12. STRONTIUM, OXYGEN, AND HYDROGEN ISOTOPE STUDIES ON PRIMARY AND SECONDARY MINERALS IN BASALTS FROM THE COSTA RICA RIFT, DEEP SEA **DRILLING PROJECT HOLE 504B, LEG 831**

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ABSTRACT

The D/H, ¹⁸O/¹⁶O and ⁸⁷Sr/⁸⁶ Sr ratios of the basaltic basement from the Leg 83 section of DSDP Hole 504B show that in that area the oceanic crust has experienced intensive but not pervasive alteration. Isotope ratios of the basalts are very heterogeneous because of an input of oxygen, hydrogen, and strontium from seawater. The hydrogen isotopic composition of many samples displays the complete thermal history of the water-rock interactions. High-temperature mineral formations (actinolites, epidotes, and chlorites) were overgrown by a mineralization at lower temperatures (mixedlayer smectites, iddingsites, and smectites) during successive stages of cooling of the oceanic crust by cold seawater. From ⁸⁷Sr/⁸⁶Sr data bulk water/rock ratios up to 5:1 have been calculated. There is evidence that some primary minerals like high-An plagioclases contain oxygen from altered basalts. We have discussed the probability that there existed a seawater/crust interface, now at a depth of 620 m sub-basement, during the high-temperature water/rock interactions. This interface was covered during later magmatism by thick flows, pillow lavas, and intrusives.

INTRODUCTION

The 5.9-m.y.-old basalts from Hole 504B have been substantially altered by seawater-rock interactions. Secondary minerals such as chlorite, mixed-layer minerals, actinolite, prehnite, epidote, and guartz formed at elevated temperatures, as did different zeolites, clay minerals, and iron-manganese oxides during the successive stages of cooling of the rocks. This interaction was not pervasive, and many primary minerals like high-An plagioclases, ortho- and clinopyroxene, and some magnetites of magmatic origin have been preserved (Alt et al., this volume). Although some of these primary minerals and the glasses contain traces of oxygen, hydrogen, and strontium from seawater, probably by the assimilation of altered basalts (Hoernes and Friedrichsen, 1977, 1979; Hoernes et al., 1978; Friedrichsen and Hoernes, 1980), we still have a good estimate for the primary isotopic composition of these elements in the mantle differentiate.

It was the purpose of this chapter to obtain additional data on (a) the temperature of the water/rock interaction, and (b) the water/rock ratio during the various phases of these reactions. Stable isotope data can provide us with more detailed information on the thermal history of the hydrothermal convection cells and their dimensions. The thermal gradient in the borehole is in agreement with a conductive heat loss model. Therefore, it is assumed that water circulation has ceased in the vicinity of Hole 504B (Becker et al., this volume).

EXPERIMENTAL METHODS

Oxygen and Hydrogen Isotopes

Sixty whole-rock samples and over 200 mineral separates were analyzed for their oxygen isotopic composition. Mineral separates were

obtained by standard techniques (heavy liquids, magnetic separation, handpicking). They were identified by X-ray diffraction.

The silicates were treated with BrF_5 at 550° to 680°C for 12 to 36 hr. in nickel bombs; the oxygen released during that reaction was converted to CO_2 . The ¹⁸O/¹⁶O ratio of the CO_2 was measured with a McKinney-type mass spectrometer. Hydrogen was extracted at elevated temperatures as a mixture of H₂ and H₂O, 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 mass spectrometer.

Isotope analyses on replicates in general yielded an analytical uncertainty of better than $\pm 0.2\%$ on the δ^{18} O value and $\pm 2\%$ of the δD value. The isotope data are reported as SMOW values.

Strontium Isotope Data

Splits of the whole rocks were crushed in a tungsten-carbide mortar, and 1 g of the sample was decomposed with HF and HNO₃ in a closed system vented by N2 from liquid nitrogen. Strontium was extracted by standard ion-exchange methods (Dowex 50 \times 8-400-cation exchange resin) and measured on three different MAT 261 solid source mass spectrometers by either single or dual filament technique. Typical errors (caused by inhomogeneities) are better than \pm 0.0002 on replicates. The errors of a mass-spectrometric run were better than 0.00004. The methods will be given elsewhere in detail.

RESULTS

Results of the isotopic analyses are given in Table 1.

Strontium Isotopes

Unaltered mid-ocean ridge (MOR) basalts have rather uniform ⁸⁷Sr/⁸⁶Sr ratios near 0.7025 to 0.7030. Barrett and Friedrichsen (1982) measured ⁸⁷Sr/⁸⁶Sr and ¹⁸O/ ¹⁶O ratios on Leg 69/70 material from this borehole and calculated a primary ⁸⁷Sr/⁸⁶Sr ratio of between 0.7025 and 0.7028, which is identical with the average value of 0.70265 given by Hart (1976) for fresh MOR basalt. Since the low Rb contents of the basalts do not contribute significant radiogenic ⁸⁷Sr in the 5.9-m.y.-old basement, any increase in ⁸⁷Sr in the basalts can be attributed to seawater strontium with an ⁸⁷Sr/⁸⁶Sr ratio of 0.709 (Veizer and Compston, 1974; Burke et al., 1982).

Unaltered basalts of Hole 504B contain 50 to 70 ppm strontium; in seawater, 8 ppm strontium dissolved. High-

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Table 1. Isotopic analyses for Hole 504B basalts.

Laboratory sample no.	Core-Section	Lithology		δD										Other
	piece no. in parenthesis)		87 _{Sr/} 86 _{Sr}			$\delta^{18}0$								
				а	a b	whole rock	plag	cpx	орх	magn	smect	chl	q	minerals
1	72-1, 34-37 (3)	Plagioclase-phyric basalt with smectite	0.70314		- 76	+ 6.7					+ 6.7			
2	72-2, 115–117 (7d)	Altered basalt with plagioclase pheno- cryst, massive	0.70269		- 98	+5.6	+ 5.8	+ 5.4			+6.4			
3	73-2, 7-9 (1A)	Plagioclase-phyric	0.70328		- 84	+ 5.6	+ 5.9	+4.8	+ 5.1		+ 7.7			
4	75-1, 87-91 (3c)	Plagioclase phyric	0.70278		- 85	+ 5.9	+ 5.2				+7.0			
5	77-1, 32-37 (3b)	Aphyric doleritic basalt with sulfide miner-	0.70300		- 55	+ 5.05	+ 6.5	+ 4.7			10.5	+ 3.0 ± 0.5		
6	77-1, 128-132 (6b)	Medium-grained dolerit-	0.70396		- 59	+ 5.2	+ 6.8		+ 5.1			+2.5 +0.5		
7	77-3,	Medium-grained dolerit- ic basalt			- 50	+ 5.2	+ 6.2	+ 5.1	+5.1					
8	78-1, 8-13 (2)	Aphyric doleritic altered basalt with greyish- green veins	0.70406		- 60	+ 5.2	+7.0	+6.5				+6.0		
9	78-1, 85-89 (3f)	and pyrite lithology as above	0.70406		- 63	+ 5.0	+ 6.7	+ 5.8	+4.9					
10	78-2, 6-10 (1B)	Aphyric basalt with green yeins	0.70315		- 57	+ 4.9	+6.1				+ 5.1		ep	+ 2.5
11	79-1, 17-20 (3a)	Aphyric basalt breccia with plagioclase phenocryst, green veins	0.70306		- 70	+ 5.3	+8.3				+3.5		ep	+3.5
12	80-1, 45-60 (4)	Fine-grained fractured basalt with plagioi- clase, quartz, zeolites*, pyrite, and sphalerite	0.70358	- 83		+5.3						+ 10.0	zeol	+ 10.5
13	80-1, 65-69 (5)	Fine-fractured basalt with plag., quartz, pyrite, sphalerite,	0.70408		- 69	+3.9	+ 8.6				+3.5			
14	80-2, 6-9 (1)	Fine-grained brecciated basalt, quartz, cc +	0.70416		- 69	+ 5.0	+ 8.5				+ 2.3	+ 8.2		
15	81-1, 12-24	Altered basalt with plag, chlorite, qu, cc + sulfide miner- als	0.70488		- 63	+6.4	+ 8.3				+ 2.5			
16	81-1, 46-60 (6)	Fine-grained basalt with quartz and chalco- pyrite	0.70338		- 74	+ 6.0						+9.1		
17	82-1, 37-38 (4A)	Greenish fine-grained basalt with calcite and sulfide	0.70289	- 98		+4.8								
18	83-1, 137-148 (10)	Olivine phyric basalt (olivine replaced by chlorite) with pyrite	0.70328		- 50	+ 3.6	+ 6.2				+2.3			
19	87-1, 67-70 (6a)	Aphyric basalt with quartz and chlorite	0.70335	- 87		+4.9		+ 4.9			+ 2.3 ± 0.3	+8.0		
20	88-1, 111-115 (4e)	Aphyric basalt with chlorite and quartz			- 45	+4.7	+ 8.0	+ 5.0			+4.0			
21	90-1, 55-57 (8b)	Fine-grained aphyric basalt altered with quartz, chlorite, zeolite and epidote	0.70382	- 76		+ 4.8								
22	90-4, 101-103 (9)	Aphyric basalts with veins of chlorite, epidote + quartz	0.70338	- 85		+ 4.5 ± 0.5								
23	90-4, 146-149 (12B)	Lithology as 90-4, 101- 103		- 73	- 48	+ 3.5	6.2	5.2			+4.9		ep	+0.1
24	91-2, 98-101 (10)	Fine-grained aphyric basalt with quartz, chlorite and pyrite	0.70366	- 90	- 45	+ 5.3								
25	93-3, 21-25 (2)	Fine-grained aphyric basalt with chlorite, epidote and actino- lite			- 55		+ 6.2	+4.7			+3.6		ep	+2.3
26	94-1, 12-16 (2)	Aphyric basalt, medi- um-grained, with smectite		- 47	+ 5.0	+ 5.1	+ 4.9				+2.4			
27	95-1, 62–66 (5)	Medium-grained basalt with chlorite, anhydrite, and zeolites, extensively altered	0.70683		- 55	+ 2.1								
28	97-2, 74–89 (6)	Medium-grained aphyric basalt with smectite veins			- 49	+ 5.0	+ 5.7	+4.8		+3.7 ±0.5				
29	99-2, 33-40 (4)	Medium-grained basalt with epidote and chlorite	0.70413	- 72		+ 2.0					+2.0		ep	+1.6

Table 1. (Continued).

Laboratory	Core-Section (interval in cm; piece no, in			δ	D	\$180							i.	Other
sample no.	parenthesis)	Lithology	⁸⁷ Sr/ ⁸⁶ Sr	а	b	whole rock	plag	срх	орх	magn	smect	chl	q	minerals
30	101-1, 110-114 (10b)	Sparsely phyric basalt with chlorite veins			- 47	+4.2	+7.2	+ 4.9			+4.0 D - 50			
31	101-2, 105-112 (12)	Medium-grained aphyric basalt with chlorite veins	0.70310	- 85	+4.8		+ 5.4		+0.3		+1.1			
32	102-1, 80-82 (7a)	Aphyric basalt with pyrite and quartz	0.70535	- 85		+ 5.3	+7.0	+ 5.1						
33	102-2, 2-6 (1)	Fine-grained gray basalt with smectite				+ 5.3	+ 5.7	+ 5.2		+ 2.0				
34	104-2, 7-11	Plagioclase phyric basalt with quartz, smectite, magnetite	0.70260	- 68		+ 4.9	+4.5 ±0.5	+ 5.0	+1.2	+3.6		+ 5.4		
35	104-2, 114-118 (8)	As above	0.70276		- 50	+4.8	+6.0	+4.9	+5.3					+4.7
36	104-3, 69-73 (10)	Medium-grained basalt	0.70280	- 65		+ 5.3	+ 5.9	+5.1	+ 5.0	+1.0				
37	107-1, 124-128 (1b)	Medium-grained aphyric basalt (dike)			- 51	+ 5.3	+ 5.7	+ 5.1	+ 5.0		+4.1			
38	108-1, 20-23 (3)	Massive fine-grained basalt			- 51	+ 5.0	+ 5.1	+4.5		+1.1	+2.6			
39	108-1, 40-44 (5)	Massive fine-grained basalt	0.70264	- 78		+ 5.0	+ 5.3				+3.7			
40	110-1, 57-60 (8)	Medium-grained aphyric basalt	0.70317	- 63		+ 5.6	+ 6.8			+0.5				
41	113-1, 53-57 (5)	Medium-grained mas- sive basalt	0.70400		- 57	+ 4.8	+ 5.9	+ 5.3		+1.2	a ²			
42	116-2, 43-49 (7)	sparsely plagioclase phyric basalt	0.70282	- 74		+ 5.4	+ 5.5	+4.9						
43	117-1, 120-130 (100)	phyric basalt	0 70270	70	- 40	. 4.0	+ 5.3	+4.7		. 1.0		+ 3.2		
44	118-1, 00-09 (3)	clase phyric basalt with sulfides	0.70279	- 78		+ 4.9		+4.0		+1.0				
45	122-1, 63-68 (5)	Fine-grained aphyric basalt	0.70425	- 107		+4.7		+ 4.7						
46	123-2, 3-5 (1)	Massive aphyric medi- um-grained basalt with zeolites and	0.70332	- 115		+ 5.4								
47	127-1, 17-20 (3)	Massive medium- grained basalt	0.70267		- 58	+ 4.9	+ 5.0		+ 4.7	+1.4				
48	127-1, 104-105	As 127-1, 17-20 cm			- 50	+4.5	+5.1		+4.7					
49	128-1, 126-130 (13)	Massive aphyric basalt			- 43	+4.3	+ 5.2	+ 5.2	+5.1					
50	129-1, 2-7 (1)	Massive medium- grained basalt with plagioclase pheno- crysts and actinolite			- 43	+4.2	+ 5.0	+4.8					act D	+ 3.5 - 42
51	129-2, 10-14 (16)	As 129-1, 2-7 cm, with talc + quartz	0.70274	- 57	- 45	+4.4	+4.7	+4.7		+0.7		+4.7		
52	130-1, 23-27 (3)	Fine-grained basalt, massive				+4.6	+4.7	+4.5		-1.2				
53	130-2, 14-17 (1B)	Plagioclase + clinopy- roxene phyric basalt			- 43	+4.3	+4.7	+4.5	+4.5					
54 55	130-2, 111-116 (7) 130-3, 78-81 (9A)	As 130-2, 14-17 cm Fine-grained basalt with	0.70263		- 51	+ 4.5	+ 4.5 + 4.7	+ 4.7 + 4.6	+ 4.7	+1.4	+ 5.2	+4.8		
56	131-1, 46-50 (5)	smectite veins Plagioclase-pyroxene phyric fine-grained basalt			- 49	+4.7	+ 4.62	+ 5.0						
57	131-1, 137-140 (13)	As above	0.70326	- 86		+4.6		+5.0		+1.5				
58	137-1, 68-90 (8)	Plagioclase-pyroxene phyric basalt, medium grained	0.70280	- 55		+4.4	+ 5.0	+4.8	+4.6					
59	138-1, 48-52 (7)	Medium-grained altered basalt			- 42	+4.6		+ 5.0	+4.7					
60	141-1, 54–57 (7)	Fine-grained plagioclase + clinopyroxene phyric basalt	0.70376	- 74			+6.2		+ 5.2					

Note: a and b are explained in Figures 5, 6.

temperature seawater-rock interactions do not significantly change the strontium budget of both phases; the black smoker fluids contain the same concentration of strontium as seawater (Edmond et al., 1979; 1982). There is, however, evidence that low-temperature water-rock interactions yield a strontium increase in the basalt and its alteration products (Barrett and Friedrichsen, 1981).

From data on the ⁸⁷Sr/⁸⁶Sr ratio and Sr contents of the basalt, a reasonable estimate for water/rock ratios can-be calculated (for a detailed discussion, see McCul-

loch et al., 1981). In Figure 1, all 87 Sr/ 86 Sr whole-rock data from Legs 69, 70, and 83 are plotted versus subbasement depth. The Legs 69/70 data show a slight decrease in the 87 Sr/ 86 Sr down to a depth of 580 m. Below 580 m sub-basement, but even more pronounced at the upper level of the stockwork mineralization, we observe a remarkable increase of the 87 Sr/ 86 Sr ratios. The large scatter of data between 0.7025 and 0.7068 indicates an influx of seawater strontium. The mean 87 Sr/ 86 Sr of all Leg 83 samples near 0.7038, yields a bulk water/rock



Figure 1. ⁸⁷Sr/⁸⁶Sr ratios versus sub-basement depth for the basalts of Hole 504B (Legs 69 and 70 samples from Barrett and Friedrichsen, 1982).

ratio of 1.4, if we assume a mean Sr content of the unaltered basalt near 65 ppm with an ${}^{87}\text{Sr}/{}^{86}\text{Sr}$ ratio of 0.7026 and a seawater strontium content of 8 ppm with an ${}^{87}\text{Sr}/{}^{86}\text{Sr}$ ratio of 0.709.

The ⁸⁷Sr enrichment in Sample 504B-95-1, 62-66 cm indicates a water/rock ratio of at least 5, based on the assumption that only unaltered seawater with a ⁸⁷Sr/⁸⁶Sr ratio of 0.7091 has reacted with this basalt. If the ⁸⁷Sr/⁸⁶Sr ratio of the water had already become lower through previous water-rock interactions, the effective water/rock ratio is even higher.

Oxygen Isotope Data

Whole-Rock Data

All δ^{18} O values of whole rocks from Legs 69, 70, and 83 are plotted versus sub-basement and sub-bottom depth in Figure 2. The powdered samples are a mixture of primary minerals with a very narrow range in isotopic composition (near + 5.8‰), low-temperature alteration minerals like iddingsite and smectite with higher δ^{18} O values (up to +30%), and high-temperature alteration minerals with lower δ^{18} O values than the primary phases. The basalts of the upper section of Leg 83 and the Legs 69 and 70 sections are enriched in δ^{18} O values to nearly +8‰. From 620 m (sub-basement) downward we observe the opposite effect, with a few exceptions. These basalts have been depleted because of higher-temperature alteration. But many samples contain minerals with higher δ^{18} O values, indicating that they have partly interacted with seawater at lower temperatures (see discus-



Figure 2. δ^{18} O SMOW values of whole rock samples versus sub-bottom and sub-basement depths. The dashed line represents the ¹⁸Ovalue of unaltered MOR basalt (Legs 69 and 70 samples from Barrett and Friedrichsen, 1982).

sion of the δD values). We observe the same trend in the sheeted dike complex of equivalent ophiolite sequences (Gregory and Taylor, 1981).

Mineral Data

We plotted the δ^{18} O values of plagioclase, pyroxene, and magnetite mineral separates versus sub-basementand sub-bottom depth (Fig. 3). In the upper 600 m (subbasement) both pyroxenes and plagioclases are more uniform than in the lower section of Leg 83. Some magmatic plagioclase phenocrysts in the dikes are enriched in their δ^{18} O values, probably by assimilation of altered δ^{18} O-rich rocks. These high δ^{18} O values of plagioclases have been mainly observed in plagiogranites (Gregory and Taylor, 1981).

Magnetite is more abundant in the lower part of the Leg 83 section, below 800 m sub-basement. Plagioclase– magnetite oxygen isotope fractionations as well as pyroxene–magnetite isotope fractionations yield a magmatic temperature of formation of between 1000 and 850°C.

In Figure 4 we plotted all δ^{18} O values of secondary minerals that could be separated by standard techniques (many fine-grained minerals of low-temperature origin could not be separated). The quartzes and smectites from the upper section of Leg 83 and the zeolites are enriched in ¹⁸O; all other minerals of the lower part (below 620 m



Figure 3. δ¹⁸O SMOW values of magmatic minerals from the basalts. Some plagioclases with lower An-content near 650 m sub-basement are enriched in their oxygen isotopic composition. Magnetites are more abundant in the lower section of Leg 83 (Legs 69 and 70 samples from Barrett and Friedrichsen, 1982).

sub-basement) are depleted, compared with the primary composition of the basalts. The low ¹⁸O smectites with δ values of between +2 and +5‰ are of high-temperature origin (>200°C). Some very low δ ¹⁸O values have been measured on epidotes (down to +0.2‰). They indicate a high water/rock ratio during formation, between 2 and 5. Heterogeneities are present even in the same mineral in two sample splits, suggesting that the fluid phase was not constant in its isotopic composition during the existence of the high-temperature hydrothermal fluid circulation. We suggest that many minerals are inhomogeneous in their oxygen isotopic composition.

Hydrogen Isotope Data

The isotopic composition of hydrogen in whole-rock splits shows an increase versus depth (Fig. 5), from a mean value near 110‰ at the upper surface of the basement to a mean value of -50% at the bottom of Hole 504B. Near 600 m sub-basement, a sharp increase from -85% to -55% was observed within a few meters. This suggests an increase of the formation temperature of the hydrous minerals. From 650 to 1075 m sub-basement we notice only a slight increase of the mean δD values. The δD values of the whole rocks are very inhomogeneous. The fine-grained minerals of the subsequent alteration

at lower temperatures are much lower in their δD values—between -50 to -115% (Fig. 6). These very low values are normally only found in sections with low-temperature alteration reactions.

DISCUSSION AND CONCLUSIONS

Below 600-620 m sub-basement, we observe a tremendous change of the ⁸⁷Sr/⁸⁶Sr, the ¹⁸O/¹⁶O, and D/H isotope characteristics. The D and oxygen isotope wholerock values give evidence for a hydrothermal system which started at temperatures near 400°C. Water/rock interactions continued to temperatures as low as 50°C or even lower. Most of the secondary minerals were formed at elevated temperatures. Low δ^{18} O values of between 0 and +4% for the secondary minerals, as well as high δD values up to -40% of the whole rocks, yield high temperatures of formation (400 to 200°C). But we observe very low δD values, to -115%, in the fine-grained mineral portions and some δ^{18} O values in separated smectites. These are typical data for low-temperature water/rock interactions. Some smectites with low $\delta^{18}O$ values of between +2% and +5% suggest a high temperature of formation for this mineral too. The occurrence of smectite only, therefore, is not an indication of low-temperature water/rock interaction. It is difficult to



Figure 4. δ¹⁸O SMOW values of secondary minerals from the basalts of the Leg 83 section. Zeolites, quartzes, and low-temperature smectites are enriched in ¹⁸O values: epidotes, actinolites, chlorites, and high-temperature smectites are depleted (Legs 69 and 70 samples from Barrett and Friedrichsen, 1982).

get exact reaction temperatures from the δ^{18} O fractionations between mineral pairs. Many minerals are inhomogeneous in their oxygen isotopic composition, and there are probably few really cogenetic minerals (in oxygen isotopic equilibrium) in the whole section. The high ⁸⁷Sr/⁸⁶Sr ratios in the whole rocks suggest that the seawater present in these rocks had not been altered in its ⁸⁷Sr/⁸⁶Sr ratios, that is, had not intensively reacted with low ⁸⁷Sr/⁸⁶Sr rocks before it circulated into this part of the crust.

In our opinion this means that there existed, at or near 620 m sub-basement, a seawater acquifer system with the original high Sr composition. Probably the best explanation might be that there existed in this region near the ridge crest an old seawater/basalt interface and a hydrothermal circulation cell with the temperature history already noted that was active for a short time (10 to 10³ yr.) and that was followed by additional magmatism with thick flows and intrusives (Legs 69 and 70 sections), and finally a reheating of the crust to the temperature profile that exists today. The higher manganese content below 620 m is evidence for a high oxidation potential during the time of hydrothermal circulation. Thus the formation of the stockwork mineralization can be easily explained by a temperature quenching of the fluids. Further data on the ⁸⁷Sr/⁸⁶Sr distribution in the different mineral generations will give us additional information

on the ⁸⁷Sr/⁸⁶Sr variations during the existence of the hydrothermal circulation system.

ACKNOWLEDGMENTS

We are indebted to Dr. M. Satir for preparation of the strontium samples and to C. Schwartz, J. Zimmermann and G. Bartholomä for mineral separation of the oxygen and hydrogen measurements. This research was supported by Deutsche Forschungsgemeinschaft contract 357/19. The mass spectrometric measurements of the ⁸⁷Sr/⁸⁶Sr ratios were carried out at the Zentrallabor für Geochronologie (Heidelberg) the Max Planck Institut (Mainz), and the Bundesanstalt für Geowissenschaften und Rohstoffe (Hannover). We gratefully acknowledge their help.

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Figure 5. δD SMOW values of whole rock samples δD_a and two smectite samples. Below 620 m sub-basement these values increase.

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Date of Initial Receipt: 11 September 1983 Date of Acceptance: 29 March 1984



