

# Stable isotopes in petrology: a brief survey

BRUNO TURI

Dipartimento di Scienze della Terra, Università di Roma «La Sapienza», Piazzale A. Moro, 00185 Roma

**ABSTRACT.** — The isotopic composition of some elements of low atomic number, notably H, C, O, N, S and Si, vary in nature as a consequence of physicochemical processes such as equilibrium exchange reactions and kinetic phenomena. In general, the equilibrium constants of the isotopic exchange reactions are temperature-dependent; this is the basis of the isotope geothermometry. Among the above elements, oxygen and subordinately hydrogen are the most useful in petrological studies. The  $^{18}\text{O}/^{16}\text{O}$  and D/H ratios (by convention expressed in  $\delta$ -units, in parts per thousand relative to the Standard Mean Ocean Water, SMOW) are currently being used to provide information on a variety of problems, like 1) the conditions and mechanisms of minerals and rocks formation, 2) the origin and evolution of magmas, 3) the interactions between magmas and country rocks, 4) the nature of the fluids involved in geological processes, 5) the evaluation of the thermal history and the scale of fluid migration during metamorphic processes, and 6) water-rock interactions. In particular, oxygen and hydrogen isotope analyses proved to be of fundamental importance to elucidate the metasomatic processes occurring in the upper mantle; they also demonstrated that high- and low-temperature interactions between meteoric waters and rocks are widespread and significant in Earth's crust.

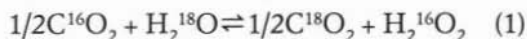
## Basic principles of isotopic fractionation

The abundance of the stable isotopes of elements having low atomic numbers display appreciable variations in nature as a consequence of fractionation processes occurring during chemical, physical, and biological reactions. The term «isotope fractionation» refers to the partitioning of the isotopes of a given element between two (or more) coexisting compounds or phases containing that element.

In general, such variations of the isotopic

abundances, or isotope effects, are produced either by kinetic processes or equilibrium isotope exchange reactions. Kinetic isotope effects arise from differences in the rate of reaction of isotopic molecules, and are normally associated with unidirectional or fast processes such as diffusion, evaporation, and dissociation reactions. The magnitudes of these effects are comparable to, or even larger than, those of the equilibrium processes. Kinetic isotope effects, however, are relatively rare in the high-temperature processes occurring on Earth.

The isotope effects associated with equilibrium exchange reactions are controlled by the constant  $K$  of the reaction. Take for example the equilibrium exchange of the oxygen isotopes  $^{18}\text{O}$  and  $^{16}\text{O}$  between carbon dioxide and water vapor:



where  $\text{C}^{16}\text{O}_2$  and  $\text{C}^{18}\text{O}_2$  mean that oxygen atoms in the  $\text{CO}_2$  molecule are  $^{16}\text{O}$  and  $^{18}\text{O}$ , respectively<sup>(1)</sup>. The equilibrium constant  $K$  for this reaction is:

$$K = \frac{(\text{C}^{18}\text{O}_2)^{1/2} \cdot (\text{H}_2^{16}\text{O})}{(\text{C}^{16}\text{O}_2)^{1/2} \cdot (\text{H}_2^{18}\text{O})} \quad (2)$$

where in parentheses are reported the concentrations of the various species.  $K$  can be also written in terms of the partition function  $Q$  of the reactants and products:

<sup>(1)</sup> It should be noted that such molecules practically do not exist in nature; this formalism, however, is largely used for simplifying calculations.

$$K = \frac{Q^{1/2}_{(C^{18}O_2)} \cdot Q_{(H_2^{16}O)}}{Q^{1/2}_{(C^{16}O_2)} \cdot Q_{(H_2^{18}O)}} = \frac{[Q_{(C^{18}O_2)} / Q_{(C^{16}O_2)}]}{[Q_{(H_2^{18}O)} / Q_{(H_2^{16}O)}]} \quad (3)$$

$Q$  is defined as follows:

$$Q = \sum g_i e^{-E_i/kT} \quad (4)$$

where  $g_i$  = statistical weight of the energy level  $i$ ;  $E_i$  of the molecule;  $k$  = Boltzmann's constant =  $1.381 \times 10^{-16}$  erg/°K;  $T$  = temperature in the Kelvin scale.

$Q$  contains all the energy information about a given molecule; therefore, the partition functions are normally used rather than concentrations for the theoretical calculation of the equilibrium constant for isotope exchange reactions.

For any isotope exchange between two compounds A and B we may define a fractionation factor  $\alpha$  as the quotient of the heavy-to-light isotope ratios of the element under study in A and B:

$$\alpha_{A-B} = \frac{R_A}{R_B} \quad (5)$$

where  $R = {}^{18}O/{}^{16}O$ ,  ${}^{13}C/{}^{12}C$ ,  $D/H$ ,  ${}^{34}S/{}^{32}S$ , and so forth.

Under equilibrium conditions, assuming that the isotopes are randomly distributed among all possible sites in the molecules,  $\alpha$  is related to  $K$  as follows:

$$\alpha_{A-B} = K^{1/n} \quad (6)$$

where  $n$  is the number of isotopes exchanged in the reaction as written. For the reaction (1),  $n = 1$  and therefore:

$$\alpha_{(CO_2-H_2O)} = \frac{({}^{18}O/{}^{16}O)_{CO_2}}{({}^{18}O/{}^{16}O)_{H_2O}} \quad (7)$$

The general equation (6), however, does not hold true for the compounds of hydrogen and for those containing two or more isotopes of the element in non-equivalent molecular position. The equilibrium constants, and therefore the fractionation factors, are temperature-dependent; this is the basis of the isotopic geothermometry. Their values are in general very close to unity, typically within the range from  $1 \pm 0.0X$  to  $1 \pm 0.00X$ . The fractionation effects are directly proportional to the relative mass difference between the

heavy (rare) and light (common) isotopes, provided other parameters such as temperature, bond strength and oxidation state are the same. For example, deuterium, the heavier stable isotope of hydrogen ( $D$  or  ${}^2H$ ), has a mass twice that of the lighter  ${}^1H$  isotope, so that the relative mass difference of these isotopes is almost 100% and the  $D/H$  fractionations are accordingly substantially larger than those of any other element of geochemical interest. For the stable isotope of heavy elements like  $Sr$ ,  $Nd$ , and  $Pb$ , the relative mass differences are very small (e.g. 1.2% for the  ${}^{87}Sr$ - ${}^{86}Sr$  pair); the natural variations of their abundances are basically related to radioactive phenomena and the ratios of the parent to daughter elements, and do not arise from physicochemical processes. Only six elements of low atomic number, namely  $H$ ,  $C$ ,  $N$ ,  $O$ ,  $S$ , and  $Si$  display variations in their isotope ratios useful in the study of geological processes. These elements (notably  $O$ ) are important constituents of a large variety of naturally occurring solids and fluids, and the abundance of their rare isotope is sufficiently high to allow precise determinations of the isotopic ratios by mass spectrometry. Inasmuch as the difference in the isotopic ratios of two substances is measured far more precisely and easier than are the absolute ratios, the isotopic compositions of the above elements are currently determined by comparing the heavy-to-light isotope ratio of the element in the sample ( $R_x$ ) with respect to the corresponding ratio in a suitable reference standard ( $R_{std}$ ). By convention, the difference  $R_x - R_{std}$  is expressed relative to the standard ratio in the so-called  $\delta$  units, in parts per thousand or permil (‰).  $\delta$  is defined as follows:

$$\delta_x = \left( \frac{R_x - R_{std}}{R_{std}} \right) \times 10^3 = \left( \frac{R_x}{R_{std}} - 1 \right) \times 10^3 \quad (8)$$

where  $R = D/H$ ,  ${}^{13}C/{}^{12}C$ ,  ${}^{18}O/{}^{16}O$ , and so forth. If  $R_{std}$  is known, the absolute ratio of any sample  $R_x$  can be readily obtained from its  $\delta$  value.

The interrelationship between the fractionation factor  $\alpha_{A-B}$  and the  $\delta$  values of A and B (expressed against the same

standard) is given by:

$$\alpha_{A-B} = \frac{1 + \delta_A/1000}{1 + \delta_B/1000} = \frac{1000 + \delta_A}{1000 + \delta_B} \quad (9)$$

The isotopic effects observed in natural samples are normally expressed as «permil fractionations». For example, for the  $^{18}\text{O}/^{16}\text{O}$  exchange reaction between  $\text{CaCO}_3$  and  $\text{H}_2\text{O}$  under equilibrium conditions,  $\alpha = 1.0056$  at  $300^\circ\text{C}$  (FRIEDMAN and O'NEIL, 1977), and the permil fractionation is accordingly 5.6 permil. Inasmuch as  $10^3 \ln(1.00X) \cong X$ , the permil fractionation is practically equivalent to  $10^3 \ln \alpha_{A-B}$ . For  $\delta$ -values  $\leq |10|$ , the approximate relationship holds up:

$$10^3 \ln \alpha_{A-B} \cong \delta_A - \delta_B = \Delta_{A-B} \quad (10)$$

Thus, the permil fractionation can be measured to a high degree of approximation by simply subtracting the  $\delta$  values of the two substances, if such values are close enough.

For reactions involving perfect gases,  $10^3 \ln \alpha_{A-B}$  varies as  $1/T$  and  $1/T^2$  at low- and high-temperatures, respectively. Similar relationships have also been established for several mineral-fluid pairs and mineral pairs. Such fractionation curves are widely used in stable isotope geothermometry. Over limited temperature ranges, they are in general represented by equations such as  $10^3 \ln \alpha_{A-B} = a + b/T$  and  $10^3 \ln \alpha_{A-B} = a + b/T^2$  (depending on the temperature range) or by a more encompassing equation like  $10^3 \ln \alpha_{A-B} = a + b/T + c/T^2$ .

It is important to be aware, however, that if extended over a wide range of temperatures, the fractionation curves do not always show such regular temperature dependencies; observations have been made of crossovers (change of sign of the fractionation factor) inflections, maxima and minima (Fig. 2). The knowledge of the shape of the fractionation curve for a given system is essential in order to avoid serious errors if the curve is used for extrapolating data far beyond the temperature range over which the curve has been established.

At infinite temperature, the fractionation factors between all substances become unity (that is, the isotopic fractionations go to zero;

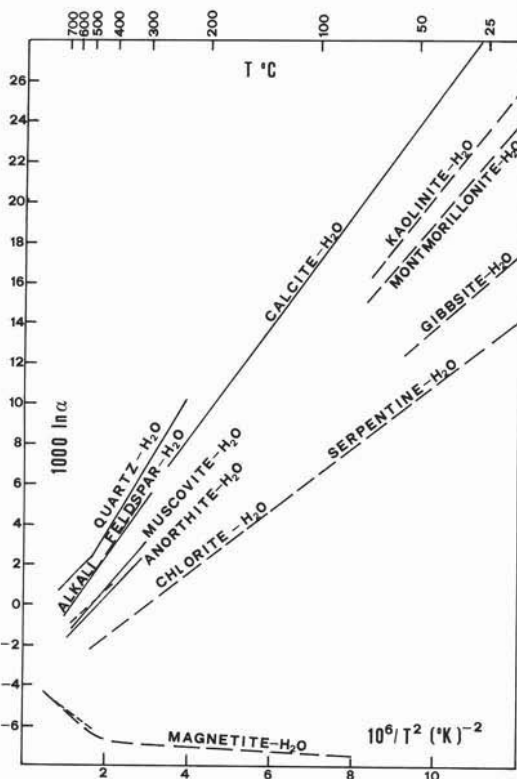


Fig. 1. — Experimentally determined  $^{18}\text{O}/^{16}\text{O}$  fractionation curves for some mineral-water systems.

BIGEISEN and MAYER, 1947). Therefore, the fractionations occurring in deep-seated assemblages are typically smaller than those occurring in supragenetic environments.

Among the 6 light elements listed above, oxygen and subordinately hydrogen proved to be the most useful in petrological studies.

Oxygen is the most abundant element in ordinary rocks, making up about 50% by weight; it is therefore a major constituent of most minerals present in igneous, metamorphic, and sedimentary rocks, as well as of a variety of fluids occurring in both surface and deep-seated environments. Hydrogen is by far less abundant than oxygen in the rocks; its concentration varies from trace amounts in many basaltic and ultramafic rocks to about 1-1.5 wt.% in clays and serpentinites. It is, however, a constituent of many important minerals (micas, amphiboles, zeolites, and so forth) and fluids ( $\text{H}_2\text{O}$ ,  $\text{CH}_4$ ,  $\text{H}_2\text{S}$ , etc.).

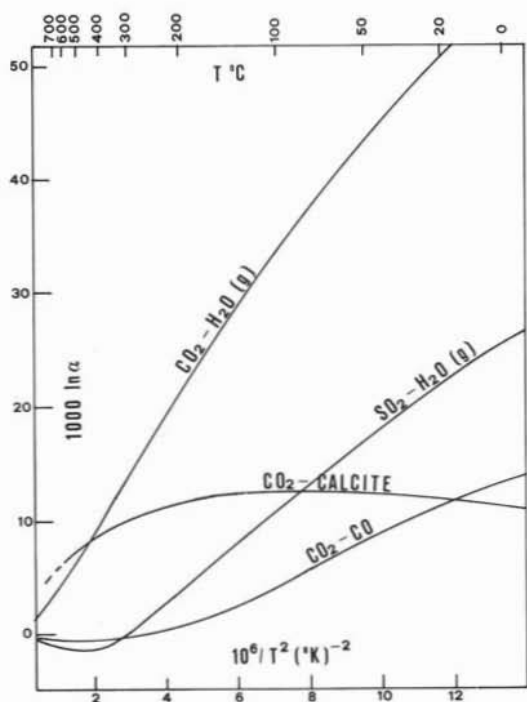


Fig. 2. — Calculated  $^{18}\text{O}/^{16}\text{O}$  fractionation curves for some systems of geological interest illustrating unusual minima, maxima and inflections.

Oxygen and hydrogen isotope analyses are currently being used in petrology to provide information on a variety of problems, like 1) the conditions and mechanisms of minerals and rocks formation; 2) the origin and evolution of magmas; 3) the interactions between magmas and country rocks; 4) the nature of the fluids involved in geological processes; 5) the evaluation of the thermal history and the scale of fluid migration during metamorphic processes; 6) water-rock interactions.

### $^{18}\text{O}/^{16}\text{O}$ variations in minerals and rocks

The  $\delta^{18}\text{O}$  values of natural materials (relative to the Standard Mean Ocean Water, SMOW), vary within the wide range from about -55 (glacier ice near the poles) to +41 (atmospheric  $\text{CO}_2$ ); see Fig. 3.

The variability of  $\delta^{18}\text{O}$  in igneous, metamorphic, and sedimentary rocks is much narrower (Fig. 4).

Sedimentary rocks display the highest  $\delta^{18}\text{O}$  values, igneous rocks the lowest ones; metamorphic rocks have in general  $\delta^{18}\text{O}$  values intermediate between those of the sedimentary and igneous rocks. Such differences in isotopic composition basically reflect the different thermal features of the geological environments where the three types of rocks developed. For example, sedimentary rocks and minerals are markedly enriched in  $^{18}\text{O}$  because of the large fractionations permitted at the low temperatures prevailing in the surface environments.

Within a given family of rocks, the  $\delta^{18}\text{O}$  variation displays some regularities due to the chemical and mineralogical features of the rock. All else being equal, the isotopic properties of a substance depend on the nature of its chemical bonds. In general, bonds to ions with a high ionic potential and low atomic mass tend to incorporate the heavy isotope preferentially. This is basically the reason why in igneous and metamorphic rocks under equilibrium conditions quartz is always the most  $^{18}\text{O}$ -rich mineral and Fe-Ti oxides are always the most  $^{18}\text{O}$ -poor minerals (TAYLOR and EPSTEIN, 1962; GARLICK and EPSTEIN, 1967; O'NEIL, 1977). After quartz, alkali feldspar and plagioclase are the most  $^{18}\text{O}$ -rich minerals; such decrease in the  $^{18}\text{O}$  content of framework silicates results from the progressive replacement of Si-O bonds by Al-O bonds.

Thus, one should expect to observe a regular order of  $^{18}\text{O}$  enrichment in equilibrium mineral assemblage. For example, in granitic rocks, coexisting minerals always concentrate  $^{18}\text{O}$  in the sequence magnetite  $\rightarrow$  biotite  $\rightarrow$  hornblende  $\rightarrow$  muscovite  $\rightarrow$  plagioclase  $\rightarrow$  alkali feldspar  $\rightarrow$  quartz. Sometimes, however, feldspar is enriched in  $^{18}\text{O}$  with respect to quartz (isotopic reversal), and in other cases the  $^{18}\text{O}/^{16}\text{O}$  fractionation between quartz and feldspar displays values like 5 or 6, that is appreciably higher than the normal ones (1.0-2.5; TAYLOR, 1978). Such granites were conceivably «disturbed» by some later event such as an isotopic exchange with external fluids at low and high temperatures, respectively; the mineral assemblages did not retain the original

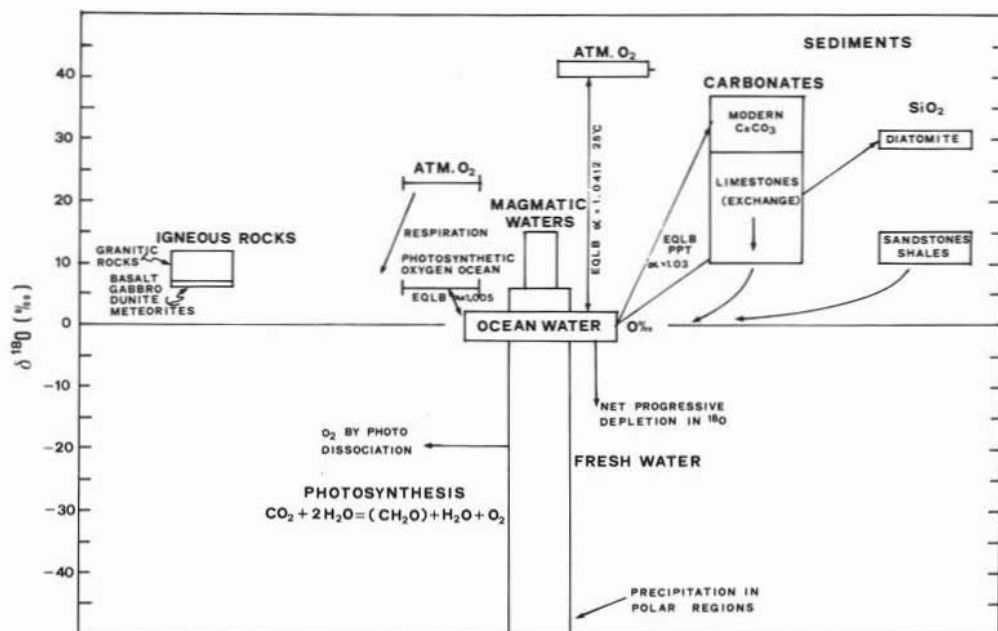


Fig. 3. — Oxygen isotope variations in nature. (Modified after BOATO, 1961)

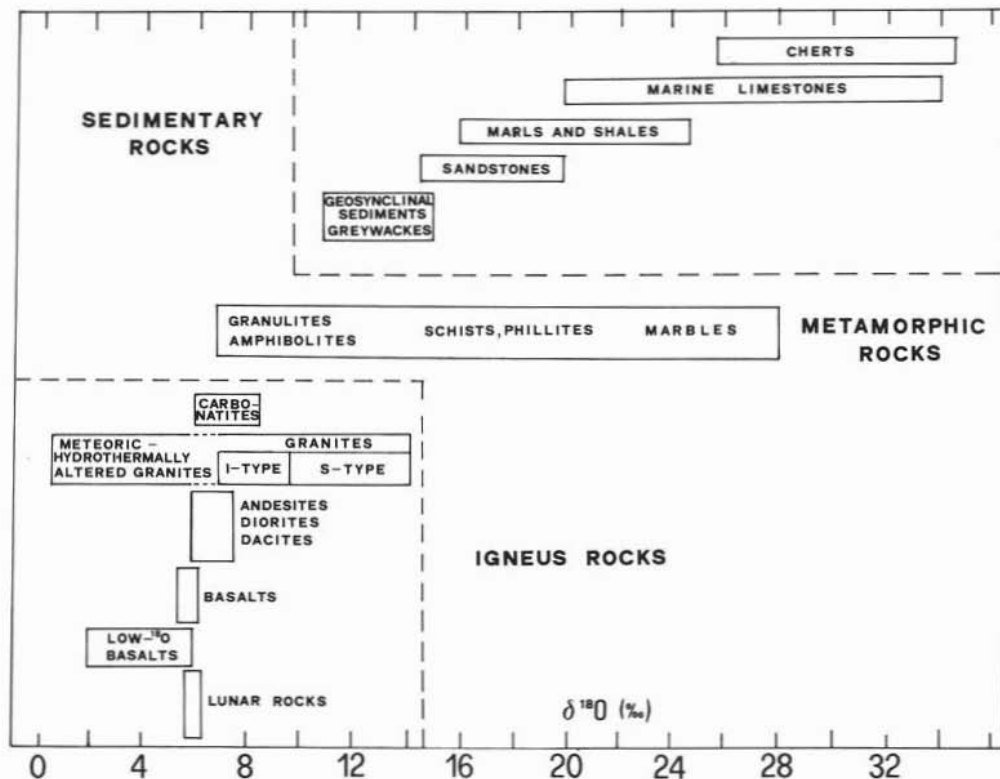


Fig. 4. — Oxygen isotope compositions of igneous, metamorphic and sedimentary rocks.

isotopic equilibrium because the various minerals exchanged to different extents with the fluids. From the above discussion it

becomes clear why, as far as «normal» igneous rocks is concerned, the more  $\text{SiO}_2$ -rich clans are progressively enriched in  $^{18}\text{O}$ , for the

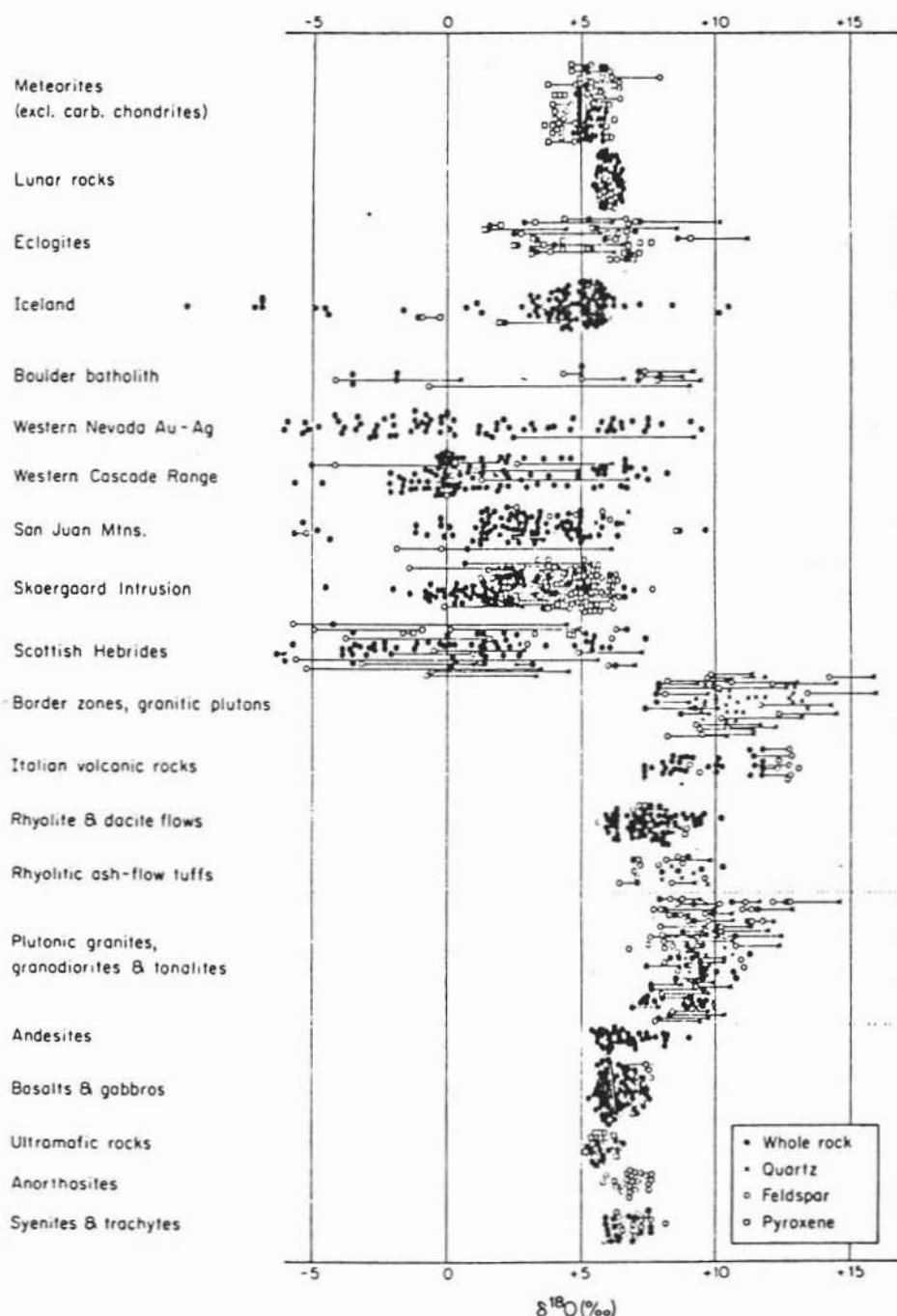


Fig. 5. —  $\delta^{18}\text{O}$ -values of igneous rocks and minerals from various localities throughout the world. (From TAYLOR, 1974; reproduced by permission of the Economic Geology Publishing Company).



sequence from ultramafic rocks through basalts and gabbros, andesites, dacites, tonalites, granodiorites, to rhyolites and granites.

In marine sedimentary rocks, a trend to concentrate  $^{18}\text{O}$  similar to that outlined above is noticeable among authigenic minerals, resulting in a progressive decrease in  $^{18}\text{O}/^{16}\text{O}$  in going from cherts through carbonates and shales to ferromanganese nodules (KNAUTH and EPSTEIN, 1976; KOLODNY and EPSTEIN, 1976; SAVIN and EPSTEIN, 1970; VEIZER and HOEFS, 1976; FIELD et al., 1983). Note that, with respect to other classes of minerals, carbonates are enriched in  $^{18}\text{O}$  because their oxygen is bonded to the small, highly charged  $\text{C}^{4+}$  ion (O'NEIL, 1977).

### Some applications of oxygen isotopes in igneous petrology

The oxygen isotopic composition of igneous rocks is portrayed in Fig. 5.

This compilation represents the state of the art in 1974; since then, of course, a huge amount of new analyses have been produced, and the data base is now so voluminous to make it practically impossible to synthesize it in a single diagram. In spite of this, Fig. 5 still represents the main features of the  $^{18}\text{O}$  variations in igneous rocks.

#### 1. Basaltic rocks

The most abundant type of igneous rocks produced at present on Earth is represented by the mid-ocean ridge basalts (MORB). Modern MORB are remarkably uniform in  $\delta^{18}\text{O}$  ( $5.7 \pm 0.3$ ); very similar values are observed in many ultramafic products (e.g. TAYLOR, 1968; KYSER et al., 1981, 1982). This strongly suggest the existence of a large reservoir in the upper mantle very uniform in  $^{18}\text{O}/^{16}\text{O}$ ; as shown by radiogenic isotope studies, however, this reservoir is «depleted» in LIL elements and radiogenic  $^{87}\text{Sr}$ .

The average  $\delta^{18}\text{O}$  of MORB is nicely

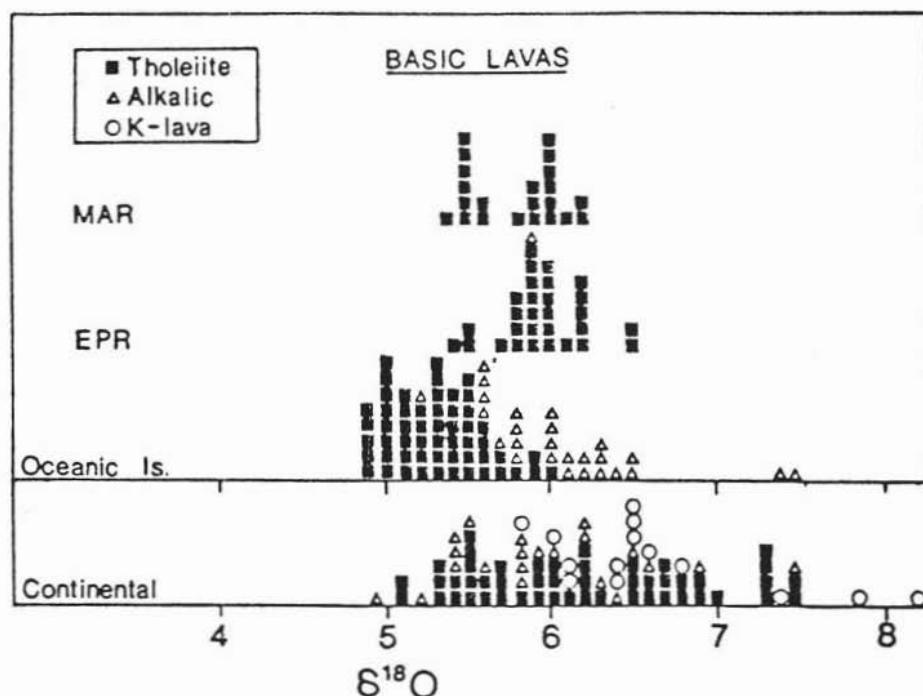


Fig. 6. —  $\delta^{18}\text{O}$ -values of fresh, uncontaminated tholeiites, alkali basalts and potassic lavas from continental and oceanic areas. EPR = East Pacific Rise; MAR = Mid-Atlantic Ridge. (From KYSER, 1986; reproduced by permission of the Mineralogical Society of America).

comparable to that obtained for lunar basalts. The extreme uniformity in  $\delta^{18}\text{O}$  of the Moon is attributed to the lack of water and consequently to the absence of low-temperature alteration processes.

It is therefore conceivable to conclude that, in terms of oxygen isotopes, only minor differences exist between the Earth and the Moon (which appeared to have formed from the same bulk reservoir), as well as between the Earth-Moon system and the ordinary chondrites, which represent the most abundant types of meteorites (CLAYTON, 1976; TAYLOR and SHEPPARD, 1986).

The oxygen isotopic composition of fresh, uncontaminated tholeiites and alkali basalts from oceanic islands (OIB) and continental basalts and potassic lavas are shown in Fig. 6. Also shown for comparison are many  $\delta^{18}\text{O}$  analyses of basalts (mostly tholeiites) from the Mid Atlantic Ridge (MAR) and East Pacific Rise (EPR); note that these two groups of MORB are practically indistinguishable.

A considerable overlap is evident in the  $\delta^{18}\text{O}$  values of OIB and MORB; however, tholeiites from oceanic islands tend to be lower in  $\delta^{18}\text{O}$  than those from oceanic ridge systems, averaging 5.4, whereas alkali basalts tend to have higher  $\delta^{18}\text{O}$  values, averaging 6.1, relative to tholeiitic basalts, whether they come from oceanic ridges or islands (KYSER et al., 1982). Tholeiitic and alkali basalts from continental areas are quite variable in  $^{18}\text{O}/^{16}\text{O}$  with  $\delta^{18}\text{O}$  mostly between about 5 and 7.5 (TAYLOR, 1968; KYSER et al., 1982).

Continental potassic lavas have typically  $\delta^{18}\text{O}$  values relatively high, from about 6 to 8 (TAYLOR et al., 1984; FERRARA et al., 1985, 1986). These variations in  $\delta^{18}\text{O}$  attest to the  $^{18}\text{O}/^{16}\text{O}$  heterogeneity in the upper mantle beneath the continents. The most plausible processes responsible of such heterogeneity are 1) subduction processes; 2) high-temperature metasomatic exchange of upper mantle minerals with external, oxygen-bearing fluids ( $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , etc.). Leucite-bearing lavas can show  $\delta^{18}\text{O}$  values as high as about 10 (TURI and TAYLOR, 1976; TAYLOR et al., 1979; FERRARA et al., 1986); much of this  $^{18}\text{O}$ -enrichment, however, is due to interactions with the  $^{18}\text{O}$ -rich continental crust. The

highest  $\delta^{18}\text{O}$  values of leucitites or nephelinites attributable to upper mantle processes are very likely around 7.5-8.0 (KYSER et al., 1982). The primitive high  $^{18}\text{O}$ -contents of some  $\text{SiO}_2$ -undersaturated alkalic magmas can be attributed to a precursor metasomatic activity that brought about an enrichment in  $^{18}\text{O}$  (and in LIL elements as well) of their source regions in the upper mantle. The relatively high- $^{18}\text{O}$  alkali basalts ( $\delta^{18}\text{O} = 6.5$  or somewhat higher) probably derived from partial melting of metasomatically  $^{18}\text{O}$ -enriched peridotites (GREGORY and TAYLOR, 1986).

## 2. Water-rock interactions

Volcanic and plutonic rocks with  $\delta^{18}\text{O}$  values much lower than 5 have been found in various localities throughout the world. Some of them, such as some low- $^{18}\text{O}$  basalts from Iceland (MUEHLENBACHS et al., 1974) and the Seychelles granite pluton (TAYLOR, 1977), definitely crystallized from anomalously low- $^{18}\text{O}$  magmas; the majority of such rocks are instead the results of sub-solidus meteoric-hydrothermal alteration.

Meteoric waters are typically depleted in both  $^{18}\text{O}$  and D relative to seawater (CRAIG, 1961). Isotopic exchange between such waters and rocks at moderate to high temperatures results in appreciable reductions of the  $\delta^{18}\text{O}$  and  $\delta\text{D}$  of the rocks, with corresponding enrichments in the  $\delta^{18}\text{O}$  and  $\delta\text{D}$  of the water. These types of hydrothermal systems, which represent the «fossil» equivalents of the deep portions of modern geothermal systems, occur wherever igneous intrusions are emplaced into permeable water-saturated rocks near the earth's surface. Silica-rich, calcalkaline magmas are most commonly involved in such systems, probably because viscous magmas tend to form stubby intrusions and because their explosive character promotes fracturing (TAYLOR, 1974, 1977).

So far, over than 50 meteoric-hydrothermal systems, very variable in size, have been recognized (CRISS and TAYLOR, 1986). The relatively smaller ones (less than 100 km<sup>2</sup>, such as Tonopah, Nevada (TAYLOR, 1973),



Bodie, California (O'NEIL et al., 1973), Skaergaard, Greenland (TAYLOR and FORESTER, 1979), Ardnamurchan, Scotland (TAYLOR and FORESTER, 1971) in general developed around small stocks and volcanic centers, whereas much larger systems, ranging from 100's to 1000's km<sup>2</sup> in extent, are associated with large calderas and batholiths; examples are the Idaho batholith (TAYLOR and MAGARITZ, 1978; CRISS and TAYLOR, 1983) the Mull and Skye volcanic centers, Scotland (FORESTER and TAYLOR, 1976, 1977), and the Lake City caldera, Colorado (LARSEN and TAYLOR, 1986).

Even larger systems (10,000 km<sup>2</sup>?) occur where oceanic spreading centers impinge into subaerial environments, like at Jabal at Tif, Saudi Arabia (TAYLOR, 1980).

The application of the stable isotope techniques to the fossil meteoric-hydrothermal systems represents a powerful and unique tool for elucidating the fluid/rock processes in the inaccessible parts of the crust. The stable isotope analyses allow us to estimate the initial isotopic composition of the fluid and the relative proportions of fluid and rock involved in the exchange. It is now known that fluid circulation is usually concentrated along major structures, although substantial quantities of fluid can also migrate along minor fractures and grain boundaries. NORTON and TAYLOR (1979) made a computer simulation of the Skaergaard meteoric-hydrothermal system. They were able to demonstrate that most of the sub-solidus hydrothermal exchange in the intrusion took place at very high temperatures (400-800°C) and that, over the 500,000-year lifetime of the system, integrated amounts of 100 to 5000 kg of water have flowed through each cm<sup>2</sup> cross-section of rock above the level of the unconformity separating a 9 km-thick pile of permeable Early Tertiary basalts from the underlying Precambrian gneiss, much less permeable.

Fluid circulation can often attain depths of 5 to 10 km (e.g. in the Skaergaard system). Taking into account the areas of these systems and the volumes of rocks involved, it turns out that a significant portion of the earth's crust has experienced such a type of meteoric-hydrothermal alteration.

Meteoric-hydrothermal fluids play an important role in ore deposition (TAYLOR, 1974, 1979; O'NEIL and SILBERMAN, 1974; BETHKE and RYE, 1979; CASADEWALL and OHMOTO, 1977; and others). Such type of fluids are almost invariably responsible for the formation of the epithermal ore deposits, a class of shallow-level mineralizations developed in environments with striking analogies with modern geothermal systems (FIELD and FIFAREK, 1985). Meteoric waters also participate in the genesis of numerous deeper, higher temperature ore deposits, usually together with fluids of different origin (e.g. magmatic). To conclude this section, it is worth noting that if the interactions with meteoric waters take place at low temperatures, like those occurring during weathering, glass hydration, and in the low-temperature portions of some meteoric-hydrothermal systems (TAYLOR, 1968; LAWRENCE and TAYLOR, 1971; CRISS et al., 1984), the  $\delta^{18}\text{O}$  of the altered rocks can actually be increased, because of the large values of the mineral-water fractionation factors at low temperatures.

### 3. High-<sup>18</sup>O igneous rocks

The majority of the igneous rocks on Earth have  $\delta^{18}\text{O}$  values lower than about 10, typically between 5 and 10 (Fig. 5). Igneous rocks with  $\delta^{18}\text{O} > 10$ , however, are not so rare, and their widespread occurrence has progressively been recognized in the last ten years. This explains why such rocks are scarcely represented in Fig. 5. The high-<sup>18</sup>O igneous rocks are mostly represented by granitoids and their volcanic equivalents. They can be divided into 3 subgroups, depending upon their anomalously high <sup>18</sup>O/<sup>16</sup>O ratios are a) inherited from the original magmas; 2) the result of high-temperature interactions with high-<sup>18</sup>O country rocks, or c) the result of a secondary event like weathering or low-temperature hydrothermal alteration, as discussed in the previous section (TAYLOR, 1978).

Subgroup a) includes plutonic and volcanic rocks crystallized from magmas of crustal origin. High-<sup>18</sup>O, alumina-rich sedimentary

and metasedimentary rocks played an important role in the genesis of such magmas. Most, but not all, of these have also high  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios (say,  $> \sim 0.710$ ); the strontium isotopic composition is in fact controlled by the Rb/Sr ratios of the source material and the difference between the age of this material and the one of the partial melting event.

One of the first examples of high- $^{18}\text{O}$  magmas reported in the literature is the Plio-Pleistocene, anatectic Tuscan Province, north-central Italy, which consists of a number of rhyolitic volcanic centers and epizonal granitic intrusions with  $\delta^{18}\text{O} = 11$  to 16 (TAYLOR and TURI, 1976 and unpublished data). The highest- $^{18}\text{O}$  magmas yet known have been observed at Tolfa, the southernmost district of the province ( $\delta^{18}\text{O}$  of K-feldspar = 15.1-16.1). More recently, several other occurrences of high- $^{18}\text{O}$  granitoids have been observed throughout the world. Examples are the Late Proterozoic to Mesozoic transformation series (analogous to the «S-type» granitoids) of South China, with  $\delta^{18}\text{O} = 9$ -14 and  $^{87}\text{Sr}/^{86}\text{Sr} > 0.710$  (D. ZHANG et al., 1984; L. ZHANG et al., 1984); the peraluminous Cenozoic adamellite and granites of the North Himalaya, High Himalaya and Paleozoic «Lesser Himalaya», with  $\delta^{18}\text{O} = 9.2$  to 14 (mostly  $> 11$ ; BLATTNER et al., 1983; VIDAL et al., 1984; DEBON et al., 1986) and  $^{87}\text{Sr}/^{86}\text{Sr}$  mostly  $> 0.720$ ; the Hercynian aluminopotassic granitoids of southwest and central Europe, with  $\delta^{18}\text{O}$  values mostly between 10.0 and 13.5 (VIDAL et al., 1984); the «S-type» (pelitic) granitoids of SE Australia (O'NEIL and CHAPPELL, 1977; O'NEIL et al., 1977), with  $\delta^{18}\text{O} \approx 10$ -12.

### Closing statement

Stable isotope geochemistry is mostly concerned with the natural variations of the isotope ratios of 6 elements of low atomic number (H, C, O, N, S, and Si); among these, oxygen is by far the most important because it is a major constituent of ordinary rocks as well as of many naturally occurring fluids. Stable isotope analyses of minerals and rocks are more and more being used to provide

information on a variety of petrological problems regarding sedimentary, metamorphic, and igneous rocks; they also proved to be very useful in understanding the origin of magmas, especially when combined with analyses of the radiogenic isotopes of heavy elements.

$^{18}\text{O}/^{16}\text{O}$  (and D/H) analyses are of fundamental importance to elucidate the role of fluids in geological processes; among other things, this approach gave a significant contribution to our knowledge of the metasomatic processes occurring in the upper mantle and demonstrated that high- and low-temperature interactions between meteoric waters and rocks are widespread and significant in the Earth's crust.

### REFERENCES

- BETHKE P.M., RYE R.O. (1979) - *Environment of ore deposition in the Creede mining district, San Juan Mountains, Colorado - Part IV, Source of fluids from oxygen, hydrogen and carbon isotope studies*. Econ. Geol., 74, 1832-1851.
- BIGEISEN J., MAYER M.G. (1947) - *Calculation of equilibrium constants for isotopic exchange reactions*. Journ. Chem. Phys., 15, 261-267.
- BLATTNER P., DIETRICH V., GANSSER A. (1983) - *Contrasting  $^{18}\text{O}$  enrichments and origins of High Himalayan and Transhimalayan intrusives*. Earth Planet. Sci. Lett., 65, 276-286.
- BOATO G. (1961) - *Isotope fractionation processes in nature*. Summer Course on Nuclear Geology, Varenna, 1960; Pisa, Laboratorio di Geologia Nucleare, 129-149.
- CASADEVALL T., OHMOTO H. (1977) - *Sunnyside mine, Eureka mining district, San Juan Country, Colorado. Geochemistry of gold and base-metal ore deposition in a volcanic environment*. Econ. Geol., 72, 1285-1320.
- CLAYTON R.N. (1976) - *A classification of meteorites based on oxygen isotopes*. Earth Planet. Sci. Lett., 30, 10-18.
- CRAIG H. (1961) - *Isotopic variations in meteoric waters*. Science, 133, 1702-1703.
- CRISS R.E., TAYLOR H.P. JR. (1983) - *An  $^{18}\text{O}/^{16}\text{O}$  and D/H study of Tertiary hydrothermal systems in the southern half of the Idaho Batholith*. Bull. Geol. Soc. Am., 94, 640-663.
- CRISS R.E., TAYLOR H.P. JR. (1986) - *Meteoric-hydrothermal systems*. In: VALLEY J.W., TAYLOR H.P. JR., O'NEIL J.R. (Eds.), *Stable Isotopes in High Temperature Geological Processes; Reviews in Mineralogy* 16, 373-424.
- CRISS R.E., EKREN E.B., HARDYMAN R.F. (1984) - *Casto ring zone: a 4,500 km<sup>2</sup> fossil hydrothermal system in the Challis volcanic field, central Idaho*. Geology, 12, 331-334.

- DEBON F., LE FORT P., SHEPPARD S.M.F., SONET J. (1986) - The four plutonic belts of the Transhimalaya-Himalaya: a chemical, mineralogical, isotopic and chronological synthesis along a Tibet-Nepal section. *Jour. Petrol.*, 27, 219-250.
- FERRARA G., LAURENZI M.A., TAYLOR H.P. JR., TONARINI S., TURI B. (1985) - Oxygen and strontium isotope studies of K-rich volcanic rocks from the Alban Hills, Italy. *Earth Planet. Sci. Lett.*, 75, 13-28.
- FERRARA G., PREITE MARTINEZ M., TAYLOR H.P. JR., TONARINI S., TURI B. (1986) - Evidence for crustal assimilation, mixing of magmas, and a  $^{87}\text{Sr}$ -rich upper mantle: An oxygen and strontium isotope study of the Vulturnian District, Central Italy. *Contrib. Mineral. Petrol.*, 92, 269-280.
- FIELD C.W., RYE R.O., DYMOND J.R., WHELAN J.F., SENECHAL R.G. (1983) - Metalliferous sediments of the East Pacific. In: SHANKS W.C., III (Ed.), *Cameron Volume on Unconventional Mineral Deposits*, Society of Mining Engineers, New York, 133-156.
- FIELD C.W., FIFAREK R.H. (1985) - Light stable-isotope systematics in the epithermal environment. In: BERGER B.R., BETHKE P.M. (Eds.), *Geology and Geochemistry of Epithermal Systems*, Reviews in Economic Geology, 99-128.
- FORESTER R.W., TAYLOR H.P. JR. (1976) -  $^{18}\text{O}$ -depleted igneous rocks from the Tertiary complex of the Isle of Mull, Scotland. *Earth Planet. Sci. Lett.*, 32, 11-17.
- FORESTER R.W., TAYLOR H.P. JR. (1977) -  $^{18}\text{O}/^{16}\text{O}$ ,  $\text{D}/\text{H}$  and  $^{13}\text{C}/^{12}\text{C}$  studies of the Tertiary igneous complex of Skye, Scotland. *Amer. Jour. Sci.*, 277, 136-177.
- FRIEDMAN I., O'NEIL J.R. (1977) - *Compilation of stable isotope fractionation factors of geochemical interest*. In: FLEISCHER M. (Ed.), *Data of Geochemistry*, 6th Ed., U.S. Gov. Printing Office, Washington, D.C.
- GARLICK G.D., EPSTEIN S. (1967) - Oxygen isotope ratios in coexisting minerals of regionally metamorphosed rocks. *Geochim. Cosmochim. Acta*, 31, 181-214.
- GREGORY R.T., TAYLOR H.P. JR. (1986) - Non-equilibrium, metasomatic  $^{18}\text{O}/^{16}\text{O}$  effects in upper mantle mineral assemblages. *Contrib. Mineral. Petrol.*, 93, 124-135.
- KNAUTH L.P., EPSTEIN S. (1976) - Hydrogen and oxygen isotope ratios in nodular and bedded cherts. *Geochim. Cosmochim. Acta*, 40, 1095-1108.
- KOLODNY Y., EPSTEIN S. (1976) - Stable isotope geochemistry of deep sea cherts. *Geochim. Cosmochim. Acta*, 40, 1195-1209.
- KYSER T.K., O'NEIL J.R., CARMICHAEL I.S.E. (1981) - Oxygen isotope thermometry of basic lavas and mantle nodules. *Contrib. Mineral. Petrol.*, 77, 11-23.
- KYSER T.K., O'NEIL J.R., CARMICHAEL I.S.E. (1982) - Genetic relations among basic lavas and ultramafic nodules: evidence from oxygen isotope compositions. *Contrib. Mineral. Petrol.*, 81, 88-102.
- KYSER T.K. (1986) - Stable isotope variations in the mantle. In: VALLEY J.W., TAYLOR H.P. JR., O'NEIL J.R. (Eds.), *Stable Isotopes in High Temperature Geological Processes*. Reviews in Mineralogy, 16, 141-164.
- LARSON P.B., TAYLOR H.P. JR. (1986) - An oxygen isotope study of hydrothermal alteration in the Lake City caldera, San Juan Mountains, Colorado. *Jour. Volcanol. Geotherm. Res.*, 30, 47-82.
- LAWRENCE J.R., TAYLOR H.P. JR. (1971) - Deuterium and oxygen-18 correlation: Clay minerals and hydroxides in Quaternary soils compared to meteoric waters. *Geochim. Cosmochim. Acta*, 35, 993-1003.
- MUEHLENBACHS K., ANDERSON A.T., SIGVALDASON G.E. (1974) - Low- $^{18}\text{O}$  basalts from Iceland. *Geochim. Cosmochim. Acta*, 38, 577-588.
- NORTON D., TAYLOR H.P. JR. (1979) - Quantitative simulation of the hydrothermal systems of crystallizing magmas on the basis of transport theory and oxygen isotope data: an analysis of the Skaergaard intrusion. *Jour. Petrol.*, 20, 421-486.
- O'NEIL J.R. (1977) - Stable isotope in mineralogy. *Phys. Chem. Minerals*, 2, 105-123.
- O'NEIL J.R., SILBERMAN M.L., FABBII B.P., CHESTERMAN C.W. (1973) - Stable isotope and chemical relations during mineralization in the Bodie Mining District, Mono County, California. *Econ. Geol.*, 68, 765-784.
- O'NEIL J.R., SILBERMAN M.L. (1974) - Stable isotope relations in epithermal Au-Ag deposits. *Econ. Geol.*, 69, 902-909.
- O'NEIL J.R., CHAPPELL B.W. (1977) - Oxygen and hydrogen isotope relations in the Barriedale batholith. *Jour. Geol. Soc. London*, 133, 559-571.
- O'NEIL J.R., SHAW S.E., FLOOD R.H. (1977) - Oxygen and hydrogen isotope compositions as indicators of granite genesis in the New England batholith, Australia. *Contrib. Mineral. Petrol.*, 62, 313-328.
- SAVIN S.M., EPSTEIN S. (1970) - The oxygen and hydrogen isotope geochemistry of clay minerals. *Geochim. Cosmochim. Acta*, 34, 25-42.
- TAYLOR H.P. JR. (1968) - The oxygen isotope geochemistry of igneous rocks. *Contrib. Mineral. Petrol.*, 19, 1-71.
- TAYLOR H.P. JR. (1974) - The application of oxygen and hydrogen isotope studies to problems of hydrothermal alteration and ore deposition. *Econ. Geol.*, 69, 843-883.
- TAYLOR H.P. JR. (1977) - Water/rock interaction and the origin of  $\text{H}_2\text{O}$  in granitic batholiths. *Jour. Geol. Soc. London*, 133, 509-558.
- TAYLOR H.P. JR. (1978) - Oxygen and hydrogen isotope studies of plutonic granitic rocks. *Earth Planet. Sci. Lett.*, 38, 177-210.
- TAYLOR H.P. JR. (1979) - Oxygen and hydrogen isotope relationships in hydrothermal mineral deposits. In: BARNES H.L. (Ed.), *Geochemistry of Hydrothermal Ore Deposits* 2nd Ed., J. Wiley & Sons, New York, 236-277.
- TAYLOR H.P. JR. (1980) - Stable isotope studies of spreading centers and their bearing on the origin of granophyres and plagiogranites. *Colloques internationaux du CNRS n° 272 - Associations mafiques et ultramafiques dans les orogènes*, 149-165.
- TAYLOR H.P. JR., EPSTEIN S. (1962) - Relationship between  $^{18}\text{O}/^{16}\text{O}$  ratios in coexisting minerals of igneous and metamorphic rocks. *Bull. Geol. Soc. Am.*, 73, 675-694.
- TAYLOR H.P. JR., FORESTER R.W. (1971) - Low- $^{18}\text{O}$  igneous rocks from the intrusive complexes of Skye, Mull and Ardnamurchan, Western Scotland. *Jour. Petrol.*, 12, 465-497.
- TAYLOR H.P., FORESTER R.W. (1979) - An oxygen and hydrogen isotope study of the Skaergaard intrusion and

- its country rocks: a description of a 55 M.Y. old fossil hydrothermal system.* Jour. Petrol., 20, 355-419.
- TAYLOR H.P. JR., MAGARITZ M. (1978) - *Oxygen and hydrogen isotope studies of the Cordilleran batholiths of western North America.* In: ROBINSON B.W. (Ed.), *Stable Isotopes in the Earth Sciences*, DSIR Bull., 220, 151-173.
- TAYLOR H.P. JR., GIANNETTI B., TURI B. (1979) - *Oxygen isotope geochemistry of the potassic igneous rocks from the Roccamonfina volcano, Roman Comagmatic Region, Italy.* Earth Planet. Sci. Lett., 46, 81-106.
- TAYLOR H.P. JR., SHEPPARD S.M.F. (1986) - *Igneous rocks: I. Processes of isotopic fractionation and isotope systematics.* In: VALLEY J.W., TAYLOR H.P. JR., O'NEIL J.R. (Eds.), *Stable Isotopes in High Temperature Geological Processes.* Reviews in Mineralogy, 16, 227-271.
- TAYLOR H.P. JR., TURI B. (1976) - *High- $^{18}\text{O}$  igneous rocks from the Tuscan Magmatic Province, Italy.* Contrib. Mineral. Petrol., 55, 33-54.
- TAYLOR H.P. JR., TURI B., CUNDARI A. (1984) -  *$^{18}\text{O}/^{16}\text{O}$  and chemical relationships in K-rich volcanic rocks from Australia, East Africa, Antarctica and San Venzano-Cupaello, Italy.* Earth Planet. Sci. Lett., 69, 263-275.
- TURI B., TAYLOR H.P. JR. (1976) - *Oxygen isotope studies of potassic volcanic rocks of the Roman Province, Central Italy.* Contrib. Mineral. Petrol., 55, 1-31.
- VEIZER J., HOEFS J. (1976) - *The nature of  $^{18}\text{O}/^{16}\text{O}$  and  $^{13}\text{C}/^{12}\text{C}$  secular trends in sedimentary carbonate rocks.* Geochim. Cosmochim. Acta, 40, 1387-1395.
- VIDAL P., BERNARD-GRIFFITHS J., COCHERIE A., LE FORT P., PEUCAT J.J., SHEPPARD S.M.F. (1984) - *Geochemical comparison between Himalayan and Hercynian leucogranites.* Phys. Earth Planet. Inter. 35, 179-190.
- ZHANG D., HUANG F., ZHENG S. (1984) - *The oxygen, hydrogen and carbon isotope studies of tungsten-bearing granitoids.* In: XU T., TU G. (Eds.), *Geology of Granites and their Metallogenic Relations.* Science Press, Beijing, China, 875-890.
- ZHANG L., GUO Y., QU P. (1984) - *A study on the oxygen isotopes of some Mesozoic granitoids in southeastern China.* In: XU T., TU G. (Eds.), *Geology of Granites and their Metallogenetic Relations.* Science Press, Beijing, China, 905-919.