4. MAJOR VOLATILES AND HELIUM ISOTOPES IN SITE 864 BASALT GLASSES

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ABSTRACT

The abundance of major volatiles and helium isotopes was measured in three basalt samples from lithological Unit 1 in Ocean Drilling Program Hole 142-864A on "zero-age" oceanic crust. Total volatile content varies from 2.71 to 3.50 cm³ STP/g in the samples, with H₂O (0.16 to 0.21 wt% for the rock as a whole) and CO₂ (0.04 wt%) as the main components. Concentration ranges of other gases are as follows (in 10^{-3} wt%): N₂ = 9–27; CO = 3–8; O₂ = 1.7–4.2; H₂O = 1.7–1.9, CH₄ = 0.45–0.92. The release behavior of different volatiles during their extraction from the rock by heating within the temperature interval 130° –1230°C was also investigated. From one-third to one-half of the total volatile content was released at 900°–1050°C, whereas the main part of He was released at <750°C. The content of He, 10^{-6} cm³ STP/g, varies from 37–39 in the gross pow-der fractions (0.5 to 1.0 mm) to 21–22 in the fine ones (<0.05 mm). The ³He/⁴He values in the same fractions are 1.18 × 10^{-5} and 1.04×10^{-5} , respectively. The C/³He value in the total mass of volatiles is ~1.9×10⁹. The obtained results are within the range of data available for normal MORB tholeiite glass.

INTRODUCTION

The studies of volatile components contained in glasses of midoceanic ridge basalts (MORB) contribute significantly to understanding the geochemical cycles of many elements as well as the general process of the Earth's degassing and evolution. Coupled with data on the contents of lithofile elements, such as K, Mg, and Fe, the evaluation of major volatile abundance has important petrological implications for the melt source reservoirs (Byers et al., 1986; Jambon and Zimmermann, 1987; Javoy and Pineau, 1991). Studies of this kind have revealed the regional features of different spreading centers (Table 1).

To recognize the origin of some volatile components, such as Cbearing gases, their contents can be normalized to the concentration of the ³He isotope (Polyak et al., 1976; Tolstikhin, 1986; Marty and Jambon, 1987; Poreda et al., 1988).

Helium isotope contents in rocks are a genetic marker that specifies source reservoirs. Sr, Nd, and Pb isotope systematics has revealed a considerable diversity for oceanic rocks in abundances of radiogenic isotopes. Together with the differences in contents of alkaline and incompatible trace elements, this diversity points to the mantle heterogeneity reflected in local or regional enrichment of the melt zone by these components (as compared to the MORB reservoir considered as the depleted mantle). The enriched source is, however, difficult to identify from data from "solid-phase" systems only, because the higher contents of radiogenic Sr and Pb isotopes and less radiogenic Nd than those in MORB are inherent to both the primitive (undepleted) mantle and the crust.

By contrast, the helium isotopic signature is quite different for all three reservoirs (Craig and Lupton, 1978, 1981; Craig and Rison, Table 1. Average volatile abundance (wt%) in basalts of mid-oceanic spreading centers (from Byers et al., 1986).

Sample location:	Spreading center					
	Mid-Atlantic Ridge, 25°-29°N	East Pacific Rise, 21°N	Galapagos Spreading Center, 95.5°W			
H ₂ O	0.201	0.120	0.098			
H ₂ O CO ₂ CO	0.132	0.163	0.097			
CO	n.d.	0.023	0.042			
CH	n.d.	0.002	0.004			
Total content	0.479	0.388	0.340			
Number of samples	7	9	3			

Notes: n.d. = not detected. Total content includes S, Cl, and F abundances.

1982; Lupton, 1983; Polyak and Tolstikhin, 1985; Azbel and Tolstikhin, 1988). According to the above-cited references, the undepleted mantle, where primordial helium with ³He/⁴He $\sim(1-3) \times 10^{-4}$ trapped during accretion is best preserved, contains helium with the maximum values of isotope ratio, ³He/⁴He $\sim(2-5) \times 10^{-5}$, observed in rocks and thermal fluids of the typical "hot spot" areas (Iceland, Hawaii, southwestern Pacific, and several others). The MORB reservoir is characterized by an intermediate ³He/⁴He value of $\sim(1.2 \pm 0.2) \times 10^{-5}$, whereas crust is enriched by U and Th as compared to the mantle and contains helium with a lower isotopic ratio down to a pure radiogenic value of $\sim 10^{-8}$. Therefore, the helium isotope data constrain possible sources of substance enriched in radiogenic Sr and Pb isotopes.

Such an approach has, for example, allowed the origin of the Azores "not so hot spot" (Bonatti, 1990) to be clarified: the basalts erupted on Sao Miguel Island of this archipelago may be derived from the MORB reservoir but contaminated by 0.3 to 0.8 wt% of continental crust material (Tolstikhin et al., 1991). A similar conclusion on the occurrence of recycled components in the mantle was reached by Graham et al. (1988) as a possible explanation for the He-Sr-Nd-Pb systematics in the seamount volcanics along the northern part of the East Pacific Rise (EPR).

The ³He excess in seawater above the EPR from 20°S to 20°N (Craig, 1981) provides evidence for the influx of mantle helium to the

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Latitude (north)	Sample	Туре	Size of fraction (mm)	Temperature of degassing (°C)	He, 10 ⁻⁶ , cm ³ STP/g ^a	³ He/ ⁴ He, 10 ⁻⁵ (±2σ)	References
≈21° CY	CYP 78*	Т		800 1700	2.511-55.390 0.003-0.064	1.21 ± 0.07	1
				total	2.514-55.392		i
	HRX 11 A2	TR	0.05-0.10	1500	1.14 ± 0.54	1.2 ± 0.04	2
	HRX 6 B2	T	0.05-0.10	1500	2.43 ± 0.98	1.44 ± 0.22	2 2,3 3 3 3 3 4,5 3 3 3 3 5 5,6
			5.0	750	4.31	1.04	3
			5.0	1650	0.51	0.96	3
			5.0	total	4.82	1.03	3
			5.0	1500	5.2	1.03	3
			0.02-0.06	1650	0.16	0.87	3
	HT plume	HTP				1.09 ± 0.2	4, 5
≈13°	CY-82-31-02	Т	5.0	750	7.67	1.04	3
			5.0	1650	0.15	0.88	3
			5.0	total	7.81	1.04	3
			0.01-0.04	1650	1.40	0.92	3
	HT plume	HTP			27-50	1.05 ± 0.01	5
	HT plume	HTP				1.10 ± 0.01	5, 6
≈11°	HT plume	HTP			20-50	1.16 ± 0.01	5,6
9°03,	R 15-56	AB	<0.1		0.00987	1.07 ± 0.03	7
8°24	SD 8-2	AB	≤2.0		0.383	1.13 ± 0.01	7
			<0.1	melting	0.390	1.12 ± 0.015	7
	00.00		total	melting	0.773	1.13	7 7 7 7 2
	SD 8-3	Т	0.05-0.10	1500	2.48 ± 1.04	1.3 ± 0.18	2

Table 2. Helium isotopes in rocks and hydrothermal plumes of the northern part of the EPR.

Notes: * = Mean 3 He/ 4 He and extreme contents of He in 10 specimens. T = tholeiite, TR = transitional basalt, AB = alkaline basalt, HTP = hydrothermal plume. *In HTP per g H₂O.

^b1 = Ozima and Zashu (1982); 2 = Kyser and Rison (1982); 3 = Marty and Ozima (1986); 4 = Merlivat et al. (1987); 5 = Welhan and Craig (1983); 6 = Kim et al. (1984); 7 = Graham et al. (1988).

ocean from the rise. It results from submarine hydrothermal discharge together with volcanic activity along the EPR crest. Hydrothermal fields have been discovered and sampled on the rise axis at 21°N (Lupton et al., 1980; Welhan and Craig, 1983), 13°N (Merlivat et al., 1984, 1987; Kim et al., 1984), and 11°N (Kim et al., 1984). According to the cited sources, these fluids contain helium with highly uniform ³He/⁴He ratios of $(1.05-1.09) \times 10^{-5}$, which conform with the MORB range. Recently, numerous active and extinct hydrothermal vents have also been discovered in the EPR segment between 9°03′ and 9°54′N (Haymon et al., 1991), where Site 864 of the Ocean Drilling Program (ODP) is located. Some of these vents were sampled during previous investigation of this segment, but the obtained ³He/⁴He data have not been published yet (M. Lilley, pers. comm., 1992).

The same MORB helium was found in the rise crest rocks (Table 2), which are dominated by tholeiites. Isotopically, the same helium is contained in the young (<7 m.y.) tholeiites produced on seamounts away from the EPR, but the seamount alkaline basalts differ noticeably from tholeiites by lower ³He/⁴He ratios, down to 0.12×10^{-5} (Graham et al., 1988, table 4 and fig. 7). The two samples of alkaline basalts collected on the rise at 9°03'N and at 8°24'N do not differ from tholeiites in their ³He/⁴He values (Table 2). However, the recent study of the EPR from 5 to 15°N and at 23°N showed that in detail the alkaline basalts along the ridge axis are measurably lower in the ³He/⁴He ratio than associated tholeiites (D. Graham, pers. comm., 1993).

All samples listed in Table 2 were obtained by dredging. Drilling operations at Site 864 recovered specimens directly from the uppermost layer of the "zero-age" oceanic crust. Therefore, the purpose of this study was to determine the abundance of major volatiles and helium isotopes in the authentic oceanic basalts of zero age of this part of the EPR for further comparison with previously studied parts of the EPR and other oceanic spreading centers.

SAMPLES

The sampled "ODP lava flow" is ≤ 1000 years old (Haymon et al., 1991). We have analyzed three samples from the roof of this flow:

Sample 142-864A-1M-2, 0–35 cm, Sample 142-864A-1M-5, 0–100 cm, and Sample 142-864A-1M-6, 0–75 cm. These represent angular to subrounded rock fragments, mostly from 5 to 25 mm across, recovered by junk basket from lithologic Unit 1.

According to on-board studies (Shipboard Scientific Party, 1993; for details and results of on-shore studies see other chapters in this volume), these rocks are very fresh, massive aphyric N-type basalts with uncommon plagioclase phenocrysts ($\leq 1\%$) ranging in size from <0.3 mm to <2.0 mm. Plagioclase is the predominant groundmass phase. The groundmass textures vary from glassy to microcrystalline (Samples 142-864A-1M-2, 0–35 cm, and 142-864A-1M-5, 0–100 cm) to very fine-grained (Sample 142-864A-1M-6, 0–75 cm). In the glassy to microcrystalline samples, well-developed quench overgrowths of individual crystals suggest rapid lava cooling.

Vesicle content is low ($\leq 1\%$). The size of the vesicles is smallest in Sample 142-864A-1M-2, 0–35 cm (<0.05 mm in diameter; vesicles are round and dispersed). It is larger in Sample 142-864A-1M-5, 0–100 cm (<1 mm across, usually 0.02–0.8 mm; vesicles are round shaped to irregular and their distribution is dispersed). In Sample 142-864A-1M-6, 0–75 cm, there are two generations of vesicles: small, round ones (≤ 0.03 mm) and larger, irregular ones (0.1–0.4 mm); there are also very few large circular vesicles up to 6 mm in diameter. It is noteworthy that some pieces from the lower part of the same section (Sample 142-864A-1M-6, 75–150 cm) are highly vesicular (up to 8%).

The contents of major volatiles and helium isotopes were determined in these samples.

ANALYTICAL PROCEDURES

Major Volatiles

Volatile components (H₂O, CO₂, CO, CH₄, H₂, O₂, N₂) were extracted from pure glass fragments crushed to 0.5-1.0 mm. The experimental methods were similar to those described by Byers et al. (1986). The samples were degassed by heating at 10°/min from 130° to 1230°C in the quartz furnace in vacuum of 10^{-5} Pa. The contents of the extracted volatiles were determined by means of a single-col-

Table 3. Volatile contents in the Site 864 basalt glasses.

	Samples				
Core, section: Interval (cm):	142-864A-1M-2 0-35	142-864A-1M-5 0-100	142-864A-1M-6 0-75		
H2O (wt%)	0.160	0.206	0.183		
CÕ ₂ (wt%)	0.041	0.043	0.042		
N2 (wt%, 10 ⁻³)	21.7	27.0	8.62		
O_2^{-} (wt%, 10 ⁻³)	1.70	4.20	1.96		
H ₂ (wt%, 10 ⁻³)	1.805	1.741	1.937		
CÕ (wt%, 10 ⁻³)	4.47	3.02	8.16		
CH ₄ (wt%, 10 ⁻³)	0.697	0.925	0.447		
Total content (cm3/g)	2.71	3.50	2.98		
Weight (mg)	34.2	36.0	34.1		

lector magnetic MS-10 mass spectrometer; for calibration we used the well-studied MIGEI meteorite material (Semenenko et al., 1987) as a standard. The volatile contents in this standard are in the ranges observed in our experiments. Reproducibility of standard values was \geq 85%. Concentrations of different components were measured with a relative error of \leq 1% for each component. These experiments enabled us to investigate the temperature-dependent features of degassing and to calculate total contents of various components and their sum in the studied samples.

The weight of specimens used in our experiments for the extraction of both major volatiles and helium varied from 29 to 47 mg.

Helium Isotopes

The measurements were made on a single-stage static MI-1201-IG mass spectrometer. Quoted accuracies are $\pm 8\%$ (1 σ) for helium isotope concentrations, and generally $\leq 1\%$ for helium isotopic ratio. A helium portion (He = 4.22×10^{-6} cm³ STP) with atmospheric ³He/⁴He ratio used as a standard (the Ne content in the standard was $\leq 5 \times 10^{-11}$ cm³ STP). Helium concentrations were calculated from the measured isotopic ratio and the ⁴He beam size were compared to those from a known aliquot of air standard. Difference in size of helium portions between the standard and the samples can distort the ³He/⁴He values; a character of this distortion depends on mass spectrometer alignment. Therefore, the appropriate calibration was used to correct meter reading, and the corrected ³He/⁴He ratios are shown in Table 3. After loading the samples into a vacuum line for helium extraction, the line was baked at 150°-200°C for over 12 hr to provide a good vacuum ($<6 \times 10^{-7}$ Pa); the samples were also preheated at ~120°C during the baking. The possible diffusive helium losses during this procedure could decrease the total He content but not the ³He/⁴He value in basalt glasses. The typical hot blank for the 1650°C fraction was ${}^{4}\text{He} = 5 \times 10^{-10} \text{ cm}^{3} \text{ STP}$.

Two powder fractions of different size (0.5–1.0 mm and \leq 0.05 mm) were prepared from each sample. Helium was extracted from both by stepwise heating in two steps at 750°C and 1650°C. The samples were heated in a tantalum crucible placed inside a high-temperature vacuum furnace. The gas released at each T-step was cleaned from chemically active components with the use of an activated charcoal trap (cooled by liquid nitrogen) and a Ti-getter. Two successive cleaning stages were used to separate the light rare gases (He + Ne) from the heavy ones (Ar + Kr + Xe). It was impossible to separate He from Ne in this experiment because the system did not include cryogenic facilities; however, the partial pressure of Ne was not significant to distort the helium isotopic ratio.

When measuring the helium isotopic ratios, the static vacuum conditions were maintained by an activated Ti mirror located near the ion source. The sorption of chemically active components on the Ti mirror surface (cooled by liquid nitrogen) ensured a negligible background of the hydrogen doublet H_3^+ -HD⁺, the ion current of which was below 5×10^{11} A. We used the secondary-emission multiplier to

detect the ³He⁺ current, and the ⁴He⁺ ion current was registered by a Faraday collector.

RESULTS AND DISCUSSION

Major Volatiles

Both the total and partial contents of volatile components in the studied samples vary significantly (Table 3). H_2O is predominant (~80% by weight of the volatiles), with the remainder of the components almost entirely of CO_2 (~17%–20%) with a small admixture of CO, CH_4 , H_2 , N_2 and O_2 (the estimate of total volatile content cited in Table 3 includes the concentrations of H_2S , SO_2 , and HCl present in the studied gases but not measured because from technical difficulties). A relative difference in the contents of H_2O does not exceed 30%. Notably, this difference is much smaller for H_2 (~11%) and especially for CO_2 (~5%). In contrast, the contents of the other components are much more variable. If Sample 142-864A-1M-6, 0–75 cm, is not included, the relative differences decrease to 25% for N_2 , 33% for CH_4 , and 48% for CO.

The content fluctuations of some components are interrelated: the increase of H_2 and CO is accompanied by a proportional decrease of CH₄, as well as of N₂. This may possibly result from chemical reactions in which H₂, CO₂ and CH₄ participate (e.g. CO₂ + 4H₂ \leftrightarrow CH₄ + 2H₂O; see: Javoy and Pineau, 1991).

Comparison with the previously studied spreading zones (Table 1) shows that the H_2O/CO_2 ratio in the Site 864 basalts is inverse to that observed at 21°N on the EPR and similar to that in Mid-Atlantic Ridge rocks. The Site 864 basalts contain 2 times as much H_2O as the Galapagos Spreading Center rocks and 1.5 times as much as those from the 21°N area. In contrast, the CO_2 and CO contents in the studied samples are the lowest values among those observed in other spreading centers whereas CH_4 is the highest.

The sum of H_2O and CO_2 contents in the Site 864 rocks is noticeably less than the total volatile contents cited in Table 1. Unlike our data, those evaluations include the concentrations of Cl, F, and S. If these components are contained in the samples from Site 864 in the same proportion, the total volatile abundance in Site 864 samples will still be the lowest ones.

The experiments reveal the release behavior of different components depending on temperature (Fig. 1). The release of CO₂ and N₂ begins at the lowest temperatures; their first concentration peaks appear at ~250°C. CO₂ has three peaks: a small one at ~750°C, a higher peak at ~1000°C, and the highest one at ~1100°C. The last peak is accompanied by the second major peak of the N₂ release. The third CO₂ peak coincides with the maximum release of H₂O. Another, lower H₂O peak is recorded at ~750°C, together with the second CO₂ peak, near the only peak of H₂. CO is released within the wide temperature interval, whereas CH₄ has two peaks, the smaller one in the range of 150°–450°C and the larger one at 900°–1200°C. The last one coincides with the N₂ and CO₂ highs. The only O₂ peak was observed at the same temperature in our experiment.

Most of the volatile components are released at >750°C (see Fig. 1). The CO₂, N₂, and CH₄ peaks at ~250°C seem to have resulted from the decomposition of some products of basalt hydrothermal alteration, because its traces were observed on some outer surfaces of rock fragments by the shipboard studies. The experiment indicated that from one-third to one-half of the total volatile content is separated within the temperature interval 900°–1050°C. This interval coincides with experimental evaluation of the temperature limits of the vacuoles decrepitation (Poreda, 1982; Jambon et al., 1986), and, hence, gas of such composition occurs within the closed vesicles included in the rock matrix. The gases extracted at higher temperatures, from 1050°C to 1230°C (the CO₂ maximum and the peaks of N₂, O₂, and CH₄) occur, evidently, within the glass matrix.



Figure 1. Mass pyrograms of basalt glasses from Hole 864A, Unit 1, showing the release behavior of different volatiles. Ion intensities are proportional to abundance.

Helium Abundance

The basalts recovered from Hole 864A are characterized by high helium contents up to $\sim 4 \times 10^{-5}$ cm³ STP/g (Table 4). These contents are similar to the maximum values found in the EPR rocks and are comparable to those observed in the water of hydrothermal plumes (see Table 2).

The total content of helium preserved in the rock fragments of different size is not the same: the He content in the gross powder fractions (0.5–1.0 mm) is noticeably higher than that in the fine ones (\leq 0.05 mm) of the same sample (Table 4). This difference is common

Table 4. Helium	isotopes in	the Site 864	tholeiites.
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Core, section, interval (cm)	Weight (mg)	Size of fraction (mm)	Temp of degassing (°C)	He content (cm ³ STP/g, 10 ⁻⁶)	³ He/ ⁴ He (10 ⁻⁵)
142-864A-	49.95	0.5-1.0	750	37.20	1.165
1M-2, 0–35		0.5-1.0	1650	0.21	1.166
	27.05	0.5-1.0	total	37.41	1.165
	37.05	≤0.05	1650	22.3	1.036
142-864A-	41.55	0.5 - 1.0	750	39.52	1.191
1M-5, 0-100		0.5 - 1.0	1650	0.35	10000
		0.5 - 1.0	total	39.17	1.191
	29.00	≤0.05	1650	20.9	1.037
142-864A-	46.75	0.5 - 1.0	750	37.17	1.185
1M-6, 0-75		0.5 - 1.0	1650	0.38	
		0.5 - 1.0	total	37.53	1.185

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(Table 2). It suggests that a significant He portion is enclosed within vesicles destroyed in the course of preparing fine powder (the size of the vesicles in the studied samples was outlined above). However, the stepwise heating experiments have shown (Tables 2 and 4) that almost the entire helium was evacuated from the rock at <750°C, i.e., before separation of the main part of the other volatiles enclosed within the vesicles (see Fig. 1). Hence, the release of helium from the vesicles has started before their destruction. In our opinion, this is explained by a preferred thermal diffusion of helium through the basalt glass as compared to most of the major volatiles, other than hydrogen. But during their extraction the only H₂ peak independent of the H₂O maximum was observed at ~820°C (Fig. 1), so the process of the He release from rocks requires further investigation.

Helium Isotopes

The powder fractions of the same size obtained from different samples contain helium with very similar 3 He/ 4 He ratio values. The average value in the gross powder fractions of the Site 864 basalt glasses is 1.18×10^{-5} . It corresponds to the generally accepted MORB value and demonstrates the similarity in helium isotopic composition between the Site 864 rocks and tholeiites dredged in other parts of the EPR axis.

At the same time, our experiments showed a difference between the gross and fine powder fractions of the same sample in their ³He/⁴He values. The values in gross fractions appeared higher than those in fine ones (unfortunately, experimental difficulties prevented us from measuring the 3He/4He ratio in the fine fraction of Sample 142-864A-1M-6, 0-75 cm; it will be remeasured later). The same relation was observed during earlier studies of some other samples of the EPR basalts (i.e., HRX 6 B2 and CY-82-31-02; Table 2). Taking into account an occurrence of the significant portion of helium within vesicles, this relation prompts us suppose that the ³He/⁴He ratio in vesicles is higher than that in rock as a whole. The similar conclusion may be drawn from the data obtained by Graham et al. (1992) for basalts of the Mid-Atlantic Ridge (MAR) between 3°S and 19°S: in helium extracted from the rocks by crushing, the 3He/4He ratios are usually higher than those in helium released by melting. Nevertheless, other experiments with the MAR basalts (Marty and Ozima, 1986; Kurz et al., 1982) show that an opposite relation also occurs. So, isotopic composition of He in vesicles and glass matrix requires further investigation and comparative analysis.

C/3He Ratio

The magnitude of this atomic ratio is presently considered the main genetic criterion of the C-bearing gases. Theoretical evaluation of the "bulk earth" ratio in the hypothetical case of an "undissipating" atmosphere is ~107 (Tolstikhin, 1986). Young basalts from the midoceanic spreading centers are characterized by a higher value of ~109 (Poreda et al., 1988), which is attributed to the depleted mantle, the MORB source reservoir. The same values were measured in some gases from the island-arc systems, although values much higher than 10º were also observed (Poreda et al., 1988). Therefore, the intermediate values of $10^7 < C/^3$ He < 10^9 can be supposedly related to the addition of substance from the undepleted mantle, whereas the higher values (>109) observed in the most natural combustible gases evidence their nonmagmatic (biogenic) origin. However, recently the high C/³He values, $(2-20) \times 10^9$, were also found in carbon dioxide fluid inclusions in ultramafic xenoliths from oceanic hotspot volcanics (Trull et al., 1993).

The C/³He ratio in the total mass of volatiles extracted from the samples from Hole 142-864A is ~ 1.9×10^9 . This relation is in very good accordance with published estimates for glasses and vesicles (Marty and Jambon, 1987). Thus, the C/³He ratio values in the basalts recovered at Hole 142-864A coincide with accepted values for the MORB reservoir.

CONCLUSIONS

The sum of H_2O and CO_2 contents in the Site 864 rocks is noticeably less than the total volatile contents in basalts from 21°N at the EPR, as well as from the areas of the Mid-Atlantic ridge (MAR) and Galapagos Spreading Center (GSC) studied earlier (Byers et al., 1986).

The H₂O/CO₂ ratio in the Site 864 basalts is the inverse of that observed at 21°N on the EPR and is similar to that in the MAR rocks. The Site 864 basalts contain 2 times as much H₂O as the GSC rocks and 1.5 times as much as those from the 21°N area. In contrast, the CO₂ and CO contents in the studied samples are the least values among those observed from other spreading centers, whereas the CH₄ content is the highest.

Partial contents of volatile components in the studied samples vary significantly, except for CO_2 . The differences in contents of some components are interrelated: the increase of H₂ and CO is accompanied by a proportional decrease of CH₄, as well as of N₂. This may possibly result from chemical reactions in which H₂, CO₂ and CH₄ participate.

A significant part of the volatile components is released from the rocks under heating at >750°C, during which the vesicles decrepitate and the specimen melts, whereas almost all the helium is released at <750°C (i.e., before the separation of volatiles enclosed within the vesicles). Hence, the release of helium from vesicles begins before their destruction, presumably as a result of preferential thermal diffusion of helium through the basalt glass.

Helium abundance in the Site 864 rocks, $(37 \text{ to } 40) \times 10^{-6} \text{ cm}^3$ STP/g, is similar to the highest He concentrations found in some glasses from 21°N at the EPR.

The values of the ³He/⁴He ratio in the Site 864 basalts vary slightly according to the size of the studied fragments. The ratio is a little lower in helium extracted from the fine powder (≤ 0.05 mm) where the most vesicles were destroyed. This suggests that the glass matrix is contaminated by seawater containing dissolved atmospheric helium. The gross powder (0.5-1.0 mm) contains helium with a ³He/⁴He ratio of 1.18×10^{-5} inherent to MORB.

The C/³He ratio in the Site 864 rocks is $\sim 1.9 \times 10^{\circ}$; it is also a typical value for MORB glasses. Thus, the rocks recovered from Hole 864A do not differ in helium isotopic composition, as well as in the abundance of helium and carbon, from normal mid-oceanic ridge basalts. There is no evidence for the contamination of their parental melts by either the recycling crust (lithosphere), or the undepleted mantle (i.e., by material from any reservoirs distinguishable from the depleted mantle).

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REFERENCES*

Azbel, I.Y., and Tolstikhin, I.N., 1988. Radiogenic Isotopes and the Evolution of the Earth's Mantle, Crust and Atmosphere: Apatity (Kola Sci. Center Publ.). (in Russian)

- Bonatti, E., 1990. Not so hot "hot spot" in the oceanic mantle. Science, 250:107–111.
- Byers, C.D., Garcia, M.O., and Muenow, D.W., 1986. Volatiles in basaltic glasses from the East Pacific Rise at 21°N: implication for MORB sources and submarine lava flow morphology. *Earth Planet. Sci. Lett.*, 79:9–20.
- Craig, H., 1981. Hydrothermal plumes and tracer circulation along the East Pacific Rise: 20°N to 20°S. *Eos*, 45:893.
- Craig, H., and Lupton, J.E., 1978. Helium isotope variations: evidence for mantle plumes at Yellowstone, Kilauea and the Ethiopian Rift Valley. *Eos*, 59:1194.
- Craig, H., and Rison, W., 1982. Helium-3: Indian Ocean hot spots and the East African Rift. Eos, 63:1144.
- Graham, D.W., Jenkins, W.J., Schilling, G.-K., Thompson, G., Kurz, M.D., and Hamphris, S.E., 1992. Helium isotope geochemistry of mid-ocean ridge basalts from the South Atlantic. *Earth Planet. Sci. Lett.*, 110:133–147.
- Graham, D.W., Zindler, A., Kurz, M.D., Jenkins, W.J., Batiza, R., and Staudigel, H., 1988. He, Pb, Sr, and Nd isotope constraints on magma genesis and mantle heterogeneity beneath young Pacific seamounts. *Contrib. Mineral. Petrol.*, 99:446–463.
- Haymon, R.M., Fornari, D.J., Edwards, M.H., Carbotte, S., Wright, D., and Macdonald, K.C., 1991. Hydrothermal vent distribution along the East Pacific Rise crest (9°09'-54'N) and its relationship to magmatic and tectonic processes on fast-spreading mid-oceanic ridges. *Earth Planet. Sci. Lett.*, 104:513–534.
- Jambon, A., Weber, H., and Braun, O., 1986. Solubility of He, Ne, Ar, Kr and Xe in a basalt melt in the range 1250–1600°C: geochemical implications. *Geochim. Cosmochim. Acta*, 50:401–408.
- Jambon, A., and Zimmermann, J.L., 1987. Major volatiles from a North Atlantic ridge glasses and calibration to He: a size fraction analysis. *Chem. Geol.*, 62:117–129.
- 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.
- Kim, K.R., Welhan, J.A., and Craig, H., 1984. The hydrothermal vent fields at 13°N and 11°N on the East Pacific Rise: *Alvin* 1984 results. *Eos*, 65:973.
- Kurz, M.D., Jenkins, W.J., Schilling, J.G., and Hart, S.R., 1982. Helium isotope variations in the mantle beneath the central North Atlantic Ocean. *Earth Planet. Sci. Lett.*, 58:1–14.
- Kyser, T.K., and Rison, W., 1982. Systematics of rare gas isotopes in basic lavas and ultramafic xenoliths. J. Geophys. Res., 87:5611–5630.
- Lupton, J.E., 1983. Terrestrial inert gases: isotope tracer studies and clues to primordial components in the mantle. Annu. Rev. Earth Planet. Sci., 11:371–414.
- Lupton, J.E., Klinkhammer, G.P., Normark, W.R., Haymon, R., Macdonald, K.C., Weiss, R.F., and Craig, H., 1980. Helium-3 and manganese at 21°N East Pacific Rise hydrothermal site. *Earth Planet. Sci. Lett.*, 50:115–127.
- Marty, B., and Jambon, A., 1987. C/³He in volatile fluxes from the solid Earth: implication for carbon geodynamics. *Earth Planet. Sci. Lett.*, 83:16–26.
- Marty, B., and Ozima, M., 1986. Noble gas distribution in oceanic basalt glasses. *Geochim. Cosmochim. Acta*, 50:1093–1097.
- Merlivat, L., Chantal, A., and Philippe, J.-B., 1984. Distribution des isotopes de l'hydrogene, de l'oxygene et de l'helium lans les sources hydrothermales sous-marines de la ride Est-Pacific, a 13°N. C. R. Acad. Sci. Ser. 2, 299:1191–1196.
- Merlivat, L., Pineau, F., and Javoy, M., 1987. Hydrothermal vent waters at 13°N on the East Pacific Rise: isotopic composition and gas concentration. *Earth Planet. Sci. Lett.*, 84:100–108.
- Ozima, M., and Zashu, S., 1982. Noble gases in submarine pillow volcanic glasses. Earth Planet. Sci. Lett., 62:24–40.
- Polyak, B.G., Kononov, V.I., Tolstikhin, I.N., Mamyrin, B.A., and Khabarin, L.V., 1976. The helium isotopes in thermal fluids. In Thermal and Chemical Problems of Thermal Waters (Proc. of the Grenoble Symp., Aug./Sep., 1975): Ann Arbor, MI (IAHS Publ.), 119:17–33.
- Polyak, B.G., and Tolstikhin, I.N., 1985. Isotopic composition of the Earth's helium and the problem of the motive forces of tectogenesis. *Chem. Geol.*, 52:9–33.

^{*}Abbreviations for names of organizations and publications in ODP reference lists follow the style given in *Chemical Abstracts Service Source Index* (published by American Chemical Society).

- Poreda, R., 1982. Helium partioning in basalt glass: comments on a paper by M.D. Kurz and W.J. Jenkins. *Earth Planet. Sci. Lett.*, 59:437–438.
- Poreda, R.S., Jeffrey, A.W.A., Kaplan, I.R., and Craig, H., 1988. Magmatic helium in subduction-zone natural gases. *Chem. Geol.*, 71:199–210.
- Semenenko, V.P., Sobotovich, E.V., and Tertychnaya, B.V., 1987. Meteorites of Ukraine: Kiev (Naukova Dumka Publ.).
- Shipboard Scientific Party, 1993. Site 864. In Storms, M.A., Batiza, R., et al., Proc. ODP, Init. Repts., 142: College Station, TX (Ocean Drilling Program), 55–72.
- Tolstikhin, I.N., 1986. Isotope Geochemistry of He, Ne and Rare Gases: Leningrad (Nauka Publ.).
- Tolstikhin, I.N., Kamensky, I.L., Forjaz, V., Polyak, B.G., Kononov, V.I., and Kudryavtsev, D.I., 1991. Helium isotopes in gases of Sao Miguel Island, the Azores plateau. *Izv. Akad. Nauk SSSR, Ser. Geol.*, 9:137–147. (in Russian)
- Trull, T., Nadeau, S., Pineau, F., Polve, M., and Javoy, M., 1993. C-He systematics in hotspot xenoliths: implications for mantle carbon contents and carbon recycling. *Earth Planet. Sci. Lett.*, 118:43–64.
- Welhan, J.A., and Craig, H., 1983. Methane, hydrogen and helium in hydrothermal fluids. In Rona, P.A., Bostrom, K., Laubier, L., and Smith, A.K.L., Jr. (Eds.), Hydrothermal Processes at Sea Floor Spreading Centers: New York (Plenum), 391–409.

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