Determination of Deuterium-Hydrogen Ratios in Hawaiian Waters

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Abstract

Previous determinations of the deuterium-hydrogen ratios in natural waters revealed the fractionation of deuterium; a fractionation resulting from differences in the vapor pressure of H_2O and HDO. Measurements of the deuterium in sea, rain, and condensate waters of Hawaii, are reported here. These results show a concentration of deuterium in sea-surface waters, and an inverse relationship of D with altitude in rain and condensate taken on a mountain side. The possible significance of these measurements for cloud physics studies is briefly discussed.

The technique of the D/H determination is essentially as follows (FRIEDMAN, 1953): 0.01 ml of water is converted to hydrogen gas by reaction with hot uranium metal. The hydrogen gas is then introduced into a mass spectrometer especially constructed for the purpose and the deuterium/hydrogen ratio in the sample gas is compared to the D/H ratio in a standard hydrogen. The standard gas was prepared from Lake Michigan water, and our D/H results are expressed as per cent enrichment or depletion of deuterium relative to our standard water:

$$\frac{(D/H)_{sample} - (D/H)_{Standard}}{D/H \text{ Standard}} \times 100$$

The precision of the method is ±0.1 per cent. Figure 1 shows the results of previous D/H analysis of natural waters from various localities. During the course of "Project Shower", water samples were taken at the positions marked D_1 to D_7 on the location map (see Figure 3).

The major source of fractionation of deuterium in nature is the difference in the vapor pressure of H_2O and HDO as shown by EPSTEIN et al. (in press). Figure 2 shows the fractionation that occurs during the change from liquid to vapor. Note that at 10°C the vapor phase is depleted by 8.8 per cent in deuterium compared to the liquid in equilibrium with it, while at 50°C the fractionation is only 5 per cent. During freezing (at 0° C) ice is enriched by about 2 per cent in deuterium relative to the water from which it is freezing.

The fractionations that take place during change of state are the ones that are important in changing the hydrogen isotopic composition of water. In the case of atmospheric water the source of the water vapor, plus the fractionation processes it has undergone, will determine its final isotopic composition. The

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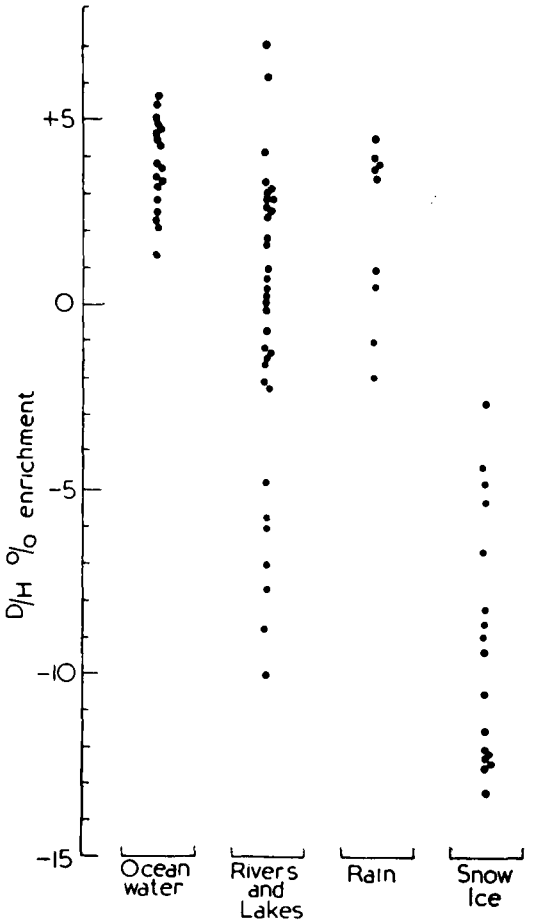

Fig. 1. Deuterium/Hydrogen ratios which have been observed in various natural waters. These results have not been previously published.

+5.0 per cent relative to our Lake Michigan standard. If we assume that evaporation occurs at about 20°C, and that the sea represents an infinite reservoir of essentially unchanging composition, the water vapor will be about 8.0 per cent "lighter" (depleted in deuterium) than the ocean, or approximately —3.5 per cent on our scale. This compares to the —3.9 per cent that we found for condensate (water from ice formed on exterior of vessel containing solidified carbon dioxide) at the windward shore of the island (see location map Figure 3 and Table 2).

Table 1 shows the D/H ratios in rain water sampled at various altitudes on the mountain side, and in lake water (station D6). Lake Waiau water is thought to come largely from

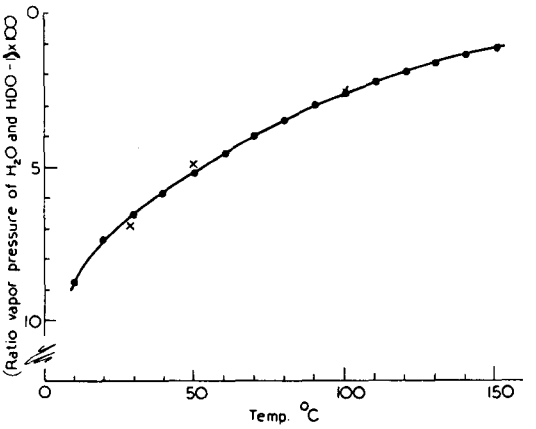

Fig. 2. Ratio of the vapor pressures of H_2O and HDO, taken from experimental data derived by measuring the isotopic composition of liquid and vapor secured during a single-stage distillation. (Epstein et al., in press.)

trade wind clouds that we are concerned with in Hawaii are composed of water which has evaporated from the open ocean.

The surface composition of the ocean in this latitude varies between about +4.0 and

melted snow near the mountain top. It is subject to excessive evaporation, due to the low water content of the air at high levels, and the D/H ratio is not therefore considered to represent that of the original precipitation

Table 1. Deuterium in rain and lake waters.

Time	Date (1954)	Elevation (feet)	Position (see map)	Source of Water	Number of Samples	D/H per cent
0930	Nov. 6	50	D1	Rain	2	+3.5 and +4.3
1030—1350	Nov. 7	2,000	D2	Rain	5	+3.5 to +4.0
—	Nov. 2	2,700	D3	Rain	1	+2.5
1500	Oct. 26	5,500	D4	Rain	2	+2.0 and +2.3
1400	Nov. 21	13,000	D6	Lake Waiau	1	+1.9

Table 2. Deuterium in sea surface and condensate waters.

Time	Date (1954)	Elevation (feet)	Position (see map)	Source of Water	Number of Samples	D/H per cent
—	—	0	D7	Sea surface	2	+4.1 and +4.5
—	Nov. 18	50	D1	Condensate	1	— 3.9
0900—1100	Nov. 21	9,500	D5	Condensate	1	— 12.1

falling at that height. The rain samples were obtained in a few seconds, using a 0.5 m^2 stainless steel funnel, and were not subject to a significant amount of evaporation after arrival at ground level. Rain samples coming from stations D2, D3, and D4 were taken within the clouds on the mountain slope. (See location map Figure 3.)

It should be mentioned that cloud motion

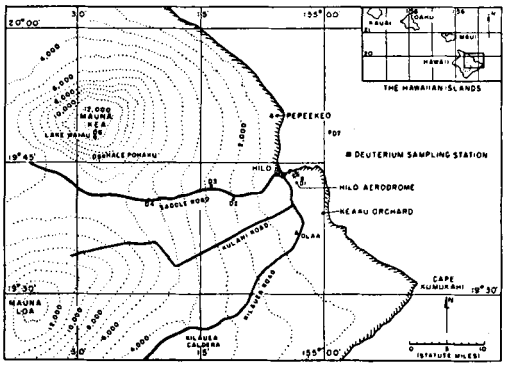

Fig. 3. Map of Hawaii showing location of the stations where rain water, sea water, and water vapor were sampled for deuterium analysis.

was, in general, from east to west; hence from position D1 up the mountain slope and through the "Saddle" which lies westward of position D4. It is interesting that the rains sampled at progressively higher elevations show a trend toward depletion of deuterium (see Table 1). A comparison of the D/H values for condensate (Table 2) obtained near sea level and at 9,500 feet altitude also shows markedly the reduction of deuterium with height.

The number of rain and condensate samples analyzed is low. It seemed pertinent, however, to point out that the trend toward decreased D/H values in rains falling at successively greater distances from the windward coast has been previously noted. (KIRSCHENBAUM, 1951.) This decrease may be explained as follows:

At the start of precipitation (assuming a wet bulb temperature of about 10° C) the first fraction precipitating will have a composition of about +4.5 per cent and the rain will get progressively lighter as the cloud becomes depleted in deuterium. Our rain samples from the 50 ft. level analyzed +4.3 and +3.5. At higher elevations we were sampling later periods in the precipitation and therefore the rain should become lighter as we proceed up the mountain and in the direction of motion of the clouds. Note that at 2,000 ft. rain varies from +3.6 to +4.0, at 2,700 ft. +2.5, and at 5,000 ft. +2.0 and +2.3.

An alternate explanation for these observed effects is that a cloud system represents a large distilling column with reflux. In this case the cool top (high altitude) will be enriched in the component of higher vapor pressure (H_2O) and the warmer bottom will be enriched in the component of lower vapor pressure (HDO). Rains formed near the bases of the orographic clouds are more likely to fall on the lower slopes of the mountain, while the rain formed near the cloud tops will be carried by the winds to the upper slopes before they fall to the ground.

In all probability the two processes (i.e. depletion of deuterium as the cloud loses water, and the distilling column effect) are both operative in the clouds. The relative importance of each process can only be decided by more

Table 3. Deuterium, salinity, and intensity in rains sampled on Nov. 7 at position D2 (see Table 1 and Figure 3).

D/H per cent	Salinity mg l^{-1}	Intensity mm hr^{-1}
+ 3.5	1.5	21.2
+ 3.8	3.4	4.8
+ 3.6	4.2	3.8
+ 3.8	4.5	9.0
+ 4.0	8.1	3.0

measurements continuing to use samples taken under known conditions.

On November 7, five rain samples were taken for deuterium measurements at position D2 at a time when rain samples were also taken for intensity and salinity determinations. Table 3 shows these results. It is interesting that there is a suggestion of a relationship between salinity and D/H. The number of samples is inadequate, however, to indicate a definite relationship.

At the present time it is not clear to what extent the D/H ratios may be useful in studying rain-forming mechanisms. The results given here clearly suggest that deuterium should be added to the list of properties of cloud, rain and condensate waters which may be useful in cloud physics studies.

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