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Hydrogen, sulphur and neodymium isotope variations in the mantle beneath the EPR at 12°50′N

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Abstract—Eight ridge and seamount glasses, from the East Pacific Rise near 13°N, have been analysed for δD, $\delta^{18}O$, $\delta^{34}S$, $^{143}Nd/^{144}Nd$, and $^{87}Sr/^{88}Sr$ of whole rocks, $\delta^{13}C$ and $\delta^{18}O$ of the dissolved carbonates, and for major and trace (Nd, Sr, H_2O^+, . . .) elements. The results from this restricted area span nearly the entire field of variations previously reported for MORB compositions: $-88 < \delta D < -54$, $-10.7 < \delta^{13}C_{carb} < -7.4$, $+23.6 < \delta^{18}O_{carb} < +26.9$, $+5.7 < \delta^{18}O < +6.1$, $+0.0 < \delta^{34}S < +1.3$, $0.702616 < {}^{87}Sr/^{88}Sr < 0.702981$, $0.513038 < {}^{143}Nd/^{144}Nd < 0.513180$, $0.09 <$ wt% $H_2O^+ < 0.49$, $218 < \Sigma C < 545$ ppm, $9 < \Sigma C_{carb} < 129$ ppm, and $877 < \Sigma S < 1104$ ppm.

Systematic chemical and isotopic variations are observed among the glasses, from those with low concentrations in incompatible elements (*e.g.* H_2O^+, TiO_2, Nd) and with low δD (≈ -84) and low $^{143}Nd/^{144}Nd$ (≈ 0.513069), to glasses with high concentrations in incompatible elements, high δD (≈ -55), and high $^{143}Nd/^{144}Nd$ (≈ 0.513173). These chemical and isotopic variations are principally reflecting within-mantle magmatic variations with effects due to degassing and/or high level contamination processes of the magma being minor. At least three mantle sources are involved as well as magma-mixing processes. The different end members may represent regions in the mantle which underwent incompatible element depletion in the past to varying extent, with the least depleted one having $\delta D \approx -80$. The H_2O^+ content of the MORB source is estimated to be 0.01–0.06 wt%, assuming 10–20% partial melting. Different degrees of partial melting, accompanied or followed by mixing, produced the observed relations among the incompatible element concentrations and isotopic ratios.

INTRODUCTION

STUDIES OF THE noble gas, Sr, Nd, and Pb isotopic compositions of MORB (Mid Ocean Ridge Basalts) have identified the existence of several reservoirs in the upper mantle. Mixing between these reservoirs can explain the major part of the observed Sr, Nd, and Pb isotopic variations and, at least in part, the noble gas variations (*e.g.* DUPRÉ and ALLÈGRE, 1983; MARTY and OZIMA, 1986; ZINDLER *et al.*, 1984; ITO *et al.*, 1987; STAUDACHER and ALLÈGRE, 1988; HART, 1988). Some of the noble gas isotopic variations, however, have been shown to be associated with phenomena occurring during the evolution of the magma chamber under ridges and eruption on the sea floor, such as interaction with seawater (*e.g.* SARDA *et al.*, 1985). At the East Pacific Rise (EPR) in particular, ZINDLER *et al.* (1984) have shown the presence of large magnitude small-scale heterogeneities which demonstrate that the source materials are intermixed on a scale ranging from ten cm to one km. Despite the large number of isotopic analyses of Nd, Sr, and Pb, relatively few analyses of light stable isotopes such as H, C, and S have been carried out on MORB samples. Contrary to Sr, Nd, or Pb isotopic compositions, initial or primary δD, $\delta^{13}C$, and/or $\delta^{34}S$ values can be more readily modified by late-magmatic or post-magmatic processes such as degassing, interaction with the oceanic crust, or even interaction with seawater. Therefore, δD, $\delta^{13}C$, or $\delta^{34}S$ variations found in MORB are thought to be related in part to such secondary processes (*e.g.* KYSER and O'NEIL, 1984; SAKAI *et al.*, 1984; PINEAU and JAVOY, 1983; MATTEY *et al.*, 1984).

A well-characterized set of samples were studied from a restricted area of the EPR at 12°50′N. The aims of the work were (1) to determine the range of variations of δD and $\delta^{34}S$ values at the EPR, and (2) to try to link these values (δD, $\delta^{34}S$) using constraints from both trace element contents and O, Sr, Nd isotope ratios to variations in magma source compositions. For this purpose eight samples of glass from pillow lavas have been analyzed for their H_2O^+, total and carbonate carbon, sulphur, neodymium and strontium contents, as well as for their δD, $\delta^{13}C$, $\delta^{18}O$, $\delta^{34}S$, $^{143}Nd/^{144}Nd$, and $^{87}Sr/^{86}Sr$ ratios.

LOCATION AND DESCRIPTION OF THE SAMPLES

The samples come from the EPR near 12°50 N (Fig. 1). The depths of collection (Table 1) range from 2163 m for the Clipperton seamount to 2600 m for samples from the axial graben (HEKINIAN and FOUQUET, 1985). Samples labelled V correspond to the external few millimetres of glassy rim of the pillow, which were handpicked from the whole sample. The maximum ages of the samples,

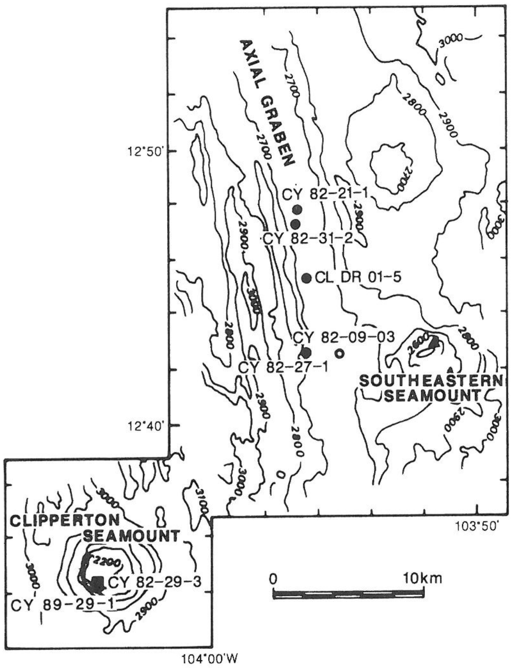

FIG. 1. Map of the East Pacific Rise at 12°50'N, with the location of the samples. CLDR samples were dredged and CY were collected by manned submersible (Cyana) (HEKINIAN and FOUQUET, 1985).

estimated from a maximum total spreading velocity of 12 cm/year (HEKINIAN and FOUQUET, 1985) and the ^{210}Pb/Pb ages on the smokers associated with the ridge (LALOU *et al.,* 1985), are less than 100 years for the axial graben and ≈2000 years for sample CY82-09-03V.

The petrology, mineralogy, and general geochemistry of the samples have been presented by HEKINIAN and FOUQUET (1985). The glasses contain between 5 and 15% phenocrysts and appear to be essentially free of microscopically visible vesicles. A vesicularity of 0.5 vol% has been reported for CY82-31-2V: this is typical of EPR glasses in general (MARTY and OZIMA, 1986). Sample CY82-21-1V also contains a few percent of microcrystalline aggregates and is therefore transitional towards the microcrystalline pillow core. The samples (Table 1, Fig. 2) include: (1) tholeiitic basalts with low TiO_2, K_2O, and FeO^T/MgO (CY82-29-3V, CY82-29-1V, and CY82-21-1V from the Clipperton seamount and axial graben, respectively) which represent the least differentiated basalts in the area; (2) TiO_2-K_2O depleted tholeiitic basalts (CY82-31-2V, CLDR01-5V, and CY82-10-02V from the axial graben zone) which are similar to basalts at 21°N; (3) a high TiO_2-K_2O alkali-enriched basalt with a composition intermediate between a typical alkali and a silica saturated tholeiitic basalt (CY82-09-03V from the southeastern constructional margin of the graben); and (4) a sample (CY82-27-1V from the axial graben) of the Ti-FeO/MgO enriched tholeiite group of HEKINIAN and FOUQUET (1985). These authors suggest that at least two different parent magmas were involved at the EPR 13°N, plus superposition of variable degrees of fractional crystallization and magma mixing (see Fig. 2).

ANALYTICAL PROCEDURES

Initially, one glass was tested for the presence of surface contaminants such as carbonates and sulphates. Several grams of sample (CLDR01-5V) were crushed to 4 mm and attacked by 1 N oxalic acid at 25°C for 12 hours. No measurable difference was observed for the sulphur and carbonate contents of this glass before and after the oxalic acid treatment.

Hydrogen was extracted by fusion of the sample, after pre-heating at either 160°C for two hours under vacuum or 120°C overnight, the water produced being reduced to H_2 by uranium at about 750°C (BIGELEISEN *et al.,* 1952). Oxygen was liberated from silicates using BrF_5 (CLAYTON and MAYEDA, 1963), and carbon and oxygen from carbonates using the 100% H_3PO_4 method (MACCREA, 1950) followed by Ag_3PO_4 purification to remove sulphur contaminants (CHAREF and SHEPPARD, 1984). Yields were measured manometrically and are accurate to ±5%. Isotopic ratios were determined with a VG602D mass spectrometer and are reported in per mil in δ notation against SMOW for H (±2 per mil), and O (±0.2 per mil) and PDB for C (±0.2 per mil) (Table 2). NBS 28 has $\delta^{18}O = +9.6$ in our laboratory.

The extraction line and procedures used for the Kiba technique (extraction of sulphur and carbonate carbon) were similar to those described by UEDA and SAKAI (1983) except that reduced and oxidized sulphur were not routinely separated. Between 0.8 and 3 g of powdered rock were reacted under vacuum at 280°C in a quartz vessel with 50 ml of Kiba solution. Kiba reagent is obtained by adding $SnCl_2$ to H_3PO_4 (>85%, $d = 1.7$ and pre-purified by heating to 250°C for one hour) in the proportion of 1.85 g of $SnCl_2$ for 100 ml of H_3PO_4 followed by heating the mixture up to 280°C (UEDA and SAKAI, 1983). The mean of the sulphur extractions is 92% while measured $\delta^{34}S$ values were constant to within ±0.3 per mil, for yields greater than 75%. Sulphur isotopic measurements are given in δ notation against CDT (±0.3 per mil).

Total sulphur, total carbon, and carbonate carbon contents were additionally determined by another technique: fusion of the sample under a stream of oxygen followed by a coulometric titration (Mr Vernet analyst, CRPG). These values were used to control the yields of the isotopic extractions. The C and S contents agree well with the Kiba technique for high contents, but for low contents (<100 ppm) the agreement was only within ±20%, especially for C. The C and S contents given in Table 2 are the mean of these different techniques.

Sr and Nd analytical procedures are those described by ALIBERT *et al.* (1983) and MICHARD *et al.* (1985). Measurements of standards are listed in Table 4.

Table 1. Chemical analyses of basalt glasses from the EPR 12°50′N.

Sample *Location*	CLDR01-5V *Axial zone*	CY82-31-2V* *Axial zone*	CY82-21-1V†* *Axial zone*	CY82-27-1V* *Axial zone*	CY82-10-02V *Axial zone*	CY82-09-03V* *Constructional high*	CY82-29-3V* *Clipperton seamount*	CY82-29-1V* *Clipperton seamount*
Depths (m)	—	2596	2586	—	—	2623	2173	2180
SiO_2	50.43	49.06	49.12	50.67	51.50	50.33	49.27	49.52
Al_2O_3	15.83	16.90	16.21	15.39	14.53	17.10	16.11	16.36
FeO^T	8.80	7.54	8.49	9.22	8.72	8.40	8.37	8.56
MgO	8.43	9.28	9.60	7.70	7.68	7.55	9.56	9.60
MnO	0.14	0.09	0.05	n.d.	0.15	0.02	0.10	0.21
CaO	12.10	12.06	12.93	11.52	12.20	11.51	12.54	12.50
Na_2O	2.92	2.63	2.14	3.08	2.73	3.15	2.12	2.22
K_2O	0.05	0.11	0.11	0.26	0.06	0.45	0.03	0.04
TiO_2	1.19	1.16	0.90	1.64	1.39	1.81	0.84	0.96
Total	99.89	98.83	99.55	n.d.	98.96	100.32	98.94	99.97
H_2O^+	0.16	0.17	0.21	0.32	0.27	0.49	0.19	0.09
S (ppm)	957	877	1056	1104	n.d.	1073	1011	n.d.
C (ppm)	273	300	327	218	n.d.	545	409	n.d.

* Data (major elements) from HEKINIAN and FOUQUET (1985).
† Contains a few percent of crystalline interior.
n.d.: not determined.

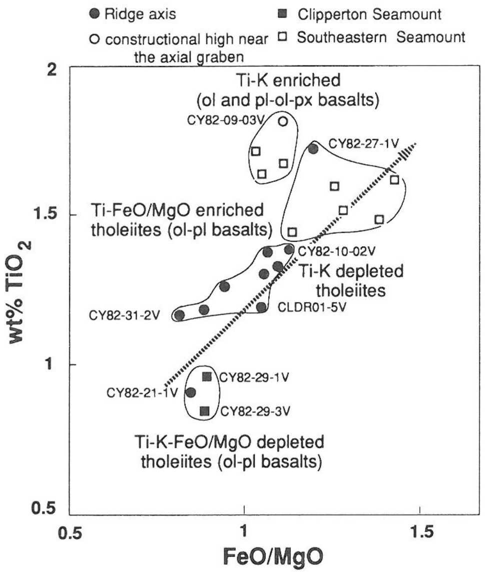

FIG. 2. Wt% TiO_2 versus FeO/MgO ratios for all available samples from the EPR 13°N (data from HEKINIAN and FOUQUET, 1985; and Table 1). The trend for differentiation predicted by HEKINIAN and FOUQUET (1985) and their four different chemical groups are represented. Note the large range of chemical variations of these basalt glasses collected in a restricted area of the EPR, and the absence of correlation between the chemistry and the location.

RESULTS

Water contents and hydrogen isotopes

Water contents show a large variation between 0.09 and 0.49 wt% H_2O^+ (Table 1), with a mean value of 0.24 wt%. They are not correlated with the depth of eruption. Similar to other localities, 13°N basalts are undersaturated in H_2O^+ (DELANEY *et al.*, 1978; BYERS *et al.*, 1983); saturation occurs around 1.5 wt% H_2O^+ for a pressure of 300 bars (extrapolated from HAMILTON *et al.*, 1964). δD values range from -88 to -54 and no direct correlation is observed with the H_2O^+ contents (Fig. 3a, Table 2). Sample CY-82-21-1V, which has the lowest δD value (-88) contains $\approx 10\%$ of micro-crystalline aggregates which were impossible to separate. This could explain a shift of δD towards more negative values by a few per mil, as the crystalline inner parts of this pillow have more negative δD values down to -103 (CHAUSSIDON, 1988). On all figures which include this sample, the tip of the arrow represents the estimated δD value of the pure glass after correction for $\approx 10\%$ content of micro-crystalline basalt.

Step heating experiments have been performed with samples CLDR01-5V and CY82-09-03V (glass chips of several mm to 1 cm or powdered to <74 μm) to examine the effect of grain size on the water release pattern. The ground glass (CY82-09-03V) lost 80% of its water between 160 and 650°C and 20% between 650 and 800°C, whilst the chips of glass (CLDR01-5V) lost $\approx 100\%$ of water between 850 and 1200°C (Table 3). Although the hydrogen release pattern and the δD of the successive fractions are related to the grain size, no difference in total δD or H_2O^+ was seen before or after crushing (sample CLDR01-5V, Table 3). Similar results were previously observed on MORB glasses (KYSER and O'NEIL, 1984), probably indicating differences in the kinetics of diffusion of H and D in the glasses at high temperatures due to variation in grain sizes. The reproducibility of the results also implies that the pre-heating process effectively removed adsorbed water.

Oxygen

The $\delta^{18}O$ values of five glasses were determined (Table 2). They all fall in the range $+5.7$ to $+6.1$, and are similar to values of other EPR basalts (KYSER *et al.*, 1982). This range corresponds to the upper part of the $\delta^{18}O$ range of MORB (*e.g.* KYSER, 1986).

Carbonates

The total carbon contents range from 218 to 545 ppm and carbonate or acid extractable carbon range from 9 to 129 ppm (Table 2). The ratio of carbonate carbon to total carbon is about 0.3 ± 0.1 for four of the glasses, but for the two samples with the highest concentrations it is very low (0.08 and 0.02) (Table 2). This difference cannot be explained by the presence of carbonates as contaminants either at the surface of the glass chips or in the many little cracks which developed in the pillows during cooling. An attempt was made to extract CO_2 by reacting with H_3PO_4 15 to 20 g sample of glass (CLDR01-5V) ground to six mesh (>3.36 mm). Less than one μmole of gas was recovered. These experiments, combined with the fact that we needed finely ground powder (200 mesh ≈ 74 μm) to obtain reproducible yields for CO_2, suggest that the carbonates are present in the rock as "internal" components such as carbonate species as identified by FINE and STOLPER (1986). Bubbles were not observed in the glasses in thin section, and no gas could be recovered during vacuum crushing (<1 μmol/15 g).

The $\delta^{13}C$ of the carbonates range from -10.7 to -7.4 and their $\delta^{18}O$ from $+23.6$ to $+26.9$. There is

Table 2. H, C, O, S quantitative and isotopic analyses.

	Hydrogen		Carbonates				Oxygen	Sulphur	
Samples	wt% H_2O^+	δD	ppm $C_{(tot)}$	ppm $C_{(CO_3)}$[a]	$\delta^{13}C_{(CO_3)}$[b]	$\delta^{18}O_{(CO_3)}$	$\delta^{18}O_{(tot)}$	ppm $S^{(c)}$	$\delta^{34}S$
Ridge axis:									
CLDR01-5V	0.16	−57	273	92	−9.9*	n.d.	6.1	957	0.0
CY82-31-2V	0.17	−54	300	107	−8.0	23.6	5.7	877	1.3
CY82-21-1V†	0.21	−88	327	129	−10.7	24.3	n.d.	1056	1.0
CY82-27-1V	0.37	−66	218	45	−7.4	26.9	6.0	1104	0.8
CY82-10-02V	0.27	−66	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
CY82-09-03V	0.49	−58	545	45	n.d.	n.d.	5.9	1073	1.1
Clipperton seamount:									
CY82-29-3V	0.19	−80	409	9	n.d.	n.d.	6.1	1011	0.4
CY82-29-1V	0.09	−67	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

n.d.: not determined.
* $\delta^{13}C$ obtained by the Kiba method only.
† Contains a few percent of crystalline interior.
(a) carbonate contents are for most samples a mean between coulometric, phosphoric acid, and Kiba techniques.
(b) mean between phosphoric acid and Kiba techniques.
(c) mean between coulometric and Kiba techniques.

no correlation between $\delta^{18}O$ and $\delta^{13}C$. The $\delta^{13}C$ values, however, tend to increase with an increase in TiO_2 (or Nd) and a decrease in CO_3 (Tables 1, 2, and 3). These $\delta^{13}C$ values are only slightly lower than those of most diamonds (≈ −5 and −8; DEINES, 1980) or of CO_2 released from vesicles or carbon liberated during high temperature (>600°C) combustion of MORB (PINEAU and JAVOY, 1983; MATTEY *et al.*, 1984; JAVOY *et al.*, 1986). However, they are very different from the very light MORB $\delta^{13}C$ values (≈ −20 to −25) which are interpreted either as traces of organic carbon contaminant or of important degassing of CO_2 of the upper mantle (*e.g.* MATTEY *et al.*, 1984; JAVOY *et al.*, 1986). The $\delta^{18}O$ values of the carbonates are within the range reported by PINEAU and JAVOY (1983) for MORB from the MAR and the EPR.

Sulphur

The glasses have sulphur contents of 1000 ± 90 ppm. Based on 35 fresh MORB glasses (MATHEZ, 1976), sulphur solubility in basaltic magmas has been shown to be principally related to Fe content. Using these data and the mean Fe content of our EPR glasses (6.6 wt%; Table 1), the value for sulphur saturation can be estimated to be about 1020 ppm. Taking into account the volume of phenocrysts present in the glasses (≈2.5 to 10% by volume olivine and ≈2.5 to 10% by volume plagioclase; HEKINIAN and FOUQUET, 1985) the actual sulphur contents of the glass are probably from 3 to 14% higher than the measured ones (Table 2). However, this correction is imprecise. Gas inclusions (SO_2 or H_2S) were not observed, but small magmatic sulphide globules (micron size) have been detected in one glass (CY82-21-1V) in accordance with saturation of the glass with sulphur. All the glasses from 13°N (except possibly CY82-31-2V) can be considered to be sulphur saturated.

The range of $\delta^{34}S$ values of the glasses is 0.0 to +1.3 with a mean of +0.8 ± 0.5 (Fig. 3b). These $\delta^{34}S$ values represent nearly the whole range of $\delta^{34}S$ already found for MORB (SAKAI *et al.*, 1984). No systematic differences are noted between samples from the ridge and the Clipperton seamount (Table 2). The "magmatic value" of $\delta^{34}S = +0.8 \pm 0.5$ for 13°N sulphur saturated glasses is a little higher than that estimated from other ridges (+0.3 ± 0.5; SAKAI *et al.*, 1984). However, data from SAKAI *et al.* (1982, 1984) show clearly that $\delta^{34}S$ values of +1.0 can be found for basaltic glasses. They have related these values to the sulphate/sulphide ratio in the rock, itself related to the water content.

Strontium and neodymium

$^{143}Nd/^{144}Nd$ and $^{87}Sr/^{86}Sr$ ratios as well as Sr and Nd contents are given in Table 4. The total spread of the isotope data from 0.513038 to 0.513180 for Nd isotope ratios and from 0.702616 to 0.702981 for Sr isotope ratios is outside the analytical uncer-

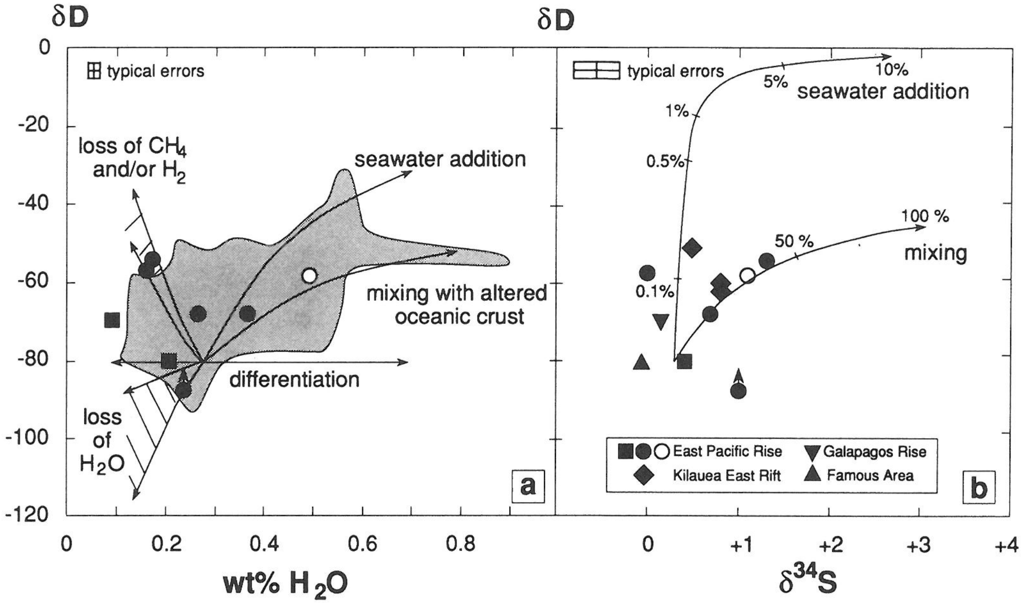

FIG. 3. δD of 13°N EPR glasses versus their water contents (Fig. 3a) and their $\delta^{34}S$ values (Fig. 3b). Data are from CRAIG and LUPTON (1976), KYSER and O'NEIL (1984), POREDA *et al.* (1986) (grey field), SAKAI *et al.* (1984), and from this study: solid square for the Clipperton seamount, solid circles for the ridge axis, and open circle for the constructional high near the axial graben, as in Figs. 1 and 2. In Fig. 3a trends are shown for loss of H_2O, loss of CH_4 or H_2, mixing with altered oceanic crust, direct seawater addition, and differentiation, for an arbitrary starting point corresponding to the mean of all the data with $\delta D < -70$ ($\delta D = -80 \pm 10$ and wt% $H_2O^+ = 0.27$). In Fig. 3b mixing lines are represented between a magmatic end member (0.27 wt% H_2O^+, $\delta D = -80$, 800 ppm S, $\delta^{34}S = +0.3$) and either seawater ($\delta D = 0$, 28.6 mM SO_4^{2-}/kg, $\delta^{34}S = +21$) or another magmatic pole (1 wt% H_2O, $\delta D = -45$, 800 ppm S, $\delta^{34}S = +3$).

tainties, and therefore reflects real sample variations at the EPR 13°N. The same range of variations has already been found for the EPR (MACDOUGALL and LUGMAIR, 1986), although their four samples from the EPR near 13°N have $^{143}Nd/^{144}Nd$ and $^{87}Sr/^{86}Sr$ ratios restricted to 0.513133 ± 7 and 0.702591 ± 19, respectively. Since the submission of the present work, PRINZHOFER *et al.* (1989) published Sr and Nd isotope analyses on some of the samples analyzed here. Their results show the same ranges of variations as those found in this study and confirm the fact that the isotopic heterogeneity is present at a very small scale, down to the sample scale. This outlines the interest of the present work which gives H, S, Sr, and Nd isotopic measurements on the same chip of sample. In a diagram of $^{143}Nd/^{144}Nd$ versus $^{87}Sr/^{86}Sr$ our data plot within the "mantle array" like all other samples from the ridge or seamounts

Table 3. H_2O step heating extractions.

T (°C)	160†–650	650–800	800–1400	Mean	Duplicate*
CY82-09-03V (powdered)					
wt% H_2O	0.42	0.1	<0.01	0.52	0.49
δD ‰	−58	−46	—	−56	−58
CLDR01-5V (chips)					
wt% H_2O	—	—	0.16	0.16	0.16
δD ‰	—	—	−57	−57	−58

† H_2O^- was removed by heating under vacuum at 160°C for 2 hours.
* Duplicate obtained on powdered samples.

of the EPR (MACDOUGALL and LUGMAIR, 1986; ZINDLER *et al.*, 1984; ITO *et al.*, 1987). No correlation is observed between the $^{143}Nd/^{144}Nd$ and $^{87}Sr/^{86}Sr$ ratios. This is not surprising on a restricted set of samples, because at the EPR one finds a large range of variations of Nd isotope ratios for a given Sr ratio, as well as the contrary (MACDOUGALL and LUGMAIR, 1986). However, our samples define a positive correlation between the Nd and Sr contents (Table 4), which is not clear in previous data.

DISCUSSION

The H and S isotope compositions of MORB glasses can be a function of both the source region of the magma and high-level late magmatic and post-magmatic processes. The relative importance of these different possibilities can be assessed by examining the nature of the relationships between δD or $\delta^{34}S$ and those parameters which directly reflect characteristics of the source regions, such as the $^{143}Nd/^{144}Nd$ ratio and certain chemical constituents. Thus, this section first considers such relationships.

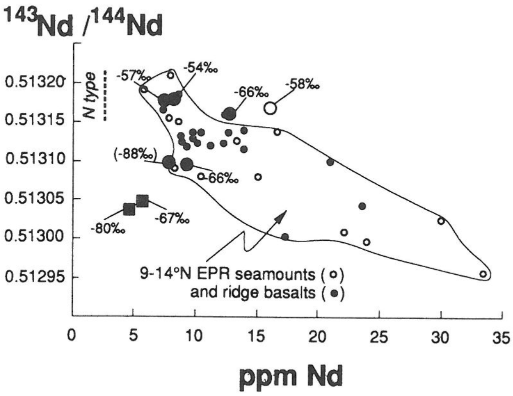

FIG. 4. $^{143}Nd/^{144}Nd$ of the EPR ridge and seamount basalts versus their Nd contents (data from ZINDLER *et al.*, 1984; PRINZHOFER *et al.*, 1989; and this work). δD values for the EPR 13°N are given for each sample. Symbols for the EPR 13°N are the same as in Figs. 1, 2, and 3. Note that the samples from this study do not plot entirely within the field of previous data and that a rough trend of increasing $^{143}Nd/^{144}Nd$ with increase of Nd contents is observed. This is best interpreted in terms of mixing between different and variably depleted sources. Most depleted N-type MORB samples typically have the highest δD values.

Relations among δD, $^{143}Nd/^{144}Nd$, and chemistry

The data for δD, $^{143}Nd/^{144}Nd$, Nd, H_2O^+, and TiO_2 contents are plotted on Figs. 4 and 5. Parameters such as Nd, TiO_2, and $^{143}Nd/^{144}Nd$ are not readily modified by late- and post-magmatic processes. For example, we do not expect any variation from a mantle $^{143}Nd/^{144}Nd$ ratio or any change in the Nd content of the magma during either the direct contamination of the magma by seawater or during assimilation of seawater hydrothermally altered oceanic crust, because the concentrations of Sm and Nd in seawater are very low, 0.545 ± 0.04 10^{-6} ppm and 2.58 ± 0.23 10^{-6} ppm, respectively (PIEPGRAS and WASSERBURG, 1982). The Nd and $^{143}Nd/^{144}Nd$ ratio variations (Figs. 4 and 5a) therefore support the interpretations of HEKINIAN and FOUQUET (1985) that at least two magmas were involved at EPR 13°N. In fact, comparison of our data with those from the ridge basalts and sea-

Table 4. Strontium and neodymium measurements of EPR (12°50N) MORB glasses.

Sample	Sr	$^{87}Sr/^{86}Sr$	Nd	$^{143}Nd/^{144}Nd$
Ridge axis				
CLDR01-5V	93	0.702616 ± 31	7.45	0.513178 ± 28
CY82-31-2V	116	0.702617 ± 28	8.15	0.513180 ± 27
CY82-21-1V	109	0.702617 ± 31	7.83	0.513099 ± 24
CY82-27-1V	159	0.702981 ± 35	12.75	0.513162 ± 29
CY82-10-02V	118	0.702623 ± 40	9.21	0.513096 ± 22
CY82-09-03V	219	0.702670 ± 30	16.00	0.513170 ± 29
Clipperton seamount				
CY82-29-03V	79	0.702666 ± 31	4.60	0.513038 ± 28
CY82-29-01V	88	0.702719 ± 31	5.63	0.513048 ± 21

Sr and Nd contents are given in ppm.

Measured values for the Eimer and Amend standard and the La Jolla standard are respectively. $^{87}Sr/^{86}Sr = 0.708030$ (±38) and $^{143}Nd/^{144}Nd = 0.511841$ (±25). $^{87}Sr/^{86}Sr$ normalized to $^{86}Sr/^{88}Sr = 0.1194$, $^{143}Nd/^{144}Nd$ to $^{146}Nd/^{144}Nd = 0.7219$. Data obtained on a Cameca 206S, single collector.

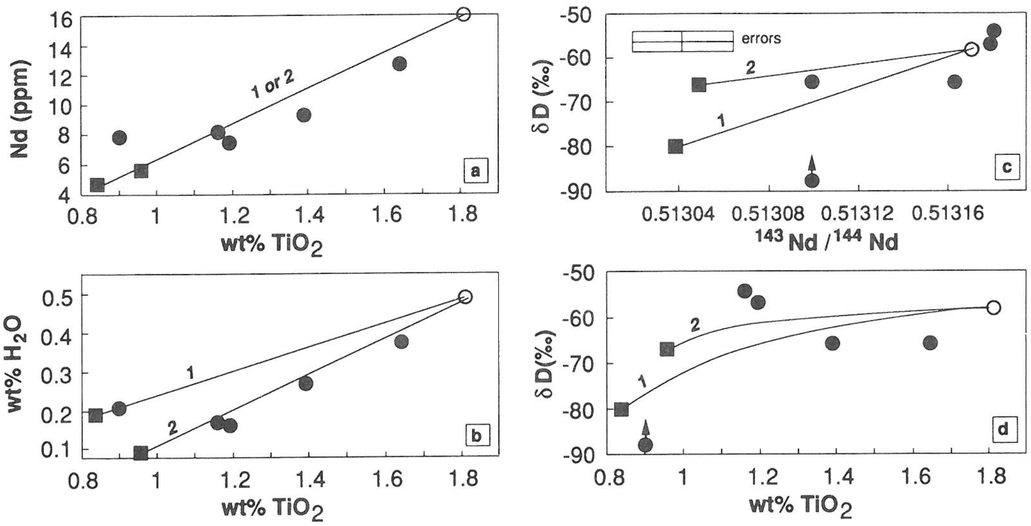

FIG. 5. Variations of the Nd (Fig. 5a), water (Fig. 5b) contents, and δD values (Fig. 5d) versus the TiO_2 contents for all the glasses from the EPR and of the δD values versus the $^{143}Nd/^{144}Nd$ ratios (Fig. 5c). Symbols are the same as in Figs. 1, 2, and 3. Mixing lines between samples with extreme Nd contents (CY82-29-3V, CY82-29-1V, and CY82-09-03V) are presented (see text). In Fig. 5c high δD values (-55 ± 5) appear to be systematically associated with high $^{143}Nd/^{144}Nd$ ratios (>0.513160), corresponding to N-type MORB.

mounts between 9° and 14°N (EPR) on Fig. 4 show that they scatter about a trend which is nearly opposite to that observed by ZINDLER *et al.* (1984) and that therefore three or more mantle sources are involved at 13°N.

On a Nd versus TiO_2 diagram any mixing between two end members gives a straight line. The line labelled 1 or 2 on Fig. 5a is such a mixing line between samples having the lowest and the highest Nd contents. The reasonable correlation shown between Nd and TiO_2 indicates that, to a first approximation, most of the Nd and TiO_2 variations can be explained by a two end-member mixing model. A similarly reasonable correlation is observed with FeO/MgO (Fig. 2), K_2O, Sr, and Nd (Tables 1 and 4). If, as suggested by HEKINIAN and FOUQUET (1985), part of the variation in TiO_2 and FeO/MgO can be explained by a fractional crystallization process, this might also explain part of the H_2O^+ variation (Fig. 5b), because water in MORB melts behaves like an incompatible element. Measurements of H_2O^+ contents in Juan de Fuca ridge basalt glasses have shown that water has a bulk distribution coefficient of ≈0.01 similar to that of La during partial melting (DIXON *et al.*, 1988). However, for TiO_2, Nd, K_2O, H_2O, etc., this would require more than 50% fractional crystallization, which is unrealistic. Noting that the various melt-mineral partition coefficients for all these elements are not similar to each other (*e.g.* COX, 1983), these correlations exclude fractional crystallization as the principal cause of the elemental variations.

The water content increases with increase in TiO_2 content (Fig. 5b) but the correlation is not so good as in Fig. 5a. Two mixing curves are shown, because of the large variations in H_2O^+ at very low TiO_2 values. These two curves are indistinguishable on Fig. 5a. The H_2O^+ contents of the different glasses can also be interpreted to be dominantly controlled by magma-magma mixing processes or other magmatic processes taking place in the upper mantle. Although two low-TiO_2 end members are necessary to account for the observed relations, note that sample CY82-21-1V on mixing curve 1 plots above the curve labelled 1 or 2 on Fig. 5a.

Figures 5c and d present the δD data as a function of $^{143}Nd/^{144}Nd$ and TiO_2 content. The mixing curves 1 and 2 are from Figs. 5a and b. Although there is no *a priori* reason why δD should be coupled to $^{143}Nd/^{144}Nd$ or TiO_2, some trends are observed. The most deuterium-depleted glasses ($\delta D \approx -80$) have $^{143}Nd/^{144}Nd$ lower than 0.51310 and low TiO_2 (<1 wt%), whilst the most D-enriched samples ($\delta D > -60$) have higher $^{143}Nd/^{144}Nd$ (>0.51316) and higher TiO_2. These relations, together with the trend of increasing H_2O^+ with an increase in TiO_2, imply that at least a major part of the δD variation must also be inherited from the mantle source regions.

Such correlations involving δD have rarely been found in MORB except for the oceanic ridges near

Iceland where Poreda *et al.* (1986) reported correlations between δD, H_2O^+, La/Sm, and $^{87}Sr/^{86}Sr$. For these ridges several local variations over a few degrees of latitude were found to be opposite to the general trend followed by samples collected over 20° of latitude. Additionally, for seamount glasses from the EPR 21°N and 12–14°N, Aggrey *et al.* (1988) reported correlations between the water contents and both the La/Sm and $^{87}Sr/^{86}Sr$ ratios. They interpreted these in terms of magma mixing between at least two different sources.

Viewing all of these relationships as a whole (Figs. 2 to 5) indicates that most of the chemical and isotopic variations in all of our glasses record within-mantle magmatic processes. At least three sources are required plus magma mixing. These conclusions specifically apply to H_2O^+ and δD. The scatter about the mixing curves on diagrams such as δD versus $^{143}Nd/^{144}Nd$ reflects the absence of perfect coupling between these parameters. However, good coupling between δD and H_2O^+ is to be expected if late magmatic processes such as degassing or interaction with seawater were dominant processes (Fig. 3). Contamination by (1) assimilation of seawater hydrothermally altered oceanic crust, which is estimated to have $\delta D = -45 \pm 10$ and $H_2O^+ = 1.5$ wt%, based on data from the Troodos ophiolite (Heaton and Sheppard, 1977; Sheppard, 1980), or (2) mixing with magmas produced by partial melting of the seawater hydrothermally altered roof rocks above the high-level magma chamber (Heaton and Sheppard, 1977; Taylor, 1977, 1980), which could have compositions comparable to plagiogranite (Coleman, 1977) and δD values of about -50 (Heaton and Sheppard, 1977) can also be excluded as dominant processes. Such processes cannot be totally excluded, but they have not contributed to the overall general trends and variations. Similarly, it is considered very improbable that the different sources had similar δD values and that processes such as degassing or direct or indirect addition of seawater (Fig. 3a) have been effective selectively for each glass.

Sulphur and carbon isotope heterogeneities

All the MORB samples (glassy rims of pillows only) yet analyzed both for δD and $\delta^{34}S$ are plotted in Fig. 3b, together with the samples from this study. The data are scattered with no well-defined trend, although samples with high δD values more often have high $\delta^{34}S$ values. This diagram emphasizes, however, that seawater addition can only be a minor process in controlling the $\delta^{34}S$ of the ridge and seamount glasses, because it would drastically increase the δD value before increasing the $\delta^{34}S$ value. A mixing line is presented in Fig. 3b between one end member with $\delta D = -80$ (0.27 wt% H_2O^+) and $\delta^{34}S = +0.3$ (800 ppm S) and another with $\delta D = -45$ (1 wt% H_2O^+) and $\delta^{34}S = +3$ (800 ppm S). The values chosen for the former correspond to the mean of all the available δD-H_2O^+ data on MORB samples having $\delta D < -70‰$ (data from Craig and Lupton, 1976; Kyser and O'Neil, 1984; Poreda *et al.*, 1986; and this study) and for sulphur to the mean of all MORB samples (data from Sakai *et al.*, 1984; and this study). The latter end member represents parts of the mantle which could have high δD and $\delta^{34}S$ values. Ion microprobe $\delta^{34}S$ measurements have shown that unaltered immiscible mantle sulphides can have $\delta^{34}S$ values of +3 (Chaussidon *et al.*, 1989). Furthermore, amphibole pyroxenite layers from orogenic spinel lherzolite massifs from Ariège (Northeastern Pyrénées, France) contain sulphides having a mean $\delta^{34}S$ value of +3 (Chaussidon and Lorand, 1990), and such massifs can contain amphiboles having high δD values (up to −47; Javoy, 1980). The origin of these variations of δD and $\delta^{34}S$ in the mantle will be addressed below, but it is striking to note that altered oceanic crust (subducted or not) is known to have such high δD and $\delta^{34}S$ values (*e.g.* Heaton and Sheppard, 1977; Sheppard, 1980; Alt *et al.*, 1989).

Despite the limited $\delta^{13}C$ data on carbonate species in glasses, the observed trends between $\delta^{13}C$ and TiO_2 or Nd, etc., imply that the $\delta^{13}C$ values are also predominantly reflecting within-mantle magmatic processes. These trends can similarly be due in part to magma-mixing processes. Degassing of CO_2 may not have been very important in so far as the trend of increasing $\delta^{13}C$ with decreasing CO_3 content is not in the expected sense (Taylor, 1986). The $\delta^{18}O$ values are not understood, as they are too ^{18}O-enriched to be in equilibrium with silicate magma and there is no other evidence to invoke low temperature exchange processes (30–60°C if in equilibrium with seawater) or mixing with marine carbonate. We note, however, that such values have also been reported from the MAR and the EPR (Pineau and Javoy, 1983).

δD variations in the mantle

The range of δD values from MORB and seamount glasses, $-90 < \delta D < -40$ (Craig and Lupton, 1976; Kyser and O'Neil, 1984; Poreda *et al.*, 1986; this study), is indistinguishable from that reported on phlogopites, kaersutitic, and pargasitic amphiboles from kimberlites, peridotites, and alkali intrusions (SHEPPARD and EPSTEIN, 1970; SHEPPARD and DAWSON, 1975; SHEPPARD *et al.*, 1977; BOETTCHER and O'NEIL, 1980; JAVOY, 1980). For all these types of samples, interpretations have fallen into two main categories. Firstly, the isotopic variations are principally related to mantle heterogeneities. Secondly, the initial δD value of the mantle is inferred to be about -70 ± 10, and the higher δD values are assumed to be a product of late-stage magmatic or post-magmatic processes acting in the continental or oceanic crustal environment. However, concerning the latter hypothesis no generally applicable arguments have been presented to exclude the possibility that some parts of the mantle have $\delta D > -60$. This study supports the original proposition of SHEPPARD and EPSTEIN (1970) that the D/H ratio of the mantle is quite variable. Moreover, D/H ratios of certain amphiboles from mantle-derived lherzolite xenoliths have recently been shown (DELOULE *et al.*, 1991) to be variable on a sub-millimetric scale, using ion microprobe techniques.

The scale of δD variations at the EPR 13°N is on the order of 100 m from our sampling, and no general relationship can be discerned between δD and the occurrence of the basalt (ridge or seamount). This suggests, as proposed by ZINDLER *et al.* (1984) for Nd and Sr, that the scale of δD heterogeneity in the mantle beneath the EPR is also very small.

The high $^{143}Nd/^{144}Nd$ ratios of normal MORB (0.513170 ± 20 for the N-type MORB of the EPR; ZINDLER *et al.*, 1984) are generally interpreted as reflecting a long-term depletion history of their mantle source. Similarly high δD values of -55 ± 2 associated with these high $^{143}Nd/^{144}Nd$ ratios (Fig. 4) are likely to be a characteristic of the "depleted mantle" source of the N-type MORB. ZINDLER *et al.* (1984) propose to explain lower $^{143}Nd/^{144}Nd$ ratios by mixing between a "normal depleted peridotite source" with either (1) subducted oceanic crust, (2) old segregation of basaltic melts, or (3) metasomatized peridotite. Such multiple hypotheses provide good explanations for the Nd contents and isotopic compositions of the samples within the field of Fig. 4 (after ZINDLER *et al.*, 1984). However, these three end members are likely to be enriched in incompatible elements relative to normal depleted peridotites, particularly in H_2O^+. Therefore, they could hardly explain our two samples from the Clipperton seamount, which have the lowest incompatible elements contents (Nd, Sr, K_2O, TiO_2, H_2O^+, . . .) as well as δD and low $^{143}Nd/^{144}Nd$ ratios. Since, as discussed previously, these two latter samples could not be related to the other ones from the EPR 13°N by either partial melting or fractional crystallization processes operating differentially, we propose that they represent a different end member in the mantle. This end member is characterized by low contents in incompatible elements, low δD values (≈ -80), and low $^{143}Nd/^{144}Nd$ ratios (0.51304), and could correspond to a more primary part of the upper mantle in which metasomatism and/or addition of external components has been limited.

In this latter hypothesis the typical N-type source of MORB, depleted in the past, would yield basalts with δD values around -55. On the other hand, a source less depleted in the past according to its $^{143}Nd/^{144}Nd$ ratios, but probably impoverished in incompatible elements in general more recently, according to its incompatible element contents, would yield more negative δD values (down to -80). Therefore, δD values of -80 ± 5 for the upper mantle seem to be the most primitive ones which can be deduced from MORB studies. This range of δD corresponds to the lowest δD values of all MORB (Fig. 3a), of unmetasomatized or unaltered alkali basalts and peridotites (SHEPPARD *et al.*, 1977; KYSER, 1986; TAYLOR, 1986; TAYLOR and SHEPPARD, 1986), and to δD values of water from glass inclusions in olivine nodules from Japanese alkali basalts and peridotites (KURODA *et al.*, 1977). Unfortunately, this cannot be more tightly constrained by δD systematics because the primordial D/H ratio of the Earth is unknown (see TAYLOR and SHEPPARD, 1986, p. 231). Meteorites with their enormous range of δD values (from -500 to $+9000$; YANG and EPSTEIN, 1983) cannot be used to constrain the problem. However, when considering the available MORB samples analyzed for δD and $\delta^{34}S$ (Fig. 3b), δD values of -80 ± 5 seem to be more typically associated with $\delta^{34}S$ values of 0 ± 0.5, which correspond to the range of $\delta^{34}S$ values of meteorites (THODE *et al.*, 1961). Assuming a distribution coefficient $D \approx 0.01$ for water between residual mantle and melt during partial melting (DIXON *et al.*, 1988) and 10 to 20% partial melting, a H_2O^+ content ranging between 0.01 and 0.02 wt% is calculated for the case of a simple batch melting model for our MORB samples having $\delta D = -80$ and $H_2O^+ = 0.1$ wt%. This water content probably represents an upper estimate for the least modified or most "primary" upper mantle.

Two principal hypotheses, subduction and degassing, can explain the origin of the variations in δD observed in the mantle. First, as suggested by the mixing line in Fig. 3b, the range of δD and $\delta^{34}S$ values observed in MORB can be attributed to addition of altered oceanic crust with $\delta D \approx -45$ and $\delta^{34}S \approx +3$ to a "primary" mantle. Second, the observed δD and $\delta^{34}S$ variations can be explained by degassing of H_2O and H_2S from parts of the mantle. This second hypothesis seems the least likely, at least for hydrogen, because mass-balance considerations suggest that degassing of the Earth, which presumably created the seawater reservoir with $\delta D \approx 0$, should have decreased the δD of the remaining water in the mantle. However, this argument is not definitive, because the initial δD of the whole system is perhaps very different from -80, particularly if the mass of protium lost to space via the atmosphere is significant during the total evolution of the Earth (HUNTEN and DONAHUE, 1976). Finally, all the processes which created variations in δD, $\delta^{34}S$, and $^{143}Nd/^{144}Nd$ may have operated within the mantle but probably selectively, which explains the lack of perfect correlation between these parameters.

CONCLUSIONS

The combined use of incompatible element concentrations and both light and heavy stable isotope ratios of glasses indicates mixing of three or more sources occurring along and near a 25 km ridge length at EPR 13°N. A major part of the total range of isotopic variations in MORB glasses is observed in this small area. Good circumstantial evidence suggests that the isotopic variations of elements such as H, C, and S, which are sensitive to near seafloor late-magmatic and post-magmatic processes, are dominantly of mantle origin. Although such later stage processes may well have contributed to the scatter in the data, it is difficult to envisage that these processes could have been dominant whilst preserving the overall consistency among all of the chemical and isotopic variations, and in particular H_2O^+ versus TiO_2 or Nd (Figs. 5a and b).

Previous H-isotope studies of MORB glasses have considered that normal values are around -75 ± 5 (KYSER and O'NEIL, 1984; POREDA *et al.*, 1986). Reexamination of their data in the light of our results reveals no compelling arguments that most of the large number of MORB glasses with $-70 < \delta D < -50$ are predominantly of secondary origin (*i.e.* due to degassing or to direct or indirect interaction with seawater). The mantle is thus considered to have variable D/H as well as $^{13}C/^{12}C$ and $^{34}S/^{32}S$ values. Based principally on the Nd and $^{143}Nd/^{144}Nd$ ratio data, the several identified mantle sources are considered to have had variable partial melting histories in time and in extent. The isotopic variations reflect these differences. The least modified or most "primary" source has $\delta D \approx -80$ and $\delta^{34}S \approx 0$. The importance of subducted oceanic crust in contributing to these variations is difficult to quantify from our results and absence of experimental isotopic fractionation data.

Water contents are relatively homogeneous with the great majority of MORB samples containing 0.2 ± 0.1 wt% H_2O^+. This implies that the H_2O^+ content of the MORB sources is around 0.01 to 0.06 wt%, assuming 10 to 20% partial melting.

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