

## 17. INTERSTITIAL WATER STUDIES, LEG 15 – ISOTOPIC COMPOSITION OF WATER

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### INTRODUCTION

The quest for samples of the ancient oceans has been concentrated, until recently, on solid materials that were in equilibrium with the ocean either chemically or isotopically. For example, the investigations of fossil shell materials and of chert have been used to give information on the O<sup>18</sup> content of the ancient seas. The availability of water squeezed from deep-sea cores collected during the various JOIDES expeditions has suggested the possibility that these samples are true fossil ocean water. However, the possibility of diagenetic changes in the sediments, and therefore in the interstitial water, makes the search for a conservative constituent in the pore water important, as a yardstick to measure changes in nonconservative components and to assess the changes in composition that the pore water has undergone.

Deuterium, present to the extent of about 150 parts per million as HDO in ordinary water, does not enter into chemical combination with most of the common constituents of the sediments. However, some water is bound to the clay minerals, and some fractionation (enrichment or depletion) of deuterium may be expected during the uptake or loss of water from these clay minerals.

In addition to the problem of identifying conservative components of the pore fluids, we must decide whether the fluid has moved vertically in the sediment. This movement can occur both by compaction of the sediment and squeezing out of the water (upward migration) or through diffusion upward or downward of deuterium from fluids relatively enriched in deuterium to fluids depleted in deuterium.

JOIDES Leg 15 was particularly interesting in as much as samples from Site 147 which represent 250,000 years, were collected at closely spaced intervals through the upper Pleistocene. These samples should allow one to determine whether self-diffusion of deuterium has been sufficiently high to erase the original differences in deuterium content between closely spaced layers in the sediment. In addition to diffusion of HDO affecting the original water compositions, we have to consider the effect of the squeezing out of water during compaction of the sediment. We also analyzed samples from Site 149, a deep core that represented about 40 million years to examine the deuterium content of pore waters as a function of time for long time periods in an attempt to decide whether deuterium is a conservative constituent of pore water.

The self-diffusion of deuterium and, incidentally, of O<sup>18</sup>, should act over a period of time to smooth out concentration differences in these isotopes between adjacent samples whose initial concentrations differed. The diffusion of deuterium, however, should have a very small effect.

The differences that we can significantly measure ( $\pm 1\%$ ) are very small in terms of true concentration differences. We can measure the difference in deuterium concentration between samples that have concentrations of 153.0 and 153.2 ppm deuterium.

### RESULTS AND DISCUSSION

The water samples were squeezed from the cores and sealed in glass ampules on board ship, as described by Sayles et al. (1969). The deuterium analysis was carried out on duplicate 10-mg aliquots as described by Friedman (Friedman and Woodcock, 1957). All analyses are reported in  $\text{‰}$  (per mil) compared to Standard Mean Ocean Water (SMOW). The analyses are precise to a  $\sigma$  of  $0.5\text{‰}$  and are usually quoted to  $\pm 1\text{‰}$  (95 percent confidence limit). The largest differences that we see in these samples are a difference of about 10 per mil or samples differing from the standard of 153 ppm by 1.5 ppm. The data are given in Tables 1 and 2 and are plotted in Figure 1.

The data from Site 147 show differences in deuterium between samples as closely spaced as 0.5 meters. These particular samples occur in the upper part of the Pleistocene and may represent time periods of less than 100,000 years. On the other hand, we also see significant differences between Middle Eocene ( $\sim 40,000,000$  years B.P.) samples of approximately 5 meters apart at Site 149.

The self-diffusion coefficient of water has been determined for the H<sub>2</sub>O<sup>16</sup>-H<sub>2</sub>O<sup>18</sup> molecules. If the same diffusion rate constant can be used for H<sub>2</sub>O<sup>16</sup>-HDO<sup>16</sup>, then we can calculate the flux of water due to diffusion. If we assume an initial sharp discontinuity in deuterium concentration of  $10\text{‰}$  between two adjacent layers of sediment each over 1 meter thick and having a porosity of 50 percent, and if we could sample the layers 10,000 years later, we would find the deuterium has diffused into the depleted layer, and that the concentration in a sample

TABLE 1  
Leg 15, Hole 147

Sample	Depth (m)	D/H ( $\text{‰}$ SMOW)
147B-1-2	2.5	+5.3
147B-1-3	4.25	+8.8
147B-1-4 (15-33)	4.75	+7.2
147B-1-4 (35-57)	4.85	+7.4
147B-1-4 (57-95)	5.1	+7.2
147B-2-2	15	+8.3
147B-2-6	21	+7.3
147B-6-2	51	+11.2
147B-7-4	63	+8.1
147B-9-4	83	+9.9
147B-11-3	100	+8.2
147C-2-1	126	+4.0
147C-4-4	148	+6.6
147C-7-4	176	+6.3

TABLE 2  
Leg 15, Hole 149

Sample	Depth (m)	D/H (‰ SMOW)
149-2-2	4	-2.3
149-4-3	23	+1.2
149-5-3	32	+1.5
149-6-4	43	+1.8
149-7-2	49	+2.9
149-8-4	62	+2.0
149-11-4	90	+5.0
149-12-5	100	+2.5
149-14-3	116	+1.5
149-16-4	135	+0.1
149-18-3	153	+1.8
149-20-4	173	-1.9
149-31-1	271	-4.0
149-33-1	289	-4.1
149-35-4	313	-7.3
149-37-3	329	-5.9
149-40-1	354	-7.0
149-41-5	369	-5.7
149-42-2	374	-6.8

collected 1 meter from the interface would be  $\pm 1\text{‰}$  rather than  $0\text{‰}$ , so that about 10 percent of the initial difference in concentration would have been erased by

diffusion. Because diffusion will be retarded due to binding effects of the sediment on the water molecules, and by the longer path of diffusion in a sediment, the effect illustrated in this example may be too high by a factor of five or more.

Another property of the sediment that might cause erasing of the record is the slow compaction of the sediment and the squeezing out of water. This squeezed-out water might slowly percolate through the upper sediment until it reached the seawater interface. An alternative path for the water could be movement laterally to cracks and then upward to the sea-sediment interface. In the latter case, we would have a minimum effect on the subsequent isotopic record in the pore water. The fact that we do see systematic composition with depth in individual cores would rule out erasing of the record by upward migration of the water. This means either that most of the compaction must have taken place in the upper part of the sediment, perhaps in the first half-a-dozen centimeters, and that very little compaction or squeezing out of water has occurred subsequently, or that compaction is occurring continuously, but that the squeezed-out water migrates laterally to cracks and along these cracks to the water-sediment interface.

Figure 1 is a plot of the deuterium concentration as a function of both age and depth for Sites 147 and 149. The

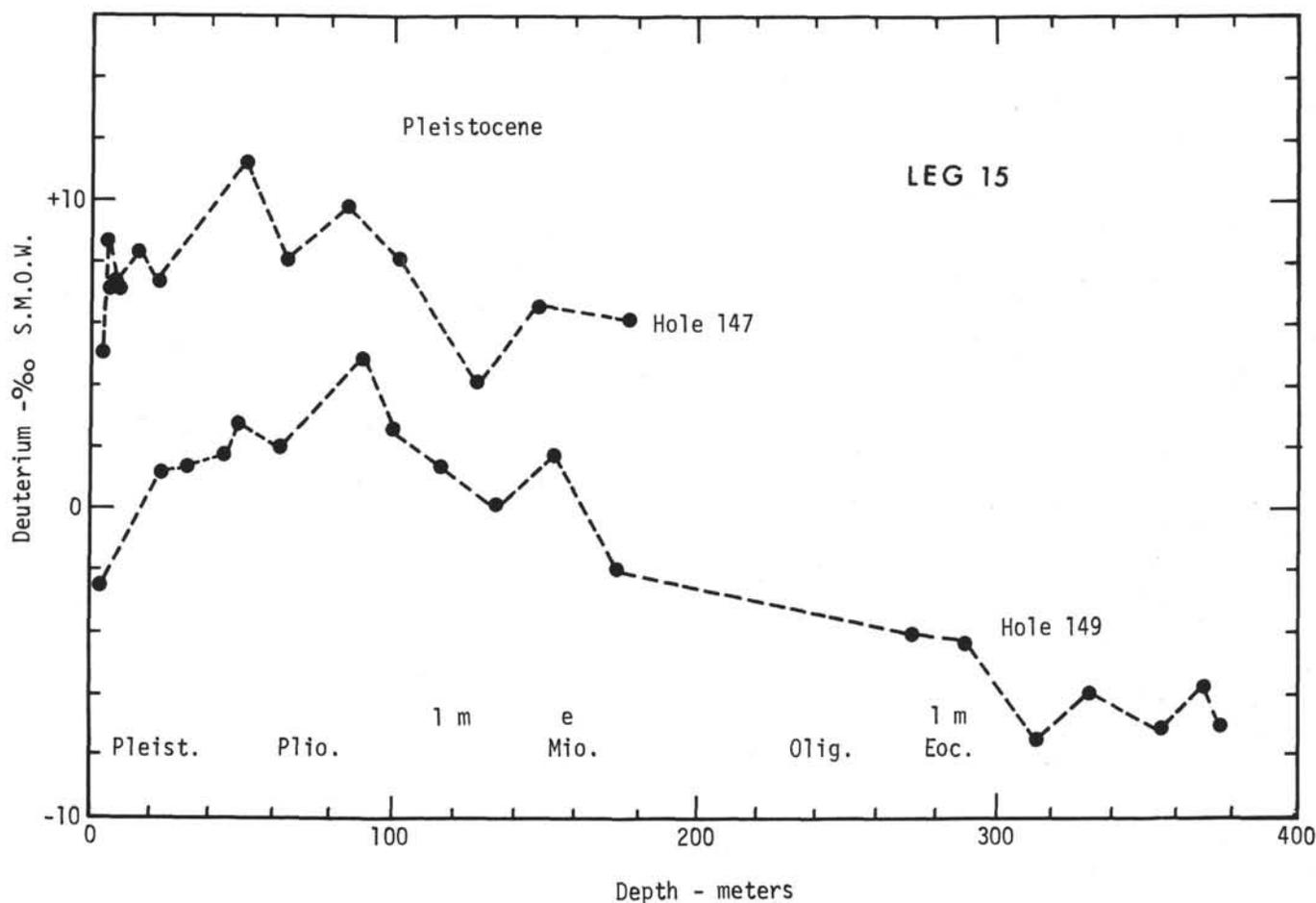


Figure 1. Deuterium concentration as a function of age and depth, Sites 147 and 149.

diagram shows that Leg 15 core samples from Pleistocene through the Miocene tended to be slightly enriched in deuterium, whereas samples of Late Eocene and earlier tend to be depleted in deuterium. It is possible that deuterium is not a conservative constituent of the pore water, and that it is slowly taken up by the sediment.

The variation in deuterium content in all Miocene samples analyzed from Legs 1, 4, 5, and 15 ranges from +8 to -9.3%. This is a greater variability than the variation in deuterium content of deep waters of the present-day ocean (Redfield and Friedman, 1965). For example, in the present-day ocean we find variations in deep waters from -1.7% for Antarctic circum-polar water to +2.2% for Arctic Ocean water, with the North Atlantic Deep Water having a value of +1.2%. However, the present-day ocean would be expected to be somewhat heavier in deuterium concentration as compared to the Miocene ocean since light water (water depleted in deuterium) is now tied up in the Arctic and Antarctic glaciers. Over a period of time, as continental glaciers wax and wane, the isotopic composition of the oceans will change. The amount of this change during the Pleistocene is a matter of debate—Emiliani (1970) favors a  $\delta O^{18}$  change of  $0.5\text{‰}$  (i.e., about 4% for deuterium) while Dansgaard (Dansgaard and Tauber, 1969) advocates a change of  $\delta O^{18}$  of  $1.2\text{‰}$  (i.e., about 10% for deuterium).

### CONCLUSIONS

1. Deuterium in deep-sea pore waters appears to be a conservative property for short periods of time (~1,000,000 years), but may change concentration due to slow reaction or exchange with the solid constituents of the sediments.

2. Mixing of water due to compactional squeezing out of water from underlying sediments is a minor effect. Either compaction is an unimportant process after the first few centimeters of burial, or if compaction continues

beyond this point, the water that leaves the compacting sediment at depth does not mix with the overlying pore water, but migrates upward through cracks.

3. Self-diffusion of HDO is slow enough so that we can still see significant differences in deuterium concentration between pore waters that are 0.5 meter apart vertically in about 100,000 years and 5 meters apart in 40,000,000 years.

4. The change in bottom water  $O^{18}$  during the Pleistocene from glacial to interglacial is 0.5 to  $1.2\text{‰}$ —additional pore water analysis should more sharply define this  $O^{18}$  change.

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