3 ± 0.3	6.39 ± 0.07	0.325	8200 ± 836	0.09	0.90	0.00	99.5	6.94
Duplicate (L.I.)	14° 11.577′	90° 25.394′	77.8	GS	5.9 ± 0.3	6.38 ± 0.06	0.468	7734 ± 789	0.14	0.85	0.01	99.3	6.91
Sulfur mine	14° 09.129′	90° 24.871′	93.1	GF	−0.7 ±0.5	5.39 ± 0.06	1.015	24,899 ± 2539					
Moyuta													
Las Guineas	14° 03.215′	90° 05.831′	85.9	GF	4.3 ± 0.4	7.39 ± 0.06	0.519	6042 ± 616	0.36	0.63	0.02	97.6	6.72
Mirram "El Volcan"	14° 00.541′	90° 06.068′	80.7	GM	1.8 ± 0.3	7.36 ± 0.09		6629 ± 676	0.72	0.26	0.02	93.6	6.24
Costa Rica													
Poas													
Crater – 1/01	10° 11.883′	84° 13.719′	76.0	GF	−1.9 ± 0.3	7.10 ± 0.10	0.020	101 ± 10	0.00	0.26	0.75	25.7§	−1.91
Crater – 3/01	10° 11.883′	84° 13.719′	92.2	GF	−2.7 ± 0.4	7.22 ± 0.07	0.023	268 ± 27	0.43	0.01	0.56	1.9	−4.78
Crater – 7/01	10° 11.883′	84° 13.719′	92.8	GF	−2.4 ± 0.5	7.14 ± 0.07	0.037	373 ± 38	0.52	0.01	0.48	<1§	−4.89
Crater – 7/01	10° 11.883′	84° 13.719′	108	GF	−3.0 ± 0.6	7.15¶ ± 0.07	0.021	156 ± 16	0.01	0.16	0.83	16.3	−3.04
Turrialba													
Summit – 1/01	10° 01.156′	83° 45.937′	89.6	GF	0.4 ± 0.3	7.74 ± 0.07	0.102	643 ± 66	0.56	0.22	0.23	48.4	0.81
Summit – 7/01	10° 01.156′	83° 45.937′	89.7	GF	−1.0 ± 0.3	8.10 ± 0.10	0.068	866 ± 88	0.80	0.00	0.20	<1§	−4.78
Irazu													
Summit landslide – 1/01	9° 59.723′	83° 47.308′	88.5	GF	1.7 ± 0.4	7.24 ± 0.06	0.537	1483 ± 151	0.59	0.31	0.10	76.4	4.16

*Corrected for the effects of air-derived helium (*55*). Error quoted at the 1σ level. †Percentage of sediment-derived nitrogen in binary sediment-mantle mixture. ‡Measured nitrogen isotope ratios are corrected for air contamination using $\delta^{15}N_C = f\delta^{15}N_M + (1 - f)\delta^{15}N_S$, where $\delta^{15}N_M = -5$ ‰, $\delta^{15}N_S = +7$‰, and f is the fraction of mantle-derived nitrogen [calculated from penultimate column: $f = 1 - (\%S/100)$]. §Estimated value derived by projecting data point onto M-S mixing curve (N$_2$/He = 200 for Poas crater 1/01; N$_2$/He = 312 for Poas crater 7/01; N$_2$/He = 750 for Turrialba). ¶Average of three other ratios at same locality.

little regional variation in the sedimentary sequences on the oceanic plate: The sediment column consists of ~175 m of hemipelagic, diatom-rich mud overlying ~250 m of pelagic carbonates (*20, 21, 24, 25*). Both units are geochemically distinct and contribute to volcanic sources along much of the strike of the arc (*24, 26*). In Costa Rica, however, the low ^{10}Be contents of arc magmas suggest that the hemipelagic portion of the sedimentary column is underplated to the overriding Caribbean Plate, leaving only the pelagic carbonates to contribute to the slab flux (*27*). This variation in the amount and type of sediment involved in petrogenesis makes Central America an ideal locality to investigate details of the transfer of N into the mantle and the associated effects on N_2/He and δ^{15}N ratios.

We measured N concentrations, N_2/He ratios, and N and He isotopic compositions of gas discharges of three volcanic centers in Costa Rica and six volcanic regions in Guatemala (Table 1) (*28*). The majority of samples have ^{3}He/^{4}He ratios in the range 5 to 8 R_A, (where R_A is the ^{3}He/^{4}He value of air = 1.4 × 10^{-6}), indicating that both segments of the arc sample He primarily from the mantle wedge (*29, 30*). In contrast, the N isotope systematics and N_2/He ratios vary between Guatemala and Costa Rica. The Guatemalan volatiles have δ^{15}N values that are mostly greater than AIR (*1*) (i.e., positive, from −0.5 to 6.3‰); they also have associated N_2/He ratios falling between 1400 and 25,000, consistent with the range found previously in arc-related volcanoes (*31*). Volatiles from Costa Rica, however, have lower N_2/He ratios (101 to 1483) and mostly negative δ^{15}N ratios (–3.0 to +1.7‰).

Addition of (sediment-derived) N to mantle sources is expected to result in higher N_2/He ratios and more positive δ^{15}N values; these trends are observed for the Guatemala samples in general and for Fuego Volcano and Laguna Ixpaco in particular (Fig. 1). Assuming that N and He are not fractionated by magmatic or hydrothermal processes (*28*), we estimated the proportion of N derived from sediment and the mantle wedge (Table 1) (*28*). We find that the Guatemala samples are dominated by sediment-derived N. In contrast, volcanic gases in Costa Rica have a much lower proportion of N derived from sedimentary material. At both Turrialba and Poas volcanoes, there is no discernible contribution from sedimentary N, and the N (after correction for air) is solely of mantle origin.

We also considered the possibility that the arc crust through which magmas are erupted may contribute to the N inventory. The presence of radiogenic helium (^{3}He/^{4}He ~ 0.05 R_A) in arc-related environments is a particularly sensitive indicator of crustal additions to the volatile budget (*32, 33*). If we define 5.4 R_A as a lower limit for mantle wedge He (*34*), then all Guatemala samples—with the exception of Zunil (4.7 R_A) and San Marcos (2.2 R_A)—record binary mantle wedge–subducted sediment mixing with a maximum contribution of ~6% sediment (Fig. 2). The two exceptions record the effects of crustal contamination leading to lower ^{3}He/^{4}He ratios than anticipated for the sub-arc mantle. The sediment contribution for Costa Rica samples reaches a maximum of ~0.7%. We conclude, therefore, that the He-N isotope systematics are compatible with binary mixing between the mantle wedge and subducted sediment, with Costa Rica recording little or no contribution from the sedimentary end member and Guatemala magmas recording up to ~6%.

The N-He isotope and relative abundance systematics identify the uppermost hemipelagic section of material being subducted as the carrier of sedimentary N to the source region of the Central American arc magmas. The lack of this component in the source region of the Costa Rica magmas—consistent with the low ^{10}Be and notions of underplating in the region (*27*)—results in samples from Poas and Turrialba being devoid of a sediment-derived N component. In addition, because the Costa Rica samples lack any sediment-derived N, the pelagic carbonates (which are subducted along the entire strike of the Central American margin) cannot contribute N to the source of arc magmas beneath Costa Rica or Guatemala. Either pelagic carbonates contain no sedimentary N (*35*) or they are sufficiently stable to retain any N throughout the subduction cycle. Given evidence that carbonate sediments do contribute to the source of arc magmas throughout Central America [based on Ba/Th ratios, for example (*24, 26*)] and the fact that CO_2/^{3}He ratios are high [≥10^{10} (*36–38*)], then the carbonate sediments probably do not contain N.

With the identification of hemipelagic muds as the principal carrier of sedimentary-derived N into the mantle, we now determine whether a mass balance exists between the input of this sedimentary-derived N via the trench adjacent to Central America and its output via volcanism along the arc. A recent estimate (*39*) of the total input of N into the Central American subduction zone is 5.5 × 10^8 mol/year, based on the flux of sedimentary material and an assumed N concentration in oceanic sediments of 0.01 wt %. This approach, however, assumes a homogeneous distribution of N throughout the entire sedimentary pile (~425 m). If sediment-derived N is present in the uppermost hemipelagic portion only [i.e., the uppermost ~175 m (*20, 21, 24, 25*)], then the above flux needs to be revised by a factor of 175/425 to give an input estimate for the entire Central American margin of 2.3 × 10^8 mol N/year.

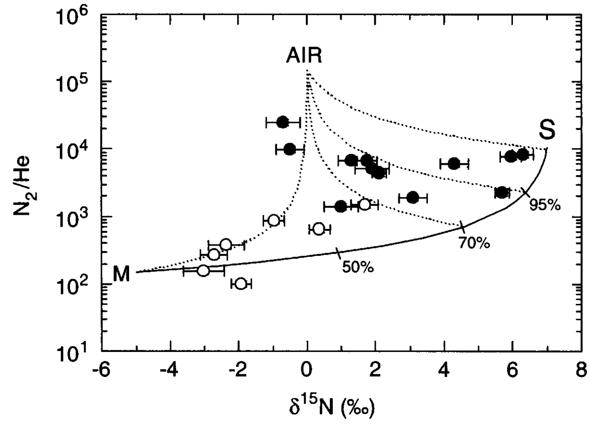

Fig. 1. Geothermal fluids from Guatemala (filled circles) and Costa Rica (open circles) compared with possible end member compositions for air (AIR), mantle (M), and sediment (S). Dotted lines reflect air addition to mixtures of mantle and sediment end members (solid line), with percentages representing the amount of sediment in the sediment-mantle binary mix. N-isotope end members from (*1–7, 13, 14*); N_2/He from (*54*).

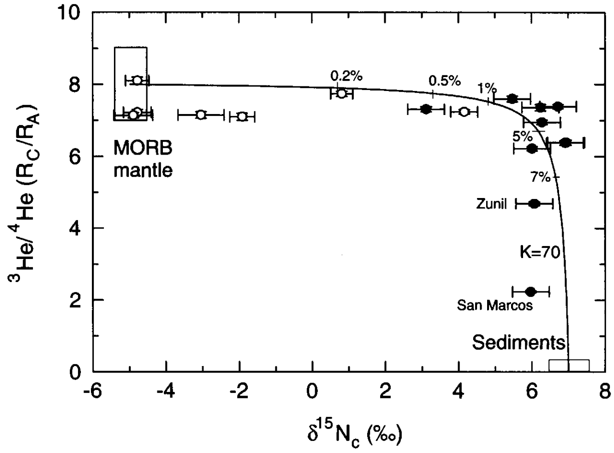

Fig. 2. Helium (^{3}He/^{4}He) versus N isotopes (δ^{15}N) (both corrected for contamination; see Table 1 for details) for geothermal fluids from Guatemala (filled circles) and Costa Rica (open circles). The solid line is a binary mixing trajectory between mantle and sediment end members, with a relative enrichment of 70 of the sediment N_2/He value relative to that of the mantle [i.e., *K* = 70 (*56*)]. Percentages marked along the trajectory indicate percent sediment in the binary mixture. See (*32, 33*) for He-isotope end members.

The total output of N along the Central

American margin has been estimated at 1.7×10^9 mol/year by combining an estimate of the total SO_2 flux (2.1×10^{10} mol/year) with the median SO_2/N_2 ratio (12.6) derived from almost 100 analyses of volcanic gas chemistries in the region (*39*). The above flux can be corrected for air-derived N on the basis of measured N_2/Ar ratios and the assumption that Ar is derived from air. The revised value for the non-air N_2 flux from the Central American arc is 2.9×10^8 mol/year (*39*). This output flux balances almost exactly the input flux of N into the trench and implies that N is efficiently released from the slab and transported through the mantle wedge to the atmosphere by arc volcanism. Thus, the Central American subduction zone acts as a "barrier" (*40*) for the transport of sedimentary N into the mantle beyond the region of magma formation below the arc; that is, the N transfer from the crust to deep mantle is short-circuited by release through arc volcanism.

If the Central American subduction zone acts to efficiently recycle subducted sedimentary N to the atmosphere, the question arises whether subduction zones worldwide behave in an analogous fashion. The output of N from arcs globally has been estimated at 3.2×10^{10} mol/year, which corrects to a value of 2.0×10^{10} mol/year when the air-N contribution is subtracted (*39*). The input from subducted sediments is 1.37×10^{10} mol N/year, based on an estimate of the N concentration of 0.01 wt % (100 ppm) and a total flux of subducted sediment of 3.8×10^{15} g/year (*39*). Given the anticipated heterogeneity in N contents of various sediment lithologies (*35*) as well as the fact that sediments subducted worldwide are characterized by large compositional differences (*41*), we consider that the apparent difference between input and output estimates falls within the level of overall uncertainty. In this case, therefore, it would seem that sediments worldwide transport N to depths of arc magma generation only, and that recycling of subducted N to the surface via arc volcanism is extremely efficient. The corollary of this conclusion is that if surficial N is recycled into the deeper mantle [see (*12*)], then it would require a source (e.g., oceanic crustal basement) other than shallow marine sediments.

References and Notes

1. The $^{15}N/^{14}N$ ratio of a sample is reported in the delta notation where $\delta^{15}N_{sample} = \{[(^{15}N/^{14}N)_{sample}/(^{15}N/^{14}N)_{AIR}] - 1\} \times 1000$. The atmosphere (AIR) is the standard (= 0.0‰), so that $\delta^{15}N_{sample}$ represents the per mil deviation from this value.
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34. Hilton *et al.* (*46*) produced a "global" estimate of the isotopic composition of mantle wedge helium (5.4 R_A) based on a compilation of >1000 $^3He/^4He$ ratios at arcs worldwide.
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54. Air has $(N_2/He)_A = 1.489 \times 10^5$ (*50*). $(N_2/He)_M$ of the mantle is taken as 150 using a compilation of global N-MORB values (*7*). $(N_2/He)_S = 10,500$ is obtained by combining an estimate of 2.1×10^4 for the crustal N_2/Ar ratio (*51*) with a $^4He/^{40}Ar$ production ratio of 2 (*50*).
55. See (*52*) for details of the correction procedure. Measured ratios are reported in (*53*).
56. $K = (N_2/He)_{sediment}/(N_2/He)_{mantle}$. Adopting end member compositions from (*54*) gives a *K* value of 70 (i.e., 10,500/150).
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Splay Fault Branching Along the Nankai Subduction Zone

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Seismic reflection profiles reveal steeply landward–dipping splay faults in the rupture area of the magnitude (*M*) 8.1 Tonankai earthquake in the Nankai subduction zone. These splay faults branch upward from the plate-boundary interface (that is, the subduction zone) at a depth of ~10 kilometers, ~50 to 55 kilometers landward of the trough axis, breaking through the upper crustal plate. Slip on the active splay fault may be an important mechanism that accommodates the elastic strain caused by relative plate motion.

Large thrust earthquakes along subduction zones pose a seismic and tsunami threat to densely populated coastal cities. These earthquakes can be generated repeatedly on a certain portion of the plate-boundary interface (*1*), which is called the seismogenic zone.