12. OXYGEN AND STRONTIUM ISOTOPE COMPOSITIONS OF HESS DEEP GABBROS (HOLES 894F AND 894G): HIGH-TEMPERATURE INTERACTION OF SEAWATER WITH THE OCEANIC CRUST LAYER 3

Christophe Lécuyer1,2 and Gérard Gruau2

ABSTRACT

The Hess Deep Rift Valley exposes a young (=1 Ma) section of lower oceanic crust generated at the East Pacific Rise (EPR). The drillers recovered 154 m of plutonic rocks from Hole 894G. The mineralogy and textures of these rocks suggest that they represent the roof of a magma chamber. These high-level gabbros, olivine-gabbros, and gabbronorites are slightly hydrated (average LOI = 0.75%, N = 27) and crosscut by a few olivine basaltic dikes. The dikes were altered under greenschist facies conditions, and the gabbros were amphibolitized. Most of the gabbros have Sr-isotopic ratios that range from 0.70247 to 0.70309, indicative of low water-rock ratios (<1), with a circulating fluid having a "Sr"/"Rb" ratio calculated at 0.7032. The δ18O values of the gabbros range from 2.2 to 6.5 and are generally much lower (average δ18O = 4.8, N = 31) than the mantle reference value (5.7 ± 0.2), whereas olivine basalt do not show any δ18O depletion. The δ18O values of clinopyroxenes are often anomalously low (5.1–5.3). Clinopyroxene-plagioclase fractionation values reach 1.5 and reveal strong isotopic disequilibrium attributed to high-temperature isotopic exchange with a discrete aqueous fluid. Clinopyroxenes with δ18O = 5 contain minute Mg-rich amphibole lamellae (1–5 mm) that represent a very early stage of high-temperature alteration before altering totally into amphibole. Except for a few samples with isotopic compositions that were reequilibrated at low temperatures (<200°C), the gabbros contain low-δ18O plagioclase (δ18O = 3–5) that recrystallized at high temperatures (400°–600°C) without exchanging major cations (An10–60). The Hess Deep gabbros record mechanisms of isotopic exchanges governed by percolation of fluids along grain boundaries and self-diffusion of oxygen through plagioclase without involving macroscopic brittle deformation. These water-rock interactions produced a sequence of low-δ18O oceanic rocks early in the spreading history of the EPR that can be compared with the gabbro sequence of the Oman ophiolite.

INTRODUCTION

The opening of the Hess Deep Rift has tectonically exhumed young (=1 Ma) lower crustal and upper mantle rocks that were generated at the East Pacific Rise (EPR). During Leg 147 of the Ocean Drilling Program (ODP), we cored gabbroic sections (Holes 894F and 894G) that provide an unique opportunity for studying the hydrothermal interactions between seawater and the lower levels of the oceanic crust generated at a fast-spreading ridge. Within the high-level gabbros of Holes 894F and 894G, a well-developed vein and crack network records low-temperature channeled fluid flow (<350°C) that was contemporaneous with the thermal contraction of the crust (Gillis, Mével, Allan, et al., 1993).

The role of solid state diffusion during fluid circulation is generally neglected in the total budget of the hydrothermal alteration of the oceanic crust even though it should provide information about the early on-axis high-temperature hydrothermal activity (>350°C). The pervasive circulation of fluids at grain boundaries through plutonic rocks must be examined at a location where hot hydrothermal fluids are expected to react with high-level gabbros. If temperatures in the hydrothermal system are high enough, hot fluids percolate along grain boundaries and react at the grain scale through dissolution-pre-

2Laboratoire de Géochimie Isotopique, Géosciences Rennes, UPR 4661 CNRS, Université de Rennes I, Campus de Beaulieu, F-35042 Rennes, France. grua@univ-rennes1.fr
3Current address: Laboratoire de Sciences de la Terre, URA 726 CNRS, Ecole Normale Supérieure, 46 Allée d'Italie, 69364 Lyon cedex 07, France. lecuyer@geologie.ens-lyon.fr
grains to examine how water-rock interactions extend down to the subgrain scale. Thus, the “background alteration” of Hess Deep gabbros will be characterized in terms of (1) metamorphic assemblages, (2) rates of hydration, (3) closure temperatures for oxygen isotopes, and (4) water-rock ratios.

**ANALYTICAL TECHNIQUES**

We determined mineral modes (volume percentages) visually or by point counting (see also Gillis, Mêvel, Allan, et al., 1993). Loss on ignition (LOI) was either determined on the JOIDES Resolution or at the University of Rennes (Table 1).

Oxygen was extracted from rock powders using the BrF₅ method (Clayton and Mayeda, 1963) and analyzed as CO₂ gas on a VG SIRA 10 mass spectrometer at the University of Rennes. Isotopic compositions are quoted in the standard δ notation relative to SMOW. Results from the NBS28 standard gave δ¹⁸O = 9.5‰ ± 0.2‰ (2σ).

We obtained δ¹⁸O values for mineral separates extracted from thick sections of rock chips; consequently, these analyses gave the compositions of individual mineral grains, not averaged values as typically provided by conventional techniques of mineral separation. The amount of material extracted by this method is typically 1-3 mg of powder. Thick sections are used to check if contamination by neighboring minerals occurs during the drilling procedure. The identification of minerals was performed by Raman spectroscopy, either in the vicinity of microcores or on residual powders.

We determined the Sr-isotope compositions (Table 1) following the method of Jahn et al. (1980). Sr blanks were lower than 1.10⁻⁶ g. 

Sr⁸⁷/Sr⁸⁶ ratios were measured using a five-collector Finnigan MAT-262 mass spectrometer. All ratios were normalized against 

Sr⁸⁷/Sr⁸⁶ = 0.1194 for isotopic fractionation. Results from the NBS987 Sr standard on 15 separate runs yielded 

Sr⁸⁷/Sr⁸⁶ = 0.71023 ± 2 (2σ), and all 

Sr⁸⁷/Sr⁸⁶ ratios presented in this paper were corrected by +0.00002 to be consistent with the NBS reference value of 0.71025.

**PETROLOGY**

Hole 894F and the upper part of Hole 894G are dominated by gabbros and olivine gabbros that are crosscut by basaltic dikes with chilled contacts against the wallrocks. Deeper in Hole 894G, gabbrobrone represents the most abundant rock type and contains a few olivine gabbrobrone layers.

The Hess Deep gabbros are characterized by a “static metamorphism” (rocks metamorphosed in the absence of deformation at the rock or grain scale) whose extent is highly variable with depth; the percentage by volume of secondary minerals ranges from 5% to 80%. Mineral assemblages suggest that this metamorphism began under amphibolite facies conditions characterized by the following mineral association: Mg-rich amphibole (tremolite) + Ca-rich plagioclase. Retrograde metamorphic reactions under greenschist facies conditions can be also found in some samples showing an association of Na-rich plagioclase (albite-oligoclase) + actinolite ± chlorite ± talc ± epidote ± prehnite ± smectite and typically associated with extensive wallrock alteration that extends at least 10 cm from the veins. The youngest macroscopic veins, commonly subvertical, are filled with a typical zeolite facies mineral association: chlorite ± smectite ± mixed-layer clays ± zeolites ± calcite, which can be found as coatings on core pieces or as late residual pore filling in earlier vein types.

Olivine is generally strongly altered in the range from 30 to 100 vol%. When olivine relics are still present, they are rimmed by a corinetic association of chlorite, iddingsite, talc, and tremolite. Replacement of pyroxenes by amphibole and minor chlorite is the main manifestation of alteration in Hess Deep gabbros but remains heterogeneous from one sample to another one (10%–100% alteration by volume). Tiny secondary clinopyroxene patches, commonly associated with brown-green amphibole lamellae, occur as replacement of migmatic clinopyroxenes, whereas discrete patches of talc sometimes invade the orthopyroxene cores.

Plagioclase looks fresh in most of the gabbro samples, but turbid grains containing numerous and very tiny iron exsolution are also present. Fluid inclusions are often abundant along the crystal rims. In highly altered zones, the formation of albite plagioclase dominates. Inclusions or patches of clays and zeolites are common in plagioclase grains close to anastomosing macroscopic vein networks filled with low-temperature minerals.

The extent of alteration in basaltic dikes is also highly variable, with 10% to 85% replacement of primary mineralogy by volume. The metamorphic mineral assemblage lacks any evidence of amphibolite facies. The mineral associations that characterize the green schist and zeolite facies observed in gabbros occur both in the background alteration of the dikes and in their associated macroscopic and microscopic veins.

For studying the mechanisms of background alteration affecting the Hess Deep gabbro succession of Holes 894F and 894G, samples were selected randomly along the core independent of the texture and primary mineralogical variations. However, except for Sample 147-894G-2R-2, 20-26 cm, which was collected close to a low-temperature macroscopic vein, sites close to any kind of macroscopic open fracture, vein network, and associated alteration halo were avoided.

**RESULTS**

**Oxygen Isotopes**

We analyzed 35 whole rocks (Table 1) and 16 microcracked minerals (Table 2) for oxygen isotope compositions. In Figure 1, whole-rock 

δ¹⁸O values are plotted vs. depth (meters below seafloor [mbsf]) for Holes 894F and 894G. The δ¹⁸O values for gabbros vary widely and range from 2.2 to 6.5, but 60% of the data range from 4.5 to 5.0, revealing a significant ¹⁸O depletion for this sequence of high-level gabbros relative to the mantle reference of 5.7 ± 0.2 (Pinoau et al., 1976). Sample 147-894G-2R-2, 26–26 cm, the only gabbro sampled close to a macroscopic vein network, has the highest δ¹⁸O value of 6.5. δ¹⁸O variations with depth commonly reach 1% by meter. The distribution of δ¹⁸O values does not show any regular trend of isotopic enrichment or depletion with depth (Fig. 1). The lowest δ¹⁸O values are found within 100 m below the surface whereas δ¹⁸O values close to 5.3% characterize Hole 894G from 100 to 150 m. Hess Deep gabbros show a combination of low δ¹⁸O values (down to 2.2) and low LOI (<0.5%). However, the inverse is also seen: δ¹⁸O values lower than 5 associated with high LOI values up to 2.5% (Table 1).

Four olivine basalts (Table 1), which are interpreted as dikes crosscutting the gabbro sequence (Gillis, Mêvel, Allan, et al., 1993), have δ¹⁸O values slightly lower (5.3 and 5.5) or slightly higher (6.1) than the mantle reference value (5.7% ± 0.2‰).

δ¹⁸O values of microcracked minerals are only available for pyroxene, plagioclase, chlorite, and ilmenite (Table 2). Amphibole was not analyzed because of the common mixing of this mineral with minute
grains of iron oxides, talc, and pyroxene. Plagioclase has a wide range of δ18O values (3.0‰–6.4‰), contrasting with the more homogeneous compositions of pyroxenes (5.1‰–5.7‰). Pyroxenes from Hess Deep have slightly lower δ18O values than those typical of fresh magmatic pyroxene from a MORB mantle source (Maclennan and Clayton, 1972; Pineau et al., 1976; Kyser, 1986). The exception is Sample 147-894G-15R-1, 32–35 cm, with a δ18O value of 5.7 (Table 2). One analysis of clinopyroxene in Sample 147-894G-20R-1, 87–91 cm, gave a surprisingly low δ18O value of 3.5. The powder produced during the microcoring was examined by Raman spectroscopy, which revealed a mixture of clinopyroxene and amphibole. P. Agrinier (pers. comm., 1994) and G. Früh-Green (pers. comm., 1994) reported δ18O values of amphibole in gabbros as low as 2‰, and this could explain the low δ18O value for our pyroxene. Analyses of two chlorites gave δ18O values of 8.2 and 5.3 in gabbro samples characterized by whole-rock δ18O values of 5.7 and 5.5, respectively. One analysis of fresh ilmenite (FeTiO3 = 96.5%, MnTiO3 = 3%, and MgTiO3 = 0.5%) yielded a δ18O value of 2.6, typical of TiFe oxides that preserve a magmatic composition with limited suboxidic reequilibration in the presence of pyroxene and plagioclase (Taylor and Epstein, 1962a, 1962b; Anderson et al., 1971).

### Strontium Isotopes

Sr-isotope compositions of Hess Deep rocks range from 0.70247 to 0.70430 but most of them are lower than 0.7027. Sample 147-894G-2R-3, 20–26 cm, the only sample close to a macroscopic vein network, has the highest initial Sr ratio and δ18O value (Table 1). This sample, which will be discussed further in the next section, clearly records late and low-temperature hydrothermal alteration and is not considered as belonging to the background alteration. Sr-isotope compositions for fresh mid-ocean ridge basalts (MORB) are commonly between 0.7023 and 0.7029, with an average value of 0.70265 (Hart et al., 1974; Barrett and Friedrichsen, 1982). Any increase in the δ87Sr/δ86Sr ratio can be attributed to the addition of seawater Sr (Dasch et al., 1973). No Hess Deep samples are totally fresh with respect to their mineralogy. Thus, to estimate the initial magmatic Sr ratio, which is required to quantify isotopic exchange with seawater, we need to use another approach. There is a rough correlation of the initial Sr-isotope compositions with the estimated volume percentage of alteration, suggesting that Sr-isotope variations within Holes 894F and 894G are mainly controlled by the extent of hydrothermal alteration (Fig. 2). By extrapolation to a percentage of alteration equal to zero, an initial “magmatic” Sr-isotope ratio of 0.7024 is inferred. This value fits well with the previous range given for fresh MORB. We do not observe any positive correlation between the Sr-isotope ratios and Sr concentrations, which suggests that the main mechanism of Sr increase in Hess Deep gabbros was isotope exchange rather than a global strontium addition caused by mineral neoformation.

### DISCUSSION

The Hess Deep gabbros show large δ18O variations (4‰) at the meter scale within 150 m of drilled rocks (Fig. 1). These whole-rock δ18O values may depend on four parameters, including (1) the modal abundance of a mineral very sensitive to isotope exchange, (2) instrumental reproducibility, (3) temperature, and (4) the isotope composition of seawater.
of the hydrothermal fluid (Brikowski and Norton, 1989). When we plot the whole-rock $\delta^{18}O$ values against the estimated volume percentages of plagioclase, we do not see any significant correlation that could reveal a "modal effect" on the oxygen isotope compositions of the gabbros (Fig. 3). Such a correlation would not be expected if fluid fluxes are larger than reaction rates (Gregory et al., 1989).

**Strontium Isotopes**

The Sr-isotope compositions of the gabbros can be used to estimate water-rock ratios and the composition of the hydrothermal fluid. The water-rock ratios can be calculated using a simple mass balance equation (Albarède et al., 1981). This calculation requires that the Sr-isotope composition of a totally altered rock should be equal to the fluid in equilibrium. Holes 894F and 894G do not provide a 100% altered rock; however, by extrapolating the linear relation of Figure 2, we can deduce a Sr-isotope composition of 0.7032 as a rough estimate of the hydrothermal fluid that reacted with the Hess Deep gabbros. For the hypothetical 100%-altered rock, the mass balance equation provides a water-rock ratio of 1.4. Consequently, most of the Hess Deep gabbros reacted with a "mature" hydrothermal fluid developed in a rock-dominated system under water-rock ratios less than 1. It means that this fluid, whose composition is far from the initial Sr composition of seawater (0.7091; Burke et al., 1982), had already exchanged Sr isotopes before altering the high-level gabbros. McCulloch et al. (1980, 1981) found a similar relationship in the Samail ophiolite. The same phenomenon was also inferred from the calculated Sr-isotope composition of the end-member fluid ($^{87}\text{Sr}/^{86}\text{Sr} = 0.7038$) that circulated through the sheeted dike complex of the East Pacific Rise sampled at Hole 504B (Kawahata et al., 1987). Sr-isotope compositions of Hole 504B veins crosscutting sheeted dikes indicate also that these hydrothermal solutions lie between 0.7031 and 0.7039 (Kawahata et al., 1987), well bracketing the calculated Hess Deep solution. These estimates also are in very good agreement with those measured in the hot fluids discharged at the East Pacific Rise at 21°N ($^{87}\text{Sr}/^{86}\text{Sr} = 0.7030$; Albarède et al., 1981) and 13°N ($^{87}\text{Sr}/^{86}\text{Sr} = 0.7041$; Michard et al., 1984).

**Oxygen Isotopes**

The study of Holes 894F and 894G gabbros provides the first evidence of the net $^{18}O$ depletion (Fig. 1) of an intact part of layer 3 formed at a modern fast-spreading ridge. The EPR basalts and dikes sampled at Hole 504B are $^{18}O$ enriched (Alt et al., 1986). Because no complete section of modern oceanic crust has been sampled, it is not yet possible to perform the types of mass balance calculations that have been done on the Samail ophiolite (Gregory and Taylor, 1981; Stakes and Taylor, 1992).

**Table 2. Oxygen isotope compositions of microcored minerals for gabbros from Hole 894G.**

<table>
<thead>
<tr>
<th>Core, section, interval (cm)</th>
<th>Piece no.</th>
<th>Depth (mbsf)</th>
<th>Plagioclase</th>
<th>Pyroxene</th>
<th>Chlorite</th>
<th>Ilmenite</th>
</tr>
</thead>
<tbody>
<tr>
<td>147-894G</td>
<td>6R-1, 94-100</td>
<td>8A</td>
<td>55.74</td>
<td>4.0</td>
<td>5.7</td>
<td></td>
</tr>
<tr>
<td>8R-2, 87-90</td>
<td>8</td>
<td>70.87</td>
<td>4.5</td>
<td>5.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9R-2, 88-93</td>
<td>5B</td>
<td>76.53</td>
<td>3.9</td>
<td>5.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11R-3, 1-3</td>
<td>1</td>
<td>87.01</td>
<td>4.8</td>
<td>5.3</td>
<td></td>
<td>2.6</td>
</tr>
<tr>
<td>12R-1, 45-51</td>
<td>6</td>
<td>94.25</td>
<td>6.4</td>
<td>5.1</td>
<td>5.3</td>
<td></td>
</tr>
<tr>
<td>15R-1, 32-35</td>
<td>6</td>
<td>119.12</td>
<td>5.7</td>
<td>8.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20R-1, 87-91</td>
<td>15</td>
<td>146.47</td>
<td>3.0</td>
<td>3.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Notes: Total uncertainty on the $\delta^{18}O$ values with respect to the SMOW is estimated to be lower than 0.1‰ to 0.15‰.

Gabbros in the Hess Deep area were recovered for the first time in 1988 during a Nautile submersible dive program (Francheteau et al., 1990). P. Agrinier (pers. comm., 1994) investigated the stable isotope compositions of a large variety of rocks and found that most gabbros have $\delta^{18}O = 5.6$, which is very close to their initial magmatic values. Calcic plagioclase has magmatic oxygen isotope compositions and does not show evidence of isotope exchange with a fluid phase. When isotope exchange occurs, this is mainly under greenschist facies conditions (P. Agrinier, pers. comm., 1994) and $^{18}O$ modified gabbros are those in which plagioclase is unstable (partly replaced by albite and/or prehnite).

The conditions of water-rock interactions recorded in the gabbros from Holes 894F and 894G are drastically different from those dredged by the Nautile and reveal the complexity and heterogeneity...
of the alteration processes affecting the oceanic crust. The $^{18}$O depletion that affects our collection of Hess Deep gabbros occurs in slightly hydrated rocks where the plagioclase remains calcic under amphibolite facies conditions ($\text{An}_{95-93}$ for plagioclases in Samples 147-894G-6R-1, 94–100 cm; 11R-3, 1–3 cm, and 15R-1, 32–35 cm). Figure 4 gives the variation of $^{18}$O values for some rock-forming minerals and shows that plagioclase ($3 < \delta^{18}O < 5$) is principally responsible for the global decrease of whole-rock $^{18}$O values. In pyroxene, $^{18}$O values range from 5.1 to 5.7. The apparent oxygen isotope fractionation between pyroxene and plagioclase can reach up to 1.5, a disequilibrium pattern already mentioned by Gregory and Taylor (1981) in the Oman ophiolite gabbros and by Ito and Clayton (1983) in samples from the Mid-Cayman slow-spreading center.

Assuming $^{18}$O values of hydrothermal fluids that range from 0 to 2, as measured in hydrothermal vents (Craig et al., 1980; Craig, 1981) or as predicted by thermodynamic models (Bowers and Taylor, 1985), and water-rock ratios lower than 1, closure temperatures of hydrothermal alteration for plagioclases are calculated in the range from $400^\circ$C to $600^\circ$C using the mass-balance equation for open systems proposed by Taylor (1977). These “isotopic temperatures” are in agreement with the pervasive presence of amphibolite assemblages throughout Hole 894G.

Most magmatic pyroxenes are characterized by $^{18}$O values in the range from 5.1 to 5.3, which are lower than the expected value of 5.7 ± 0.2 for mantle-derived pyroxenes (Taylor and Epstein, 1962a, 1962b; Anderson et al., 1971). Ito and Clayton (1983) analyzed clinopyroxenes from Mid-Cayman Rise gabbros that also have low $^{18}$O values (from 4.8% to 5.0‰). Ito and Clayton (1983) attributed these isotope compositions to subsolidus exchange between clinopyroxene, plagioclase, and Fe-Ti oxides during the slow cooling of the plutonic rocks. As a consequence of the subsolidus isotope reequilibration, plagioclase becomes $^{18}$O enriched (slightly higher than 6), whereas pyroxene (4.8–5.0) and Fe-Ti oxide (down to 0.5) become $^{18}$O depleted. A few mineral separates from Hess Deep gabbros do not support this hypothesis (Table 2). The existence of clinopyroxene...
gabbros that experienced some retrograde reactions into the green-

θ = 5.5). Chlorite is generally present in
θ = 5.7), and Sample 147-
Sample 147-894G-15R-1, 32-35 cm (δ

... surprisingly, in gabbros that show mantle-like oxygen ratios such as
δ... Sample 147-894G-12R-1, 45-51 cm (δ... Chlorites (δ
O = 5.3) crystallized also at higher temperatures (~300°C) in the stability field of greenschist facies assemblages that occur in Sample 147-894G-12R-1, 45-51 cm (Table 2; Fig. 4). Früh-Green et al. (this volume) calculated approximate temperatures of 400°-450°C for chlorites in serpenitized peridotites from Holes 895C and 894E, which are characterized by lower δ O values (from 1.5 to 3) than those analyzed in gabbros from Holes 894F and 894G. The large range of oxygen isotope compositions measured in chlorites from Hess Deep rocks reveals that this mineral is stable over a large span of temperatures during the hydrothermal alteration of the oceanic crust.

These results suggest that in some restricted areas the low-temperature fluids can overprint the high-temperature event that characterizes the background alteration (Fig. 5). This isotopic overprint is linked to the high densities of anastomosing macroscopic vein networks (0.3 cm⁻¹) that occur in Cores 147-894G-2R, 4R, 6R, 12R, 15R, and 20R (Gillis, Mével, Allan, et al., 1993; Manning et al., this volume). Apparently, the low-temperature fluids percolated through the wallrock and precipitated the greenschist facies or zeolite facies minerals responsible for the strong oxygen isotope disequilibrium between minerals observed in these gabbros.

CONCLUSION

Pervasive background alteration of the gabbros occurred without deformation under amphibolite facies conditions (400°-600°C) and was responsible for 18O depletion of these rocks (δ 18O = 4.8, N = 31). Plagioclase controls most of the oxygen isotope exchanges with the aqueous fluid phase. As a consequence, many low δ 18O gabbros are only weakly hydrated (LOI ≤ 0.7%).

Water-rock ratios lower than 1 were calculated using Sr concentrations and isotope ratios. However these probably underestimate the real water-rock ratios because, as suggested by the oxygen isotope study, the δ 18O value of plagioclase grains was lowered by self-
diffusion of oxygen under hydrothermal conditions without modification of the major element chemistry (An$_{80-60}$).

A low-temperature fluid circulated in gabbroic levels where the vein density reaches 0.3 cm$^{-1}$. This circulation led to whole-rock $\delta^{18}$O values close to normal mantle values (5.5–5.7) or slightly higher values (6.5), and stronger hydration (LOI = 1%–2%).

Holes 894F and 894G define, for the first time, a remarkable section of low $\delta^{18}$O gabbros hydrothermally altered beneath a fast-spreading ridge. We do not yet know whether the $\delta^{18}$O depletion of Holes 894F and 894G is representative of the entire lower oceanic crust. In the absence of $\delta^{18}$O-depleted gabbro zones, the oceans should evolve to lower $\delta^{18}$O values.

The existence of these low $\delta^{18}$O gabbros clearly validates the models of oceanic hydrothermal circulation elaborated on the basis of the Oman ophiolite. Gregory and Taylor (1981) presented an oxygen isotope profile in which gabbros clearly show a $\delta^{18}$O depletion similar to our Hess Deep samples.

These observations confirm that seawater-derived fluids react with the deep layers of the oceanic crust generated at fast-spreading ridges.

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