# 14. <sup>18</sup>O/<sup>16</sup>O AND D/H INVESTIGATIONS ON BASALTS OF LEG 46

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## INTRODUCTION

The results of oxygen and hydrogen isotope studies on oceanic crust basalts can only be explained if we assume an intense exchange of these nuclei with seawater. Whole-rock isotope data and oxygen-isotope fractionations between coexisting minerals of the crust samples from Legs 37 and 45 and this leg indicate that ocean water has reacted with the basalts at magmatic temperatures, as well as at the low temperatures at the basalt/water interface.

Reactions of oceanic basalts at high temperatures (>100°-200°C) yield an increase of the <sup>18</sup>O in the seawater and a decrease in the basalt and its reaction products. In a low-temperature reaction (formation of clay minerals) of the silicates, <sup>18</sup>O decreases in the fluid phase and increases in the low-temperature silicate minerals. Muchlenbachs and Clayton (1976) have pointed out that the opposite <sup>18</sup>O-shifts in the two reaction types cancel. They argue that because of exchange reactions between the basalts and the water, there is no drastic change of the 18O/16O ratio of the seawater with time. Since we now have strong indications for hightemperature seawater interactions with the basalts, we must conclude that the deeper layers (layer 3) probably contain appreciable amounts of seawater oxygen. Further chemical and isotope investigations of these rocks will be necessary to get better information on exchange reaction between the oceanic crust and seawater.

Until now, only a very thin upper layer of the oceanic crust has been investigated. Stable isotope results on altered basalts indicate that seawater penetrated into the deeper regions. Further core recovery from these regions is desirable to gain better understanding of the silicate-seawater interactions during the uplift of mantle differentiates at the mid-oceanic ridges.

### **EXPERIMENTAL PROCEDURE**

We analyzed 13 slabs from Leg 46 cores (sub-bottom depth 80 to 170 m) for their oxygen and hydrogen contents. Using standard separation techniques, we separated 13 plagioclases (mainly the coarse-grained fractions), 10 olivines, and 2 magnetites, and determined their <sup>18</sup>O/<sup>16</sup>O ratios.

The silicates were treated with  $BrF_5$  at 550° to 680°C for 12 to 36 hours in nickel bombs; the oxygen released during that reaction was converted to CO<sub>2</sub> (Clayton and Mayeda, 1963). The <sup>18</sup>O/<sup>16</sup>O ratio of the CO<sub>2</sub> was measured with a McKinney-type mass spectrometer (McKinney et al., 1950). Hydrogen was extracted at elevated temperatures as a mixture of H<sub>2</sub> and H<sub>2</sub>O, the water was reduced with uranium at 800°C, and hydrogen was sampled on activated charcoal at liquid nitrogen temperature. D/H measurements

were carried out on a Nier-type 15-cm-radius mass spectrometer (in principle a McKinney-type instrument).

Isotope analyses on replicates in general yielded an analytical uncertainty of better than  $\pm 0.1 \ ^{0}/_{00}$  on the  $\delta^{18}$ O value and  $\pm 1 \ ^{0}/_{00}$  of the  $\delta$ -D value. The isotope data are reported as  $\delta$ SMOW values.

#### **RESULTS AND DISCUSSION**

#### Mineral Isotope Data (Table 1)

The plagioclase and olivine fractions separated from the 0.3 to 0.2 (min 0.1) mm diameter are portions of the phenocrysts, which are not much affected by low-temperature alteration. We obtained  $\delta^{18}O$  values for plagioclases of 5.6 to 7.2  $^{\circ}/_{00}$  and  $\delta^{18}$ O values for olivines of 4.7 to 5.3  $^{0}/_{00}$ . The magnetites were separated from the dust fraction. If we calculate the whole-rock composition from these data, including a pyroxene  $\delta$  value of  $+ 5.5^{\circ}/_{\circ \circ}$  on the SMOW scale, we get  $\delta^{18}$ O values for the whole rocks of +5.5 to  $6^{0}/_{00}$ , which is very close to an accepted  $\delta^{18}$ O value for mantle material. The phenocrysts of all samples yield  $\delta$ values distinctly lower than the  $\delta$  values of the whole rock including the groundmass (Table 2). The plagioclase and olivine fractionations of the samples are plotted against the  $\delta$  values of these phases in Figure 1. Large  $\Delta$  plag-ol fractionations coincide with higher  $\delta^{18}O$  values for the plagioclases and lower  $\delta^{18}$ O values for the olivines. The general pattern of Figure 1 proves that, at least for the oxygen isotopes, these phases crystallized in a closed

TABLE 1 Mineral Isotope Data, Leg 46, Hole 396B

Core-Section (Int. no. in parens) 15-2 (520)	Interval, cm 141-147	Piece 2D	Minerals plagioclase magnetite	ε <sup>18</sup> 0 + 7.2 + 4.75	Min-Fractionations		T (°C)
					plag-mag	2.45	1020
15-4 (590	132-141	8A	plagioclase	+ 6.2			
16-2 (630)	107-113	9	plagioclase magnetite	+ 5.8 + 3.9	plag-mag	1.9	1200
17-1 (710/720)	12-14	1	plagioclase olivine	+ 5.7 +5.2	plag-ol	0.5	
17-2 (730)	43-49	3	plagioclase	+ 5.9			
17-3 (750/760)			plagioclase olivine	+ 6.35 + 5.1	plag-ol	1.25	
20-1 (856)	56-62	4C	plagioclase olivine	+ 6.0 +5.0	plag-ol	1.0	
20-2 (910)	58-67	5B	plagioclase olivine	+ 5.8 + 4.9	plag-ol	0.9	
20-4 (1000)	112-121	12F	plagioclase olivine	+ 5.8 + 4.7	plag-ol	1.1	
20-5 (1020)	60-68	8	plagioclase olivine	+ 5.9 + 5.25	plag-ol	0.65	
22-1 (1100)	125-134	14	plagioclase olivine	+ 6.2 + 5.2	plag-ol	1.0	
22-2 (1140)	122-144	7D	plagioclase olivine	+ 5.65 +4.8	plag-ol	0.85	
22-3 (1170)	49-56	3A	plagioclase olivine	+ 5 85 + 5.0	plag-ol	0.85	

TABLE 2 Whole-Rock Oxygen and Hydrogen Isotope Data, Leg 46, Hole 396B

Core-Section (Int. no. in parens)	Interval (cm)	Piece	Sub-Bottom Depth (m)	δ <sup>18</sup> 0	δD
15-2 (520)	141-147	2D	88.4	+ 7,8	123
15-4 (590)	132-141	8A	92.3	+ 7,5	118
16-2 (630)	107-113	9	102	+ 7,8	117
17-1 (710 + 720)	12-14	1	117	+ 7,9	127
17-2 (730)	43-49	3	119	+ 6,6	117
20-1 (850)	56-62	4C	136.7	+ 7,9	135
20-2 (910)	58-67	5B	138.5	+ 6,15	125
20-4 (1000)	112-121	121	142.7	+ 7,7	132
20-5 (1020)	60-68	8	143.8	+ 8,0	116
22-1 (1100)	125-134	14	157.3	+ 7,85	- 105
22-3 (1170)	49-56	3A	161	+ 7,85	- 104
22-2 (1140)	122-144	71	160	+ 7,7	124



Figure 1. Plot of  $\delta^{18}O$  plagioclase and  $\delta^{18}O$  olivine versus the plagioclase-olivine fractionation.

system (as far as seawater is concerned). By contrast, a considerable addition of oxygen from seawater has been traced in the high-temperature phases of rock samples of Leg 45. For details see our report in Volume 45 of the *Initial Reports* (1978).

The higher plag-ol-fractionations indicate a lower isotope equilibration temperature. The equilibrium temperatures can be estimated from the  $\Delta^{18}$ O-(plag-ol) values. The lower fractionations yield temperatures around 1200 ±100°C, and the higher fractionation values give temperatures of 1050 ±50°C. The plagioclase-olivine thermometer is relatively insensitive and inaccurate. Two plagioclase-magnetite isotope-temperatures have been calculated: 1020°C for an <sup>18</sup>O-rich specimen (Core 15-2), and 1200°C for a sample with "normal" composition (Core 16-2). The  $\delta^{18}$ O values of the phenocrysts of Leg 46 samples show, when compared with those of Legs 37 and 45, that seawater was a less abundant component during the crystallization of these phases (Hoernes and Friedrichsen, 1977).

### Whole-Rock Data

The <sup>18</sup>O/<sup>16</sup>O and D/H composition of powdered whole-rock samples are compiled in Table 2. All samples except two (with  $\delta$ SMOW of 6.2 and 6.5 <sup>0</sup>/<sub>00</sub>) have been enriched in <sup>18</sup>O owing to low-temperature alteration of the groundmass (Figure 2). The hydrogen isotope composition of these samples reflects the low-temperature formation of the OH-bearing clay phases. Since only a very limited amount of core sample was recovered on Leg 46 (80 to 150 m subbottom depth), all with rather similar T-conditions for formation of the clay minerals, the total spread of the D/H-isotope composition is smaller than in the Leg 45 D/H profile (Figure 3).

## CONCLUSIONS

The basalt samples recovered on Leg 46 have been altered at low temperatures. Parts of the groundmass have exchanged oxygen with seawater, yielding an increase of



Figure 2. Whole-rock  $\delta^{18}O$  composition, Hole 396 B.



Figure 3. Hydrogen isotope composition ( $\delta D$ -values) of Leg 45 and Leg 46 basalts.

oxygen in the solid phase because of newly formed <sup>18</sup>O-rich clay minerals. About 10 to 20 per cent of the total oxygen of the matrix has been exchanged with seawater. Also the D/H ratio of the clay minerals indicates low-temperature interaction between solid and fluid phase (Suzuoki and Epstein, 1976).

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