Chapter 10
Hydrogen and Oxygen Isotopic Composition of Minerals of Magmatic and Metamorphic Rocks and Fluid Inclusions

10.1 Role of Water in Hydrothermal Alteration of the Rocks and Minerals

The results of stable hydrogen and oxygen isotope studies in minerals of magmatogenic rocks and fluid inclusions are in common use in geology mainly when the problem of hydrothermal ore deposition is concerned. Valuable evidence concerning the genesis of ore-forming fluids and mineralization sources of hydrothermal solutions, temperature conditions of the formation of mineral constituents, magmatogenic, metamorphic, and hydrothermally altered rocks and ore minerals may be obtained from isotope investigation (Taylor 1974, 1978; Hall et al. 1974; Rye et al. 1974; Robinson 1974; Sheppard and Taylor 1974; Ohmoto and Rye 1974; White 1974; Javoy 1978; Taylor and Silver 1978; Matsuo et al. 1978; Borshchevsky 1980; Shukoliukov 1980; Vlasova et al. 1978).

Of indubitable scientific and practical interest in this field is the study of water genesis of ore-forming hydrothermal fluids. As White (1974) has pointed out, the most authentic data on the fluid genesis may be obtained by studying the isotopic composition of fluids and accompanying minerals of the ore deposits against a background study of natural waters and, in the first place, of hydrothermal system waters. The data of water isotopic composition provide valuable information on the conditions of ore deposition and the role played by groundwaters of different origin. This question has been studied in a number of works by various authors (see, for example, a special issue of the journal *Economic Geology*, Vol. 69, No. 6, 1974).

White (1974) has distinguished six major types of natural waters involved to some degree in hydrothermal processes: (1) meteoric waters; (2) sea waters of the modern ocean; (3) connate waters of ancient oceans (the waters of sedimentary basins); (4) metamorphic waters associated with rocks in the course of their metamorphism; (5) magmatic waters coming out of magmatic rocks independently of their origin; (6) juvenile waters evolved during degassing of the mantle which were not previously in the hydrosphere.

The possible variations of isotopic composition of the majority of these water types have already been considered. We shall dwell here only on the results of
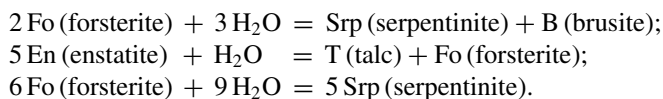
isotopic composition studies of metamorphic, magmatic, and juvenile waters which were obtained by some researchers in their investigations of hydrogen and oxygen isotopic composition of magmatic, metamorphic, and hydrothermally altered rocks of various geologic formations.

A vast data review on hydrogen and oxygen isotope content in magmatic and metamorphic rocks was reported by Taylor in his review paper (Taylor 1974) and is shown in Figs. 10.1 and 10.2, which were composed according to the results of numerous authors.

The calculation of hypothetical isotopic composition of metamorphic and primary magmatic (according to the classification of Sheppard et al. (1969) or juvenile waters is based, as was pointed out earlier, on the usage of data on hydrogen and oxygen isotope content in minerals of metamorphic and mafic rocks, taking into account the experimental evidence of isotopic fractionation factors in the mineral-water system at various temperatures. For qualitative consideration, one can take into account that $\Delta\delta D$ and $\Delta\delta^{18}O$ values for the mineral-water systems are similar to the values of these parameters in the following systems: feldspar-water, biotite (chlorite)-water, muscovite (phlogopite)-water, hornblende-water, and serpentine-water. The estimations of Δ-values at different temperatures are shown in Table 10.1 in accordance with data obtained by Taylor (1974), Suzuoki and Epstein (1976); and Sakai and Tsutsumi (1978).

We shall point out once more that the data presented in Table 10.1 are tentative. These data were obtained by extrapolation in the range of temperatures above 800°C and below 400°C. For the chlorite-water system, only one experimental point has been reported by Suzuoki and Epstein (1976), obtained at 400°C ($\Delta\delta D = -20‰$). Therefore, the values presented in the table for biotite (chlorite)-water system were obtained analogously with the help of the fractionation factor dependence on temperature for other hydroxide-bearing minerals.

Pugin and Khitarov (1978) assumed that during the passage of the mantle ultramafic substance up to the Earth's surface, with the accompanying decrease in temperature and pressure besides the solid phase transformations, the main process is that of serpentinization, resulting in radical changes of its phase composition and the loosening of its substance. There occurs together, not on such a large scale, the metasomatism change of ultramafic rocks which is manifested in the form of amphibolization, mica formation, and talc formation. All these processes are carried out with the participation of water, for example by the following reactions:

$$2\,Fo\,(\text{forsterite}) + 3\,H_2O = Srp\,(\text{serpentinite}) + B\,(\text{brusite});$$
$$5\,En\,(\text{enstatite}) + H_2O = T\,(\text{talc}) + Fo\,(\text{forsterite});$$
$$6\,Fo\,(\text{forsterite}) + 9\,H_2O = 5\,Srp\,(\text{serpentinite}).$$

As Pugin and Khitarov (1978) have pointed out, at present there are many reasons to suppose that water involved in the serpentinization of ultramafic substance can be both of juvenile and nonjuvenile character. According to Dmitriev (1973), who studied isotope abundances of sulfur and boron in serpentines sampled from the ocean bottom and the copper content in them, the juvenile waters play the main role in processes of rock serpentinization at great depths. Pugin and Khitarov do not share
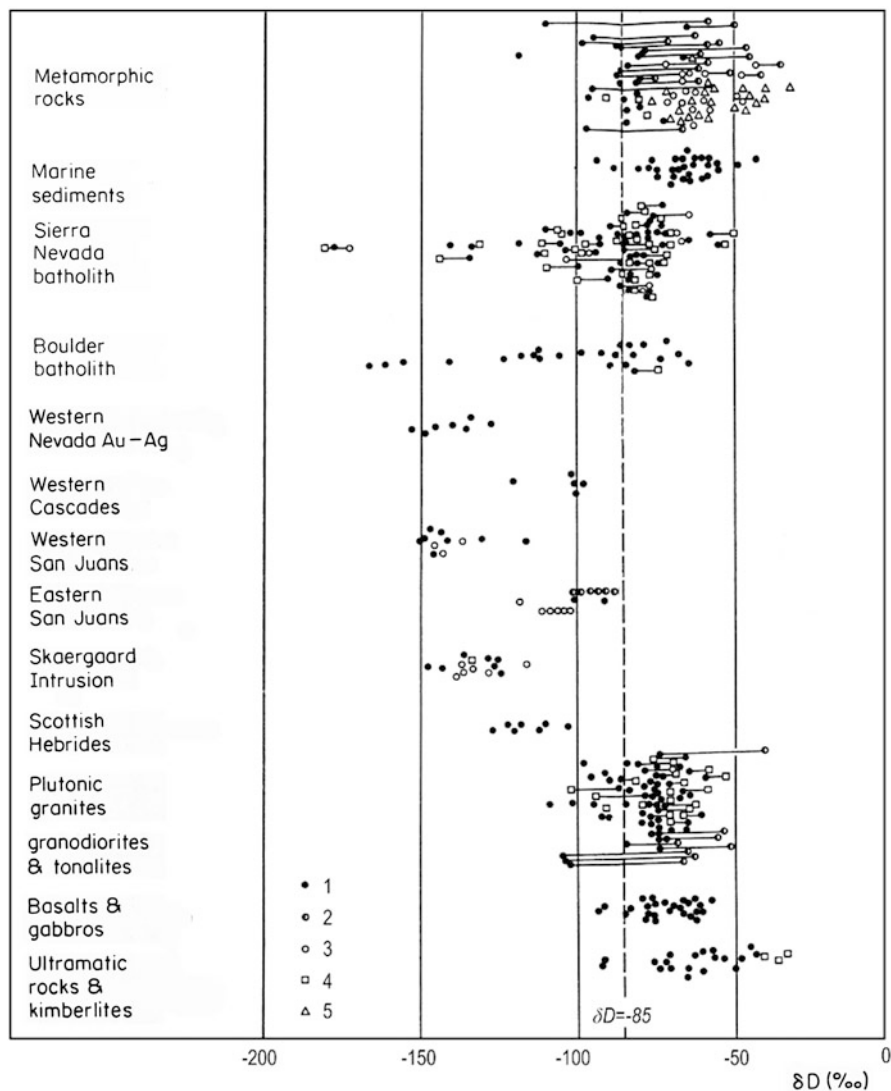
Fig. 10.1 A compilation of δD analyses of minerals from magmatic, metamorphic, and hydrothermally altered rocks from variety of locations and obtained by different authors: (*1*) biotite and whole rock; (*2*) muscovite; (*3*) chlorite or talc; (*4*) hornblende; (*5*) antigorite. (After Taylor 1974)

this view, stating that the amount of water in the mantle's substance does not exceed 0.025–0.1%. The amount of water in serpentinized rocks is dozens of times as great, amounting to several percent. It is difficult to prove that such large-scale processes take place in natural conditions, taking into account juvenile (mantle) waters only, on the basis of these arguments.
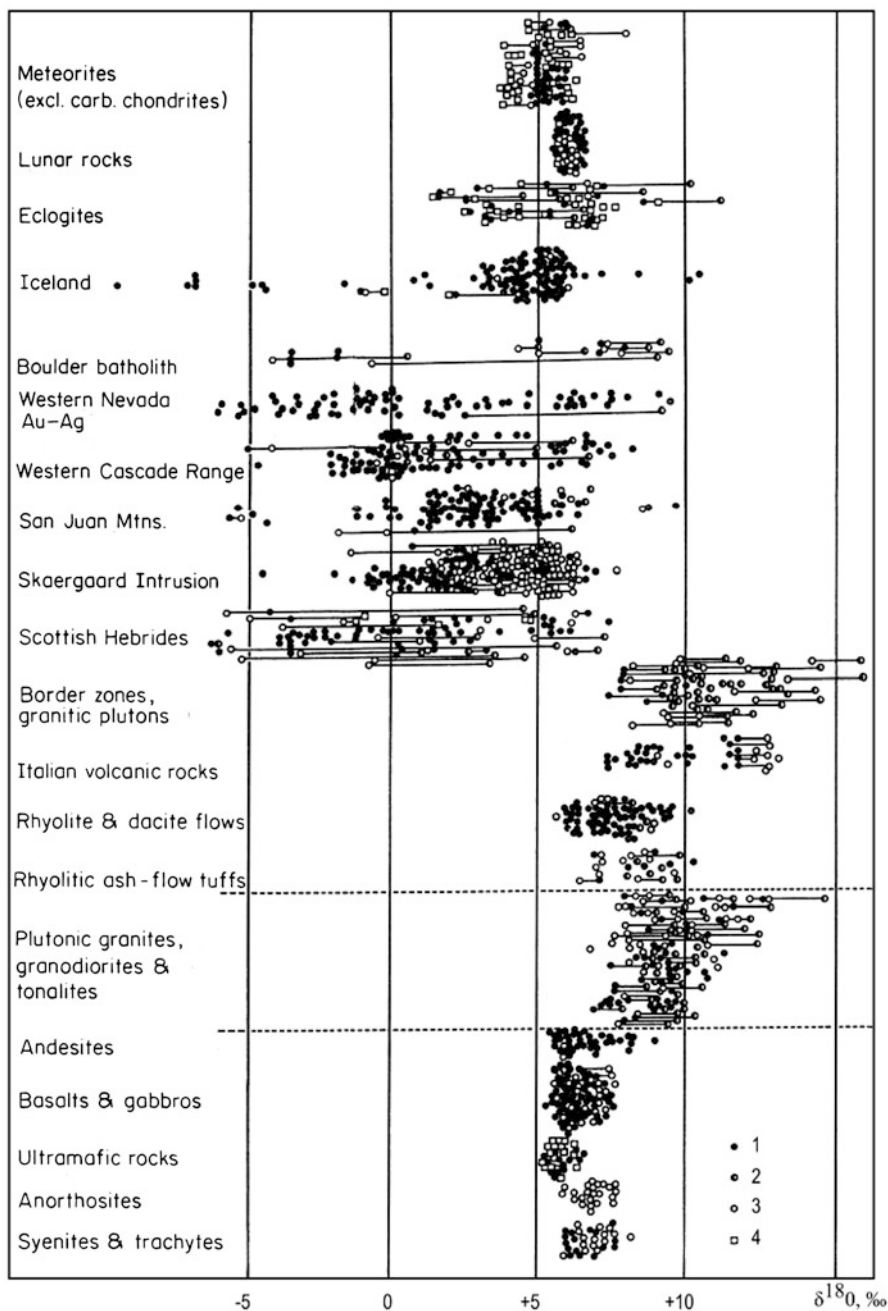
Fig. 10.2 A compilation of ^{18}O analyses of minerals and whole-rock samples of magmatic rocks from variety of locations and obtained by different authors: (*1*) whole rock; (*2*) quartz; (*3*) feldspar; (*4*) pyroxene. (After Taylor 1974)

Table 10.1 Approximate Δ-values for various temperatures. (© IAEA, reproduced with permission of IAEA)

Δ(‰)	Temperature (t°C)					
	1,100	900	700	500	300	200
$\Delta\delta^{18}O_{feldspar-water}$	0	0	+0.5	+0.1	+4.5	+8.5
$\Delta\delta^{18}O_{serpentine-water}$	0 (?)	0 (?)	0–2 (?)	0–2 (?)	0	+1
$\Delta\delta D_{biotite-water}$	−12	−18	−25	−38	−45	−50
$\Delta\delta D_{muscovite-water}$	0	0	−5	−20	−25	−30
$\Delta\delta D_{hornblende-water}$	−5	−10	−19	−32	−40	−45
$\Delta\delta D_{serpentine-water}$	0 (?)	0 (?)	−20	−18	−10	−3

Analysis of the hydrogen and oxygen isotope composition of more than 150 samples of serpentinized rocks taken from the pre-Cambrian formations of various regions of the former Union of Soviet Socialist Republics (U.S.S.R.) have been carried out by Polyakov. The results of these studies show that δD values of the minerals' hydroxide groups vary over a wide range from −50 to −150‰ with an average value of $\delta D = -95‰$. Since the processes of serpentinization in nature take place at temperatures of 300–350°C (Pugin and Khitarov 1978), then, taking into account that $\Delta\delta D_{serpentinite-water}(300°C) = -10‰$, it is possible to obtain the δD of water involved in the serpentinization of ultramafic rocks which varies from −40 to −140‰. A wide range of δD variations shows that main role in serpentinization has been played by meteoric waters but not juvenile fluids.

This assumption is confirmed also by the data for oxygen isotope measurements for water extracted at 800°C by thermal destruction of the hydroxide group, which range between −10 and +8‰ with an average value of −2‰. There is reason to believe that serpentinization of rocks occurs at conditions of isotopic equilibrium and that in this case the oxygen isotope composition of the water also reflects the isotopic composition of serpentine. Making such an assumption, it is possible to conclude that either serpentine at isotope equilibrium with forsterite at a temperature of about 500°C or lower has been depleted in oxygen-18 by 7–9‰ compared with forsterite or in the course of serpentinization large amounts of water depleted in ^{18}O have been involved. The latter conclusion seems to be more reasonable. Thus investigations of minerals of the serpentine group cannot give reliable evidence on variations of the isotopic composition of original magmatic or juvenile water.

Taylor discussed the problem of primary magmatic water from a theoretical viewpoint. He pointed out that magma exists over a restricted temperature range from 700 to 1000°C. At these temperatures, the isotopic composition of water released from magma minerals in isotopic equilibrium with it should be practically identical to mantle minerals in oxygen isotope composition and heavier in hydrogen by a value ranging from 0 to 20‰ (on average 10‰). It is known that the majority of plutonic and volcanic rocks have $\delta^{18}O$ ranging from +5.5 to +10‰ (Fig. 10.2) and δD in 95% of cases ranging from −50 to −85‰. At these values of δD and $\delta^{18}O$, taking into account fractionation at $t > 700°C$, the primary magmatic water should have $\delta^{18}O = +5.5$ to +10‰ and $\delta D = -40$ to −75‰. Taylor with his co-authors, in their

earlier work (Sheppard et al. 1969), for the primary magmatic water accepted values of $\delta^{18}O = +7$ to $+9.5\%o$ and $\delta D = -50$ to $-80\%o$.

Similar data estimating the hypothetical isotope composition of primary magmatic (juvenile) water have been reported by the other researchers (Epstein and Taylor 1967; Rye 1966; Sheppard and Taylor 1974). White (1974) has pointed out that the δD value for the hypothetical juvenile waters genetically related to the mantle should most likely be close to $-50\%o$. This value of δD is similar, for example, to eaters of the fumarole condensates from the Surtsay volcano, Iceland, for which $\delta D = -53\%o$ (Arnason and Sigurgeirsson 1967). For the glassy border of juvenile pillow lavas, emerged at high pressures on the ocean floor, it has been found that $\delta D = -60\%o$ (Moore 1970).

According to Sheppard and Epstein (1970), who studied the hydrogen isotopic composition of phlogopites of ancient ultramafic rocks genetically related with the mantle substance, the average value of $\delta D = -58 \pm 18\%o$. Taking into account the fractionation factor of deuterium between water and phlogopite at $t = 700°C$ ($\Delta\delta D_{phlogopite-water} = -10\%o$ at this temperature according to the author's accounts), the value for juvenile water in contact with rock has been estimated at $-40 \pm 20\%o$ ($\delta^{18}O = +7 \pm 2\%o$). The hypothetical juvenile water involved in the transformation of ultramafic and mafic rocks of the Kitakami granite massif, northeastern Japan (Kuroda et al. 1974) lie in the range of $\delta D = -29$ to $-37\%o$ as do majority of water in Western Turkmenia, in which the δD and $\delta^{18}O$ values range between -28 and $-65\%o$ and $+3.7$ and $+5.0\%o$, respectively (Seletsky et al. 1973). The δD values in primary amphiboles of high-temperature peridotites in a number of regions of Morocco and France range from -48 to $-88\%o$, which indicates, according to Javoy (1978), the existence of a deep (juvenile) hydrogen source.

The above-mentioned estimates of the isotopic composition of hydrothermal juvenile (or primary magmatic) water are based on a number of assumptions which do not exclude other considerations. For example, from the viewpoint of plate tectonics one can assume that in the zones of ocean plate movement (zones of oceanic trenches), large amounts of pelagic and other oxygen-bearing minerals which were formed under surface conditions are involved in the mantle. In the course of dehydration of these minerals at high temperatures, water with an isotopic composition ranging from -60 to $-80\%o$ may be released. This possibility is discussed in Chap. 2. It is obvious that a 'juvenile' appearance may be obtained by meteoric waters as a result of isotopic exchange during the metamorphism of rocks. In fact, metamorphic waters are characterized by a wide range of $\delta^{18}O = +4$ to $+25\%o$ and a comparatively narrow range of $\delta D = -20$ to $-65\%o$ (Taylor 1974; Magaritz and Taylor 1976a, b).

The hypothetical isotope composition of juvenile waters might possibly be explained from the viewpoint of the condensational theory of the formation of planetary bodies which is developed by the authors of the present book (see Chap. 20). According to this theory, at the stage of 'cold' condensation of siliceous compounds ($T \leq 537°C$), their partial hydration could occur with the formation of a great number of hydroxide-bearing minerals. If condensation occurs at equilibrium conditions between the solid siliceous phase and water vapor, then the siliceous minerals formed in accordance with fractionation factors become enriched in oxygen-18 by 5–10‰ and

depleted in deuterium by 25–50‰. Large amounts of captured inertial gases, and in particular 'primary' helium enriched in ^{3}He isotope, are evidence in favor of a low temperature at the beginning of the condensation of planetary bodies. In the course of the warming of the protoplanetary cloud during its gravitational contraction, the released juvenile water should have an isotopic composition $\delta D = -25$ to $-50‰$ and $\delta^{18}O = +5$ to $+10‰$. The hypothesis of condensational origin results in initial inhomogeneity of juvenile waters' isotopic composition since, in this case, the processes of isotope exchange between water and condensing minerals occur in the closed system at varying temperatures.

10.2   Meteoric Water in the Processes of Hydrothermal Formation of Minerals

Let us consider now the results of some experimental investigations concerning hydrogen and oxygen isotope studies and liquid-gaseous inclusions which provide valuable information about the evolution of the Earth's core. The majority of investigations on this question, initiated by Friedman (1953), have made it possible to conclude that the main role in the transformation of the upper lithosphere belongs to the hydrosphere's water and a large part of metamorphic and magmatic waters which we are studying now has more than likely passed through a cycle of meteoric circulation.

Friedman and Smith (1958), studying the deuterium content of igneous rocks, found that δD ranges from -80 to $-150‰$ in obsidians from five geographical regions. The relationship between these concentrations and those of local meteoric water has not been found, whereas in the accompanying perlites this relationship is evident. Therefore, it has been acknowledged that the latter are secondary formations. In the course of biotite and hornblende investigations in rhyolite lavas (New Mexico, USA), the same authors (Friedman et al. 1963) found that the relative deuterium content in 11 samples varied from -33 to $-14‰$. It has been found that the inverse relationship holds between the amount of water in the sample and the deuterium content. A similar relationship has been obtained by Friedman et al. (1963) under laboratory conditions in the course of heating biotite up to 700°C. It has been stated on this basis that the deuterium content in the investigated samples is a record of the history of rhyolite glass cooling during which iron reacted with water and oxidized and a light isotope of hydrogen had been preferentially lost. Therefore, the less water that remained in the glass, the more it was enriched in deuterium.

Analyzing numerous experimental data on the hydrogen and oxygen isotope composition of granite plutons, Taylor (1978) pointed out the following: The δD values of biotites and hornblende in granite batholites range everywhere between -50 and $-80‰$. These data are similar to typical δD values detected in metamorphic and marine sedimentary rocks and also in the majority of rocks which are products of weathering in the moderate climate. On this basis, Taylor has stated that primary

water involved in the process of granitization of igneous rocks were not juvenile waters. Typical $\delta^{18}O$ values for the majority of granitic rocks range from $+7$ to $+10‰$. He concluded that the formation of batholiths was accompanied by the formation of a gigantic meteoric hydrothermal convection system.

Studying different igneous rocks and minerals, Kokubu et al. (1961) found that the relative deuterium content in their water ranges from -25 to $-160‰$. No correlation has been found between the content of water and deuterium in these specimens. The same authors analyzed several samples of liquid inclusions in basalts from the Japanese Islands, where δD values were found to range from -33 to $-60‰$. The authors, using results of chemical analyses carried out earlier by other researchers, concluded that these liquid inclusions represent 'juvenile' water. The ^{18}O content was measured simultaneously in the samples. Later on, Craig (1963) showed that the experimental D and ^{18}O values of that water fit the straight line of local meteoric water.

According to Godfrey (1962), the relative deuterium content in amphiboles (35 specimens), biotites (36 specimens), and chlorites (8 specimens) from different regions in the USA range from -203 to $-76‰$.

It should be pointed out that long before mass spectrometric measurements upon water and minerals, Vernadsky et al. (1941) reported data on deuterium and oxygen-18 content in two water samples from metamorphic rocks of igneous origin using a method based on water density and refraction measurements. It was found that only heavy oxygen is enriched in the water of the rocks, whereas it becomes depleted in deuterium. These data obtained in the 40s of the previous century are in good agreement with later conclusions derived by other researchers and are related to the way in which ^{18}O enrichment may reflect, to some degree, the Earth's magmatic activity.

The authors of this book have measured the deuterium content of two perlite specimens sampled from the Kecheldagsky ore deposits location in the central region of the North Caucasus. The water was extracted under two temperature regimes: up to $600°C$ (the first stage of burning with extraction of 'perlite water') and in the range $600–1,000°C$ (second stage of burning with extraction of 'obsidian water'). Relative deuterium content in these specimens was -82 and $-88‰$, which is in accordance with the data of other researchers obtained for this type of rock.

Interesting investigations were carried out by Hall and Friedman (1963) on the determination of chemical composition and deuterium content in primary liquid inclusions in ore, lead-zinc vein, and fluorite deposits on the Upper Mississippi and Cave-in-Rock (USA). It was found that in liquid inclusions of different minerals (white, yellow, and blue fluorite, quartz, calcite, barite, etc.) of the fluorite Cave-in-Rock deposit, relative deuterium concentrations range from -64.6 to $-32.9‰$. The ancient sedimentary waters in this region had δD values from -31.7 to $-26.6‰$ and in one case this value was $-147.5‰$. The following principle has been obtained: liquid inclusions of more ancient minerals have a higher content of both salts and deuterium compared with the younger ones. A similar picture is also evident for liquid inclusions of minerals (calcite, galenite, sphalerite, etc.) in the lead-zinc deposition in

the Upper Mississippi. The δD values there range between -101 for ancient minerals and $-25.4‰$ for younger ones.

Hydrogen and oxygen isotope techniques, applied to hydrothermal altered rocks and their liquid inclusions, have made it possible to elucidate the role of groundwater of different origin in the formation of ore deposits. In the review papers by Taylor (1974) and White (1974), analysis of isotope data and the role of groundwaters of different type in the metamorphism of rocks and accompanying ore deposition process in hydrothermal deposits of various types are shown. Besides the elucidation of this role of groundwater in ore formation, isotope techniques are useful in the determination of ore formation temperatures as isotope thermometers involving co-existing minerals (see Chap. 9). They are also useful for mean ratio estimations of ore-forming fluids to rocks.

We shall not discuss this problem in detail; only note that the existence of isotope investigations of hydrothermal alteration of ores and the formation of ore deposits of various geological ages makes it possible to conclude that the main role in these processes belongs to groundwaters of meteoric genesis. Thus, Taylor (1974) has pointed out that, from data on hydrogen and oxygen isotopic composition studies, the most widespread types of water in hydrothermal systems of the subsurface layer of the continental crust (3–6 km in thickness) are meteoric and 'connate' formation waters or a mixture of the two. Further, the author has pointed out that though the aim of this work was to prove the importance of magmatic and metamorphic waters, the latter, as Taylor pointed out, are the most important components of hydrothermal solutions, being waters separated from magmatogenic rocks during their evolution. In this case, the terms 'magmatogenic' and 'metamorphic' correspond not only to water circulation in the crust-hydrosphere system. As mentioned earlier, experimental evidence suggests that the water content in the mantle rocks is minimal and insufficient for regional transformations of rocks. This has been proved experimentally, for example, by the laboratory studies of the serpentinization processes of ultramafic rocks (Pugin and Khitarov 1978).

In relation to this problem, White (1974) has also reported that meteoric waters play the dominant role in the majority of hydrothermal systems. He has also added that the present accuracy of measurements and slight variations of isotope composition of the thermal and meteoric waters in each of the studied regions suggest the presence of 5–10% of water of nonmeteoric origin and other isotopic composition in the studied thermal systems. The assumption may be confirmed by a number of experimental results which have appeared in the last few years. For example, Vlasova et al. (1978) examined the origin of hydrothermal solutions associated with trap volcanic activity of the Siberian Platform, on the basis of hydrogen, oxygen, and carbon isotope techniques. They found that δD variations, ranging from -75 to $-54‰$, in waters in equilibrium with basalts at the temperature of 200–300°C indicate the common meteoric-marine origin of the solutions responsible both for the hydrothermal ore deposition and the chloritization of basalts.

At present, attempts are being made to widen the circle of studied isotope ratios applied for the determination of the genesis of hydrotherms and hydrothermal ore-forming fluids. Considerable success has been achieved in the investigations of

isotopic composition of noble gases (^{3}He/^{4}He, ^{36}Ar/^{40}Ar), in hydrothermal liquid inclusions (Naydenov et al. 1978; Kamensky et al. 1976; Fedorov 1999), in strontium isotopes (Faure and Powell 1972; Hedge 1974; Lepin et al. 1975), in strontium and lithium isotopes (Sandimirova et al. 1978; Plyusnin et al. 1978a, b), in silicon (Ustinov et al. 1978), and also in isotopes of other elements such as sulfur, carbon, and lead.(Doe and Stacey 1974; Ohmoto and Rye 1974).

In conclusion, we should like to note that isotope studies of water inclusions in ancient rocks and minerals are of unique interest for understanding the history of water itself and for the elucidation of both the conditions of rock metamorphism and formation of hydrothermal deposits of minerals. Further investigations involving not only stable isotopes of water as the solvent but also dissolved substances will provide new facts which will be of value in solving important scientific and practical problems.