

The isotope geology of oxygen*

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ABSTRACT

Natural silicates vary in their O^{18}/O^{16} ratios by as much as 2.4%. This difference is largely due to an exchange reaction between silica and water during the processes of erosion and sedimentation, as a result of which sedimentary rocks are richer in O^{18} than are the igneous rocks. The temperature coefficient for the silica-water exchange has been estimated to be -0.128‰ per degree Centigrade.

The O^{18} content of basic igneous rocks is low and confined to a narrow range (6.4 to 7.0‰). The alkalic and granitic igneous rocks are richer in O^{18} , and their isotopic ratios are more variable (7.7 to 12.2‰). In granitic rocks, quartz shows a greater preference for O^{18} than does orthoclase; the distribution coefficient is 1.20 in favor of the quartz.

The isotopic constitution of stony meteorites is identical to that of the basic igneous rocks, but tektites resemble the sedimentary rocks in their isotopic composition. The analysis of a granophyre-gabbro sequence revealed an isotopic gradient which suggests solid diffusion as the mode of origin for the intermediate rock. The mechanism of metamorphism has been studied from the standpoint of isotopic composition. The results are not conclusive, but suggest that metamorphism is associated with a depletion of O^{18} .

INTRODUCTION

The existence of measurable variations in the isotopic composition of the silicate oxygen of the lithosphere, and the significance of these differences have already been suggested [1], [2]. The purpose of this paper is to consider these variations and their implications in the light of current knowledge of isotopic phenomena.

The dependence of the energy, and consequently all thermodynamic properties, of vibrating and rotating molecules upon the masses of their constituent atoms [3], [4], [5] is responsible for the slight differences in the properties of isotopic substances. The validity of these fundamental principles have been assured by the success with which they have been used to predict the experimental results of isotope separations, isotopic exchange reactions, and isotopic reaction rates in the laboratory. The application of these principles, wherever possible, may serve to reveal the chemical and physical processes responsible for the distribution of oxygen isotopes in nature.

Oxygen is the most important element from a geochemical standpoint since it comprises about 46% of the lithosphere, 86% of the hydrosphere, and 23% by weight of the atmosphere. The relative abundances of oxygen isotopes in the hydrosphere [6], [7], [8] and in the atmosphere [9], [10], [11] have already been determined. The less accessible oxygen combined in the rocks of the lithosphere remains a relatively unexplored field.

Variations in the oxygen isotopic composition of limestones have been utilized in the determination of the temperatures at which these sediments have been deposited [8], [12], [13], [14]. The oxygen isotopic composition of some iron ores [15].

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[16] and of the water contained in certain metamorphic rocks and minerals [17] have also been investigated.

TOKUDA and KASHIDA [18] measured the oxygen isotope abundances in silicates by treating the samples with potassium acid fluoride at 230° C, and the water formed by this reaction was purified in "an appropriate way" and its density compared with that of Osaka tap water. The sensitivity of this method in terms of the O^{18}/O^{16} ratio was reported to be about $\pm 1.4\text{‰}$ (± 0.3 ppm in density units), yet the authors state that they were unable to find any difference between igneous and metamorphic rocks. The slight differences reported by TOKUDA and KASHIDA are significant, but the absence of large differences may have been due to inherent purification difficulties in the density method for isotopic analyses and in some cases due to incomplete oxygen yields.

The oxygen separated from silicates by reaction with chlorine trifluoride and hydrogen fluoride [1], [2] have yielded O^{18}/O^{16} ratios reliable to $\pm 3.0\text{‰}$. The isotopic abundances reported in this paper have been obtained from oxygen liberated by fluorine and hydrogen fluoride [2]. The average deviations in O^{18}/O^{16} ratios for duplicate measurements by this method were less than 0.5‰ for over 70 % of the samples analyzed, and in only one case was the average deviation greater than 1.0‰ .

TERRESTRIAL ABUNDANCES

The relative abundances of the three stable isotopes of oxygen, $O^{16}:O^{17}:O^{18}$, in air have been reported by NIER [19] as $2670 \pm 20:1:5.5 \pm 0.1$. The results of previous relative abundance measurements of the oxygen isotopes in nature have been compiled by THODE [20] and by RAINBRIDGE and NIER [21]. THODE's compilation, which denotes variations in O^{18} abundances ranging as high as 4%, is reproduced here as Table 1.

The differences in O^{18} abundances given in Table 1 are encouraging because they are readily explained by theoretical principles. For example,

it should be expected that the process of evaporation be accompanied by depletion of the heavy isotope in the vapor phase since the vibrational energy of a molecule is inversely proportional to the square root of its reduced mass. In other words, water molecules containing only the light isotope (O^{16}) should have a higher vapor pressure than water molecules containing the heavy isotope (O^{18}). Accordingly, fresh water is depleted in O^{18}

Table 1. Distribution of O^{18} in nature *

Source	Relative abundance of O^{18}
<i>Water:</i>	
Fresh water, Lake Ontario	1.00
Ocean water	1.009
Atmospheric water vapor over Lake Ontario	0.991
Glacier water, Lake Louise	0.977
Dead Sea water	1.020
<i>Air:</i>	
Atmospheric oxygen	1.033
Atmospheric carbon dioxide	1.040
Photosynthetic oxygen	1.006
<i>Rocks:</i>	
Limestone	1.039
Cuprite	1.00
Swedish magnetite	1.00
Iron ores	1.00

* From THODE, H. G.; Research 1949 2 157.

(Table 1) relative to ocean water. The same relation applies to water vapor derived from fresh water, as evidenced by a decrease of 9‰ in the O^{18} abundance of water vapor over Lake Ontario as compared to that of Lake Ontario water. The high concentration of O^{18} in Dead Sea water represents the anticipated enrichment of the heavy isotope in a residual liquid after loss of the O^{16} -rich water by evaporation. The water formed by the melting of glacial ice is 23‰ lower in O^{18} than fresh water. This is in agreement with the concept that isotopic fractionation could occur during the

Table 2. Oxygen isotopic composition in silicate rocks †

Sample and Number	O^{18}/O^{16}	Average	Number of Determinations
	‰	Deviation ‰	
Chicago tap water	-3.2	—	1
Hawaii sea water No. RT-6.	0.0	0.2	2
Columbia River basalt No. 79-PG-5	6.4	0.2	3
Disco basalt No. R-7696	6.6	0.7	3
Mt. Etna lava No. B-1-74	6.7	0.2	4
Dunite No. 25.	6.8	0.5	2
Olivine basalt No. 1	7.0	0.1	3
Yellowstone obsidian No. 47	7.7	0.8	2
Gneissic granite No. 4	7.9	0.2	2
Nepheline syenite No. 14	8.3	0.0	2
Paricutin lava No. K-12	8.5	0.2	4
Cheshire orthoquartzite No. 410	10.2	0.0	3
St. Peter sandstone No. 46	10.9	0.2	2
Arkose No. 2698.	11.4	0.5	2
Basal breccia No. 45	13.2	0.3	2
Quartz vein No. 89	14.0	0.2	4
Brazil quartz No. 26	14.0	0.2	2
Grafton orthoquartzite No. 778	14.7	0.3	2
Wishart orthoquartzite No. F-75	15.1	1.4	2
Potsdam sandstone No. 2039	15.5	0.0	2
Maquoketa shale No. 9	15.5	0.5	2
Atmospheric oxygen	19.2	0.9	2
Dover flint No. 2	29.3	0.5	2
Diatomite No. 13	30.3	0.0	2

† Sources and other information pertaining to these samples are listed in the appendix.

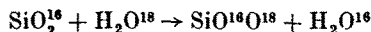
fusion of ice, in which case the O^{16} -rich water molecules, being the most energetic of the possible isotopic combinations, would be prevalent in the early fractions of the liquid phase.

The relative abundances of the oxygen isotopes in igneous, sedimentary, and metamorphic rocks, determined by mass spectrometric analysis of the oxygen liberated by the fluorine method [2], are listed in the order of increasing O^{18}/O^{16} ratio in Table 2. The values are given as deviations of the O^{18}/O^{16} ratio, in parts per thousand (‰), from the same ratio in an arbitrary standard*. The results were adjusted to the Hawaii sea water value which was arbitrarily set equal to zero. On this scale

* The standard used in all analyses was the oxygen derived from pure quartz (Randville pegmatite, No. 10).

Chicago tap water has an abundance of -3.2‰ , which supports our earlier contention that the cycle of evaporation and precipitation should deplete the heavy isotope in fresh water relative to sea water.

The analyses in Table 2 indicate that sediments are consistently higher in O^{18} than are the igneous rocks. This implies that the deposition of silica from solution is accompanied by enrichment of the heavy isotope in the precipitated phase. In accord with this conclusion, diatomaceous deposits (diatomite, No. 13), composed entirely of silica precipitated from solution, have the highest abundance of O^{18} . From the $\text{O}^{18}/\text{O}^{16}$ ratios in sea water and diatomite, the equilibrium constant for the exchange reaction:



may be estimated to be 1.03 at the specific temperature of this precipitation. The equally high abundance of O^{18} in Dover flint (No. 2) implies that this material is

Table 3. Relation of isotope abundances in siliceous sediments to amount of authigenic silica

Sample	$\text{O}^{18}/\text{O}^{16}$ ‰	Per Cent Secondary Silica	Per Cent Increase in $\text{O}^{18}/\text{O}^{16}$ Ratio Difference
St. Peter sandstone No. 46	10.9	0	0
Basal breccia No. 45	13.2	10-15	12
Wishart orthoquartzite No. F-75	15.1	20	21
Dover flint No. 2	29.3	100	95
Diatomite No. 13	30.3	100	100

also a product of chemical precipitation. The correlation of the O^{18} abundances with authigenic silica content (Table 3) indicates that the enrichment of the heavy isotope in sediments is due to surface exchange between the clastic fragments and water.

Of the group of orthoquartzites considered in Table 3, only the St. Peter sandstone is uncemented. The complete absence of interstitial quartz is marked by its low O^{18} abundance relative to other sediments. The Dover flint and diatomite, representing the upper limits of chemically-precipitated silica, are about 20‰ higher (than St. Peter sandstone) in $\text{O}^{18}/\text{O}^{16}$ ratios. The basal breccia, with siliceous overgrowths estimated at about 10-15 %, is 2.3‰ higher in O^{18} than the St. Peter sandstone. This increase is about 12 % of the $\text{O}^{18}/\text{O}^{16}$ ratio difference (Table 3, column 4) between St. Peter sandstone and diatomite. The Wishart orthoquartzite, which contains about 20 % authigenic silica, is 21 % of the above ratio difference higher in O^{18} than the St. Peter sandstone.

The arkose (No. 2698), a deposit attributed to a minimum of sedimentary action, fittingly shows an increase of only 0.5‰ over the $\text{O}^{18}/\text{O}^{16}$ content of St. Peter sandstone.

The relation of the Grafton and Cheshire orthoquartzites is also interesting. Both are from the same general locality; the Grafton occurs as a lens (100 ft in its greatest dimension) included in a deformed, but not recrystallized, shale. The Cheshire is a thick bed (1000 ft thick) unconformably overlying the pre-Cambrian Mt. Holly granite gneiss [22]. Petrographically, the Cheshire orthoquartzite is crystalloblastic

in texture. Original clastic grain boundaries are completely obliterated, and the undulatory extinction characteristic of metamorphic quartzites is evident throughout. Furthermore, the presence of traces of epidote and crystalline sericite serves to classify the rock as a metaquartzite [23] belonging to the epidote-amphibolite facies.

The Grafton also shows indications of metamorphic change, but not as intense as that encountered in the Cheshire. Clastic grain boundaries and overgrowths are still faintly visible, although crystalloblastic textures are prevalent.

The Cheshire orthoquartzite has an isotopic composition of 10.2‰ , which is 0.7‰ lower than that of the St. Peter sandstone. The Grafton, which is the less completely metamorphosed of the two, is higher than the Cheshire by 4.5‰ in its

$\text{O}^{18}/\text{O}^{16}$ ratio. Since the O^{18} abundance of St. Peter sandstone has been taken to represent a lower limit for the undeformed sediments listed in Table 3, it is tempting to conclude that metamorphism results in a decrease in O^{18} content. This implies that metamorphic transformation is accompanied by a transfer of material.

The $\text{O}^{18}/\text{O}^{16}$ ratios of the quartz vein (No. 89) and Brazil quartz (No. 26) are too high to class them among the igneous rocks. This is

Table 4. Temperature coefficients for $\text{O}^{18}/\text{O}^{16}$ fractionations in several exchange reactions*

Exchange Reaction	Temperature Coefficient (‰ per degree Centigrade)
$\text{SO}_4^{2-}-\text{H}_2\text{O}$ (liq.)	-0.188
$\text{CO}_3^{2-}-\text{H}_2\text{O}$ (liq.)	-0.176
$\text{SiO}_2-\text{H}_2\text{O}$ (liq.)	-0.128
$\text{PO}_4^{3-}-\text{H}_2\text{O}$ (liq.)	-0.068

* The values for the carbonate, sulfate, and phosphate exchange reactions have been calculated over the temperature range 0° to 25°C ; that for the silicate covered the range 15° to 140°C .

in accord with present theories which ascribe their origin to precipitation from vein-forming solutions [24]. The lower O^{18} concentrations in these samples than that of diatomite (No. 13) are believed to be due to higher deposition temperatures.

INGERSON [25] has estimated the formation temperature of Brazil quartz to be about 140°C . This figure is based on two "probable best values," 100° and 180°C . Assuming that the diatomite was precipitated at a temperature of 15°C , we have two points on the temperature-isotopic composition scale. Although this relation is not linear, it is not possible to consider it from any other viewpoint in the light of the crude and insufficient data used. Furthermore, because of the inherent differences between fresh and sea water, the O^{18} content of silica precipitated from fresh water should be lower than that deposited in sea water, and this may account for the slight difference between the diatomite (No. 13) and Dover flint (No. 2).

The fractionation factors at 15°C and 140°C (K_{15} and K_{140}) are 1.030 and 1.014, respectively, for the silica-water equilibrium, which indicates a difference of -0.128‰ per degree centigrade. In 1947, UREY [5] noted the similarity in temperature coefficients for the carbonate-water exchange and the sulfate-water exchange and predicted at that time that similar coefficients should exist for the phosphate-water and silica-water exchanges. The temperature coefficients for the carbonate, sulfate, and phosphate exchange reactions have been calculated from experimental data [14] over the temperature range from 0° to 25°C . These values are given in Table 4 along with the temperature coefficient for the silica-water exchange reaction which has been computed as indicated above for the temperature range 15° to 140°C .

The significance of a diminishing isotopic fractionation with increasing temperature will become more evident in later sections of this paper. If we were to retain our erroneous assumption that the silica-water exchange constant is linearly dependent upon the temperature, the last traces of fractionation would be expected to vanish at about 160° C. In any event, at sufficiently high temperatures the thermal contribution to the vibrational energy of the silicate molecule would become great enough to eclipse the mass contribution due to the isotope effect. Under these conditions the exchange constant becomes equal to unity and no fractionation should occur.

The differences in oxygen isotopic abundances which exist between sedimentary and igneous rocks are the results of interactions and redistributions which have occurred since the formation of the earth's crust. Since fractionation of isotopes is not expected at high temperatures, it is reasonable to assume that the oxygen isotopes were uniformly distributed during the molten stage of the earth's crust. The composition of this completely mixed and uniform state shall be referred to as the primordial composition. To determine the primordial composition, it is necessary to obtain a sample of the lithosphere which has been unaltered by erosional processes and uncontaminated by remelted or assimilated sediments. Most geologists will agree that the Plateau and Oceanic basalts fulfill these requirements since they are believed to have arisen from the basaltic shell underlying the earth's crust. The samples selected as representative of this "Mother Magma" were an olivine basalt (No. 1) from Tahiti, the Columbia River basalt (No. 79-PG-5) from Oregon, and the Disco basalt (No. R-7696) from Ovigssak, Greenland.

The olivine basalt is a good example of the Oceanic Province, the Columbia River basalt is typical of the Plateau basalts, and the noble metal content in the metallic phase of the Disco basalt bears a striking similarity to the composition of meteorites [26]. The analyses fall into the range of 6.4 to 7.0‰ (Table 2) and this range of oxygen isotopic composition may be regarded as the primordial composition. The dunite (No. 25), believed to have been formed at great depth, falls within this range with a value of 6.8‰.

The Mt. Etna lava (No. B-1-74), which has an isotopic abundance of 6.7‰, presented no problem, since these lavas are basaltic to andesitic in composition.

The alkaline and granitic rocks are somewhat richer in O¹⁸, with values ranging from 7.7 to 8.3‰. Parícutin lava (No. K-12), although originally basaltic in composition, has been studied by SHAND [27], who calls attention to granitic inclusions, and the high value (8.5‰) of this sample may be due to assimilation of alkalic rocks and sediments.

It is difficult to explain the higher O¹⁸ abundances in granitic rocks as compared with the basic rocks. If the granitic rocks have originated by differentiation from a magma, then on the basis of energy considerations, the earlier crystallizing fraction, i.e. the basic rocks, should be richer in the heavy isotope than the later fractions (granitic rocks). This is not the case, and the discrepancy is given further consideration below in the section dealing with fractional crystallization.

Since the increased O¹⁸ content of sediments is due to an exchange reaction associated with the precipitation of silica from solution, an equivalent amount of O¹⁸ must have been lost by the seas. Using the estimates of KOSSINA [28] and KUENEN [29] for the total masses of the oceans and sediments as 1.4×10^{24} g and 1.9×10^{24} g

respectively, it should be possible to calculate the primitive oxygen isotopic composition of the ocean. Accepting KRYNINEs [30] breakdown of continental sediments and KUENENs [29] estimate for the ratio of continental to deep-sea deposits as 2:5. the overall weighted average for the isotopic composition of sedimentary rocks was calculated to be 23.0‰ .

Since water contains 89 % by weight of oxygen, and sediments an average of 48 %. the total oxygen content of the oceans is 1.2×10^{24} g, and for sediments, 0.9×10^{24} g. The isotopic composition of the oceans at present may be taken as 0.0‰ , the present overall value for sediments is 23.0‰ . Allowing that these deposits evolved from rocks with an original $\text{O}^{18}/\text{O}^{16}$ ratio of 7.0‰ , and letting Y designate the primordial composition of the seas, then the balance may be expressed by:

$$1.2 \times 10^{24}(Y - 0.0) = 0.9 \times 10^{24}(23.0 - 7.0)$$

and Y equals 12.0‰ .

Since deep-sea deposits (mainly clays, muds, and siliceous and calcareous oozes) are assumed to have precipitated chemically, or deposited as very fine clastic particles with very large surface area exposed to the action of sea water, a high value (30.0‰) was assigned to them in the calculation of the weighted average. If KUENENs estimate of 5×10^8 cubic kms for the total volume of deep-sea deposits is too large by a factor of two, we then obtain for the primitive isotopic composition of the seas a value of 7.5‰ which is close to the primordial abundance designated for igneous rocks.

In an earlier estimate, CLARKE [31] has given 3×10^8 cubic kms as the highest possible volume of decomposed igneous rocks. Using this figure and retaining the computed average isotopic abundance for sediments as 23.0‰ , we are now concerned with 8.4×10^{23} g of rock of which 45 % is oxygen. This results in a value of 5.0‰ for the primordial isotopic abundance of the oceans.

Thus far we have barely taken into account the metamorphic and granitic rocks which are shown below to be generally richer in the heavy isotope than are the average basic igneous rocks. If these higher values are the results of sea water (or ground water) action preceding metamorphism and granitization, then the entire sialic layer underlying the continents to a depth of 30 kms must enter into our calculations. For a total land area of 1.5×10^8 square kms, we are now concerned with a volume of 4.5×10^9 cubic kms which weighs 1.3×10^{25} g. Deducting the 1.9×10^{24} g already taken as sedimentary deposits, 1.1×10^{25} g of sialic material remains to be considered. Ninety five per cent of this is granitic [32] and composed of about 48 % by weight of oxygen. If we assign to the 5.0×10^{24} g of oxygen in these rocks an average value of 8.0‰ for the $\text{O}^{18}/\text{O}^{16}$ ratio, it will be necessary to add 4.2‰ to our previous value for the primitive isotopic composition of the seas.

On the grounds that their contribution is negligible, the volume and isotopic composition of ground water, of the oxygen content of the biosphere, or of water vapor and fresh water on the continental masses were not considered in these calculations. Moreover, complete information is still lacking for a precise knowledge of the present distribution of the oxygen isotopes in the oceans. In view of these deficiencies and the questionable estimates used in the above calculations, it is not possible at this time to offer a reliable figure for the primitive composition of the oceans.

COSMIC ABUNDANCES

The only non-terrestrial materials that lend themselves to this method of investigation are meteorites. Four specimens in this category have been analyzed. Of these, the nortonite (No. 24) (achondritic stony meteorite) is the largest meteorite of any type of witnessed fall [33], [34]. Two tektites, moldavite (No. 38) and tektite (No. 40) are included in this group although their origin is still problematic. The results are given in Table 5.

Table 5. Oxygen isotopic abundances in stony meteorites and tektites

Sample	O^{18}/O^{16} ‰	Average Deviation	Number of Determinations
Nortonite No. 24	6.3	0.4	4
Stony meteorite No. 37	6.5	0.8	3
Moldavite No. 38	10.4	0.5	2
Tektite No. 40	10.4	0.1	2

The oxygen isotope ratios for the stony meteorites, 6.3‰ and 6.5‰, fall within the range assigned to the primordial composition of our planet, and may be taken as evidence that meteorites form a counterpart of the subsurface composition of the earth. Previous comparisons of the isotopic composition of iron [35] and oxygen [36] in terrestrial and meteoritic matter have led to the same conclusion. On the strength of observed isotopic shifts in the band spectra of M-type stars, MCKELLAR [37] has concluded that the relative abundances of oxygen isotopes in stellar atmospheres show no significant departure from terrestrial abundances. This statement may now be extended to include the planetary bodies of the Solar System.

The higher isotope ratios for the tektite and moldavite bring them within the range of sedimentary rocks. This is interesting, since chemically the tektites resemble the aluminum-rich argillaceous sediments [38]. If tektites are derived from extra-terrestrial sources, do these data imply that erosional processes are operating on other planets? The analyses of the two samples given above neither add nor detract from the meager evidence for the nonterrestrial origin of tektites. Since all available information indicates that the structure and composition of all the planetary bodies of the Solar System are similar [39], isotopic abundances cannot be used to prove or disprove the extra-mundane origin of matter.

FRACTIONAL CRYSTALLIZATION

The process of fractional crystallization of one component from a melt may or may not be accompanied by fractionation of isotopes. This would depend upon the degree to which equilibrium is attained and the temperature at which crystallization occurs.

In the calculation of equilibrium constants by use of statistical mechanics, the fractionation factor is determined from the ratio of the partition functions Q_2/Q_1 for the molecules with different isotopic compositions. This ratio is given by the expression [5]:

$$\frac{Q_2}{Q_1} = \frac{\sigma_1}{\sigma_2} \pi_i \left\{ 1 - \frac{1}{24} \left[\left(\frac{h c \omega_{2i}}{k T} \right)^2 - \left(\frac{h c \omega_{1i}}{k T} \right)^2 \right] \right\}$$

where σ_1 and σ_2 are the symmetry numbers of the two different isotopic configurations [40], and the $hc\omega$ terms are the corresponding vibrational frequencies for each molecular configuration. π_i signifies the product over all the internal quantum states of the molecules.

At high temperatures the ratio of the partition functions, Q_2/Q_1 , reduces to the ratio of the symmetry numbers, σ_1/σ_2 , and the fractionation factor for the distribution of the oxygen isotopes between the two modifications (solid and liquid, or solid and solution) is determined by this ratio alone. For the oxygen exchange in the silicate ion, which has been shown to possess the same symmetry in both the liquid and the solid states [41], [42], [43], [44], the ratio of the partition functions Q_2/Q_1 (solid) approaches Q_2/Q_1 (liquid) as the temperature assumes high values. Under such conditions, the distribution coefficient for oxygen isotopes between solid and liquid states approaches unity, which implies that isotopic fractionation should not occur during crystallization at the temperature of silicate melts.

In order to verify this assumption, quartz and potash feldspar were separated from rocks of granitic composition, and the isotopic constitutions of these separated components were determined. If the rock was formed by crystallization from a melt at equilibrium conditions, the isotopic abundances of oxygen in the component minerals would disclose whether or not isotopic fractionation had occurred. The size of the mineral grains might be taken as a measure of the degree to which equilibrium was attained. Three sets of samples were analyzed, and these results are given in Table 6.

Table 6. Isotopic fractionation between quartz and potash feldspar

Sample	Quartz			Potash Feldspar			Difference *
	O^{18}/O^{16} ‰	Average Deviation	Number of Deter- minations	O^{18}/O^{16} ‰	Average Deviation	Number of Deter- minations	
Randville pegmatite No. 10 and 11 . . .	10.3	0.2	4	8.8	0.2	4	1.5
Balmoral granite No. 35	7.9	0.4	2	6.2	0.4	2	1.7
Graphic granite No. 31	13.1		1	11.3	—	1	1.8

* O^{18}/O^{16} (quartz) less O^{18}/O^{16} (potash feldspar).

In each case the quartz is richer in the heavy isotope than is the potash feldspar, and from the values in Table 6, the distribution coefficient for O^{18} enrichment between quartz and potash feldspar is 1.20 in favor of the quartz.

With regard to the equilibrium requirements, the Randville pegmatite is very coarse-grained, the graphic granite moderately so, and the Balmoral granite has a typical granular texture. Our criterion for equilibrium was apparently of no noticeable consequence to the isotopic fractionation in these rocks.

In a preceding section it was noted that granitic rocks were richer in O^{18} than the basic rocks which was incongruous with the prediction that the granitic minerals, being the latest crystallizing components of a magma, should have concentrated the

light isotope. The reaction principle [45] establishes a differentiation sequence in which potash feldspar crystallizes at a higher temperature than quartz, and here again the quartz is richer in the heavy isotope.

From the data presented in Table 2, it might appear that each mineral or group of minerals has a specific affinity for a definite oxygen isotopic composition. This thesis could be explained by way of the specific lattice energy associated with each mineral species, since the consequent specific bonding forces could be responsible for the selection of the different isotopes in fixed proportions during crystallization. Thus the isotopic composition of any mineral would depend solely on its chemical and structural composition and be independent of its mode of origin. This hypothesis can be discarded by noting the oxygen isotopic abundances in the three rocks in Table 6. Each is composed of approximately equal amounts of quartz and feldspar. The Balmoral granite has an average O^{18}/O^{16} composition of 7.1‰ which is practically within the primordial composition range. The Randville pegmatite, with an O^{18}/O^{16} value of 9.6‰ , occupies a position intermediate to the alkalic rocks and sediments, and the graphic granite, averaging 12.2‰ , is well within the sedimentary class.

In certain respects, the choice of quartz and potash feldspar was unfortunate. These minerals are the major constituents of granitic rocks, and in view of the present uncertainty of a direct magmatic origin for granites, the results may be entirely irrelevant to the process of fractional crystallization from a melt. These minerals may have formed as a result of solid state reactions; or if the rock had originally crystallized from a melt, the present ratios may be the result of isotopic redistribution over a very long period of time at sub-solidus temperatures. Neither of these alternatives would be contradictory to our earlier assertion of a vanishing fractionation at high temperatures.

It should be noted that the basic igneous rocks have a narrow range of isotopic compositions (6.4 to 7.0‰), and from the standpoint of alteration and contamination, this justifies the acceptance of these rocks as representative material from the depths of the earth. The isotopic abundances of the acidic differentiates are more variable (7.1 to 12.2‰), and this suggests corresponding variations in modes of origin. The detrital constituent of an orthoquartzite, whether derived from igneous rocks, metamorphic rocks, or earlier sandstones, is thus a source of isotopic variation in itself, and the positive correlation of O^{18} abundance with amount of authigenic silica as shown in Table 3 must be discarded as fortuitous.

DIFFUSION IN THE SOLID STATE

Among the foremost of the controversial subjects in geology today is the credence that many of the so-called igneous rocks (*i.e.* those presumed to have crystallized from a primary melt or magma) may have been formed by the introduction and incorporation of atoms or ions into pre-existing sedimentary, igneous, or metamorphic rocks [46]–[51]. The preferential diffusivity of certain ions through solids has been attributed to the differences in the chemical activities of the different ions [51], [52].

If we assume that a given source or center of migrating ions consists of an association of minerals with a definite oxygen isotopic composition, then at the temperature and pressure conditions at any point in this center molecules or ions with

differing isotopic constitutions will have different free energies, and consequently unequal migration tendencies.

The ions richer in the lighter isotope, in view of their higher chemical potential, will have a higher mobility than ions rich in the heavy isotope. For any given amount of movement, a gradual increase in the separation of isotopes should be experienced with increasing distance from the source. This principle of isotope separation by migration of ions through solids was discussed by LINDEMANN [53] in 1921, although subsequent attempts to separate isotopes by ionic migration through gels have been unsuccessful [54].

Laboratory methods are limited by space and time, but such limitations are non-existent in geologic processes. In order to determine whether isotopic separations of this kind have occurred in nature, it is necessary to select a series of properly-spaced samples of rocks from a region in which the silicate ion concentration increases gradually along a definite direction. If the silicate ion is the migrating particle, then the samples farthest from the source of migration should be enriched in the lighter isotope relative to the materials closer to the source.

A sequence which fulfilled these requirements was brought to the attention of the writer by M. W. LEIGHTON, who was kind enough to supply the specimens and field details*.

The specimens were selected from a region in Bayfield County, Wisconsin, where, in a lateral extent of 20 ft, a granophyre passes gradationally into a gabbro. The granophyre is composed of approximately equal amounts of quartz and alkalic feldspar, while 82% of the gabbro is labradorite and the remainder a mixture of hypersthene and augite.

In all, six samples were selected to represent the transition from gabbro to granophyre. Running from north to south, the gabbroic end-member (No. W-187) passes into an intermediate rock (No. W-137-4), which is seven feet north of the site of specimen No. W-137-3. One foot away is No. W-137-2, and two feet farther south is No. W-137-1, which blends into the main granophyric body (No. W-136-4). The samples are listed in Table 7 in the order of their position in the sequence.

The oxygen content of each member, taken as a measure of the silicate ion abundance, is given in column 5 of table 7 as the ratio of cc of oxygen per mg of sample. The trends in the isotope ratios and silicate ion concentrations meet the requirements given above for positive evidence for solid diffusion.

Table 7. Oxygen isotope abundances in the Bayfield County granophyre-gabbro sequence

Sample and Number	O^{18}/O^{16} ‰	Average Deviation	Number of Determina- tions	cc O_2 mg. Sample
Gabbro No. W-187	6.1	0.4	4	0.28
Intermediate rock No. W-137-4	7.7	0.0	2	0.33
Intermediate rock No. W-137-3	8.4	0.3	4	0.35
Contact rock No. W-137-2	8.7	0.3	4	0.36
Granophyre No. W-137-1	9.0	0.2	3	0.39
Granophyre No. W-136-4	9.9	0.8	3	0.36

* A detailed description of the field relations by M. W. LEIGHTON will appear elsewhere.

A petrographic analysis of any part of this rock sequence shows properties which indicate that the mineral assemblage is, directly or indirectly, the product of a crystallization process. Evidence of microscopic or macroscopic channelways which might explain the intrusion of foreign substances is absent. Neither is there any indication, in the form of embayments or other solution effects, that the rocks have assumed their present form as a result of assimilation processes.

In explaining the oxygen isotopic gradient in this extent of rock, it should be noted that in every laboratory method, to date, for isotope separation, reflux is necessary for the production of a measureable effect. If similar limitations apply to isotope separations produced in the course of geologic processes, a closed system must be conceived in which a cyclic geologic process can occur in order to account for the Bayfield County rock sequence. A silicate melt confined in a closed space in nature may experience isotopic separations as a result of the cyclic process known as the Soret effect, which is a crude equivalent of a thermal diffusion column in the laboratory [55]. The Soret effect could not have been responsible for the Bayfield County rock sequence on two counts. Ordinarily, in a Clusius-Dickel thermal diffusion column, the heavy isotope would be expected to concentrate at the "cold wall." In this case the gabbroic country rock would represent the "cold wall" in relation to the included silicate melt, and the rocks closest to the country rock are depleted in the heavy isotope relative to those crystallized at greater distances. Furthermore, the absence of sharp limiting boundaries in the Bayfield County sequence is evidence against the existence of the necessary "cold wall."

Gravitational forces may be discarded since the variation is horizontal. Another alternative is incomplete mixing.

Field evidence suggests that the granophyre has been intruded as a melt into the gabbroic country rock, or that some process of remelting has occurred. This is based on the presence of unoriented xenoliths of gabbro included in the granophyre. A common explanation given for this type of sequence is that the granophyre has been intruded into the gabbro, reacting with it to form the intermediate rock [56], [57]. A progressively decreasing assimilation of rocks low in O^{18} by a fluid high in O^{18} could account for the trend in isotope ratios found here. This requires that the granophyric melt reacts with, or partially remelts, the solid gabbro upon contact with it.

BOWEN [58] has shown that the assimilation of a gabbroic solid by a granitic melt is extremely improbable, if not impossible. This is especially pertinent in this instance since the granophyre is believed to be the product of a "filter-press" type of action, being separated from an early gabbroic fraction at greater depth and forced upward to its present position. A residual melt arising in this manner would obviously not possess sufficient superheat to remelt a gabbro.

Petrographic studies of the intermediate rocks show features which cannot be explained by an assimilation mechanism. For example, idiomorphic hornblende crystals are completely enclosed by idiomorphic microcline crystals. Elongate prismatic hornblende crystals transect rows of other crystals without disturbing in any way the internal structures of the transected crystals. Plagioclase crystals are completely severed by other plagioclase crystals with no visible offset of the twinning lamellae in the transected plagioclases. Orthoclase with perthitic-type blebs of hornblende are common, and hematite-rich zones of reaction rim appearance occur

in plagioclase crystals with very distinct and straight inner borders. Idiomorphic crystal forms are prevalent, and nowhere is there any sign of solution effects or embayments. These are criteria for replacement mechanisms.

The O^{18}/O^{16} ratio of the granophyre is 9.9‰ , which is higher by about 1.5‰ than the granitic rock with the highest O^{18} concentration in Table 2*. The O^{18}/O^{16} ratio falls to 6.1‰ in the gabbro, which also shows many of the replacement features described above. This transition cannot be explained by assimilation, by crystal settling, or by incomplete mixing. On the grounds of the evidence presented above in the section on fractional crystallization, the oxygen isotopic gradient cannot be dismissed as the result of inherent specific isotopic compositions of the different mineral species. Above all, it is inconceivable that the oxygen isotopes of the intermediate rock could have assumed their present distribution as a result of direct crystallization from a silicate melt. Consequently, it must be concluded that oxygen in one form or another, is free to redistribute itself by some mechanism in solid rock.

There may be many mechanisms capable of producing the textural and chemical features described here, and whatever they may be, they must abide by the following restrictions:

1. The action of the mechanism should not transform the pre-existing rock completely into the liquid state, for then it would be difficult to avoid complete mixing.
2. The mechanism should not produce any microscopic or macroscopic inhomogeneities in the structure of the resulting rock.

In other words, this mechanism should involve the transfer of material by some process of permeation, solution, or diffusion in a solid.

THE EFFECT OF METAMORPHISM ON ISOTOPIC COMPOSITION

In a preceding section, a premature guess was ventured that metamorphism results in a decrease in O^{18} content. The Dutchess County metamorphic rock sequence is suited for further investigation of this possibility. This sequence consists of Paleozoic argillaceous sediments in southeastern New York state which show a progressively increasing intensity of metamorphism from northwest to southeast. The structure and petrology of the region have been described by BALK [59] and BARTH [60].

The sequence of samples selected for analysis fall along a line perpendicular to the axis of the northeasterly trending geosyncline. The isotope abundances from this series may therefore be regarded as a measure of the effect of differing degrees of metamorphism on a sediment which is assumed to have had an originally uniform composition. The samples are listed in Table 8 in the order of increasing metamorphic change, with the exception of the black phyllite (No. 22), which was collected from a point about five miles northeast of the site of specimen No. 18. The locations of samples No. 22 and 18 are equidistant from the geosynclinal axis, and both should have experienced the same degree of metamorphic transformation.

The olive gray slate (No. 18) and the black phyllite (No. 22) have been assigned to the muscovite slate facies by BARTH [60]. The black phyllitic slate (No. 20) falls

* This enrichment in O^{18} may be due to the preferential loss of the lighter isotope in the migration process.

on the biotite isograd*, but belongs to the muscovite slate facies; this sample comes from a locality five miles east-southeast of the source of specimen No. 18. The garnet schist (No. 19) is located about eight miles due east of the black phyllite (No. 22) site, and is well past the garnet isograd and belongs in the kyanite schist facies. The chlorite schist (No. 30), from a point two miles south of the garnet schist (No. 19) locality, also fits into the kyanite schist facies. The biotite garnet schist (No. 28), occurring five miles southwest of sample No. 30, falls just west of the sillimanite isograd, and also belongs to the kyanite schist facies.

The results listed in Table 8 indicate no immediately apparent correlations. The assumption that we are dealing with a sediment of initially uniform composition is not strictly true, since the Hudson River slate, of which the olive gray slate (No. 18)

Table 8. Isotopic abundances in rocks of the Dutchess County metamorphic sequence

<i>Sample and Number</i>	O^{18}/O^{16} ‰	<i>Average Deviation</i>	<i>Number of Determina- tions</i>
Olive gray slate No. 18	15.4	0.1	2
Black phyllite No. 22	12.1	1.0	2
Black phyllitic slate No. 20	15.7	0.4	2
Garnet schist No. 19	12.7	0.5	2
Chloritic schist No. 30	12.5	0.2	2
Biotite garnet schist No. 28	12.9	0.0	2

should have been a representative sample, is interbedded with lenses of conglomerate, arkose, and greywacke [61]. The authenticity of a sample taken from an average-sized hand specimen may therefore be questioned.

With the exception of the black phyllite (No. 22), the rocks of the muscovite slate facies (low grade of metamorphism) are higher in O^{18} than those of the more intensely metamorphosed kyanite schist facies, but this should not be taken as conclusive evidence for the depletion of the heavy isotope during metamorphism. It does suggest that isotopic analyses of rock sequences which extend over large areas are more subject to contamination from unrelated materials than are those selected from less widely scattered sources.

CONCLUSION

The fundamental principles of isotopic chemistry have been applied to a number of geologic problems. All conclusions and interpretations are based on the evidence reported in this paper. In no case has the investigation been sufficiently exhaustive to preclude the possibility of erroneous conclusions. More extensive studies will surely follow, because differences in isotopic abundances are extremely sensitive measures of the energy relations in chemical substances.

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* See Plate 1, reference [59].

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APPENDIX

*Rock specimen descriptions**

<i>Number</i>	<i>Specimen and Data</i>
1	Olivine basalt, from Pt. Tahera, Tahiti.
2	Flint nodule, from Dover Cliffs, England.
4	Gneissic granite, from Little Elk Creek, South Dakota. Migmatitic, with inclusions of biotite schist. Sample analyzed was free from biotite schist.
9	Maquoketa shale, from Belleview, Iowa (Upper Ordovician).
10	Randville pegmatite, (quartz), from Randville, Michigan. Oxygen from this sample used as standard.
11	Randville pegmatite, (orthoclase), from Randville, Michigan.
13	Diatomite, (diatomaceous earth), from Santa Barbara County, California.
14	Nepheline syenite, from Pulaski County, Arkansas.
18	Olive gray slate, from road cut 1.5 miles west of Lagrangeville, Poughkeepsie Quadrangle, New York, [59] p. 799: specimen No. 1.
19	Garnet schist, from site two miles south-southwest of Dover Plains, Clove Quadrangle, New York, [59] p. 804: specimen No. 9.
20	Black phyllitic slate, one-half mile north-northwest of Beekman, Clove Quadrangle, New York, [59], p. 799: specimen No. 4.
22	Black phyllite, from road cut north of Moores Mills, Clove Quadrangle, New York, [59] p. 799: specimen No. 2.
24	Nortonite (stony meteorite), fell at boundary of Norton County, Kansas, and Furnas County, Nebraska on February 18, 1948 [33].
25	Dunite, from Mooihoek, Union of South Africa.
26	Quartz, from Minas Gerais, Brazil [24].
28	Biotite garnet schist, from north side of Tennile River, just northeast of Webatuck, Clove Quadrangle, New York. Occurs as a lens in dolomitic marble immediately west of sillimanite isograd, [59] p. 802: specimen No. 8.
30	Chloritic schist, from road cut, two-thirds mile northwest of Dover Furnace, Clove Quadrangle, New York, [59] p. 802: specimen No. 7.
31	Graphic granite, Lincoln pegmatite, Custer, South Dakota. Quartz and perthitic microcline components separated by Dr. I. FRIEDMAN.
35	Balmoral granite, Scotland. Quartz and orthoclase components separated by Dr. I. FRIEDMAN.
37	Stony meteorite, from Varpais järvi, Finland. An analysis of this meteorite will be published by W. WAHL and H. B. WILK.
38	Moldavite, a tektite from Radomilice, C.S.R.; this is Dr. TUCEK's specimen No. 12.
40	Tektite (Americanite), Santa Mesa Site, Phillipines.
45	Basal Breccia, from Federal Exploration Mine, Menominee Range, Michigan. Upper Cambrian, Iron Formation.
46	St. Peter sandstone, from St. Paul, Minnesota.
47	Yellowstone obsidian, from Obsidian Cliff, Yellowstone Park, black variety, rhyolitic, [62] p. 98.
79-PG-5	Columbia River basalt, from Picture Gorge, Oregon.
89	Quartz vein, from 12th level, Dome Mine in Timiskaming conglomerate, Porcupine District, Ontario.

* Number in square brackets indicates literature references.

Rock specimen descriptions (Continued)

<i>Number</i>	<i>Specimen and Data</i>
410	Cheshire orthoquartzite, from road cut at north edge of Highway 9, on Bennington-Woodford town line, two miles east of Bennington, Vermont. Specimen is of Lower Cambrian age (Olenellus zone).
778	Grafton orthoquartzite, from 5/8 mile east-southeast of Southwest Hoosick, Grafton Quadrangle, New York.
2039	Potsdam sandstone, from Ablemans, Sauk County, Wisconsin.
2698	Arkose, Triassic age, from Fair Haven, New Haven, Connecticut.
B-1-74	Lava, from Mt. Etna, Sicily.
F-75	Wishart orthoquartzite, Huronian (?) age, from Gasson Lake, Labrador.
K-12	Lava, from active flow 100 m north of triangulation station "Paricutin," approximately 3 km northwest of volcano, Michoacán, Mexico. Collected May 20, 1948 by R. E. WILCOX.
R-7696	Disco basalt, from Ovifak, Greenland.
W-136-4	Granophyre-gabbro sequence, T 45 N; R 5 W, SW $\frac{1}{4}$, Sec 25-Bayfield County, Wisconsin. These specimens will be described fully at a later date by M. W. LEIGHTON.
W-137-1	
W-137-2	
W-137-3	
W-137-4	
W-187	

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