

Chapter 3

Isotopic Composition of Ocean Water

On an average, there are 320 molecules of HDO, 420 molecules of H_2^{17}O , and about 2,000 molecules of H_2^{18}O for each 10^6 molecules of H_2^{16}O in natural waters of the Earth. The ratio of isotopic abundances of deuterium (D) to protium (H) is $\text{D}/\text{H} = 0.000155$ (0.0150 atom.%) and that of oxygen is $^{18}\text{O}/^{16}\text{O} = 0.002$ (0.2 atom.%).

3.1 Distribution of Hydrogen and Oxygen Isotopes and Water Dynamics

The maximum limits of the variation in D concentrations, which have been found, are about 70% and those of oxygen-18 (^{18}O) are about 9%. As one may expect, precipitation over the Southern polar region is most depleted in heavy water isotopes: $\text{D}/\text{H} = 0.0109$ atom.% and $^{18}\text{O}/^{16}\text{O} = 0.1887$ atom.% (Schotterer et al. 1996). The most enriched waters are in the closed reservoirs of the arid zone: $\text{D}/\text{H} = 0.0178$ atom.% and $^{18}\text{O}/^{16}\text{O} = 0.2055$ atom.% (Fontes and Gonfiantini 1967). For other natural objects, the fixed limits of the D content variations are about 150% (in atmospheric molecular hydrogen $\text{D}/\text{H} = 0.0079$ atom.% (Begemann and Friedman 1968) and in the chondrites and lunar rocks $\text{D}/\text{H} = 0.0195$ atom.% (Briggs 1963; Friedman et al. 1971). For oxygen, these limits are about 10 atom.% (in the polar regions, the precipitation $^{18}\text{O}/^{16}\text{O} = 0.189$ atom.% (Gonfiantini 1978), and for the oxygen dissolved in ocean waters $^{18}\text{O}/^{16}\text{O} = 0.2083$ atom.% (Craig and Gordon 1965)).

It follows that the differences in the limits of D variation are one or more orders of magnitude higher than those of heavy oxygen. This can be explained by the more effective separation of D and H in natural processes than that of any other pair of stable isotopes due to the large difference in their atomic weights (Table 3.1).

For this reason, D can be considered as one of the most interesting isotopes from the geochemical viewpoint. Since the end of the 1950s, researchers studying the isotopic composition of natural waters have preferred to determine both isotopes of water hydrogen and oxygen simultaneously.

Ocean waters account for 90% of the total amount of water in the hydrosphere (Poldervaart 1955; Ronov and Yaroshevsky 1967; L'vovich 1969) (see Table 3.2).

Table 3.1 Limiting values of stable isotope variations for some elements in natural objects. (From Larionov 1963; Begemann and Friedman 1968; Briggs 1963; Craig 1963; Hoefs 1973; Gonfiantini 1978)

Element	Isotope ratio	Variation limits (absolute values)	Relative variation of limiting values
H	D/H	0.000079–0.000195	147
Li	⁸ Li/ ⁷ Li	0.079–0.084	6
B	¹¹ B/ ¹⁰ B	0.226–0.234	3.5
C	¹³ C/ ¹² C	0.01079–0.01225	13
O	¹⁸ O/ ¹⁶ O	0.001893–0.002083	10
Si	³⁰ Si/ ²⁸ Si	0.0332–0.0342	0.5
S	³⁴ S/ ³² S	0.0427–0.0491	13

Table 3.2 Total amount of water in the hydrosphere reservoirs. (From Poldervaart 1955 and L'vovich 1969)

Reservoir	Amount of water (million km ³)		Time of water exchange, L'vovich 1969
	Poldervaart 1955	L'vovich 1969	
Oceans	1370	1370.323	2,600 years
Lakes and rivers	0.5	0.231	From 12 days to 3.3 years
Ice sheets	22	24	~11,000 years
Atmospheric waters	0.013	0.014	10 days
Water in marine and continental sediments	196	–	–
Groundwaters	–	60	~5,000 years
Soil waters	–	0.075	0.9 year
Bounded waters in the Earth's crust (Ronov and Yaroshevsky 1967)	180	380	–
Total amount in the hydrosphere	1968.513	1834.643	–

According to Ronov and Yaroshevsky (1967), Poldervaart (1955), and Vinogradov (1967a), the total amount of water in the Earth's crust and oceans is estimated to be 1,800–2,700 million km³ ($1.82.7 \times 10^{24}$ g).

Of all natural waters, the ocean, which is a unique reservoir, remains most constant regarding its isotopic and other physicochemical properties. Several authors (Craig and Gordon 1965; Craig 1961b; Epstein and Mayeda 1953; Friedman et al. 1964) have shown that ocean water at depth of more than 500 m is homogeneous in isotopic composition. This allowed Craig (1961b) to propose it as a standard for reporting concentrations of D and ¹⁸O content in natural water. The standard of the ocean water (SMOW) has the following values of hydrogen and oxygen isotope ratios: D/H = $(155.76 \pm 0.08) \times 10^{-6}$ (Hagemann et al. 1970) and ¹⁸O/¹⁶O = $(2005.20 \pm 0.45) \times 10^{-6}$ (Baertschi 1976). Fluctuations in the ratios of the absolute values for hydrogen and oxygen isotopes arise from the difficulties incurred in the precise preparation of the synthetic isotope mixtures for mass spectrometer calibration.

The variation in the relative content of D in deep ocean layer is about 4‰ and that of ¹⁸O is of 0.3‰. In the surface ocean layer, the regional variations, depending upon water temperature, are 35‰ for D and about 3‰ for ¹⁸O. The lowered content of D in the surface ocean layer occurs in those regions where ice-melting water

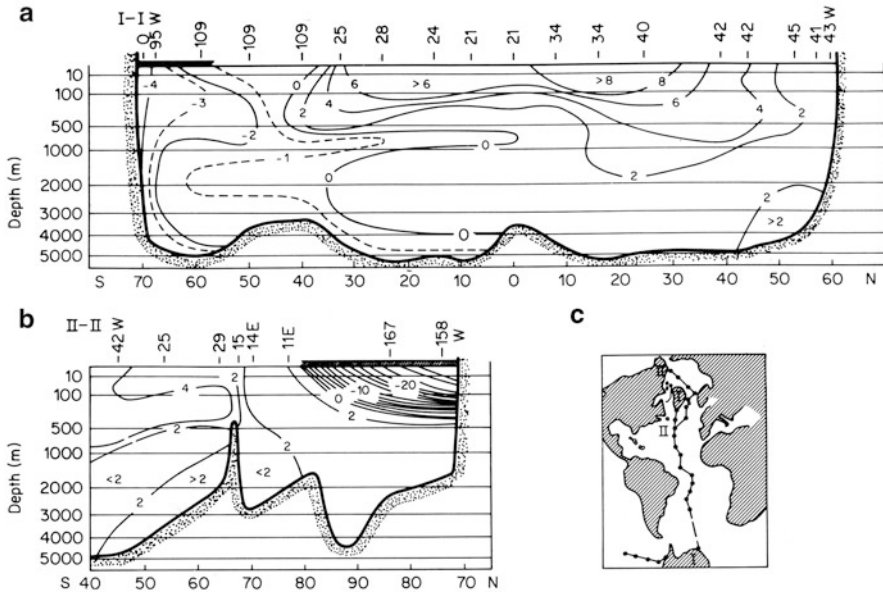


Fig. 3.1 Distribution of D concentrations (in δD ‰) in a vertical section of Atlantic Ocean and Arctic basin waters. **a** section from Antarctic through the Atlantic Ocean to Greenland. **b** section from North Atlantic across the Norwegian Sea and Arctic Ocean to Alaska. **c** schematic plan of sections. (After Redfield and Friedman 1964)

affects isotopic composition. In high latitudes, where the surface layer of the ocean is freezing, isotopic fractionation factor is ~ 1.0180 for D and ~ 1.0030 for ^{18}O . In the equatorial region of the ocean where intensive evaporation of water takes place, there is an enrichment of the surface layer with heavy isotopes.

Despite the considerable homogeneity of the isotopic composition of ocean water, the ranges of D and ^{18}O variations with latitude and depth are wide enough to be reliable indicators of processes occurring in the ocean. These ranges, for deep ocean waters, are about ten times greater than the accuracy of mass spectrometer measurements with which modern techniques and apparatus permit determination of D (± 0.2 ‰) and ^{18}O (± 0.02 ‰).

On the basis of investigations carried out by Epstein, Friedman, and Craig with co-authors (Epstein and Mayeda 1953; Friedman et al. 1964; Redfield and Friedman 1964; Craig and Gordon 1965), we can compose a sufficiently detailed picture of D and ^{18}O distribution in ocean waters. Numerous samples of ocean water obtained during expeditions in the main oceans have been studied. The number of water samples is finite due to the ocean size; however the choice of samples, which have been taken from the most characteristic points of individual basins according to oceanographic data in common use, combined with the high precision of measurement and the coincidence of experimental data with principal conclusions which have been made by different authors, suggests that the results obtained are reliable.

Figure 3.1 and 3.2 show isolines of D distribution in the profile and in the surface layers of the Atlantic and Arctic Oceans plotted by Redfield and Friedman (1964).

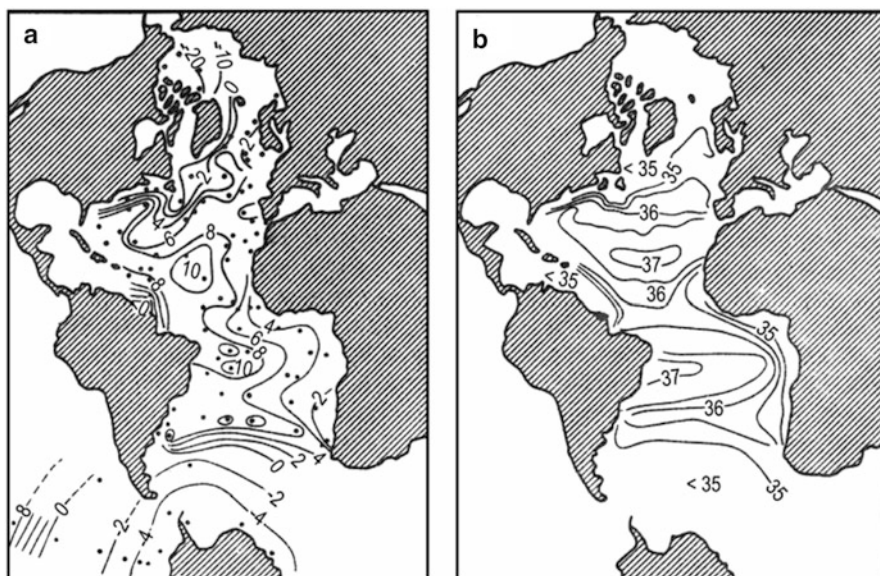


Fig. 3.2 Distribution of **a** D concentrations (in $\delta D\text{‰}$) and **b** salinity (in ‰) on the surface waters of the Atlantic Ocean. (After Redfield and Friedman 1964)

Table 3.3 Regional distribution of average D concentrations in deep oceanic-water masses. (From Redfield and Friedman 1964)

Ocean	$\delta D, \text{‰}$	Number of stations	Number of samples
Arctic Ocean	$+2.2 \pm 1,0$	6	22
Norwegian Sea	$+2.2 \pm 0,7$	6	22
North Atlantic	$+1.2 \pm 0,8$	18	44
South Atlantic	$-1.3 \pm 0,6$	7	11
Pacific Ocean	$-1.4 \pm 0,4$	5	8
Antarctic Intermediate	$-0.9 \pm 0,8$	10	19
Antarctic Circumpolar	$-1.7 \pm 0,8$	6	16

Three layers are commonly distinguished according to the conditions of the distribution of individual isotope concentrations and the observed picture of the ocean water mixing at different depths. The surface layer (down to ~ 500 m) is characterized by the greatest ranges of local and regional variations of isotopic composition. The deep layer (below $\sim 1,000$ m) is distinguished by thorough mixing of water and uniform isotopic composition in the entire ocean. The intermediate—or mixing—layer (from ~ 500 to $\sim 1,000$ m) is characterized by some intermediate parameters. Sometimes in the oceanic water profile, a bottom layer can be distinguished which has characteristic regional peculiarities in some basins.

The deep ocean layer, including approximately three-quarters of its total mass, can be practically considered representative of all the Earth's hydrosphere. On the basis of experimental data, Redfield and Friedman give the following average D δ -values (in relation to the SMOW standard) for the major deep water masses in individual oceans (see Table 3.3).

Table 3.4 Regional distribution of average ^{18}O concentrations in deep oceanic-water masses. (From Craig and Gordon 1965)

Ocean	$\delta^{18}\text{O}$, ‰	Salinity, ‰
North Atlantic	+0.12	34.93
Antarctic (bottom water)	-0.45	34.65
Indian Ocean	-0.18	34.71
Pacific Ocean:		
Antarctic basin (55–65°S)	-0.21	34.700
Shouern region (22–40°S)	-0.17	34.707
Equatorial basin (6°S–30°N)	-0.17	34.692
Northern region (44–54°N)	-0.17	34.700
Antarctic Circumpolar	-0.3 to 0.2	34.69

The picture of ^{18}O δ -values for deep ocean waters according to data of Craig and Gordon (1965) is given in Table 3.4.

From the analysis of these data, the following principles of D and ^{18}O variations in deep ocean waters were obtained (Craig and Gordon 1965).

1. The ocean waters in the northern hemisphere are heavier in D and ^{18}O than those of the southern hemisphere.
2. The waters of the Arctic Ocean are highly uniform in isotopic composition and differ a little from those of the Norwegian Sea but differ significantly from the North Atlantic deep waters.
3. The waters of the Atlantic Ocean are mixing preferentially northward and have considerable variations even in the subtropical latitudes of the northern hemisphere.
4. The deep waters of the Indian and Pacific Oceans are highly homogeneous in isotopic composition but have some variations in high southern latitudes. The isotopic composition of water becomes heavier in the direction of low latitudes.
5. The Pacific and Atlantic ocean waters and circumpolar Antarctic waters are approximately similar in isotopic composition.
6. In deep Pacific trenches, the water is enriched with ^{18}O by about 0.2‰ in relation to the bulk of deep waters in this ocean.
7. For deep ocean waters as a whole there is a relationship between D and ^{18}O content which is sufficiently close to linear: $\delta\text{D} = n\delta^{18}\text{O}$. The value of n is approximately equal to 10, with some regional deviations.

It appears from the information on heavy isotope distribution that waters of the ocean display a natural tendency towards constant isotopic composition. The main factors governing the observed D and ^{18}O variations are the processes which occur in surface ocean waters and have a regional character. In surface waters, the constant enrichment or depletion of water with heavy isotopes takes place due to evaporation of water and exchange with the atmosphere. Further redistribution of isotopes in the ocean proceeds as a result of mixing of surface and deep waters on global and regional scales.

The data on ^{18}O variations in the North Atlantic surface waters, obtained by Epstein and Mayeda (1953)—and recalculated by Craig in relation to the SMOW standard—are given in Table 3.5, which supplements Fig. 3.2.

Table 3.5 Variation of ^{18}O concentration in North Atlantic surface waters

Location of sampling place	$\delta^{18}\text{O}$, ‰	Salinity, ‰
43°04'N, 19°40'W	+0.68	35.8
Off Bermuda	+1.11	36.1
Off Bermuda	+1.00	36.4
Off Bermuda	+1.30	36.8
28°05'N, 60°49'W	+1.32	36.78
Golfstream, off Norway	+0.26	35.2
44°09' N, 68° 18'W	-0.95	33.0
Off Greenland	-11.33	16.2
East cost, Greenland	-3.34	29.3

The isotopic composition of the surface ocean waters undergoes considerable variations with latitude; however, for equatorial and temperate latitudes the linear relationship between D and ^{18}O contents in the form $\delta\text{D} = n\delta^{18}\text{O}$ remains the same. The variation of n for a given region depends on the ratio of the amounts of evaporation and precipitation and is equal to 7.5 for the North Pacific, 6.5 for the North Atlantic, and 6 for the Red Sea.

3.2 Effect of Evaporation and Vertical Water Exchange

The factors governing regional isotopic variations in the surface ocean waters are: the ratio between evaporation and precipitation; the continental run-off and in a number of cases the submarine discharge of groundwater run-off; the freezing of sea water; the contribution of water from Polar and Circumpolar glaciers and also ice-melt water; the mixing of surface and deep ocean waters. Among all the enumerated factors, the most important is evaporation from the ocean surface and its ratio with precipitation in a given region.

According to Craig and Gordon (1965), the values of the ratio of evaporation to precipitation is 0.67 for the equatorial belt, 2.0 (maximum value) for the subtropical trade winds region, and 0.5 for high latitudes (above 40°).

The isotopic composition of precipitation varies with latitude in accordance with principles given in Chap. 4. The primary precipitation, condensing from vapor, has the maximum content of heavy isotopes, since the standard vapor pressure for heavy molecules of water is lower than that for the light ones and, thus, they are condensing preferentially before the light molecules. Practically, the first precipitation has an isotopic composition close to that of the sea water in a given region. Consequently, during the movement of vapor away from the evaporation region they are depleted in heavy isotopes. Therefore, in those latitudes where the balance of evaporating and precipitating moisture is observed, the isotopic composition of surface waters remains constant and is close to the mean ocean isotopic composition. In those regions, where evaporation exceeds precipitation, enrichment D and ^{18}O of the surface waters occur. In the Polar Regions where precipitation exceeds evaporation and the incoming water vapor has the lowest D and ^{18}O composition, the surface waters are considerably depleted. Craig and Gordon (1965) have given the following regional limits for

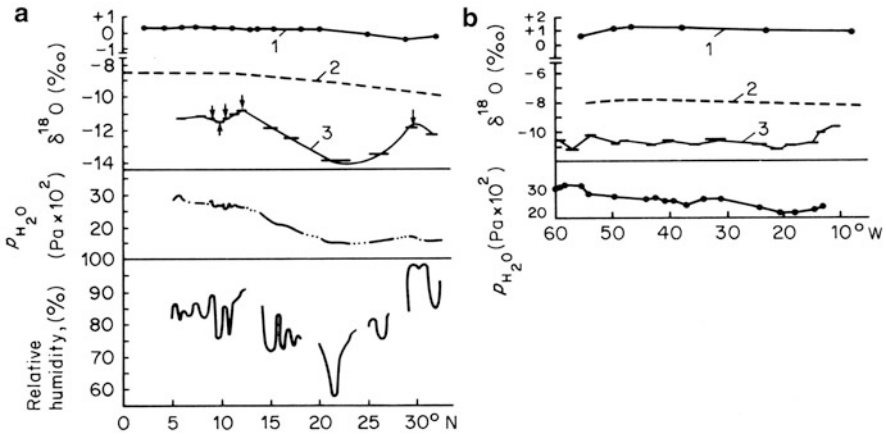


Fig. 3.3 ^{18}O variations in vapor over sea surface for **a** North Pacific latitudes and **b** North Atlantic longitudes: (1) sea surface water; (2) equilibrium vapor; (3) observed vapor data. (After Craig and Gordon 1965)

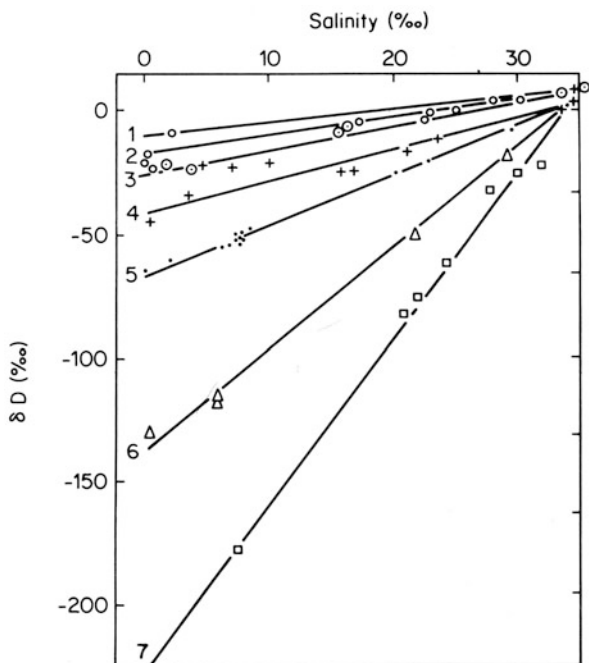
^{18}O variations in precipitation: from 0 to -5‰ for tropical and subtropical regions, from -5 to -15‰ for temperate latitudes, and below -15‰ for the polar regions.

The process of vapor isotopic composition formation during evaporation and molecular exchange above the ocean surface has a complicated and non-equilibrium character. Figure 3.3 shows the results of Craig and Gordon's work, for determining ^{18}O variations in water vapor, which had been carried about in the Pacific Ocean. The samples of vapor were taken at the height of the ship's mast. The figure also shows the curve of ^{18}O variation in surface waters in the regions under investigation and the curve of ^{18}O content in equilibrium vapor in relation to surface waters at the observational temperatures.

While comparing the experimental data with those calculated for equilibrium vapor, one can see that the observed difference in ^{18}O content is 4.5‰ and occurs in the northern part of the trade winds region ($18\text{--}26^\circ\text{N}$), that is in the region of maximum evaporation. The analogous investigations carried out by Craig and Gordon across the North Atlantic along 20°N latitude have shown that, within small regional deviations, the isotopic composition of vapor is sufficiently homogeneous and is about 3‰ lighter than that at equilibrium. Thus, the following conclusion has been drawn: the latitudinal isotopic variations of vapor are more easily observed than longitudinal variations. The physicochemical effects provided by non-equilibrium conditions of condensation and water evaporation from the surface are considered in Chap. 4.

Further fractionation of oxygen and hydrogen isotopes proceeds with the freezing of water in the Polar Regions. The process goes further at equilibrium conditions and results in enrichment of ice in relation to the surface water by approximately 2‰ in ^{18}O and 20‰ in D (Craig and Gordon 1965; Redfield and Friedman 1964). In general, this effect is not huge. The main influence upon the formation of isotopic

Fig. 3.4 Relationship between D content and salinity for various coastal waters: (1) Gulf of Venezuela; (2) Georgia Coast; (3) Albemarle, NC; (4) Chesapeake Bay, VA.; (5) Baltic Sea; (6) Labrador, Hamilton Inlet; (7) Greenland Fjords. (After Redfield and Friedman 1964)



composition of surface water in polar basins is expected by melt-waters from glaciers and snow formed by the accumulation of atmospheric precipitation. The analogous effect arises from continental run-off and the submarine discharge of groundwaters in the continental shelf area. The formation of the isotopic composition of the ocean waters finally depends on the process of surface and deep water mixing. The observed picture of D and oxygen isotope distribution, together with other classical experimental data, may be applied to investigate ocean water dynamics.

It is commonly known that the classical approach for experimental oceanographic studies is based on the relationship between the temperature and salinity of ocean water. The logical question arises whether or not data on isotopic composition of sea water contains any new information. It appears they do for the following reasons. Salinity characterizes sea water in terms of a solution, whereas D and ^{18}O composition characterizes just water, which is a solvent. During changes of salinity and heavy isotope composition in surface ocean waters, due to evaporation and precipitation, the salinity depends on the isotopic ratios of water in precipitation and evaporation. Therefore, the data of isotopic composition and salinity of sea water complement each other, characterizing the solution from different sides: from the side of components dissolved in it and from the side of water, the solvent.

Experimental data obtained from a number of coastal regions (Redfield and Friedman 1964) representing the relationship between D content and salinity are shown in Fig. 3.4. From this figure, it is evident that the experimental points fall on lines representing different proportions of fresh and salt water with gradients representative of given regions. All the lines meet at a point, which is characteristic of the

relationship between D content and salinity for North Atlantic deep waters or their modifications at lower latitudes and shallower depth.

The D content corresponding to zero salinity is characteristics of fresh water, it varies with latitude over a wide range, attaining extreme values in the fjords of Greenland. These data are close to those for the D content in continental surface waters of corresponding regions.

3.3 Dynamics of the Ocean Water

The relationship between the isotopic composition and salinity for subsurface and deep ocean waters is illustrated by the experimental evidence provided by Craig and Gordon (1965) which is shown in Fig. 3.5 for the Pacific and the Atlantic Oceans. Craig and Gordon gives the following interpretation of the data on the relationship and motion of subsurface and deep ocean waters.

1. The position of deep waters on the isotopic composition-salinity plot reflects the average chemical and isotopic composition of ocean water. The starting point for near-surface waters on this plot is their geographical position, corresponding to zero balance of water in the precipitation–evaporation process. The position of this point is determined by the intersection of equatorial, trade winds, and polar relationships. On a geological time scale, the composition of near-surface and deep ocean waters should vary over a certain range. The variations of oxygen isotopic composition with time are limited by products of ocean activity and provide the base for oxygen paleothermometry.
2. In Pacific Ocean deep waters (see Fig. 3.5a), the identical relationship between isotopic composition and salinity found for near-surface waters of this **basic** are not observed, which suggest the absence of convective transfer water masses between near-surface and deep waters in this ocean. The South Pacific waters have a higher salinity than waters of the North Pacific although they have similar ^{18}O content. The near-surface isotopic composition of water in high southern latitudes of the Pacific and Atlantic Oceans is approximately similar and is governed by circumpolar conditions of the Antarctic region. The slope of the straight line which is characteristic for the isotopic composition-salinity relationship for near-surface waters of the southern hemisphere is greater than that for the northern hemisphere, which suggest different latitudinal variations of water composition in the two hemispheres, probably reflecting the continental effect of the northern hemisphere. In addition, high latitudes in both hemispheres generally have a greater isotopic composition-salinity ratio than low ones, reflecting the latitudinal dependency of isotopic ratios in precipitation. In the southern hemisphere in the Pacific Ocean from 30°S to the equator, an isotopic loop is observed, whereas in waters with similar ^{18}O contents the salinity varied from 35 to 34.5‰. The nature of this loop has not yet been explained.
3. From the data given in Fig. 3.5a, it is evident that the Pacific Ocean surface waters do not exert a significant influence on the formation of its deep waters.

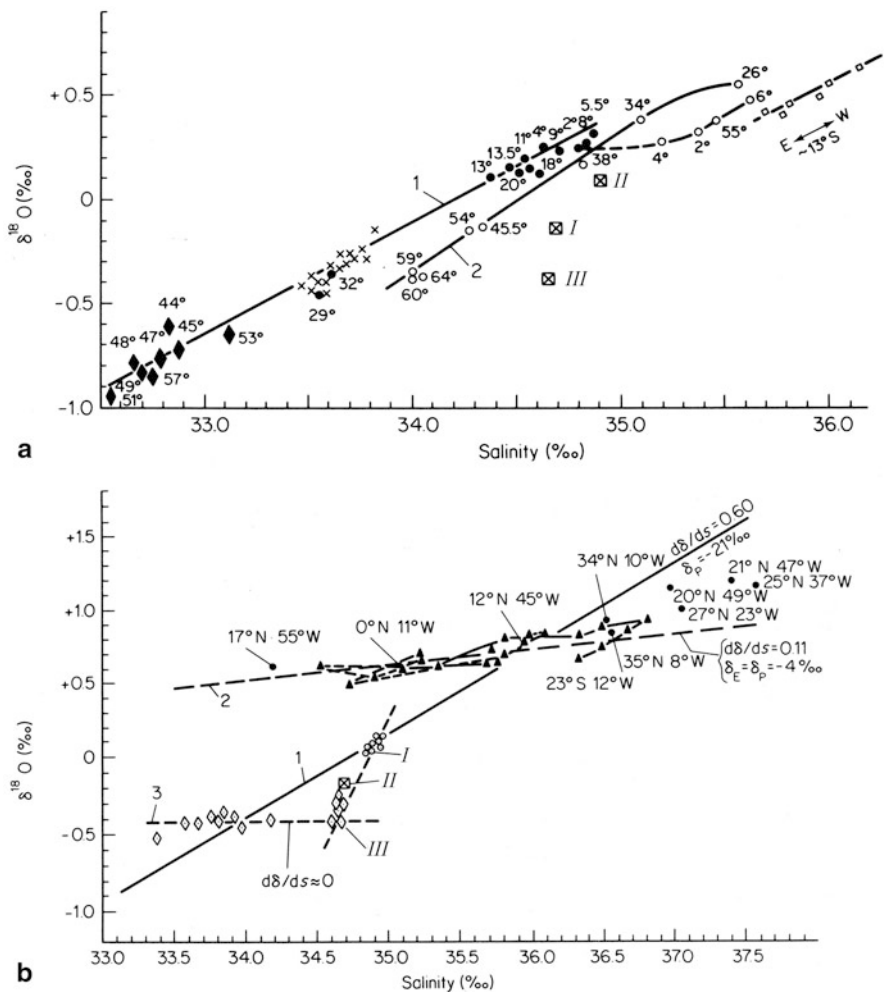


Fig. 3.5 Relationship between ^{18}O content and salinity. **a** for northern (1) and southern (2) latitudes of the surface Pacific Ocean: (I) deep and bottom Pacific; (II) North Atlantic; and (III) Antarctic waters. (The samples are from different expeditions). **b** for northern (1) and equatorial (2) regions of the Atlantic and Weddell Sea (3) waters and for deep North Atlantic (I), Indian and Pacific (II) and Antarctic waters (III). Here δ_E and δ_P refer to the isotopic composition of vapor and precipitation respectively. (After Craig and Gordon 1965)

An analogous picture is observed in the Indian Ocean. Waters of the Pacific and Indian oceans being replenished from the Atlantic and Antarctic deep and bottom waters are not simply formed by the mixing of these two components, because they lie off the range of the line connecting these two source waters. To obtain the water of the required composition, a third component is needed which has less water but the same isotopic composition. Investigations by other authors based on

a temperature–salinity relationship are leading to the same conclusion. As a third possible component, the Pacific and Indian intermediate waters are considered. Besides the possibility of these waters taking part in the formation of Pacific and Indian deep waters, Craig and Gordon have also considered circumpolar deep waters having the necessary isotopic composition and salinity and being found in the South Atlantic in the Weddell Sea waters. To answer this question, more involved investigations are required.

The circumpolar waters in the North Pacific (see Fig. 3.5a) are characterized by a mean slope of the isotopic composition–salinity line of about 0.54. In contrast to Epstein and Mayeda (1953), who considered the continental run-off of fresh waters to be of great importance, Craig and Gordon (1965) found that in the formation of water composition in the sub-arctic region, the decisive role is played by the typical prevalence of sea precipitation over evaporation.

4. The North Atlantic deep waters, in contrast to the Pacific waters, are formed due to mixing with subsurface. This is observed from their position on the line of subsurface waters on the isotopic composition–salinity diagram (see Fig. 3.5b). This conclusion is in agreement with certain classic data on the convective mixing of subsurface and deep waters in this region. The data on the isotopic composition of near-surface waters are also in agreement with those of precipitation in high latitudes.

A sharp difference in the average values of the isotopic composition–salinity ratio between the equatorial region and the trade winds belt on the one hand and the high latitudinal region on the other is typical for the Atlantic subsurface waters. In equatorial regions of this ocean, in contrast to the Pacific Ocean at low salinity, rather high concentrations of ^{18}O content are observed in subsurface waters.

According to Ereemeev (1972), who has studied the isotopic composition of ^{18}O in Atlantic surface waters, there is an empirical relationship between ^{18}O content and salinity of water. For high latitudes from 60°N and 40°N this relationship is

$$\delta_{34.8}^{18}\text{O} = 0.64S - 21.1\text{‰},$$

where $\delta_{34.8}^{18}\text{O}$ is ^{18}O content in a sample relative to that in intermediate ocean waters with salinity 34.8‰; that is the observed salinity of the surface waters per mille.

For middle latitudes between 40°N and 20°N the relationship is

$$\delta_{34.8}^{18}\text{O} = 0.26S - 6.7\text{‰}.$$

For the equatorial region, $0\text{--}15^\circ\text{N}$.)

$$\delta_{34.8}^{18}\text{O} = 0.17S - 5.4\text{‰}.$$

For southern latitudes

$$\delta_{34.8}^{18}\text{O} = 0.34S - 11.8\text{‰}.$$

These data were used by Ereemeev for calculating the evaporation–precipitation ratio in corresponding latitudes.

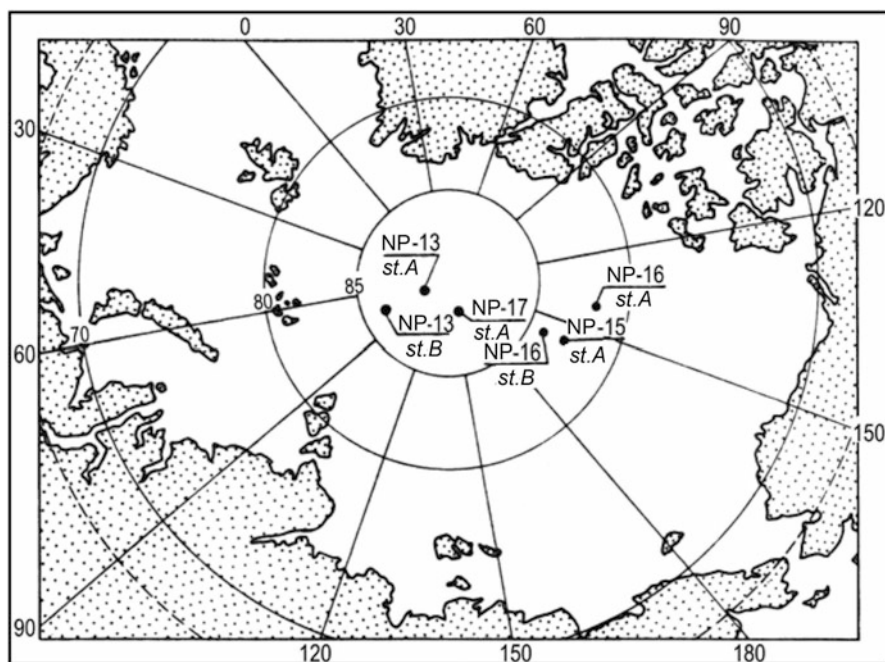


Fig. 3.6 Location of water sampling places for study of ^{18}O distribution in waters of Arctic basin. (After Vetshtein et al. 1974)

In the South Atlantic, the surface and near-surface waters in the Weddell Sea are characterized by a relatively constant ^{18}O content within a considerable range of the salinity variations ($^{18}\text{O} = -0.45\text{‰}$, when salinity ranges from 33.4‰ to 34.6‰). The salinity of these waters is not much lower than that of Pacific surface waters. The decrease of salinity in the circumpolar waters of this region reflects the dilution effect provided by ice melting.

The Antarctic bottom waters studied in two locations ($64^{\circ}55'\text{S}$ and $52^{\circ}10'\text{W}$ at depth 2,935 m; $64^{\circ}00'\text{S}$ and $40^{\circ}50'\text{W}$ at depth 4,609 m) have the same values of salinity, 34.66‰ and $^{18}\text{O} = -0.45\text{‰}$, which corresponds to the minimum value of salinity required for sea water at freezing temperature to sink to the bottom. The isotopic composition of this water is the same as that of the surface water. Therefore, the process of Antarctic bottom water formation due to sinking of the surface waters agrees with the data obtained by both ^{18}O and D isotope studies (see Fig. 3.1).

In Fig. 3.5b, one can see that the Antarctic intermediate water may possibly contribute to the Pacific and Indian deep waters as the elusive 'third component'.

Isotopic composition of oxygen in the Antarctic basin during drifting expedition stations, 'North Pole-13, 15, 16 and 17' has been studied.

Figure 3.6 shows location of water sampling places during these investigations and Table 3.6 demonstrates the analysis results. On the basis of interpretation of the obtained data the authors derived, in the Arctic basin, the surface water layer up to

Table 3.6 Experimental data of $\delta^{18}\text{O}$ values obtained in the central part of Arctic basin. (From Vetshtein et al. 1974)

Sampling depth, M	Temperature, °C	Salinity S‰	$\delta^{18}\text{O}$, ‰
<i>Station NP-13 (winter 1967)</i>			
15	-1.71/-1.80	31.13/32.79	-2.3/-1.0
75	-1.82/-1.79	33.22/33.33	-2.0/-1.5
400	+0.88/+0.82	34.85/34.88	+0.2/+0.1
3500	-0.80/-0.80	34.92/34.90	-0.4/-0.8
<i>Station NP-15 (winter 1967)</i>			
5	-1.71/-1.67	31.04/30.97	-3.6/-3.8
35	-1.68/-1.66	31.00/31.00	-2.8/-2.6
130	-1.54/-1.50	33.75/33.68	-1.4/-1.6
400	+0.76/+0.76	34.87/34.88	+0.1/+0.5
<i>Station NP-15 (winter 1969)</i>			
10	-1.8/-1.78	29.65/32.14	-4.5/-2.5
50	-1.32/-1.74	31.73/32.14	-2.7/-2.1
100	-1.56/-1.67	32.68/33.13	-2.0/-1.4
250	+0.04/+0.38	34.63/34.72	-0.6/-0.4
400	+0.71/+0.88	34.87/34.79	-0.2/0.0
750	+0.16/-0.01	34.88/34.87	-0.2/+0.2
1500	-0.49/-0.56	34.92/34.90	-0.6/-0.3
2000	-/-0.77	-/35.92	-/+0.3
3000	-/-0.83	-/34.92	-/-0.3
4000	-/-0.70	-/34.92	-/-0.4

/Variation limits of values measured by a number of samples

the depth of 250 m, which is characterized by -4.5 to -0.8‰ value of $\delta^{18}\text{O}$ with the temperature of water from 1.65 to 1.75°C and salinity up to 32‰ (Vetshtein et al. 1974). The water layer of the depth from 250 to 750 m is characterized by higher value of $\delta^{18}\text{O}$ equal to $-0.4 \pm 0.3\text{‰}$, temperature from 0.04 to 0.88°C , and salinity up to 34.88‰ . The bottom waters have small fluctuations in $\delta^{18}\text{O}$ values in the range of 0 to -0.7‰ , temperature about -0.8°C , and salinity close to 34.92‰ .

By the above investigation, the surface waters located to the west from Lomonosov Ridge are formed with the Atlantic waters having high salinity and $\delta^{18}\text{O}$ about 1.0‰ . The waters of the east part of the basin are formed by the ice-melting waters, with the influence of river run-off and also with the Pacific waters coming through the Bering's Strait. The following experimental relationship between $\delta^{18}\text{O}$ and salinity for the Arctic basin is found by the study of Vetshtein et al. (1974): $\delta^{18}\text{O} = 0.7S - 24.6\text{‰}$. This dependence gives general idea about the degree of dilution of the regional waters by fresh waters, which has slope of the straight line as $\Delta\delta^{18}\text{O}/\Delta S = -0.7$. At zero value of salinity, one has $\delta^{18}\text{O} = -25\text{‰}$, which relates with the mean value of $\delta^{18}\text{O}$ for the fresh waters of the Arctic latitudes. The mean value of content of the fresh waters in the Arctic basin is estimated to be about $0.2\text{--}0.3\%$.

Only the initial steps in investigation of the conditions and principles of oxygen and D isotopic distribution in oceanic waters have been undertaken, mainly to study their transfer on global and regional scales. The studies have shown the considerable potential of stable isotope techniques which together with the classical parameters of

the ocean water, salinity, and temperature, greatly expand our experimental ability to study the ocean dynamics.

3.4 Isotopic Composition of Ocean Water in the Past

Paleotemperature studies based on oxygen isotopic analysis of the ancient ocean sediments and glaciers (Emiliani- 1970, 1978) show that the temperature variations of the ocean surface in the equatorial region during the last 730,000 years have not exceeded 5–6°C. With regards to the variations of $\delta^{18}\text{O}$ values of the sea water, they have not deviated by more than 0.5‰ from the modern level. Similar results were obtained based on the analysis of the D content in water of the clay minerals of ocean origin and of different ages.

By Imbrie's (1985) data, temperature of the surface oceanic layer during the ice epoch has felt down not by 5–6°C, as it follows from works of Emiliani, but only by 2°C. Imbrie notes that Emiliani's curves express not the temperature change of the ocean surface waters, but changes in isotopic and chemical composition due to pumping-over the oceanic part of water to the continental access. In this case a change of A parameter in the Epstein and Mayeda isotope paleothermometry formula (see Chap. 1) takes place. The parameter A is characterized oxygen isotopic composition of water, in which the foraminifera's shells are growing in the surface layer of water and after their death falling down to the bottom and forming the bottom sediments.

The isotopic and chemical composition of the ocean water has more than likely remained the same at least during the last 250–300 million years. This is confirmed by many facts summarized during paleotemperature studies and based on the analysis of the isotopic composition of oxygen in the shells of modern and ancient mollusks (Bowen 1966) and also of oxygen and hydrogen isotopes in the charts of different ages (Kolodny and Epstein 1976).

Arguments in favor of the stability of isotopic and chemical composition of the ocean water were considered by Lowenstam (Bowen 1966). They are:

1. The crystalline form of carbonate of the castle brachiopodas remained the same from the Mississippian time. This supports the theory that the crystallochemical process of Mg and Sr accumulation has remained stable during the last 250 million years, the period which corresponds to the time interval of the studied samples.
2. Modern organisms, living in ocean waters of variable chemical composition, have different ratios of Sr/Ca and Mg/Ca. This fact demonstrates the absence of any homeostatical mechanism due to which the definite Sr/Ca and Mg/Ca ratios might remain constant.
3. Differences in the Sr and Mg content found in fossil species of mollusks are analogous to those observed in modern ones. The interdependence between Sr and Mg content and oxygen isotopic ratios in both the fossil and modern mollusks is very close.

Bowen notes that since the isotopic composition of oxygen, the concentrations of SrCO_3 and MgCO_3 , and the values of the Sr/Ca and Mg/Ca ratios in those shells of the fossil mollusks studied by Lowestam always varied within the limits which are characteristic for modern samples, it seems probable that the concentration of ^{18}O in ocean waters has remained constant, at least during the last 250 million years.

One may suppose that isotopic composition of hydrogen in ocean waters has also remained unchanged during geological time. This conclusion does not contradict theoretical and experimental results related to the value of isotopic balance of hydrogen on the Earth during its geological history (Soyfer et al. 1967).

The total accumulation of D on the Earth might occur as a result of the interaction of initial cosmic rays with the atmosphere and the Earth's surface, but according to Korff's data, the output of D in nuclear reactions of neutron capture (the secondary component of cosmic rays) by H nuclei, assuming that the intensity of the cosmic rays was a constant during 3.2×10^9 years, would make up only $1/10^{10}$ part of all the D in the hydrosphere at present.

In the literature, the question of the accumulation of D in the Earth's hydrosphere caused by the preferential loss of H—by the escape of the free hydrogen from the gravitational field of the Earth—has been discussed.

It should be noted that estimations of the isotopic composition of ocean water in the Precambrian era remain uncertain. The study of the isotopic ratios of oxygen in sea carbonates and siliceous sediments shows that the ^{18}O content decreases progressively from modern time to ancient geological epochs (Degens and Epstein 1962, 1964; Perry 1967; Chase and Perry 1972, 1973; Knauth and Epstein 1975, 1976; Kolodny and Epstein 1976; Veizer and Hoefs 1976; Becker and Clayton 1976; Bowen 1991).

At present, there are three possible reasons for this phenomenon: (1) the change in the isotopic composition of rocks during their metamorphism as a result of the isotopic exchange with 'light' meteoric waters; (2) the lighter isotopic composition of waters of ancient oceans; (3) higher average temperatures of the ocean waters in ancient geological epochs. A reliable solution to this problem has not yet been obtained. Degens and Epstein (1962, 1964) explain the observed tendency in the siliceous and carbonate sediments in terms of isotopic exchange process with meteoric waters. Perry (1967), Perry and Tan (1972), and Chase and Perry (1972, 1973) have assumed on the basis of the oxygen isotopic composition analysis of the charts that the possible depletion of the ocean in Precambrian era had attained the maximum value of 20‰. Knauth and Epstein (1975, 1976) and Kolodny and Epstein (1976) have come to a conclusion based on hydrogen and oxygen isotopic composition analysis that the isotopic composition of ancient oceans was already close to the modern one in the late Precambrian era and the change with time of the oxygen isotopic composition of the charts should be completely explained by higher temperatures of the Earth's surface (up to 70°C) in the Precambrian era. Becker, and Clayton (1976), analyzing the isotopic composition of oxygen of Precambrian sediments in Western Australia of the age of 2.2×10^9 years, assume that the oxygen isotopic ratios in the Precambrian oceans could have been 10–11‰ lower than those of modern times, assuming that modern temperatures are valid for the past. If one assumes that forma-

tion of the investigated sediments occurred at $t = 60^\circ\text{C}$ (the temperature determined by the isotopic composition of the co-existing minerals), then the $\delta^{18}\text{O}$ value of the ancient ocean waters had an upper limit equal to -3.5‰ .

The process of the isotopic exchange in the system water–oxygen-bearing sediments should play an important role during the evolution of the isotopic composition of the ocean water in geological history. If one assumes that all the oceans were formed due to degassing of the mantle, then the initial ocean waters should have been enriched with ^{18}O relative to the recent waters by $6\text{--}8\text{‰}$, and depleted in D by $50\text{--}80\text{‰}$. This assumption follows from the supposition that the water degassing occurred at high temperatures, of which the equilibrium constant of the isotopic exchange in the water–rock system tends to unity. The hypothesis of the cold accretion of the Earth followed by the processes of warming up and mantle degassing has led several researchers (Taylor 1974) to search for the mechanism which could provide the ocean with zero values of $\delta^{18}\text{O}$ and δD during geological history. The ^{18}O in charts ($\delta^{18}\text{O} = +30 \text{--} +38\text{‰}$), carbonates ($\delta^{18}\text{O} = +25 \text{--} +30\text{‰}$), clays ($-18 \text{--} +25\text{‰}$), and other authigenic minerals may provide an example of such processes. By assuming that the ocean has had a constant volume during geological history, Savin and Epstein (1970c) and earlier Silverman (1951) have shown that, due to sedimentation, the oxygen isotopic composition of the ocean water could undergo variations of about 1‰ during 5×10^8 years. The process of weathering and sedimentation during the whole Earth's history, according to data of Savin and Epstein (1970c), might result in the enrichment of its hydrosphere with D by 0.3‰ and depletion in oxygen by 3‰ .

The accumulation of D in ocean waters resulting in an increase in its mean value from about $\delta\text{D} = -65\text{‰}$ (characteristic for the upper mantle minerals) to the recent 'zero' level can be explained, as mentioned above, by the processes of H dissipation. However, we do not possess evidence in favor of this process taking place.

The authors of the present book are developing the hypothesis of the condensational formation of the Earth and its hydrosphere (see Chap. 19) based on the solutions obtained in Jacobi dynamics. This hypothesis allows one to assume that the isotopic composition of the ocean water has remained constant during the whole history of the Earth by conditions of the hydrosphere formation.

At present, an attempt can be made to estimate the hydrogen and oxygen isotopic balance from the viewpoint of plate tectonics (Le Pichon et al. 1973). If we assume that the residence time of substances in the ocean plates does not exceed 1.5×10^8 years (for continents 1.5×10^9 years), then we can assume that during geological history the ocean plates have undergone about 30 exchange cycles and the continental crust about 3 cycles. During each cycle, there were large masses of hydroxide and oxygen-bearing minerals with $\delta^{18}\text{D}$ from -50 to -80‰ and $\delta^{18}\text{O}$ from $+18$ to $+38\text{‰}$ (Taylor 1974). These processes should result in enrichment of the ocean waters with D and depletion in ^{18}O . On the contrary, however, in the region of the destructive boundaries of the plates at the middle-ocean ridges, some enrichment of waters in oxygen-18 and depletion in D may occur as a result of the exchange reactions of ocean water with basalts and serpentinization and chloritization processes

at high temperatures ($t = 280\text{--}380^\circ\text{C}$; Taylor 1974; Hoernes and Friedrichsen 1979). These two processes have continued further during geological history in such a way that the isotopic composition of the ocean waters, as Taylor (1974) suggested, may be 'buffered' in time near a value of zero, but this conclusion is not indisputable and requires more detailed study. At the same time, the approach to the problem of the circulation of waters in the Earth's crust and mantle from the viewpoint of plate tectonics permits one to assume that the isotopic composition of hydrogen and oxygen in igneous rocks, and therefore magmatogenic and juvenile waters, reflects the isotopic composition of the sea hydroxide-bearing minerals cycling through the mantle (Taylor 1974).

Glacial epochs may have played an important role in varying the isotopic composition of ocean waters. The total amount of water in the ocean in non-glacial time, for example during the Mesozoic, was 5% greater than that in glacial periods according to Fairbridge (1964). If we accept that all excess water was provided by ice melting, then the amount of D in the ocean in non-glacial time would be 10‰ less than during glaciation. Fairbridge estimated the amount of continental ice during glaciation to be 80 million km³, which exceeds by factor 2 the data given by other authors. According to Bowen (1966), the excess of ice during the Pleistocene was 40.2×10^6 km³, which corresponds to an ocean volume increase of 4% in non-glacial times. According to Emiliani (1970), the increase in the ¹⁸O content of the ocean in glacial time was equal to 0.5‰. In order to carry out these calculations, the increase in the volume of ice during Pleistocene was assumed to be equal to 40.106 km³ and the average isotopic composition of ice to be $\delta^{18}\text{O} = -15\text{‰}$.

Emiliani assumed that during the Pleistocene glaciation, the average ¹⁸O content in the North American ice sheet was -9‰ . At the same time, Yapp and Epstein (1977) found from the analysis of the hydrogen isotopic composition in the cellulose of plants of glacial age that, for the Pleistocene glaciers of North America, the characteristic values are $\delta^{18}\text{O}$ from -12 to -15‰ . Assuming during the Wisconsin maximum glaciation, the value of $\delta^{18}\text{O} = -15\text{‰}$ for North American glaciers, $\delta^{18}\text{O} = -30\text{‰}$ and $\delta^{18}\text{O} = -40\text{‰}$ for all the others, Yapp and Epstein calculated the average enrichment of ocean waters with ¹⁸O as -0.8‰ . This value is in agreement with the results obtained by Craig and Gordon (1965) and Craig (1966). A greater value, $\delta^{18}\text{O} = -1.1\text{‰}$, of the average enrichment of the ocean in that period was given by Shackleton and Opdyke (1973). This result was obtained on the basis of the oxygen isotope analysis of the shells of foraminifera of Pleistocene and recent ages in equatorial parts of the Pacific ocean. However, as Yapp and Epstein (1977) have pointed out, the deep ocean waters could have been depleted in ¹⁸O by 0.2‰.

Therefore, the variations in concentrations of D and ¹⁸O in the oceans during glacial and non-glacial times do not exceed $\pm 10\text{‰}$ in D and $\pm 1\text{‰}$ in ¹⁸O. The isotopic composition of the oceans has remained practically unchanged at least during the last 250 million years. There is some evidence to suppose that the D and ¹⁸O contents in the oceans in more ancient period (e.g., during Cambrian era) also did not differ considerably from those in the recent ocean waters.