

1. DOWNHOLE VARIATION OF NITROGEN IN HOLE 504B: PRELIMINARY RESULTS¹

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ABSTRACT

We report the first data of nitrogen downhole variation in a 2-km-thick section of the ocean crust at DSDP/ODP Site 504. N concentrations in the volcanic section (275–856 mbsf) of Hole 504B are 0.73 ± 0.13 ppm, similar to the N contents of average MORB. The lower sheeted dike complex (SDC) is characterized by significantly lower N contents of 0.29 ± 0.17 ppm. We interpret this loss of N as a result of leaching processes at high temperatures. N data display a similar downhole trend as Zn, which is also depleted in the lower SDC. Therefore the lower SDC may be not only a source for base metals but also for nitrogen. Maximal estimates of the nitrogen flux through hydrothermal leaching, on the basis of the novel N data presented here, are 1.2×10^8 mol N₂/yr. This is less than 8% of the estimated present N₂ flux at mid-ocean ridges, indicating that hydrothermal leaching plays a minor, though not negligible, role in the geochemical cycle of nitrogen. The effect of addition of NH₄⁺ through oxidative alteration of the upper volcanic sequences needs to be evaluated in our ongoing investigations.

INTRODUCTION

The geochemistry of nitrogen in the oceanic crust is still poorly understood. Whereas the majority of nitrogen data are from basaltic glasses and fresh crystalline basalts, the behavior of nitrogen during alteration and nitrogen concentrations of altered rocks are virtually unknown.

The total nitrogen content of a rock is the sum of chemically bound nitrogen (mainly as NH₄⁺) and molecular nitrogen (N₂), which can be physically dissolved and/or a portion of vesicle gas or fluid inclusions.

Mass spectrometric determinations of N concentrations in basaltic glasses range from 0.2 to 2.8 ppm (Sakai et al., 1984; Exley et al., 1987; Marty and Lenoble, 1992; Bach and Erzinger, 1995). Marty and Lenoble (1992) suggested that a small amount of N (<1 ppm) released below 600°C could be of organic origin. In the upper extrusive sequences, NH₄⁺ is very likely to be enriched in clay minerals formed during oxidative seawater alteration (similar to K⁺ and Rb⁺). Spilitized basalts of the Cornubian massif in southwest England have ammonium contents up to 200 ppm (Hall, 1989). These basalts, however, rest on continental crust and therefore the addition of ammonium may not solely be a result of rock-seawater interaction.

Both N₂ and NH₄⁺ are thought to behave as incompatible elements during partial melting and fractional crystallization, with N₂ behaving similar to noble gases and NH₄⁺ behaving like large ion lithophile elements (e.g., K⁺, Rb⁺).

In basaltic glasses, variable portions (20%–60%) of N are trapped as N₂ in CO₂-rich vesicles, similar to the relative proportion of He in vesicles (Javoy and Pineau, 1991; Bach and Erzinger, 1995).

One can conclude that numerous secondary processes (alteration, degassing, diffusion) probably have affected the observed N concentrations in fresh and altered oceanic basalts.

DSDP/ODP Hole 504B is the only drill hole in the oceanic crust where we can study the chemical and mineralogical results of high-temperature alteration in situ. Site 504 is located 201 km south of the modern Costa Rica Rift in 5.9-Ma-old crust. The hole penetrates 274.5 m of sediment, a 571.5 m volcanic section, a 209 m transition zone (TZ), and 1056 m into a sheeted dike complex (SDC). The upper 310 m of volcanics were partly altered to Fe-oxyhydroxides, celadonite, saponite, calcite, and zeolites at high seawater/rock ratios and temperatures less than 50°C. The lower volcanics were partly altered to saponite, pyrite, calcite, zeolites, talc, and mixed-layer smectite-chlorite at low water/rock ratios and temperatures less than 150°C. Greenschist mineral assemblages (chlorite, actinolite, albite, titanite, quartz, and epidote) indicating temperatures up to 380°C appear abruptly at 898 meters below seafloor (mbsf) and are present to the bottom of the hole showing increasing temperatures of pervasive background alteration (Alt et al., this volume).

This study has determined nitrogen concentrations of 32 samples from Hole 504B, using a combined vacuum heating/mass spectrometry method. The samples represent almost the entire drilled crustal section.

SAMPLE PREPARATION AND ANALYTICAL METHODS

The investigated samples are variably altered rocks drilled during DSDP Legs 69, 70, and 83, as well as ODP Legs 111, 137, and 140. Detailed petrographic descriptions and chemical composition are given in the respective *Initial Reports* and *Scientific Results* volumes of the legs (see also the note in Table 1).

The degrees of alteration (i.e., the amount of secondary minerals) in samples from Leg 137 and 140 were visually estimated (cf. Zuleger et al., 1995). Samples were divided into three groups according to the style of alteration. Group D comprises relatively fresh dark diabases, Group L are light diabases, and Group P are patches of strong alteration (Table 1; see Alt et al., 1995, for a detailed description).

All samples were crushed and fragments of 1- to 2-mm grain size were selected for vacuum heating. After cleaning the fragments ultrasonically in distilled water, about 500 mg were vacuum-heated at 1300°C to release the gaseous content of the samples. Nitrogen concentration was determined by a quadrupole mass spectrometer (QMS) Balzers™ QMG 112, combined with a gas separation and calibration line. A schematic diagram of the equipment is shown in Fig-

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Table 1. Concentration of nitrogen together with water, carbon dioxide, and zinc data of selected samples from Hole 504B.

Leg	Hole	Core, section, interval (cm)	Rock type	Alt. (%)	Depth (mbsf)	N (ppm)	H ₂ O (wt%)	CO ₂ (wt%)	Zn (ppm)
69	504B	6R-2, 108-112			301.1	0.81	0.99	0.13	81
69	504B	9R-2, 80-83			327.8	0.46	0.83	0.08	82
69	504B	19R-1, 98-103			404.0	0.83	1.20	0.10	69
69	504B	27R-1, 105-110			467.1	0.73	0.63	0.09	76
70	504B	37R-2, 94-96			555.0	0.68	0.61	0.46	57
70	504B	46R-2, 129-131			631.8	0.83	0.46	0.09	67
70	504B	65R-1, 20-25			782.2	0.80	0.46	0.09	63
83	504B	90R-4, 146-149			1000.5	1.28	3.40	0.34	96
83	504B	129R-2, 58-62			1272.1	1.00	1.60	0.08	81
111	504B	142R-1, 14-17			1353.0	0.69	1.08	0.05	69
111	504B	145R-3, 92-94			1382.2	0.60	1.08	0.05	57
111	504B	148R-1, 110-112			1407.9	0.66	0.91	0.05	76
111	504B	154R-1, 85-87			1455.2	1.29	1.24	0.04	74
111	504B	161R-1, 7-9			1504.2	0.48	0.95	0.07	68
111	504B	163R-2, 1-3			1513.1	0.85	1.48	0.03	54
137	504B	174R-2, 23-26	D	10	1578.0	0.14	1.21	0.06	72
137	504B	181M-2, 95-97	P	25	1622.8	0.09	1.29	0.06	60
140	504B	189R-2, 15-17	P	85	1653.5	0.45	3.09	0.08	60
140	504B	190R-1, 10-14	P	60	1655.2	0.38	5.98	0.08	61
140	504B	194R-1, 36-40	D	20	1680.8	0.53	1.29	0.06	67
140	504B	197R-1, 123-126	D	15	1704.0	0.40	1.71	0.09	68
140	504B	200R-3, 115-117	D	15	1732.8	0.40	2.16	0.08	92
140	504B	203R-1, 15-19	L	45	1756.7	0.18	1.98	0.14	43
140	504B	207R-1, 22-26	D	40	1768.6	0.29	1.10	0.07	50
140	504B	208R-1, 110-114	D	18	1779.1	0.70	1.25	0.04	56
140	504B	210R-1, 80-87	D		1795.7	0.12	1.29	0.06	49
140	504B	214R-1, 36-40	D	50	1819.0	0.29	1.84	0.06	39
140	504B	222R-1, 115-120	D	45	1885.8	0.17	2.42	0.07	39
140	504B	225R-2, 29-32	D	15	1914.0	0.19	1.38	0.07	63
140	504B	227R-1, 40-46	D		1924.9	0.14	1.55	0.08	44
140	504B	231R-1, 0-3	L	60	1953.5	0.13	1.38	0.08	36
140	504B	238R-1, 8-9	D	25	1992.0	0.32	1.60	0.07	40

Notes: D = dark diabase, L = light diabase, and P = alteration patch. Data sources, except for nitrogen, are Hubberten et al. (1983), Emmermann (1985), Zuleger et al. (1995), and unpublished data from our laboratory. Alt. = alteration.

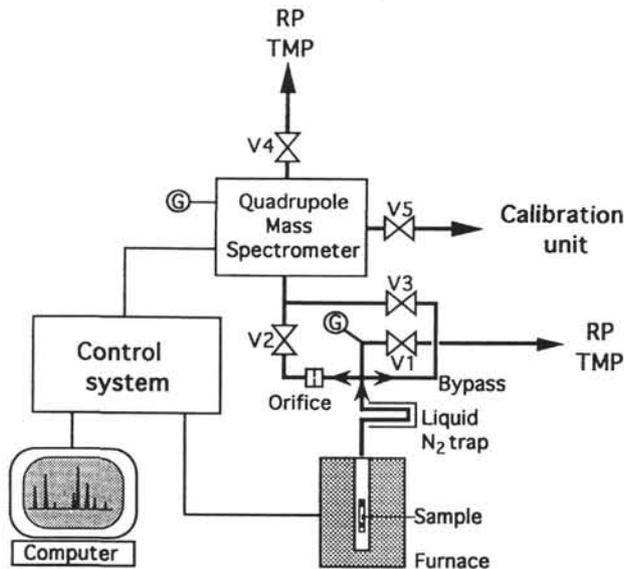


Figure 1. Schematic sketch of the equipment employed for gas analysis. G = ionization gauges; V1-V5 = valves; TMP = turbo-molecular pump; and RP = rotary pump.

ure 1. Total gas contents were determined after heating the sample material in a molybdenum crucible, which was employed in an alumina tube. Before analysis, this tube and the crucible were heated to 1400°C to decrease the blank values to an acceptable level ($<2 \times 10^{-5}$ cm³ STP, which is below 0.1 ppm N for a sample of 500 mg). The samples were baked at 120°C in vacuum overnight to remove adsorbed gases and moisture from the fragment surfaces. The furnace then was heated to 1300°C, with a heating rate of 30°C/min. During

heating, a cold trap at liquid nitrogen temperature separated H₂O, CO₂, H₂S, and other condensable gases from the noncondensable gases (N₂, He, Ar, H₂, CH₄, CO). The noncondensable fraction was led into the mass spectrometer via an orifice after the maximum temperature was maintained for 30 min. After the furnace had cooled, the same procedure was repeated to obtain the blank values, which were subtracted from the sample intensities before the concentrations were calculated. Blank values were always below 0.1 ppm N. The mass spectrometer is calibrated periodically with both pure gases and certified gas mixtures. Mass interferences are corrected using the intensities of subsidiary masses (i.e., $m/e = 15$ for CH₄, $m/e = 12$ for CO, and $m/e = 14$ for N₂). Mass interferences with CO have been a minor problem because the CO concentrations in the released gas are an order magnitude lower than N₂ concentrations. He and Ar concentrations were, at that time, below the detection limits of our method. Four replicates of a basalt laboratory standard yielded 0.30 ± 0.05 (2σ) ppm N.

Discussion of Possible Analytical Problems

Common mass spectrometric methods cannot distinguish between molecular nitrogen (N₂) and other N (NH₄⁺, organic N). With our method, we determine N by analyzing N₂ concentration in a gas mixture released upon vacuum heating. The measured N₂ may reflect three possible situations. First, all N is converted to N₂ and we measure total N concentrations. Second, only molecular N₂ is released during heating and oxidation of reduced N did not occur. Third, reduced N is partly converted to N₂.

We think that our N data represent concentrations of molecular N₂ for the following reasons. First, our studies of biotites and muscovites from different locations yielded generally high NH₄⁺ concentrations (determined by ion-chromatography following Kjeldahl distillation), whereas the N concentrations determined by mass spectrometry are an order of magnitude lower (Bach and Erzinger, 1993). This at least proves that a complete conversion of NH₄⁺ to N₂ does not occur in the

furnace and gas separation line. Second, all samples from Hole 504B, where mass pyrograms have been monitored, exhibit a unimodal release pattern of N_2 , which is unlikely if N_2 were released by different processes (e.g., degassing of N_2 and production of N_2 through oxidation of reduced N). Some samples show a second peak of N_2 at high temperatures around 1450°C that could be possibly related to artificially produced N_2 . Third, our N data from fresh mid-ocean ridge basalt (MORB) glass (Bach and Erzinger, 1995) indicate that ratios of N_2 in vesicles (crushing-released) and total N released upon heating are similar to the corresponding ratios for He and CO_2 , which have similar (or slightly lower) solubilities in basaltic melts. This indicates that the measured total N cannot be influenced by production of large quantities of N_2 through oxidation of NH_4^+ .

We cannot completely rule out that, in some cases, oxidation of reduced N could have led to slightly elevated N_2 values, but, commonly, partial oxidation of NH_4^+ appears to occur only at temperatures above 1400°C.

Reliable analyses of total N are extremely difficult to obtain. Previous workers (e.g., Sakai et al. 1984, Exley et al., 1987) oxidized NH_3 to N_2 in their gas separation lines, but it is very unlikely that the chemically bound NH_4^+ is quantitatively volatilized upon heating. The substantial differences between Instrumental Neutron Activation Analysis (INAA) determination of total N in fresh basaltic glass (7–10 ppm; Norris and Schaeffer, 1982) and mass spectrometric N determination (0.3–2.8 ppm; e.g., Sakai et al., 1984) could possibly result from the incomplete volatilization of NH_4^+ during pyrohydrolysis. Unfortunately, no international reference rocks or basaltic glasses with certified N values are available to verify the precision of the applied method.

Our future work will provide data on NH_4^+ concentration and mass spectrometrically measured N in fresh and altered basalts to better understand the distribution of N in the oceanic crust and its implications for the nitrogen geochemical cycle. N data presented in this paper are very likely to be concentrations of molecular N_2 . In the following sections, however, we refer to the measured N_2 concentrations as N contents because we cannot clearly prove the correspondence to the concentration of molecular N_2 in the rock.

RESULTS AND DISCUSSION

The results of the N determinations are listed in Table 1 together with H_2O^+ , CO_2 , and Zn values, and, where available, percentage of alteration minerals.

Figure 2 shows the downhole variation of N, H_2O^+ , and Zn. As a reference line, the mean N-concentration of oceanic basalt glasses of 0.8 ppm was drawn (Exley et al., 1987; Marty and Lenoble, 1992). The Zn reference line of 70 ppm was calculated as the average Zn concentration of the volcanic section of Hole 504B.

The lines in the H_2O vs. depth plot were calculated as two average values for the volcanic section from 275 to 850 mbsf and for the SDC from 1060 to 2000 mbsf, respectively.

The nitrogen content of Hole 504B samples is relatively uniform within the volcanic section from the top of the basement to 800 mbsf. The average N concentrations of the volcanic section are 0.73 ± 0.13 ppm. This is close to the N concentration of average MORB (0.7 ppm, Exley et al., 1987; 0.9 ppm, Marty and Lenoble, 1992). Sample 83-504B-90R-4, 146–149 cm ($N_2 = 1.28$ ppm) was derived from 1000.5 mbsf, the stockwork mineralization zone. Chemically this sample has a higher water content and contains disseminated Cu- and Zn-rich sulfides. In the SDC below 1350 mbsf, N contents continuously decrease from 0.7 ppm to 0.15 ppm. The average N concentrations of the lowermost part of the SDC (from 1600 to 2000 mbsf) is 0.29 ± 0.17 ppm, indicating a significant loss of N in the lower SDC. At present we have no explanation for the higher N content in Samples 83-504B-129R-2, 58–62 cm; 111-504B-154R-1, 85–87 cm; 111-504B-163R-2, 1–3 cm; and 140-504B-208R-1, 110–

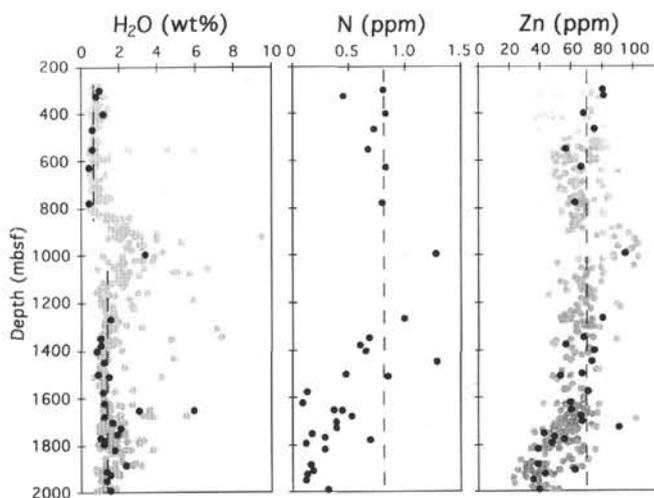


Figure 2. Downhole variations of H_2O , N, and Zn. Solid dots are from Table 1, stippled dots are data from Autio and Rhodes (1983), Hubberten et al. (1983), Marsh et al. (1983), Emmermann (1985), Kempton et al. (1985), Tual et al. (1985), Autio et al. (1989), Zuleger et al. (1995), and unpublished data from our laboratory. See text for details.

114 cm. All these samples are mineralogically and chemically similar to the others, except for enrichments in Cu and occasionally in sulfur. Because no data on N-contents in sulfides are available, and because primary differences in N contents cannot be ruled out, we cannot determine whether these higher N contents are of primary or secondary origin.

All investigators (e.g., Hubberten et al., 1983; Emmermann, 1985; Zuleger et al., 1995) have pointed to the remarkable uniformity of both major- and trace-element abundances throughout Hole 504B. Still observed changes in mineralogy and chemistry with depth are generally consistent with increasing temperatures downward, variable water/rock ratios, and degrees of oxidation. Several elements and parameters such as K_2O , S, Ti, H_2O , CO_2 , the iron oxidation ratio, and also the abundance of the rare gases Ar, Kr, and Xe (Mitchell and Terrell, 1985) show significant changes in concentration at the base of the oxalic alteration zone at 585 mbsf. Changes in nitrogen concentrations cannot be observed around the oxalic/anoxic transition.

Among all major and trace elements determined in the rocks of the sheeted dike section of Hole 504B and published to this date, only H_2O , Zn, and N show significant general changes in concentrations downhole (Fig. 2). H_2O is slightly enriched below the transition zone towards the bottom of the hole resulting from the increasing amount of water-rich secondary alteration minerals at increasing temperatures (Alt and Emmermann, 1985; Zuleger et al., 1995). Zn depletion in the basal SDC is interpreted as a result of hydrothermal leaching processes and may be a source for Zn in hydrothermal vent fluids and the Zn-enrichment in the mineralized transition zone (Sparks, 1995; Zuleger et al., 1995; Bach et al., this volume).

We therefore interpret the strong depletion of nitrogen downward in the SDC clearly as being the result of a hydrothermal leaching process. Overall, the degrees of alteration, the intensities of fluid-rock interactions, and the background alteration temperatures increase downward in Hole 504B (Alt et al., 1995). The upper volcanic section displays N concentrations typical of MORB (around 0.7 ppm N), which is mainly molecular N_2 trapped in vesicles and dissolved in glass. High-temperature hydrothermal alteration of the lower SDC diabases resulted in the breakdown of primary minerals and almost complete alteration of glassy interstitial material. The depletion of N in the lower SDC rocks therefore indicates that large quantities of the molecular N_2 obviously were removed by high-temperature hydrothermal processes.

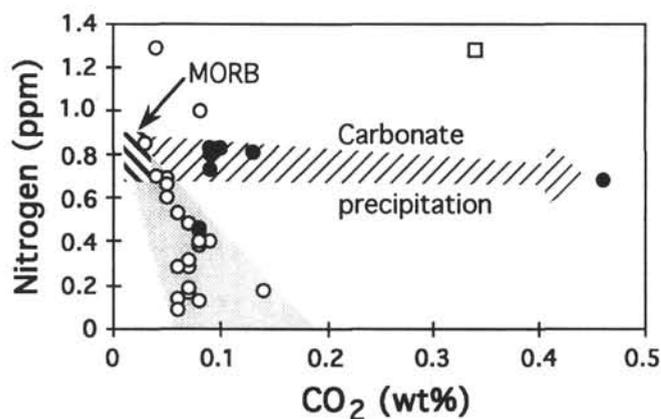


Figure 3. Plot of nitrogen vs. CO_2 . Open circles indicate rocks from the sheeted dike complex, solid circles are basalts from the volcanic section, and the square represents a sample from the transition zone. The MORB field is drawn from average N data of Marty and Lenoble (1992) and Exley et al. (1987) and from the CO_2 data of Fine and Stolper (1986). See text for discussion.

Implications for the Nitrogen Geochemical Cycle

Degassing of nitrogen from active ridges during emplacement of the magmas occurs via exsolution and segregation of CO_2 bubbles (e.g., Javoy and Pineau, 1991). The actual outgassing rate of N_2 is, however, difficult to constrain because N_2 was rarely determined in vesicle gases. Marty and Lenoble (1992) estimated a maximum N_2 flux of 4×10^9 mol/yr based on mean $\text{N}/^3\text{He}$ ratios of MORB. Zhang and Zindler (1993) used ^{36}Ar outgassing rates and average N_2/Ar ratios in vesicles of 54 (Javoy and Pineau, 1991) to estimate a N_2 outgassing rate of $3.2 (+3.2, -1.6) \times 10^9$ mol/yr.

Leaching of nitrogen from the upper oceanic crust during high-temperature alteration reactions is a provable addition to the net flux of N_2 at spreading ridges. Nitrogen has been detected in gas samples taken from submarine hydrothermal vents at the Juan de Fuca Ridge (JdFR) and the Valu Fa Ridge in the Lau Basin (VFR). N_2 makes up about 12% of the total amount of dissolved gas (JdFR; Evans et al., 1988) and 20%–40% (VFR; Fouquet et al., 1993; unpublished data corrected for air-contamination of our laboratory), respectively. In case of the VFR, only 10%–30% of the nitrogen in vent fluids possibly originated from N_2 dissolved in the downwelling seawater (calculations are based on the seawater N concentration of Craig et al., 1967). However, the majority of N_2 is clearly leached from the basement rocks.

Whereas the degassing of MORB magmas is strictly controlled by melt-vapor partitioning of volatiles, the hydrothermal leaching is not. It is interesting that the depleted mantle is variably degassed in respect to different volatiles. For instance, the depletion of ^{36}Ar is 99.7%, ^3He 97%, the depletion of N is 88%, and that of CO_2 is only 28% (Zhang and Zindler, 1993, and references therein). These discrepancies contrast the similar solubilities of N_2 and Ar on the one hand and He and CO_2 on the other hand (e.g., Jambon and Zimmermann, 1987). This can be interpreted as indicating recycling of C and N by means of subduction (e.g., CO_2 as carbonate and organic C in sediments, and N as an organic component in sediments). The compiled values indicated that C must have been preferentially recycled as compared to N. This was explained by recycling of carbonate sediments through subduction or partitioning of N in the Earth's core (Marty and Lenoble, 1992).

Hydrothermal alteration could also contribute to a preferential recycling of C, if the basaltic oceanic crust acts as a sink for C but a

source for N. Figure 3 depicts the measured N concentration plotted against CO_2 concentrations. It becomes obvious that CO_2 concentrations of all Hole 504B rocks are higher than MORB (maximum of 360 ppm dissolved CO_2 ; Fine and Stolper, 1986) but N concentrations are lower in most rocks from the SDC. This indicates a net loss of N from the oceanic crust through hydrothermal alteration. In contrast, CO_2 concentrations in Hole 504B are much higher than in fresh MORB glasses. Carbonate precipitation in the upper part of the crust adds CO_2 to the rock but apparently does not change the N contents. Oxidative seawater alteration is, however, likely to add nitrogen through enrichments of NH_4^+ . If NH_4^+ behaves indeed like large alkali ions, it would be enriched in the upper oxic volcanic section but leached during nonoxidative high-temperature hydrothermal alteration. In short, overall enrichment of CO_2 in the altered crust and drastic depletion of nitrogen in the lower SDC might be a possible additional effect for the preferential recycling of carbon into the mantle. We need more information on ammonium contents in Hole 504B to quantify this model.

Simple mass-balance calculations can prove the importance of hydrothermal leaching for the outgassing rates of N at mid-ocean ridges. The total volume of the oceanic crust is about 2×10^9 km³ (Kay and Hubbard, 1978). If the average N_2 concentration of MORB is 0.8 ppm (2.9×10^{-8} mol/g), the oceanic crust would contain 1.7×10^{17} mol N_2 (assuming an average density of 3 g/cm³). This is low as compared to the content of the atmosphere (1.38×10^{20} mol N_2 ; Ozima and Podosek, 1983) and the continental crust (4×10^{19} mol N_2 ; Wlotzka, 1972). Assuming the yearly production rate of basalts at mid-ocean ridges is $3.3\text{--}4.3 \times 10^{16}$ g (Kay and Hubbard, 1978) the amount of N transferred from the mantle to the ocean crust would be $0.9\text{--}1.2 \times 10^9$ mol N_2 /yr. This is less than the lower limit for the estimated outgassing rate of N (about 1.6×10^9 mol/yr; Zhang and Zindler 1993), indicating that a substantial fraction of the N_2 degasses upon magma ascent and eruption. If we assume that hydrothermal leaching, on average, removes 0.5 ppm molecular N_2 from a SDC of 1 km thickness, the yearly degassing rate would be $0.94\text{--}1.25 \times 10^8$ mol N_2 /yr (assuming the average crustal thickness is 6 km). This makes up at most 8% of the present outgassing rate of N_2 .

CONCLUSIONS

From the results of this preliminary study we conclude that molecular nitrogen, which is originally dissolved in the basaltic matrix or a constituent of vesicle filling, is being leached or degassed from the deeper oceanic crust as a result of increasing temperatures with depth.

Hydrothermal leaching of N is a potential additional source for the nitrogen flux from the mantle. It is, however, not efficiently changing net nitrogen fluxes and therefore plays a minor role in the nitrogen geochemical cycle.

The question whether the effects of hydrothermal alteration can contribute to the preferential recycling of C as compared to N cannot be answered yet. The analytical technique used here cannot determine total nitrogen contents or clearly distinguish between N_2 and NH_4^+ ; thus, a possible enrichment of total nitrogen in the upper oxic volcanic section was not detectable. Continuation of this work, including determination of NH_4^+ and nitrogen isotopes, is planned.

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REFERENCES

- Alt, J.C., and Emmermann, R., 1985. Geochemistry of hydrothermally altered basalts: Deep Sea Drilling Project Hole 504B. In Anderson, R.N., Honnorez, J., Becker, K., et al., *Init. Repts. DSDP*, 83: Washington (U.S. Govt. Printing Office), 249–262.
- Alt, J.C., Zuleger, E., and Erzinger, J.A., 1995. Mineralogy and stable isotopic compositions of the hydrothermally altered lower sheeted dike complex, Hole 504B, Leg 140. In Erzinger, J., Becker, K., Dick, H.J.B., and Stokking, L.B. (Eds.), *Proc. ODP, Sci. Results*, 137/140: College Station, TX (Ocean Drilling Program), 155–166.
- Autio, L.K., and Rhodes, J.M., 1983. Costa Rica Rift Zone basalts: geochemical and experimental data from a possible example of multistage melting. In Cann, J.R., Langseth, M.G., Honnorez, J., Von Herzen, R.P., White, S.M., et al., *Init. Repts. DSDP*, 69: Washington (U.S. Govt. Printing Office), 729–745.
- Autio, L.K., Sparks, J.W., and Rhodes, J.M., 1989. Geochemistry of Leg 111 basalts: intrusive feeders for highly depleted pillows and flows. In Becker, K., Sakai, H., et al., *Proc. ODP, Sci. Results*, 111: College Station, TX (Ocean Drilling Program), 3–16.
- Bach, W., and Erzinger, J., 1993. Geochemistry of volatile components in rocks from the KTB-HB. In Emmermann, R., Lauterjung, J., and Umsonst, T. (Eds.), *NLFb, KTB-Report 93-2*: Stuttgart (Schweizerbart-Verlag), 465–468.
- , 1995. Volatile components in basalts and basaltic glasses from the EPR at 9°30'N. In Batiza, R., Storms, M.A., and Allan, J.F. (Eds.), *Proc. ODP, Sci. Results*, 142: College Station, TX (Ocean Drilling Program), 23–29.
- Craig, H., Weiss, R.F., and Clarke, W.B., 1967. Dissolved gases in the equatorial and south Pacific Ocean. *J. Geophys. Res.*, 72:6165–6181.
- Emmermann, R., 1985. Basement geochemistry, Hole 504B. In Anderson, R.N., Honnorez, J., Becker, K., et al., *Init. Repts. DSDP*, 83: Washington (U.S. Govt. Printing Office), 183–199.
- Evans, W.C., White, L.D., and Rapp, J.B., 1988. Geochemistry of some gases in hydrothermal fluids from the southern Juan de Fuca Ridge. *J. Geophys. Res.*, 93:609–616.
- Exley, R.A., Boyd, S.R., Matthey, D.P., and Pillinger, C.T., 1987. Nitrogen isotope geochemistry of basaltic glasses: implications for mantle degassing and structure? *Earth Planet. Sci. Lett.*, 81:163–174.
- Fine, G., and Stolper, E., 1986. Dissolved carbon dioxide in basaltic glasses: concentrations and speciation. *Earth Planet. Sci. Lett.*, 76:263–278.
- Fouquet, Y., von Stackelberg, U., Charlou, J.L., Erzinger, J., Herzig, P.M., Mühe, R., and Wiedicke, M., 1993. Metallogenesis in back-arc environments: the Lau Basin example. *Econ. Geol.*, 88:2154–2181.
- Hall, A., 1989. Ammonium in spilitized basalts of southwest England and its implications for the recycling of nitrogen. *Geochem. J.*, 23:19–23.
- Hubberten, H.-W., Emmermann, R., and Puchelt, H., 1983. Geochemistry of basalts from Costa Rica Rift Sites 504 and 505 (Deep Sea Drilling Project Legs 69 and 70). In Cann, J.R., Langseth, M.G., Honnorez, J., Von Herzen, R.P., White, S.M., et al., *Init. Repts. DSDP*, 69: Washington (U.S. Govt. Printing Office), 791–803.
- Jambon, A., and Zimmermann, J.L., 1987. Major volatiles from a North Atlantic MORB glass and calibration to He: a size fraction analysis. *Chem. Geol.*, 62:177–189.
- Javoy, M., and Pineau, F., 1991. The volatiles record of a “popping” rock from the Mid-Atlantic Ridge at 14°N: chemical and isotopic composition of gas trapped in the vesicles. *Earth Planet. Sci. Lett.*, 107:598–611.
- Kay, R.W., and Hubbard, N.J., 1978. Trace elements in ocean ridge basalts. *Earth Planet. Sci. Lett.*, 38:95–116.
- Kempton, P.D., Autio, L.K., Rhodes, J.M., Holdaway, M.J., Dungan, M.A., and Johnson, P., 1985. Petrology of basalts from Hole 504B, Deep Sea Drilling Project, Leg 83. In Anderson, R.N., Honnorez, J., Becker, K., et al., *Init. Repts. DSDP*, 83: Washington (U.S. Govt. Printing Office), 129–164.
- Marsh, N.G., Tarney, J., and Hendry, G.L., 1983. Trace-element geochemistry of basalts from Hole 504B, Panama Basin, Deep Sea Drilling Project Legs 69 and 70. In Cann, J.R., Langseth, M.G., Honnorez, J., Von Herzen, R.P., White, S.M., et al., *Init. Repts. DSDP*, 69: Washington (U.S. Govt. Printing Office), 747–763.
- Marty, B., and Lenoble, M., 1992. Nitrogen in MORB: a CO₂, He, Ar study. *Eos*, 73(Suppl.):349. (Abstract)
- Mitchell, J.G., and Terrell, D.J., 1985. Downhole variation of potassium, inert gas abundance, and apparent K-Ar age in basalts from the Costa Rica Rift, Hole 504B, Leg 83, Deep Sea Drilling Project. In Anderson, R.N., Honnorez, J., Becker, K., et al., *Init. Repts. DSDP*, 83: Washington (U.S. Govt. Printing Office), 305–312.
- Norris, T.L., and Schaeffer, O.A., 1982. Total nitrogen content of deep sea basalts. *Geochim. Cosmochim. Acta*, 46:371–379.
- Ozima, M., and Podosek, F.A., 1983. *Noble Gas Geochemistry*: Cambridge (Cambridge Univ. Press).
- Sakai, H., Des Marais, D.J., Ueda, A., and Moore, J.G., 1984. Concentrations and isotope ratios of carbon, nitrogen and sulfur in ocean-floor basalts. *Geochim. Cosmochim. Acta*, 48:2433–2441.
- Sparks, J.W., 1995. Geochemistry of the lower sheeted dike complex, Hole 504B, Leg 140. In Erzinger, J., Becker, K., Dick, H.J.B., and Stokking, L.B. (Eds.), *Proc. ODP, Sci. Results*, 137/140: College Station, TX (Ocean Drilling Program), 81–98.
- Tual, E., Jahn, B.M., Bougault, H., and Joron, J.L., 1985. Geochemistry of basalts from Hole 504B, Leg 83, Costa Rica Rift. In Anderson, R.N., Honnorez, J., Becker, K., et al., *Init. Repts. DSDP*, 83: Washington (U.S. Govt. Printing Office), 201–214.
- Wlotzka, F., 1972. Nitrogen. In Wedepohl, K.-H. (Ed.), *Handbook of Geochemistry* (Vol. 2/1): Berlin (Springer-Verlag).
- Zhang, Y., and Zindler, A., 1993. Distribution and evolution of carbon and nitrogen in Earth. *Earth Planet. Sci. Lett.*, 117:331–345.
- Zuleger, E., Alt, J.C., and Erzinger, J.A., 1995. Primary and secondary variations in major and trace-element geochemistry of the lower sheeted dike complex: Hole 504B, Leg 140. In Erzinger, J., Becker, K., Dick, H.J.B., and Stokking, L.B. (Eds.), *Proc. ODP, Sci. Results*, 137/140: College Station, TX (Ocean Drilling Program), 65–80.

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