Chapter 7
Isotopic Composition of Formation Waters

7.1 Relationship Between Hydrogen and Oxygen Isotopes in Formation Waters

It is observed from the previous chapters that the processes of water evaporation and condensation are of great importance in the fractionation of isotopes of natural waters. At the same time, the evaporation is primarily an attribute of surface conditions. It might occur in shallow underground waters but it is generally agreed by hydrogeologists that groundwater evaporation does not occur on a regional scale (Zaitsev 1967; Stankevich 1968; Smirnov 1971); however, in local zones, the underground evaporation is likely to take place. An example of such phenomenon is the evaporation of groundwater accompanying oil and gaseous deposits (Sultanov 1961). As a rule, these processes of water evaporation occur at elevated temperatures ($\sim80^\circ$C). In this case the isotopic fractionation factors are $\alpha_D = 1.032$ and $\alpha_{18_O} = 1.0042$. The vapor phase differs insignificantly in isotopic composition from layer waters to a deposit. The water vapor which has been formed migrates with oil gases. During the migration of the vapor–gaseous mixture through porous layers at lower temperatures, underground fresh water deposits with mineralization less than 1 g/l and δD and $\delta^{18}O$ values greater than, those which are characteristic of meteoric waters might form.

Thus, in the region of the Dnieper–Donets depression at depths exceeding 2,000 m waters with mineralization of up to 4 g/l and values of δD from $-21‰$ to $-53‰$ and ^{18}O from $-2.5‰$ to $-4.6‰$ were found. In this region for oil waters with mineralization ranging from 150 to 330 g/l, the deuterium (D) and oxygen-18 (^{18}O) content varies within the limits δD from -21 to $-54‰$ and ^{18}O from $+2.0$ to $-4.6‰$ (Yakubovsky et al. 1978).

Analogous waters were also found in the east part of the Terek–Sundzha oil and gas region at depth of 4–5.5 km (Nikanorov et al. 1980), but naturally underground evaporation cannot result in considerable changes of the isotopic composition of the layer waters since the amount of evaporated water is always negligible in comparison to the amount of native water.

The basic process determining the isotopic composition of water undergoing underground circulation is that of isotopic exchange in the water–rock system. The

isotopic exchange of water with gases (H_2S, H_2, CH_4, CO_2) and liquid hydrocarbons of oil also takes place, but these processes are considerably less effective than the exchange processes with water-bearing rocks. For example, according to Soyfer et al. (1967), the change in the isotopic composition of hydrogen in groundwaters due to exchange reactions with gaseous hydrogen and hydrogen sulfide is negligible.

The absence of the influence of isotopic exchange in the H_2O–H_2S system upon the isotopic composition of formation waters has been demonstrated by Clayton et al. (1966) and Hitchon and Friedman (1969). By indirect means, the possible scale of changes of hydrogen isotopic composition in groundwater due to exchange processes with liquid hydrocarbons of the oil series can be estimated. Thus, Mason (1966), with reference to Smith, has pointed out that the formation of oil deposits in the USA, in the Gulf of Mexico region, Louisiana, and Saint Croix in California, was accompanied by the release of about 3.4×10^5 t of liquid hydrocarbons from 1 km^3 of sediments ($\sim 2 \times 10^9$ t). Assuming that moisture made up 10% of the mass of sediments at the stage of diagenesis, that is there were $\sim 2 \times 10^8$ t of water in 1 km^3 of sediments, than the ratio of hydrogen atomic fractions in water and oil becomes $w/o \approx 300$. Here we have assumed that the exchangeable amount of hydrogen in oil per mass unit is twice as large as that of water. It is obvious that for such a low value of w/o, the isotopic composition of water remains even when the isotopic equilibrium between hydrocarbons $\delta D_n = -200‰$ and water is maintained such that $\alpha = 1$ ($\delta D_{oil} - \delta D_{water} = 0$). This was confirmed by Clayton et al. (1966) studies of isotopic composition of groundwater in the oil deposits mentioned above. The results of this research are presented in Figs. 7.3 and 7.5. Some observable changes in the hydrogen isotopic composition are likely to be expected in the region of water–oil contact, when $w/o \ll 300$.

The change in oxygen isotopic composition of water due to exchange with carbon dioxide may take place under certain conditions in hydrothermal systems of groundwater gas CO_2. Thus, Ferrara et al. (1965) observed the negative 'oxygen shift' in the thermal waters of Toscana which they explained in terms of the exchange of water with carbon dioxide. These results are presented later on.

Isotopic exchange with water-bearing rocks at high temperatures has the greatest influence upon the isotopic composition of the water. These processes mainly affect the oxygen isotopic composition of groundwater since, in sedimentary rocks, oxygen content amounts to 40% while hydrogen is only 0.3%. In granite rocks, these values amount to 48% and 0.12% and in basalt a 46% and 0.1%, respectively (Beus 1972).

The scales of changes of δD and $\delta^{18}O$ values of water provided by isotopic exchange reactions with water-bearing rocks depend on the following factors (Ohmoto and Rey 1974). (1) The initial isotopic composition of water δ_w and rocks δ_r, participating in isotopic exchange reactions. (2) The ratio of the amount of exchangeable oxygen or hydrogen atoms in water to the same in rocks (w/r). (3) The temperature which determines the equilibrium isotopic fractionation factor between water and rocks. As pointed out earlier, the effect of isotopic fractionation between the two phases, for example between rocks and water, can be approximated by the difference of the values $\Delta = \delta_r - \delta_w \approx 10^3 \ln \alpha$. (4) The degree of exchange in the rock-water system, depending on the average residence time of the water in the aquifer.

Assuming that water and rocks are in isotopic equilibrium at a given temperature, the final isotopic composition of water δ_w^f can be expressed as (Ohmoto and Rey 1974)

$$\delta_w^f = \frac{\delta_r - \Delta + (w/r)\delta_w}{1 + w/r}.$$

This formula can be used not only for calculating the isotopic composition of water in isotopic equilibrium with rocks but also for estimating the ratio (w/r) when the parameters are known (Sheppard et al. 1969, 1971; Taylor 1974, 1978).

Using the above formula, let us estimate the change in the isotopic composition of hydrogen and oxygen of normal sea water ($\delta D_w = 0$, $\delta^{18}O_w = 0$) syngenetic with the clay sediments. For example, this process may occur by wringing out the inner-layer water of the clay minerals during the formation of deep waters in sedimentary basins (Kartsev and Vagin 1973). Sergeev et al. (1963) have shown that the dominant clay minerals in the rocks of Mesocainozoic sediments are those of the more ancient ages are hydromicas. Next in abundance are minerals of the montmorillonite group and then of the kaolinite group. The clay minerals of hydromicas and montmorillonites are very similar in their crystalline structure and hydrogen (water) content of the hydroxide groups coming into the crystalline lattice of the complete dehydrated minerals (Lazarenko 1958; Kulchitsky 1975). For minerals of these groups, the values of hydrogen isotopic fractionation factors are also close to each other in the same way as the oxygen ones. They most readily start the oxygen exchange with water (Savin and Epstein 1970a, c; James and Baker 1976; O'Neil and Kharaka 1976).

These circumstances permit one to consider, in reliable details, isotopic exchange in the montmorillonite-water system as an illustration of the scale of changes in water of δD and $\delta^{18}O$ from initial values. The assumption is made that during clay diagenesis, isotopic exchange occurs under conditions of a closed system that is only the water which was bounded by rocks at the stage of sedimentation is involved in isotopic exchange reactions with clay minerals. Let us take into consideration the following parameters of the process: the humidity of the clay is 20% of the total mass; the hydrogen content in hydroxide groups per mass unit of the dry rock is 0.4% (which is equivalent to about 4 mass % of H_2O). Then $w/r \approx 5$ for hydrogen atoms and 0.3 for oxygen atoms. Let us consider further that prior to sedimentation, the clay minerals were formed under hypergeneous conditions in regions with a temperate climate. The isotopic composition of atmospheric precipitation may then be taken as $\delta D_w = -90‰$ and $\delta^{18}O_w = -12‰$ and the isotopic composition of the clay minerals of the montmorillonite group, equilibrated with meteoric waters, is $\delta D_r \Delta = -15‰$ and $\delta^{18}O_r = +15‰$ (Savin and Epstein 1970a). For the purpose of estimation, we consider the isotopic composition of pore water, at the initial stage of sedimentation, to be the same as that of normal sea water, and isotopic exchange in system to occur at 100°C. For these conditions, one has $\Delta D_{mineral-water} \approx -50‰$ and $\Delta^{18}O_{mineral-water} \approx +12‰$. The values Δ for oxygen isotopic exchange in the mineral-water system are estimated on the basis of data provided by Taylor (1974). For the isotopic exchange of hydrogen between montmorillonite and water at normal

temperatures of hypergenic processes, the value Δ will be obtained using Savin and Epstein's (1970a) data. In addition, let us consider that fractionation factor of hydrogen isotopes between hydroxyl-bearing minerals and water does not doesn't undergo any significant changes up to $\sim$400°C (Taylor 1974; Suzuoki and Epstein 1976).

Now putting δ_w, δ_r, Δ, and w/r into the Ohmoto-Rye formula, one obtains $\delta D_w^f = -17‰$ and $\delta^{18}O_w^f = +2.3‰$. Note that the conditions described above are the most favorable for the isotopic exchange (due to filtration of water through the clay). If such filtration takes place, the value of w/r calculated per unit of mass of rock should be increased by factor n (where n is the number of water exchange cycles). For $n = 2$, $\delta D_w^f \approx -9‰$ and $\delta^{18}O_w^f \approx +1.2‰$.

From these estimations, it is observed that the isotopic exchange of water with the clay minerals at layer temperatures below 100°C will not result in significant changes in the content of D and ^{18}O in groundwater. In natural conditions ($w/r = 1$), the interaction of water with basic (basalts, $\delta^{18}O \approx +7‰$) and acid (granites, $\delta^{18}O \approx +10‰$) volcanic rocks at temperatures above 400°C, when the value of $\Delta_{\text{rock}-\text{water}} \to 0$, may result in a maximum oxygen shift from 3 to 5‰ when $\delta^{18}O = 0$. The value of oxygen shift increases as $\delta^{18}O_w$ decreases; the maximum oxygen shift for the above conditions is 10‰ when $\delta^{18}O_w = -10‰$ and 12‰ when $\delta^{18}O \approx -15‰$. Other conditions being equal, the maximum oxygen shift will take place at isotopic equilibrium for groundwater in circulation in carbonate rocks composed of limestones and dolomites with $\delta^{18}O_r = +30‰$.

The hydrogen isotopic exchange with hydroxyl-bearing minerals of siliceous rocks of volcanic genesis does not, in practice, play any significant role in the change of the isotopic composition of underground waters since the hydrogen content in these rocks does not exceed an average of 0.1% (Beus 1972).

Many studies have shown how this process occurs on a very limited scale. For example, according to Arnason and Sigurgeirsson (1967), who studied Iceland's thermal waters, there is reason to believe that during the movement of groundwater, large distances from the infiltration zone to the place of discharge changes in D content do not occur.

By analyzing numerous experimental data in various hydrothermal regions of the world, Craig (1963, 1966) has shown that D content in hydrothermal waters corresponds to its content in meteoric waters in region where the former is fed by the latter. According to data of several researchers (Clayton 1961; Craig 1963, 1966; Clayton et al. 1966; Hitchon and Friedman 1969; Savin and Epstein 1970a; Bottinga and Javoy 1973; Taylor 1974; Becker and Clayton 1976; Kawabe 1978), at higher temperatures the water is enriched with heavy oxygen due to isotope exchange with oxygen-bearing rocks (limestones, silicates, and so on). This phenomenon of oxygen isotopic exchange has been called the oxygen shift. Figure 7.1 demonstrates the data obtained by investigation of geothermal brines brought out through boreholes in the Salton-Sea region of California, USA (Craig 1966)[1].

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[1] The work was undertaken to refute that the above-mentioned brines are deep ore-bearing fluids.

Fig. 7.1 Isotopic composition of waters in the Salton-Sea geothermal area: *1* a spring at the base of the Chocolate Mountains (17°C); *2* water from the 'mud volcanoes' on the east shore of the lake (39°C); *3* water from the old CO_2 production wells about 300 m deep (42°C); *4* steam and brine from the two geothermal wells WGS and IID-1; *5* brine from a deep geothermal well (>300°C). (After Craig 1966)
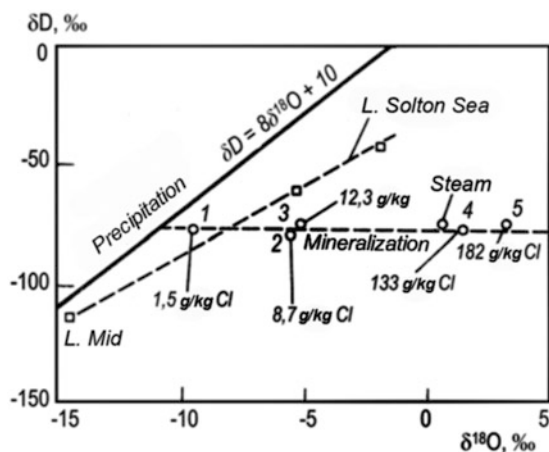
It follows from Fig. 7.1 that with increases in temperature of the waters being studied, the D concentration remains constant at the level corresponding to its content in atmospheric moisture in this region, while the ^{18}O content increases sharply for the same conditions. In contrast, on the surface (for the Salton-Sea and Mead Lakes) the content of these isotopes changes in parallel.

Thus, it should be noted that the statement made by several authors (Soyfer et al. 1967) on the parallel behavior of D and ^{18}O concentration in groundwater cannot be considered as universal. It holds only for waters of the surface cycle as Craig (1961a) has shown. For groundwater, the behavior of D and ^{18}O differs due to oxygen isotopic exchange between water and water-bearing rocks, especially at elevated temperatures, and this must be taken into consideration in the course of isotope studies. The variation of ^{18}O concentration in rocks and groundwater is illustrated by another example characteristic of the Larderello region of Italy (Ferrara et al. 1965). The sea limestones, for which values of $\delta^{18}O = +30‰$ are typical, are notably depleted in this isotope. At the same time, for water migrating through these limestones, range from $\delta^{18}O = -7.3‰$ in the region of supply -4.8 and even $-1.9‰$ in the areas of emergence at springs on the surface or in the boreholes. Nevertheless, the D concentration is practically a constant equal to that in meteoric waters in the supply region.

Coplen and Hanshow (1973) have studied the isotopic composition of oxygen and hydrogen in ultra-filter and sedimentary solution by infiltration of distilled water and NaCl solution through the montmorillonite membrane. The porosity of the disk under pressure has reached 35%. They have found that the liquid being infiltrated through the montmorillonite membrane becomes depleted in δD and $\delta^{18}O$ by 2.5‰ and 0.8‰, respectively. The concentration of NaCl up to 0.01 NH does not affect the process of isotopic fractionation. Higher saline concentrations are likely to exert influence upon the isotopic separation in the course of infiltration of a liquid through the clayey membranes. It should be noted that the experimental data obtained by Coplen and Hanshow concerning the δD and $\delta^{18}O$ deviations in the infiltrated liquid

may be considered as insignificant and the scale of the experiment does not apply itself to natural conditions where, in the range of experimental error, this phenomenon has not been observed.

It is worth to note that in the study of Yeh and Epstein (1980) the authors, with reference on Coplen and Hanshow, by the process of ultra-filtration explains some increase ($\sim$20‰) of D content in pore waters in the clays profile opened by boreholes in the Gulf of Mexico, but this phenomenon has another explanation. For example, the observed fact can be related with decrease with the depth in the fractionation factor of hydrogen in the water-rock system because of increase in temperature; the effect can be also explained by the *w/r* ratio decrease due to decrease of the moisture in the clayey thickness and by the climate changes in the area of the North America in the previous epochs. The latter explanation must effect on isotopic composition of the hydroxide group of the clay minerals discharged by Mississippi.

On the other side, on the basis of study undertaken, it has been shown (Soyfer et al. 1967) that fractionation of hydrogen isotopes does not occur during the motion of groundwater in sandstones and argillites of the Hot Springs suite, North Caucasus, within a distance of hundreds of meters (photoneutron methods are accurate within ±3%). By using more accurate mass spectrometric measurements, Degens (1961) found that the oxygen isotopic composition remains essentially unchanged during filtration at a distance of 1,100 km through the sandstone aquifer of the Numibian suite in Northern Africa (deviations of only 9%). Forty samples of water were taken at intervals of 35–40 km along the profile. It is obvious that although in this case the chemical composition of groundwater has undergone considerable change, the conditions for oxygen isotopic exchange did not exist.

Other natural processes of groundwater isotopic fractionation are practically unimportant. In fact, the process of gravitational isotopic fractionation of hydrogen is buffered by the more powerful hydrodynamic process. The process of bacterial fractionation, which is rather intensively energetic under laboratory conditions, can be considered as insignificant under natural conditions since even at the maximum value of bacteria content (tens of millions per ml) their total weight does not exceed 1 mg/l. This conclusion is a natural one since isotopic exchange is not only a result of practical process but also indicates the scales of their activity. The latter effects of hydrogen separation in natural waters were classified as second-order effects (Soyfer et al. 1967).

7.2 Isotopic Composition of Formation Water in Sedimentary Basins

The formation of the deep groundwater of sedimentary basins of the Earth has had a long and complicated history. The deep waters of sedimentary basins were formed within the ancient seas and lagoons located at the edge of continents. A close relationship exists between sedimentary thickness and horizontal tectonic displacements

of lithospheric plates (Le Pichon et al. 1973; Bullard 1978) resulting in the vertical tectonic displacements of the Earth's crust (Verhoogen et al. 1970).

The main sedimentary basins which originated in various geological times have been related to boundaries of plates, that is with those places on the Earth's crust where the maximum vertical tectonic displacements have occurred. It is no coincidence that the majority of giant petroleum fields discovered before 1970 are related to sedimentary basins and located in the shelf areas of modern continents (Moody 1978).

While studying the processes of groundwater formation in a sedimentary basin with the help of commonly used techniques, researchers are normally faced with considerable difficulties. These consist of a marked transformation in the chemical composition of primary marine water both during the stage of the surface exposure and as a result of interaction of the groundwater (primary or infiltrational) with water-bearing rocks. Studies of the isotopic composition of sedimentary basin groundwater help to overcome these difficulties to a great extent.

As mentioned earlier (see Chap. 4), during the exposure of a sedimentary basin where the precipitation of evaporites have occurred, the hydrogen and oxygen isotope composition of the water could have been a little different from that of the sea water recharging it, due to evaporation. During evaporation, there is an increase in the concentration of salts in such a basin resulting in a decrease of water activity and, also, of the evaporation rate. This, in turn, affects the water hydrogen and oxygen isotope composition at the final stages of evaporation. As Sofer and Gat (1975) have shown, the D content in such basins could decrease compared with the primary marine water ($\delta D = 0$), depending upon humidity. Thus, at a relative air humidity of 40–50% and a vapor isotope content $\delta D = -80\%o$, when the sedimentation of bishofite might occur, the water hydrogen isotope composition is greater than the D content of the ocean water at practically all stages of evaporation. At humidity of 80%, when basin in natural conditions may be evaporated to the stage of halite sedimentation, the hydrogen isotope composition of the remaining water might decrease, reaching $\delta D = -20\%o$.

In the underground conditions at the stage of diagenesis of the sedimentary strata, the isotope composition of the groundwater could also have been changing. As a rule, at elevated temperatures compared with the surface, oxygen isotope exchange between groundwater and water-bearing rocks occurs, resulting in an increase of the ^{18}O content in groundwater. The D content also changes but its variation, provided by the exchange processes with the hydroxide-bearing minerals such as clays, is more diminished than that for oxygen because the oxygen content exceeds the hydrogen content by more than one order of magnitude (Taylor 1974; Ohmoto and Rye 1974).

Therefore, the original groundwater of sedimentary rocks differ considerably, in terms of their D content, from the infiltration meteogenic water entering the basin during its period of exposure at the surface. All this leads to the conclusion that, in the groundwater of ancient sedimentary basins, it is possible to distinguish connate marine water from infiltration meteogenic ones, even when their chemical composition is the same, by virtue of the D content (Degens et al. 1964; Graf et al. 1965, 1966; Craig 1966; Clayton et al. 1966; Taylor 1974; White 1974; Hitchon and Friedman 1969; Kharaka et al. 1973; Gutsalo 1980).

Concentration of ^{18}O in groundwater is a less conservative parameter. Its high values are explained not only by the marine origin but also by the isotopic shift. This is why high concentration of ^{18}O cannot be an indicator of marine origin of the studied water. At the same time, the ratio of concentration of D and ^{18}O can be an index of the depth of sedimentary basins.

Many studies have been devoted to the principles of stable isotope distribution in deep sedimentary waters and rocks and on the determination of the isotopic content in water using its physical properties (the techniques based on density measurements and other). Later on, due to their accuracy and restricted applicability, these techniques were replaced at first by the photoneutron method and later by modern mass spectrometric methods which are presently in use.

Alekseev et al. (1966) and Tyminsky et al. (1966) used the photoneutron method measurements to carry out studies of the D distribution in the deep formation waters of the Tashkent artesian basin. With the help of experimental data they found that the infiltrating waters of this basin are depleted in D and the ancient waters are enriched in it.

While studying the absolute ages of groundwater in the chalky water-bearing complex in the Tashkent artesian basin using the helium–argon method, which was suggested by Ovchinnikov, it was found that the most ancient waters (up to 5 million years) are situated in the immersed parts of the depression and the side-wards regions and the northern part of the depression, with rocks of the Cretaceous age at the surface, have waters of more recent age (tens or hundreds of thousands of years). It was found that D content increases with increases of groundwater age. In the northern and north-eastern part of the basin, relatively young waters occur (up to 60,000 years) having a lower D content (from −160 to −120‰). The maximum D content (from −26 to −7‰) was found in waters at depths of about 2,000 m below the land surface, the age of which is about 4–5 million years.

For the paleohydrological consideration, the dilution proportions of infiltration and sedimentary waters in chalky sediments of a basin were calculated. The proportions were determined with the help of mixing formulae in common use. The D concentrations accepted were −160‰ for infiltration waters and +26‰ for sedimentary waters. The researchers distinguished zones of abundance of waters with proportions of infiltration waters in the mixture up to 0.25, from 0.25 to 0.5, and more than 0.5.

Using these studies, and also investigating the D content in waters of a number of oil and gas field regions (Brezgunov et al. 1966), the applicability of isotope techniques has been shown for the identification of formation and infiltration waters in artesian basins.

Seletskt et al. (1973), Ferronsky et al. (1974), and other researchers have carried out a considerable amount of mass spectrometric measurements for the investigation of D and ^{18}O distribution in deep groundwater in the former USSR. The results of these studies are generalized in Table 7.1.

The isotopic composition of groundwater in the North Caucasus region was studied for two hydrogeological levels Nikanorov et al. (1976). The waters of the neogen-quaternary upper floor are of infiltration origin (δD from −67 to −46‰,

Table 7.1 Distribution of D and ^{18}O in groundwater of the artesian basins within the former USSR

Artesian basin	δD, ‰	$\delta^{18}O$, ‰	Reference
Near Baltic	From −119 to −48	From −18.8 to −6.3	Pelmegov et al. (1978)
Pripyat Depression	From −95 to +2	From −12.7 to +4	Tkachuk et al. (1975)
Ukrainian Carpathy	From −108 to −7	From −13.1 to +3	Babinets et al. (1971) Vetshtein et al. (1972) Polyakov et al. (1974)
Near Carpathy Mineral Waters type 'Naftusya' and 'Shklo'	From −102 to −6	–	Vetshtein et al. (1973)
Dnepr-Donetsk	From −55 to +11	From −7.2 to +0.3	Vetshtein et al. (1973)
Near Caspian Depression (north-west)	From −107 to −33	From −10.1 to −2.4	Alekseev et al. (1975)
North Caucasus	From −67 to −15	From −12 to −5.8	Nikanorov et al. (1976)
Azov-Kuban	From −120 to −28	From −17.7 to +7	Sokolovsky et al. (2007)
Caucasus Mineral Waters	From −118 to −42	From −12.7 to +1.1	Seletsky et al. (1973)
Sochi-Adler	From −73 to −35	From −9.8 to −0.5	Gorbushina et al. (1972, 1974)
Middle Caspian	From −125 to −17	From −12.4 to −2.2	Seletsky et al. (1973)
West Turkmenian	From −79 to −4	From −13.4 to +4.4	Seletsky et al. (1973) Alekseev et al. (1975)
Yaskhan Lens of Fresh Water	From −89.2 to −54.4	From −12.4 to −2.5	Seletsky et al. (1973)
Mud Volcanoes of West Turkmenia	From −57 to −31	–	Seletsky et al. (1973)
North Caucasus3	From −115 to −28	From −14.2 to +5	Alekseev et al. (1975)
Moscow	From −114 to −22	From −14.5 to −5	Sokolovsky et al. (1999)
Ferganian	From −106 to −78	From −10.9 to ±1.7	Seletsky et al. (1973)
Amu-Darian	From −102 to −20	From −12.3 to −6.1	Alekseev et al. (1974, 1975)
Sibirian Platform	From −180 to −23	From −21.5 to 0.0	Pinneker et al. (1973, 1974, 1975)

$\delta^{18}O$ from −12.0 to −6.8‰). The waters of the lower floor are separated from the upper one by a thick layer of Maykop argillaseous suite. These waters are enriched in heavy isotopes (δD from −55 to −15‰, $\delta^{18}O$ from −4 to +5.8‰) and are similar to thalassogenic ones in terms of origin.

Investigations carried out in the Azov–Kuban artesian basin have shown that the D content in waters of oil and gasfield ranges from −68 to 58‰. These values corresponds to an intermediate, average D content in meteoric (−107.5) and sea waters, which is evidence in favor of the presence of connate sea sedimentary waters up to about 50%. About 50% of Yessentuki saline–alkali waters (Nagut aquifers) are also of marine origin, which refutes the existing opinion that these types of water originate from meteoric local recharge areas.

A greater portion of ancient sea waters are contained in mud volcanoes in this region, where δD ranges from -56.9 to $-54.9‰$. At the same time, a considerably lower D content has been detected (from -80.8 to $-80.0‰$) in the iodine waters of the Slaviano–Troitsk aquifers. These data indicate that these waters are diluted with meteoric water to a greater extent, which is in disagreement with the option that there is a genetic relationship between the former waters and those occurring in oil and gas field.

Within the region of the Caucasus mineral waters, it has been reported (Seletsky et al. 1974) that the waters of the Olkhovsk prospecting area have the lowest D content ($\delta D = -118‰$). These waters are typically fissured and are completely recharged by precipitation.

The 'Narzan' group of waters in Kislovodsk as a whole, are intermediate, in terms of D content ($D = -108$ to $-76‰$), between the waters of the Olkhovsk prospecting area and waters of the deep wells situated in the Yessentuki area.

The 'Yssentuki-20' spring is clearly distinguished by its D content ($\delta D = -117‰$) from other waters in the region of the Yssentuki aquifer. The low D content is the result of the spring being recharged by groundwater flowing from the sandy-pebble sediments of the Podkumok River, starting at a height of more than 2 km. The other waters in the Yessentuki area have greater values of δD (up to $-42‰$). This suggests that they also contain ancient waters of marine genesis from the more deeply lying complexes, in particular the Valazhinsky complex which exerts great influence on the formation of all main aquifers of the Caucasus mineral waters.

The relative D content in formation waters of the oil–gas fields in the South Mangyshlal Peninsula ranges from -82.3 to $-16.5‰$. The waters most depleted in D have been contaminated by fresh water pumped into the productive oil-bearing layers. In water of the West Turkmenian artesian basin δD ranges from -76.6 to $-37.3‰$. The elevated D concentrations in waters of the Jurassic complex in the Mangyshlal Peninsula is evidence that waters of marine genesis participate in their formation to a greater extent compared with waters of the Tertiary sedimentation in the Western Turkmenia.

The investigations of deep waters of Pliocene sediments in the Western Turkmenia artesian basin (Seletsky et al. 1973; Alekseev et al. 1975) have shown, by ^{18}O and D isotope analyses that brines in the red colored sediments contain a large portion of marine waters.

The hydrothermal ore sediments in the Cheleken area (Gutsalo et al. 1978; Esikov et al. 1979) have been reported to be colored sediments (δD from -41 to $-31‰$, $\delta^{18}O$ from -3.5 to $-2.1‰$). They are likely to be similar in origin to connate marine waters, being metamorphosed in salt composition. However, in order to elucidate the conditions of high salt saturation and enrichment with heavy metals, further prospecting of this area is required.

While studying the isotope composition of the Yaskhan Lens fresh water in West Turkmenia (Seletsky et al. 1973), considerably different conditions of the lens water formation from those of the underlying Kara Kum saline waters have been reported. The lower δD and $\delta^{18}O$ values in waters of the diffusion zone of the lens are evidence

that waters of pluvial age exist in the underlying aquifer, whereas the waters of the lens are likely to have been formed in conditions of arid climate.

In the Fergana artesian basin, more careful studies of the sulfide mineral water fields of Chimion and Obi-Shiro (Gorbushina and Tyminsky 1974) have been carried out. The D content variations were reported to be insignificant (δD from -98 to -70‰), although there are large differences in mineral content (0.7–120 g/l), δD values (from -16.1 to -3.7‰) shows that processes resulting in oxygen isotope shift are involved. The low D content in the Fergana artesian basin waters probably reflect the importance of the mountains surrounding the depression is supplying infiltrating waters to recharge the basin complexes.

In the Amu-Darya artesian basin (Alekseev et al. 1974, 1975) it has been reported that δD and δ^{18}O variations are respectively -52–(-20‰) and -6.3–($+6.1$‰) in waters of the Jurassic aquifer; -102–(-43‰) and -11.8–(-5.1‰) in the Lower Cretaceous aquifer; -93–(-57‰) and -11.7–(-6.8‰) in the Upper cretaceous aquifer; and -97–(-60‰) and -12.3–(-8.4‰) for the surface waters. On the basis of these data, the authors have reported that waters of the Jurassic sediments are preferentially of marine genesis and the Cretaceous complex waters originated due to the dilution of marine connate waters with modern meteoric ones which follows from the fact that the corresponding points fit the line plotted for δD–δ^{18}O coordinates connecting the plots of ocean and meteoric waters. Assuming δD $= -25$‰ for sea waters and δD $= -90$‰ for meteoric waters, Alekseev et al. have calculated that the proportion of infiltrational waters composing sedimentogenic waters may vary from 9 to 94%.

The relative D content in highly saline calcium chloride brines in the Angara–Lena artesian basin ranges from -70 to -23‰ and in this respect are similar to the waters of petroleum and gas provinces in the South Mangyshlak and West Turkmenia. The D content in NaCl brines of this basin is considerably lower. They vary from -168 to -75‰ and differ insignificantly from local meteoric waters. The D content of waters here is even lower than that sampled in the artesian basin.

The ^{18}O concentrations in the considered basins are characterized by the following ranges of values. In the Fergana artesian basin, they range between -10.9 to $+1.2$‰; in the Western Turkmenian basin from -7.6 to $+3.4$‰. The data obtained from these two basins support the idea that large portion of infiltrating waters dilute the Fergana basin waters and the process of oxygen isotope exchange with water-bearing rocks takes place in these two basins. There are no great differences in the range of ^{18}O values compared with to the amplitude of D content variations. By comparing the data from both isotope studies in the West Turkmenia artesian basin, the relatively high ^{18}O content can be explained both in terms of the inheritance of marine concentrations and isotopic exchange with rocks. In the Fergana basin, it can be explained as a sequence of oxygen isotopic exchange.

In the Angara–Lena artesian basin, the ^{18}O content ranges between -17.0 to -0.6‰, which agrees with the D content variations for this basin. Using the above-mentioned knowledge corresponding to the examined basins, it was concluded that the calcium chloride brines in the Angara–Lena artesian basin contain a considerable proportion of waters of marine genesis, thus being distinguished from all other

waters of this region. The brines of sodium chloride composition do not differ from waters which are obviously of meteoric origin. Thus, the experimental data on water isotope composition disagree with the existing opinion that initial sedimentary water resources of this region have been completely renewed.

The isotope studies in the West Turkmenian artesian basin suggest that the origin of the red colored Pliocene aquifer was not completely sedimentary in origin and that the degassation process from the interior may have occurred.

The isotope data obtained for waters of the Alb-Senoman and Jurassic complexes in the South Mangyshlak Peninsula are in agreement with the hypothesis of the sedimentary origin of the latter and in conflict with the hypothesis suggesting a common hydrodynamic model for all the complexes.

The low D content in waters of the Fergana artesian basin reflects the important role of the mountain surrounding the depression in recharging all complexes in the basin from infiltrating waters.

The waters of mud volcanoes are distinguished from all other deep waters occurred in the Earth's sedimentary shell. The D content in them, according to mud volcano studies in Western Turkmeniya and Northern Caucasus, normally corresponds to the D content of waters of oil and gasfields of the artesian basins. As to the ^{18}O concentrations, they attain the highest values for all known groundwaters, not only in the former USSR area but on the Earth as a whole. The $\delta^{18}O$ values detected in them range from $+3.4$ to $+5.0‰$. More detailed discussion on the above results may be found in Seletsky et al. (1973), Alekseev et al. (1975), and Esikov et al. (1979).

While studying the formation conditions of the Matsesta mineral waters in the Sochi–Adler artesian basin (Gorbushina et al. 1972, 1974), it was found that $\delta^{18}O$ values in these waters range from -9.8 to $-2.0‰$, in the Black Sea waters from -4.0 to $-2.3‰$, and in local lakes and rivers from -14.5 to $-10.9‰$. On the basis of these data, it was concluded that recharge to mineral springs up to depths of 500 m occurs due to precipitation and melt waters flowing from the snow-packs, and deeper mineral waters (at depth of 1,200–2,000 m) are formed due to the dilution of sea water with surface water.

In the sulfide waters of the Jurassic sediments in the same region (Gorbushina et al. 1972), the δD values have been reported to vary from -51 to $-35‰$ and $\delta^{18}O$ from -5.8 to $-0.5‰$. In the sulfide waters of chalky sediments, these values for D and ^{18}O range from -73 to $-52‰$ and from -9.7 to $-5.0‰$, respectively. Comparing these data with those of the surface waters of the region, the authors concluded that the sulfide waters of the Jurassic sediments are connate marine waters and the waters in chalky sediments ate marine and meteoric waters mixed in some proportion.

For the conditions of the distant parts of the Baltic artesian basins the hypothesis of the glacial origin of the Strelninsky aquifer and the weathering core water has been confirmed, as was the assumption of the hydraulic isolation of the Strelninsky and Gdovsky aquifers from each other and from the overlying water-bearing complexes (Sobotovich et al. 1977). Moreover, isotopic data on the solutions shows that the formation waters of the Strelninsky aquifer are situated in the reduced water exchange

zone and their recharge by the surface waters is about 5% per thousand years. Analogous waters with anomalous light isotopic composition (δD up to $-170‰$ and $\delta^{18}O$ up to $-22.2‰$) were also found in Cambrian–Vendian sediments near the shore of the Tallinn in Estonia Bay (Yezhova et al. 1996).

Within a complicated region of the southern slope of the Ukrainian crystalline shield dipping towards the Black Sea depression, the hydrogen isotope composition was investigated in a profile of the South Belozersk iron ore deposits area (Voytov et al. 1976). It was found that waters of the Buchakovsky and chalky aquifers and weathering core waters are depleted in heavy isotopes ($\delta D = -107–(-90‰)$) compared with the fissured waters of the iron–siliceous formation ($\delta D = -92–(-70‰)$ and even $-33‰$). On the basis of these data the authors have assumed that the mine waters are a mixture of two water types. The first being a relict of the pluvial period, since they are considerably lighter than the recent waters of the river run-off ($\delta D = -77–(-61‰)$). The second type of water has the modern meteoric origin.

With the north-western region of the Caspian depression, D and ^{18}O abundances have been studied in a profile from surface waters to those of the deep Paleozoic aquifer. In this region, high δD values (up to $-33‰$) are observed in waters of the Devonian sediments. The reduction of the δD values ($-64–(-47‰)$) is a feature of the carboniferous sediments as a whole (for depths from 500 to 3,200 m). At depth of 50–300 m, the D content is even lower ($\delta D = -107–(-74‰)$). On the basis of the isotope analysis data (Alekseev et al. 1975), it was reported that within the Don-Medveditsk heights the water of the carboniferous sediments were formed under certain influence from infiltration processes involving the dilution of the marine sedimentary waters with those of the surface discharge. The influence of the infiltration processes is observed up to depths of 1,200–1,400 m. The waters of the Devonian sediments are the connate marine waters which have been insignificantly diluted by meteoric waters probably during the short periods of infiltration regime.

The $\delta^{18}O$ values have been found (Vetshtein et al. 1973) to range from -7.2 to $+0.3‰$ in waters of deep (1,900–4,000 m) Devonian, carboniferous, and Lower Permian brines (150–300 g/l) of the oil and gas in the Dniepr–Donetsk depression, whereas in the surface waters of this region, the $\delta^{18}O$ values range from -11.1 to $-8.6‰$. The relative D content ranges from -55 to $+11‰$. This suggests these waters are 'connate' waters of the sedimentary basin (metamorphosed by the salinity content). Using the isotope evidence while studying the genesis of groundwater in the Dniepr–Donetsk depression, the authors have found that the hypothesis of the juvenile of infiltration origin of the Paleozoic waters fails to explain the fact that the content of stable isotope of water (solvent) is close to that in recent sea waters.

The carbonic acid saline groundwater in the Ukrainian Carpathy region (Babinets et al. 1971; Vetshtein et al. 1972), mineralized to 4 from 13 g/l and taken from the internal flush zone have, in three cases, shown a high ^{18}O content ($-3–(+6‰)$) and in the fourth case it was $-8.6‰$. The authors related the first three samples with relicts of the ancient seas and the last one with water of meteoric origin. In aquifers of the same region used for balneological purpose (Vetshtein et al. 1972), the δD varies between -108 and $-67‰$ and $\delta^{18}O$ from -13.1 to $-9.4‰$. Therefore these

Table 7.2 D content in Japanese gasfield formation waters. (Kobayakawa and Horibe 1960)

Sampling area	Sampling depth, below surface (m)	δD (‰)
Niigata wells	180	−48
	460	−77
	800	−42
	1500	−47
Shinagawa wells	1100	−9
	1300	−7
Chiba wells	136	+15
	505	−5
	507	−8
	508	−9
Miyazaki mine	–	+2

waters are recharged from surface waters despite considerable differences in gas and salt composition.

D and ^{18}O content was studied in deep waters of the Pripyat depression oil field (Tkachuk et al. 1975). It was found that waters from the aquifer, situated above the salt-bearing sediments, have δD content between −95 and −75‰ and δ^{18}O content between −12.7 and −10.5‰ and are of meteoric origin. The brines situated between the salt-bearing sediments with δD values ranging from −65 to −10‰ and δ^{18}O from −9.7 to +4‰, and waters below the salt-bearing sediments with δD values ranging from −49 to −8‰ and δ^{18}O values ranging from −6.4 to +2‰, where attributed to ancient marine origin by the authors.

While studying the ^{18}O content in saline formation waters sampled in the Sibirian Platform, it was found (Pinneker et al. 1973, 1974, 1975) that in the sulfate hydrocarbonate fresh and saline waters δ^{18}O ranges from −20.3 to −17.8‰. In the sodium and calcium chloride saline waters and brines of the salt-bearing—and above the salt-bearing sediments—sulfate hydrocarbonate ranges from −20.1 to −15.5‰; for the calcium chloride brines from −7 to −1.3‰; and for the calcium chloride brines below the salt-bearing sediments from −8.7 to −7.3‰. The relative ^{18}O content in the surface waters in this region ranges from −19.9 to −15‰ (in the Baikal Lake δ^{18}O = −16.5‰ is characteristic of meteoric waters in the south of Eastern Siberia). On this basis, the authors concluded that the sulfate and hydrocarbonate calcium-sodium waters have a completely meteoric origin and the deep brines originated from waters of marine genesis being markedly diluted with meteoric waters. In spite of the low temperatures (below 44°C) and almost complete absence of carbonic acid in brines, oxygen isotope exchange with rocks had obviously not markedly affected the formation of their isotopic composition.

The study of the D content in the concomitant waters of the Japanese gas fields was reported by Kobayaki and Horibe (1960) (Table 7.2: data recalculated relative to the SMOW standard). The D concentrations in the formation waters of Niigata, Shinagava, Chiba, and Miyazaki Prefectures are approximately equal to those of sea water. The authors have suggested that this should result from the penetration of sea water into the gas field waters. Unfortunately, Kobayaki and Horibe did not give

Table 7.3 The results of oxygen isotope measurements in the formation of some oil and gas fields In the United States. (From Degens et al. 1964)

| Geological age of water-bearing rocks	Number of samples	Total dissolved solids (g/kg)		$\delta^{18}O$ (‰)	
		Variation range	Average	Variation range	Average
Marine sediments					
Cambrian	12	77–206	146	−9.98–(−1.39)	−4.1
Ordovician	4	231–262	256	−0.06–(−1.77)	+0.4
Devonian	1	132	132	−0.46	−0.5
Carboniferous	6	79–269	153	−2.63 ± 2.05	+0.7
Creteceous	9	2.9–5.4	4.0	−11.67 ± 10.29	−11.08
Tertiary	2	103–104	104	+3.04 ± 3.34	+3.2
Freshwater sediments					
Tertiary	10	0.2–15.8	5.6	−16.86–(−3.03)	−12.7
Data for comparison					
Oceans	–	–	35	–	0.0
Surface waters (Utah)	–	–	0.5	–	−16.8
Great Salt Lake	–	–	220	–	−7.4

the geologic structural peculiarities of the profiles studied. It is obvious that such a conclusion, though probably true, cannot be drawn from the D content alone, since similar D concentrations could be exhibited by ancient sedimentary waters.

In the concomitant waters of the Niigata field, the D concentrations were reported to be close to the Tokyo standard (0.01489 ± 0.00005 at. %) which is the tap water of Tokyo University. The similarity of the isotope ratios for those two waters should be explained by the percolation or pumping of the local surface waters into the productive gas layers. The particularly low D content has been found in waters at depths of about 400 m. The different chemical composition of these waters and those lying above or below the mentioned level indicates differences in their origin.

Degens et al. (1964) studied the oxygen isotopic composition in 44 samples of different ages from water-bearing layers in the oil and gas-bearing fields of Oklahoma, Texas, Colorado, and Utah, USA. The data are shown in comparison with those for surface water in Table 7.3 and are recalculated relative to the SMOW standard.

Both in highly and partly mineralized waters there is a tendency for the ^{18}O content to increase with increasing mineralization (Fig. 7.2). The $\delta^{18}O$ values in highly mineralized waters are similar to those for modern ocean waters. Negative deviations from the ocean mean values of ^{18}O agree well with decreasing mineralization, resulting in the penetration of the recent meteoric waters or dilution with ancient infiltration waters, during the geological history at positive tectonic dislocations. The positive deviations of ^{18}O content in some samples were explained by the authors to be a result of continuous evaporation before the waters were connected, for example, during the isolation of small parts of the ocean from the whole basin, that is during lagoon formation.

Fig. 7.2 Relationship
between ^{18}O values and
mineralization of the oil-field
formation waters from marine
and fresh water sediments:
Cambrian–Odrovician
(Oclahoma) *1* Devonian
(Oklahoma) *2* Pennsylvanian
(Oklahoma) *3* Tertiary
(Texas) *4* Cretaceous
(Colorado) *5* Tertiary (Utah)
6. (From Degens et al. 1964)
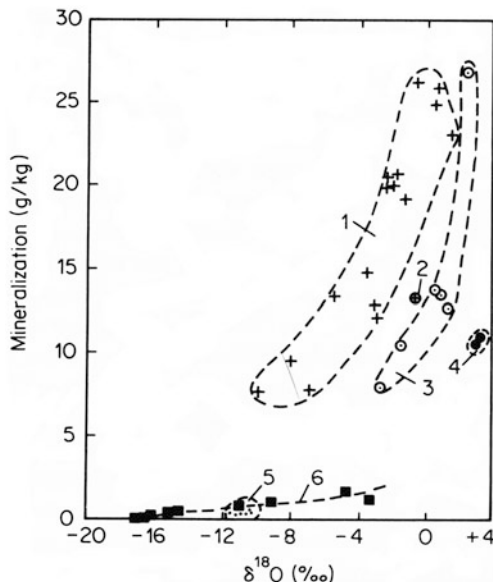
From this data, the authors (Degens et al. 1964) concluded that the brines under
study represent ancient marine water, assuming that the ratio in sea waters has re-
mained more or less unchanged since Cambrian times. This suggestion is confirmed
by the fact that calculations fossils of Paleozoic age, according to Compston, have
the same ^{18}O content as analogous modern fossils. Further, Degens has pointed out
that the similarity of the isotope characteristics of ground brines and less mineral-
ized recent ocean waters suggests that the concentration of inorganic salts was not
completed by evaporation. The completion of such a process might possibly oc-
cur during the process of compaction of sediments accompanied by ion infiltration
through the clays. Degens has shown that isotopic data might serve as an indicator
of the proportions of meteoric and 'connate' water in samples under study.

Wight (1965) also reported his results of isotopic composition of formation waters
of oil-field sedimentary rocks. He carried out rather detailed investigations in the
course of which both ^{18}O and D isotopes were determined (Table 7.4).

White, citing Friedman, has pointed out that the majority of highly saline oil-field
brines have lower D content than those of the sea water, ranging from 0 to −50‰.
As Table 7.4 shows, the D variations for the investigated waters from oil-bearing
sediments fall within these limits and are typical. Brines with lower D content are
not considered to be of sea water origin.

From Table 7.4 it is observed that, according to the results obtained, heavy oxygen
is present in large amounts than in modern sea waters. The author has obtained this
in terms of equilibrium exchange reactions of ^{18}O between water and water-bearing
rocks at high temperatures which takes place in deep parts of pressurized water
systems. Therefore, White stresses that the temperature of waters and the degree of

Table 7.4 D and ^{18}O content in some saline waters and brines of California, United States. (From White 1965)

Sampling location	Chemical composition	δD (‰)	$\delta^{18}O$ (‰)
Cympric oil-field, 900 m depth from Miocene sandstones	$M_{17.7} \dfrac{Cl}{Na}$	−17.1	+2.93
The same place, 1400 m depth	$M_{17.7} \dfrac{Cl}{Na}$	−16.1	+3.14
The same place, 1600 m depth from Eocene sandstones	$M_{25.09} \dfrac{Cl}{NaCa}$	−11.4	+5.93
El Dorado oil-field, 870 m depth from Mississippian limestones	$M_{146.4} \dfrac{Cl}{NaCa}$	−22.0	–
Wilbur oil-field, from Cretaceous rocks	–	−17.9	+3.07
Wilbur Springs, mixture of 'relict' and meteoric waters	–	−22.2	+5.58
Tuscany Springs, 'relict' waters	–	−13.8	+5.27
Searls Lake, nonmarine evaporitic brines	–	−26.0	+4.20
Sulfur Bank, metamorphic waters	–	−24.1	+5.62
Salton Sea, thermal waters	–	−75.3	+3.27

equilibrium between the brines and solid phases are factors which should always be taken into account during more detailed investigations.

Miller et al. (1966) pointed out that oil-field brines are similar in heavy oxygen isotope content to normal sea water and may exhibit mineralization to a great extent. The insignificant enrichment in ^{18}O content might be due to low evaporation occurring during sedimentation. They pointed out another process involved, that of isotopic exchange with water-bearing rocks, and also emphasized that ^{18}O decrease in oil brines is always accompanied by the process of dilution of the aquifer with meteoric waters.

The data on ^{18}O isotope ratios have been used by these authors to explain the origin of hot acid highly mineralized (310 g/l) brines, localized in the central part of the Red Sea at depth of about 2,000 m. Before the investigations, it was supposed that studies would confirm one of three possible hypotheses of their origin: (1) due to inflow of brines, concentrated by local surface evaporation; (2) due to evaporation from the whole surface of the Red Sea during its isolation stage; (3) due to submarine outflow of the brines.

The ^{18}O concentrations in brines and surface waters in the Red Sea and other sea waters insignificantly enriched by evaporation are similar to each other. Therefore, the observed values of oxygen isotope ratios do not support the idea that the investigated brines are evaporates of the normal Red Sea waters. In the last case, the ^{18}O content should be considerably higher. In relation to this, the authors Miller et al. (1966) concluded that the hypotheses of submarine discharge of deep groundwaters into the Red Sea are more convenient. Later Craig (1969) studied in detail the abundances of D, ^{18}O, and argon dissolved in water and the temperatures and salinities of the Red Sea waters. He concluded that Red Sea brines are forming in the near-surface layer of the southern part of the sea near the Bab-el-Mandeb Strait under conditions of the high temperature and salinity. An important role of the process which took

place in the past, during glacial times when the sea level had markedly dropped, and in more distant times when the sea was dried up forming large amounts of evaporates, has been emphasized by the author. Craig's model uses a similar argument. White (1974) pointed out that, in accordance with this model, the existence of the groundwater flow 500–900 km long and passing along the Middle Rea Sea valley should be assumed. Moreover, the brines, in some incomprehensible manner, avoid some other basins which are deeper than those containing hot brines.

There are also some other models, explaining the formation of the chemical and isotope composition of the Red Sea brines, which are free of the hydrogeological contradictions present in Craig's model. For example, White (1974) has assumed the hot brines to be recharged from the nearby edges of the Red Sea which are represented by highly evaporated sea waters often diluted with meteoric waters due to discharge from inland Saudi Arabia. In any case, White noted that the hot brines are genetically connected with the Red Sea waters.

The most detailed studies of isotopic composition of the formation waters in the United States were carried out by Clayton and Graf with co-authors (Clayton et al. 1966; Graf et al. 1965, 1966). They studied formation waters in the Illinois, Michigan, Alberta, and Gulf Coast artesian basins which have a relatively simple geological structure, vast geologic documentation, and a considerable number of boreholes available for sampling. In the profile of the Michigan basin, there are thick deposits of salts and anhydrites and in the Illinois basin only anhydrites of restricted thickness were found. According to the data of isotope studies, it has been discovered that meteoric waters play a significant role in the formation of deep saline waters on the Alberta and Gulf Coast basins. Ninety-five water samples were taken in order to determine D and ^{18}O content. D content variations about $\pm 20\%$ were indicated in each basin. In the Michigan and Golf Coast basins, the total mineralization is, in general, insignificantly related to the D concentration. In the Illinois and Alberta basins, the D content increases proportionally with mineralization (Fig. 7.3).

In general, while comparing data obtained for individual basin, marked variations in D content were observed. For example, the Gulf Coast basin waters are similar in D content to sea water, while in the Alberta basin the D content of water is about 100% lower than that in the ocean.

More objective conclusions on the water's genesis, as emphasized by the authors, may provide a hypothesis that original marine waters were pressed-off during compaction from syngenetic rocks and were then mixed with meteoric waters formed under climatic conditions close to modern ones.

Clayton et al. (1966) reported that the main process affecting the observed D/H variations from basin to basin is climatic change with time which has altered the isotopic composition of meteoric waters. The effect of climatic variations can be demonstrated by a few extreme values indicating very low D and ^{18}O contents, which correspond to climatic conditions during the Pleistocene glaciation.

The authors have concluded the processes of isotope exchange between water and other hydrogen-bearing geological objects as a result of hydrogen dispersion to be of no importance since only slight variations in D content have been detected in each basin. These slight variations should more likely be due to isotope fractionation by filtration of water through micropores in clay minerals (Clayton et al. 1966).
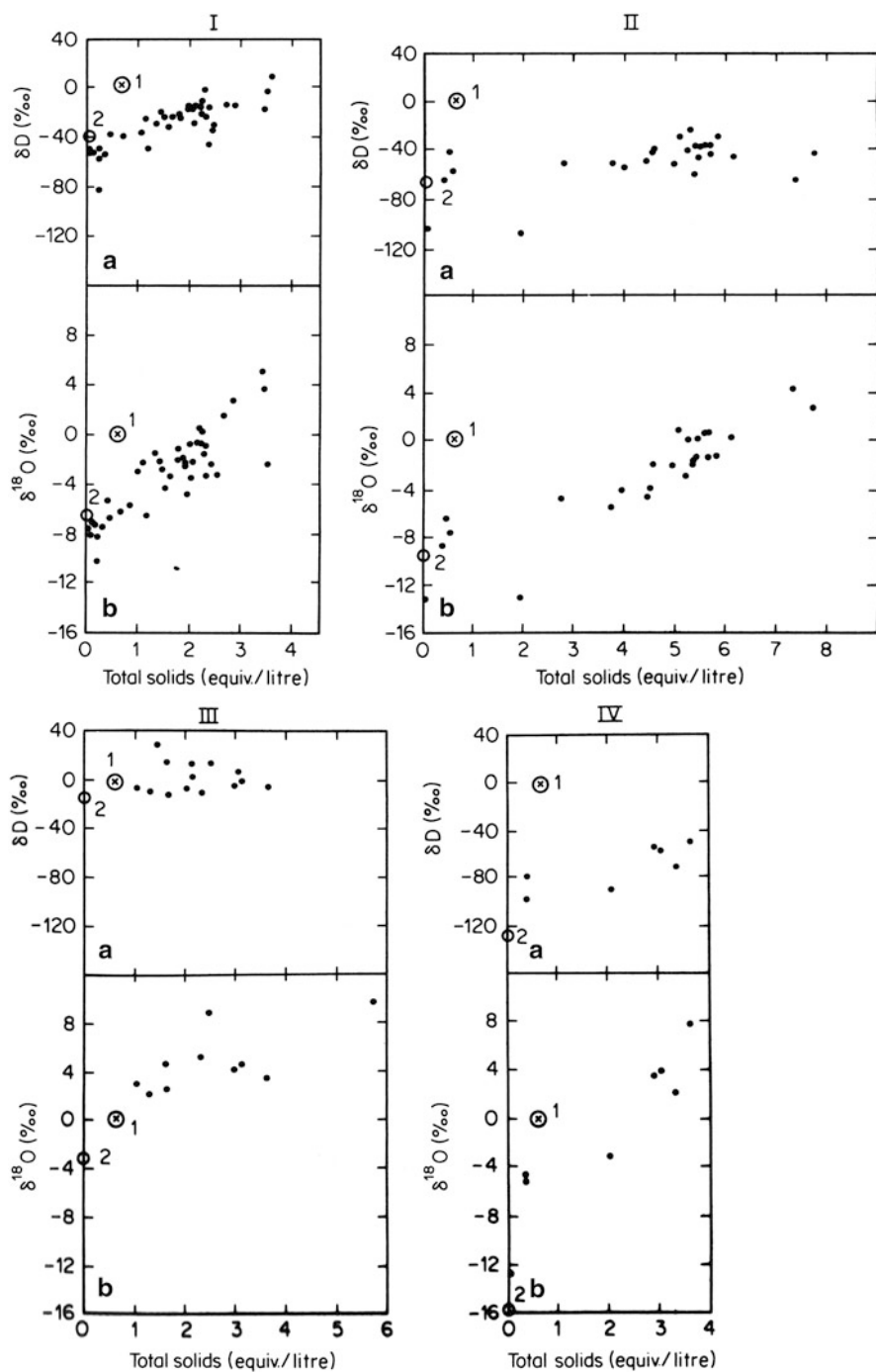
Fig. 7.3 Variation of brine isotope composition with salinity for Illinois (**I**), Michigan (**II**), Gulf Coast (**III**), and Alberta (**IV**) basins: *1* ocean water; *2* present-day meteoric water. (After Clayton et al. 1966)
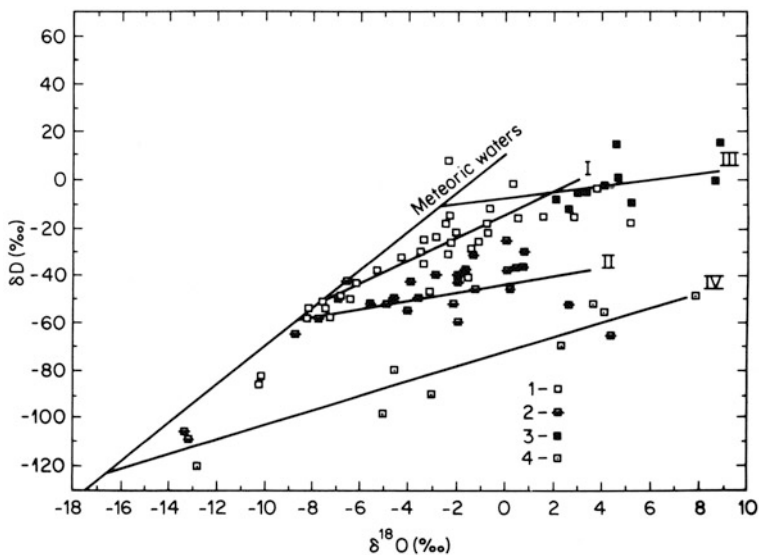
Fig. 7.4 Relationship between $\delta^{18}O$ and δD values for Illinois (**I**), Michgan (**II**),Gulf Coast (**III**), and Alberta (**IV**) basins. *1* Ocean water; *2* meteoric waters throughout the world. (After Clayton et al. 1966)

Marked ^{18}O content variations, strongly correlated with salinity variations, were detected in the investigated basins. Measurements of the ^{18}O content at zero mineralization coincide with its content of meteoric waters. At first sight, this seems to be due to the dilution of formation water with meteoric water. This argument was reported by Degens with his co-authors (1964), but Clayton et al. (1966) found another explanation of the observed data. From Fig. 7.4, it is observed that the least saline waters and the highly saline waters corresponding to D and ^{18}O content in meteoric waters and the highly saline waters fall markedly off this line. This picture resembles the case of hot springs such as the sets of points obtained within each basin lie aside from the meteoric water line so that a slight D enrichment corresponds to a great enrichment in ^{18}O. In fact, there is an oxygen shift in this case. The authors pointed out that a wider range of oxygen shift here is observed than in hydrotherms. This is likely to be due to a marked time of water exchange with rocks in the exchangeable system of the considered brines.

The main factor governing oxygen isotope composition in oil brines is water exchange between water and water-bearing rocks.

Figure 7.5 shows the theoretical curves corresponding to the isotope equilibrium between calcite and formation waters relative to the heavy oxygen content in the latter and dependent on temperature. The relative oxygen contents reported in the calcite of water-bearing limestones are +24.2, +25.3, +22.8, +22.3‰ in the Illinois, Michigan, Gulf Coast, and Alberta, respectively. It has been found that the majority of points lay within the 'band' of the theoretical line ranging about ±20‰ side of this line. Thus the following two conclusions have been drawn: (1) in all the basins

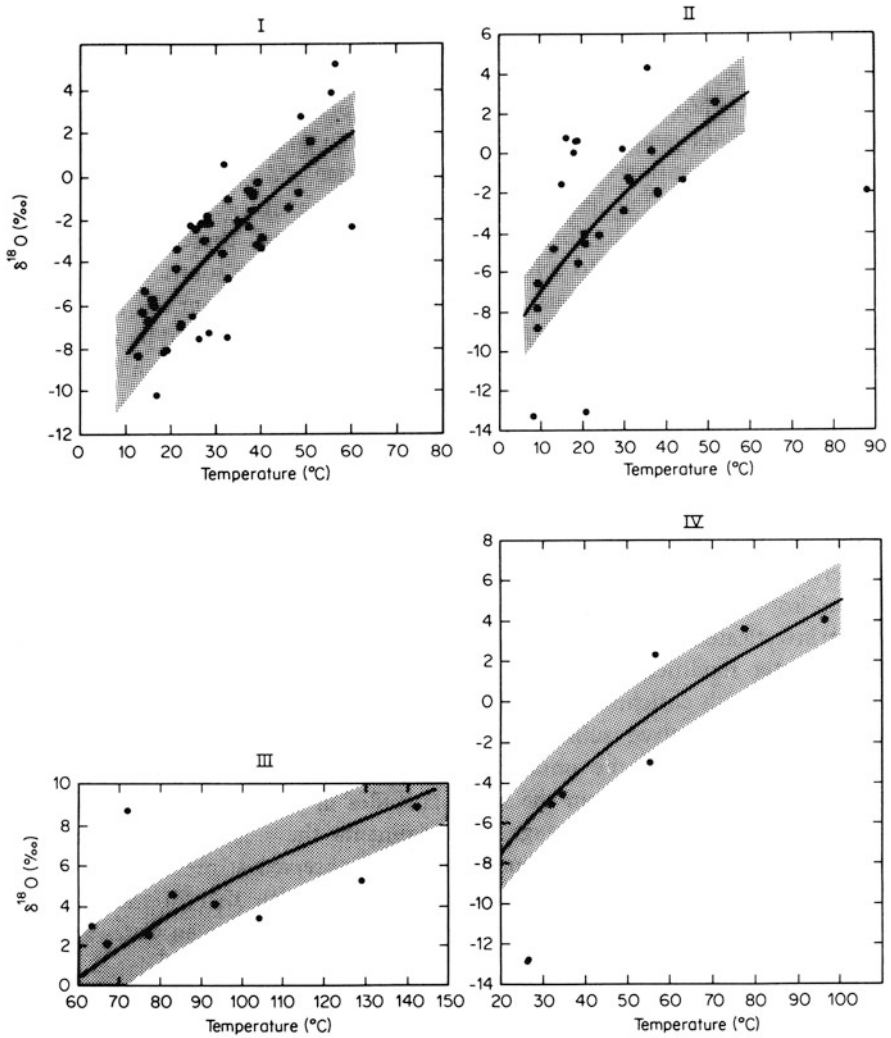**Fig. 7.5** Variation of brine $\delta^{18}O$ value with groundwater temperature for Illinois (**I**), Michgan (**II**), Gulf Coast (**III**), and Alberta (**IV**) basins. The equilibrium curve is drown for calcite of $\delta^{18}O$ equal to +24.2, +25.3, +22.8, +22.3‰. (After Clayton et al. 1966)

and at all possible temperatures the $\delta^{18}O$ content corresponds to isotope equilibrium lines; (2) the ^{18}O abundances in calcite are practically the same for all the basins. The scatter of points around the equilibrium line may be result of: (a) the lack equilibrium between the waters and the carbonates (especially in the case of the low-temperature waters and calcite-deficient rocks); (b) temperature-measurement errors; (c) local deviations of the oxygen isotope content of carbonates from the mean value.

Graf et al. (1966) investigated the conditions of formation of saline waters and brines in the Illinois and Michigan basins. They found that during the formation of the chemical composition of these basins, the marine and fresh waters participated to different degree. Further, the processes of substitution of magnesium for calcium during the dolomite formation are of importance. These processes involve the transition of calcium into solution and filtration of the solution through clay sediments working as ultra-filters. It was found that brines from the Illinois basin originated mainly from marine waters, the volume of which should be five times as much as the pore volume in the modern basin. For more calcium-rich brines in the Michigan basin, the role of fresh waters was highly essential. According to the author's estimation, the formation of these brines required a mixture of marine and fresh waters in the proportion of 1:200.

Hitchon and Friedman (1969) reported their results of formation waters in the western Canada sedimentary basin from the Upper Cretaceous waters to the Upper Devonian. They took 20 samples of surface waters, 8 samples from shallow aquifers, and 79 samples from different regions of gas and oil fields. Analyzing the data on isotopic composition of waters the authors concluded that formation waters of the investigated artesian basin originated by the mixing of surface water and marine water modified during the process of diagenesis. This process has been accompanied by enrichment of waters in heavy oxygen. The material balance of D and dissolved substances in the basin water shows that the observed D content can be obtained by the mixing of diagenetically modified marine and fresh waters from the same latitudes in proportions not greater than 1:2.9. During its passage through the sediments, the fresh water redistributed dissolved substances up to the salinity variations observed at past. The oxygen shift results from the oxygen exchange of water with that in the carbonate minerals. The effect of the process depends on the ratio between water and rock masses.

On the basis of works of Clayton et al. (1966), and Hitchon and Friedman (1969), Taylor (1974) has come to the conclusion that, in the majority of the North American sedimentary basin, meteoric waters are the main component of the brines. Thus, Taylor suggested the use of the term 'metamorphic connate waters' or 'formation waters' instead of 'connate waters', which is the term commonly used. These formation waters, in Taylor's opinion, are present in all sedimentary basins. In a number of cases these waters may be important, ore-forming fluids.

Rozkowski and Przewlocki (1974) studied the hydrogeological conditions of two coal basins in Poland with the aid of isotope techniques. In the Lublin coal basin, located at the boundary of the pre-Cambrian and Paleozoic platforms, the infiltration waters contribute greatly to sediments of different ages up to a depth of about 900 m. This phenomenon has been identified by decreases of mineralization and D and ^{18}O concentrations and also by a charge in the chemical making up of water from the carbonate sediments (of the Cambrian times) below the reference 900 m (Fig. 7.6). In the lower branch of the curve, the mineralization increases from 2.4 g/l (sample 17) up to 25 g/l (sample 27). The results of the chemical analyses have not been reported by the authors for sample 12. In water of the Cambrian formation, the mineralization

Fig. 7.6 $\delta^{18}O$ and δD values plotted against depth for Lublin Coal Basin waters from Cretaceous *1*, Jurassic *2*, Carboniferous *3*, and Cambrian *4* formations. (After Rozkowski and Przewlocki 1974)
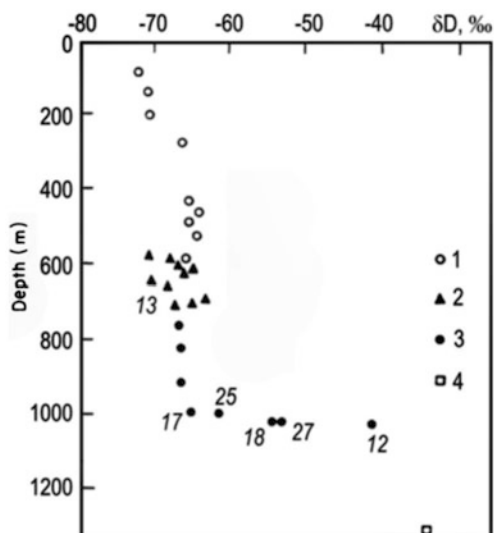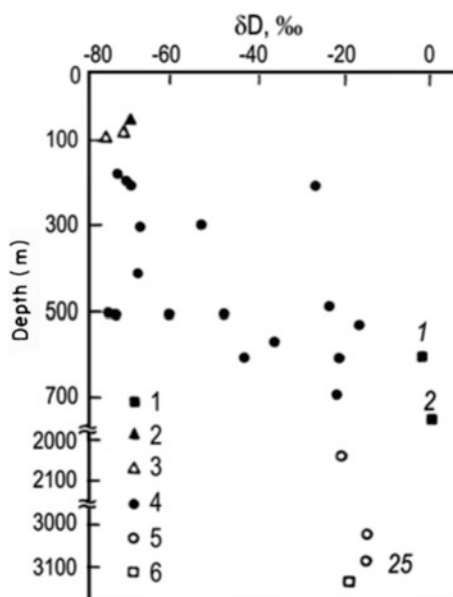

Fig. 7.7 ^{18}O and δD values plotted against depth for Upper Silesian Coal Basin waters from Tertiary *1*, Jurassic *2*, Triassic *3*, Carboniferous *4*, Devonian *5*, and Cambrian *6* formations. (After Rozkowski and Przewlocki 1974)

is 65 g/l ($\delta D = 33.2‰$). The type of water in a series (samples 17, 25, 18, 27) varies from the chloride–hydrocarbonate–sodium to the chloride–sodium one.

The Upper Silesian coal basin exhibits different characteristics. Here, the infiltration component is seen up to depth of about 500 m. Below this, the mineralization of water and the heavy Tertiary formation have the greatest hydrogen and oxygen isotope ratios, close to that of SMOB (Fig. 7.7). The mineralization of these chloride–sodium
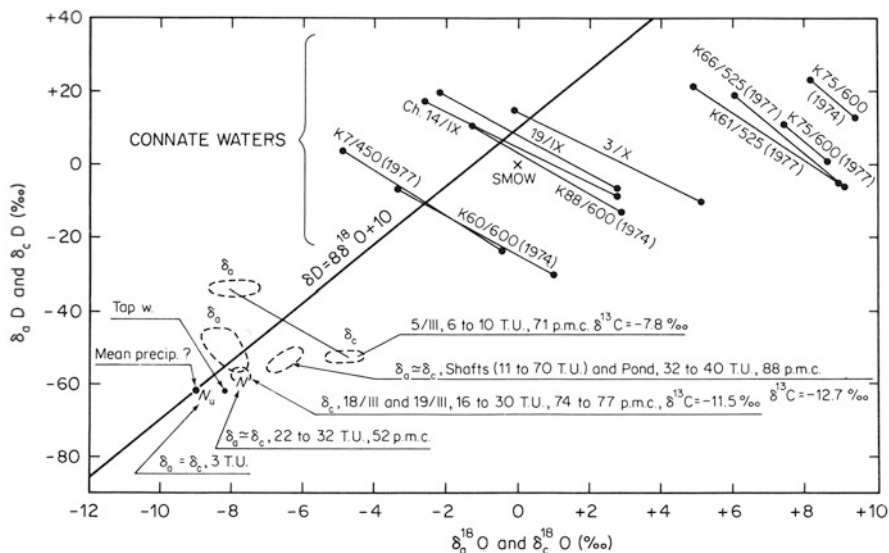
Fig. 7.8 Isotope data used for investigating brines of the Wapno and Klodava salt mines (Poland): δ_a is isotope activities; δ_b is isotope concentrations. (After Zuber et al. 1979)

waters is equal to 32 g/l ($\delta D = -3.6‰$, $\delta^{18}O = +0.07‰$) and 52 g/l ($\delta D = -1.2‰$, $\delta^{18}O = +0.34‰$). The highest values of mineralization (223 g/l, sample 25) are found in the Devonean. The authors have reported this to be a result of infiltration and relict waters mixing in the deep basin horizons. This process began at the end of the Tertiary period after regression of the sea. In the Lublin, there are more favorable conditions for the contribution of infiltration waters in the productive sandy–clay horizons of the carboniferous complex since the Cretaceous and Tertiary rocks are markedly thinner than in the Upper Silesian basin.

Zuber et al. (1979), with the help of a complex of isotopes (D, ^{18}O, T, ^{14}C), studied the genesis of water recharge in three salt mines in Poland. In particular, on the basis of the D and ^{18}O distribution in the aquifers at different mine horizons, it has been found that the amount of connate metamorphic waters, characterized by increased D and ^{18}O content, increases with depth. This is particularly evident for the Klodava salt mine located in the salt dome of the Zeichstein formation (Upper Permian). It is indicated also that in a number of cases, a considerable amount of modern infiltrational water ends up in the deep aquifers of the mines. Thus, at the third level of the Vapno mine values have been obtained for the tritium content (20–30 TU) and radiocarbon (74% relative to the modern standard), the total mineralization ranging from 360 to 422 g/l. The chlorine–bromine coefficient reached 80 in these typical alkaline brines with a chloride–magnesium type of water. Some of the results of the isotope studies at the Vapno and Klodava mines are shown in Fig. 7.8.

Moser et al. (1972) determined the D content in 110 water samples from the pressurized aquifers in the Styria basin, carried out paleoclimatic reconstructions, and identified several local zones related to different ages of groundwater formations.

At present, sufficiently comprehensive information on the isotopic composition of deep groundwater in sedimentary basins in the former USSR territory and other countries is available, making it possible to further develop isotope techniques and apply them in solving problems of deep groundwater origin. The most successful solution of problems concerning the conditions affecting the formation of sedimentary basin waters may be attained by the interpretation of both isotopic composition data and other hydrological and hydrochemical evidence (IAEA 1976; Bath et al. 1979; Sonntag et al. 1979; Gutsalo 1980; Dubinchuk et al. 1988; Cook and Herzeg 2000; Glynn and Plummer 2005).