

## Stable Isotopes in Mineralogy

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**Abstract.** Stable isotope fractionations between minerals are functions of the fundamental vibrational frequencies of the minerals and therefore bear on several topics of mineralogical interest. Isotopic compositions of the elements H, C, O, Si, and S can now be determined routinely in almost any mineral. A summary has been made of both published and new results of laboratory investigations, analyses of natural materials, and theoretical considerations which bear on the importance of temperature, pressure, chemical composition and crystal structure to the isotopic properties of minerals. It is shown that stable isotope studies can sometimes provide evidence for elucidating details of crystal structure and can be a powerful tool for use in tracing the reaction paths of mineralogical reactions.

### Introduction

The fractionation of light stable isotopes between minerals is a function of the vibrational frequencies of the minerals and the frequency shifts attendant on isotopic substitution (Urey, 1947; Bigeleisen and Mayer, 1947; Bottinga and Javoy, 1973). Consequently isotope effects depend on fundamental properties of minerals and bear on several topics of mineralogical interest.

Chemical extraction techniques and mass spectrometry have developed to the point where it is possible to make precise determinations of the isotope ratios of the mineralogically important elements H, C, O, Si, and S in almost any material. The ability to make these determinations routinely has resulted in a veritable explosion of stable isotope data in the last few years. Critical to the interpretation of isotope effects in mineral systems is a knowledge of (1) equilibrium isotope relations among minerals and between minerals and fluids, (2) rates of these isotopic exchange reactions and (3) factors that influence the equilibrium and kinetic isotopic properties of minerals. Such information is obtained from the analyses of natural materials as well as from laboratory studies and theoretical considerations.

Investigations have been made of the importance of temperature, pressure, chemical composition, and crystal structure to the isotopic properties of minerals.

In favorable cases, stable isotope studies provide evidence that can elucidate certain details of crystal structure where alternate structures have been proposed. Of particular interest is the use of stable isotopes as tracer materials to follow the reaction paths of mineralogical reactions.

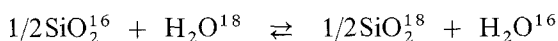
In this paper some of the important published applications of stable isotope techniques to mineralogy are reviewed and new data concerning crystal structures and mineralogical reaction mechanisms are presented.

### Equilibrium Fractionation Factors

The isotopic fractionation factor between two substances  $a$  and  $b$ ,  $\alpha_{a-b}$ , is defined as

$$\alpha_{a-b} = R_a/R_b$$

where  $R$  is the isotope ratio of  $O^{18}/O^{16}$ ,  $C^{13}/C^{12}$ , etc. At equilibrium,  $\alpha$  is related, to a very good approximation, to the equilibrium constant,  $K$ , for the isotope exchange reaction between the two substances. For example, the oxygen isotope exchange reaction between quartz and water may be written



and

$$K = \frac{Q(SiO_2^{18})}{Q(SiO_2^{16})} \bigg/ \frac{Q(H_2O^{18})}{Q(H_2O^{16})} = \alpha$$

where  $Q$  is the partition function and  $SiO_2^{16}$  means that both oxygen atoms are  $O^{16}$ . In general,  $\alpha = K^{1/n}$  where  $n$  is the number of atoms exchanged in the reaction as written. As true equilibrium constants, the isotopic fractionation factors are functions of temperature and this is the basis of their use in geologic thermometry.

The fractionation factors, or equilibrium constants, can be determined directly by laboratory exchange experiments or by semi-empirical calculations using the methods of statistical mechanics and the measured vibrational frequencies of the molecules or crystals. The changes in vibrational frequencies on isotopic substitution have been measured in only a few cases and the shifts normally are calculated assuming some force-field model. Isotopic partition function ratios can be calculated quite accurately for simple gaseous molecules, but for condensed mineral phases, insufficient knowledge of the lattice dynamics usually precludes such calculations. This is a severe limitation because experimental determinations of fractionation factors can normally be made only at relatively high temperatures where isotopic exchange rates are more rapid. Precise theoretical calculations could provide much needed information at low temperatures. Calculations have been reported for some sulfide minerals (Sakai, 1968; Bachinski, 1969; Elcombe and Hulston, 1975) diamond and graphite (Bottinga, 1969), quartz (Shiro and Sakai, 1972; Becker and Clayton, 1976) and calcite (McCrea, 1950; O'Neil et al., 1969; Bottinga, 1968; Shiro and Sakai, 1972). Excellent spectral and thermochemical data as well as good models for lattice modes and the internal modes of

the carbonate ion are available for calcite. The calculated carbon and oxygen isotopic partition function ratios for calcite can be used to calculate fractionation factors which are in good agreement with experimentally determined values. Calculations for the other minerals are less refined. The main limitations are the approximations used in the treatment of lattice modes and frequency shifts. With the availability of materials highly enriched in heavy isotopes, like  $\text{H}_2\text{O}^{18}$ , it should be possible to synthesize isotopically heavy minerals and measure the frequency shifts directly.

Laboratory "calibration" experiments have been performed on many of the major rock-forming and ore-associated minerals. In Table 1 these minerals are listed in order of decreasing tendency to concentrate the heavy isotope. In these experiments a mineral undergoes an isotope exchange reaction with another phase (normally a fluid because of enhanced rates) until the equilibrium distribution of isotopes between the phases is attained. In a true isotope exchange reaction, there is no change in chemistry or mineralogy of either phase and equilibrium can be demonstrated by approaching the equilibrium distribution from opposite directions. However, exchange rates at moderate temperatures are very sluggish and workers have perforce resorted to experiments in which the attainment of equilibrium can only be inferred and not strictly proved. Some techniques or

**Table 1.** Experimentally calibrated minerals. Listed in order of decreasing tendency to concentrate the heavy isotope

Minerals	References
$O^{18}/O^{16}$	
Quartz	Clayton et al. (1972)
Anhydrite	Lloyd (1968)
Barite	Robinson and Kusukabe (1975)
Feldspars	O'Neil and Taylor (1967)
Carbonates (see Table 2)	O'Neil et al. (1969); Northrop and Clayton (1966)
Muscovite	O'Neil and Taylor (1969)
Garnet	Taylor (1976)
Biotite	Bertenrath and Friedrichsen (1975)
Rutile	Addy and Garlick (1974)
Magnetite	Bertenrath et al. (1972)
$D/H$	
Muscovite	Suzuoki and Epstein (1976)
Phlogopite	Suzuoki and Epstein (1976)
Hornblende	Suzuoki and Epstein (1976)
Biotite	Suzuoki and Epstein (1976)
Trona	Matsuo et al. (1972)
$S^{34}/S^{32}$	
Pyrite	Grootenboer and Schwarcz (1969) <sup>a</sup>
Sphalerite	Kajiwarra and Krouse (1971) <sup>a</sup>
Chalcopyrite	Czamanske and Rye (1974) <sup>a</sup>
Galena	

<sup>a</sup> Authors examined all four sulfides

criteria employed are (1) synthesis of a mineral by some mineralogical reaction or crystallization of a gel, (2) synthesis with but a minor departure from a true exchange reaction as in a cation exchange reaction or a transition from an unstable to a stable polymorph, (3) extrapolation of partial exchange data to 100% exchange, (4) recrystallization in a temperature gradient, (5) apparent cessation of exchange with time. These techniques often yield results which are "reasonable" and "compatible with natural data" and as such are usually interpreted as equilibrium or near-equilibrium data. Nature being perverse, such an interpretation may be completely misleading. O'Neil and Taylor (1969) have suggested that equilibrium may be assumed to have been established when the results of the application of two or more experimental techniques are in agreement. It would be highly fortuitous if kinetic or other nonequilibrium processes in completely different experimental procedures produced identical isotopic fractionations.

There is lack of agreement between some laboratory calibrations but both theoretical calculations and experimental determinations of equilibrium isotope fractionation factors are, in general, consistent with each other and with nature. For example the regular order of  $O^{18}$  enrichment normally observed among coexisting minerals in nature is the same as that observed in the laboratory. Departures from the regular order ("isotopic reversals") are used as indicators of disequilibrium in mineral systems. Oxygen, carbon, and sulfur "isotopic temperatures" are often in agreement with temperatures obtained by other methods. The outstanding scientific advances made by use of the oxygen isotope paleotemperature scale of Epstein et al. (1951) provide the best example of the exploitation of equilibrium isotope fractionations in understanding nature.

## **Factors Affecting Isotopic Properties of Minerals**

### *Chemical Composition*

The isotopic properties of a mineral depend most importantly upon the nature of the chemical bonds within the mineral. The oxidation state, ionic charge, atomic mass and electronic configuration of the elements to which the isotope is bonded need to be considered. In general, bonds to ions with a high ionic potential and low atomic mass are associated with high vibrational frequencies and have a tendency to incorporate the heavy isotope preferentially in order to lower the free energy of the system. For example, consider the difference between the bonding of oxygens to the small, highly charged  $Si^{4+}$  ion as opposed to the relatively large  $Fe^{2+}$  ion. In common natural equilibrium assemblages, quartz is always the most  $O^{18}$ -rich mineral and magnetite is always the most  $O^{18}$ -deficient mineral and this relationship has been confirmed by laboratory experiments (Clayton et al., 1972; Bertenrath et al., 1972; Becker and Clayton, 1976).

Taylor and Epstein (1962) and Garlick and Epstein (1967) drew attention to the regular order of  $O^{18}$  enrichment found in minerals of igneous and metamorphic rocks. After quartz, the alkali feldspars and plagioclase are the next most  $O^{18}$ -rich minerals in the rocks in which they coexist. The most important corresponding

chemical change in this sequence of framework silicates is the progressive replacement of Si—O bonds by Al—O bonds. At temperatures above 350°C, the isotopic properties of alkali feldspars are not measurably affected by changes in the Na<sup>+</sup>/K<sup>+</sup> ratio either in laboratory systems (O'Neil and Taylor, 1967) or in nature (Schwarcz, 1966). Even substitution of the heavy Rb<sup>+</sup> ion in the feldspar structure produces no detectable effects at 500°C (O'Neil, unpub. data). These observations imply only a weak electronic interaction between alkali ions and aluminosilicate oxygen in feldspars. The O<sup>18</sup> differences between end members of the plagioclase series are relatively large (1–2‰) even at high temperatures (O'Neil and Taylor, 1967). It is difficult to assess the importance of replacing alkali ions by alkaline earth ions in the series, but based on the previous discussion it is certainly minor compared to the concomitant replacement of Si by Al.

Taylor (1976) has measured a relatively large permil fractionation of 1.68 between grossularite and andradite at 600°C, demonstrating the magnitude of the isotopic effect attendant on substituting Al—O bonds for Fe—O bonds. Both Al and Fe are in the same oxidation state (III) in grandite garnets and consequently the effect is caused primarily by the difference in atomic mass between Al and Fe, and the effect this difference has on the vibrational frequencies of the mineral. This mass effect is also apparent in S<sup>34</sup> distributions among sulfides, where, for example, ZnS always concentrates S<sup>34</sup> relative to coexisting PbS. Lawrence and Taylor (1972) found that Fe-rich smectites are about 3‰ depleted in O<sup>18</sup> relative to Fe-poor smectites from the same sampling location. In keeping with this mass effect, the generally most O<sup>18</sup>-depleted minerals in nature are found in uraninites (Hoekstra and Katz, 1956).

Detailed studies have been made of the relationship between chemical composition and the isotopic properties of carbonate minerals. In relation to other classes of minerals, carbonates are O<sup>18</sup>-rich due to the fact that oxygen is bonded to the small highly charged C<sup>4+</sup> ion. While important, the nature of the divalent cation is only secondary in importance to the C—O bonding in determining the overall isotopic characteristics of carbonates. Tarutani et al. (1969) investigated the effect of magnesium substitution on oxygen isotope fractionation between calcium carbonate and water at 25°C and found that O<sup>18</sup> concentrates in magnesian calcite, relative to pure calcite, by 0.06‰ for each mole-percent MgCO<sub>3</sub> in calcite. O'Neil et al. (1969) examined the oxygen isotope relations in a series of divalent metal carbonates, the majority of these experiments being made with CaCO<sub>3</sub>, SrCO<sub>3</sub> and BaCO<sub>3</sub>. As expected, the tendency to concentrate O<sup>18</sup> was CaCO<sub>3</sub> > SrCO<sub>3</sub> > BaCO<sub>3</sub> at all temperatures studied (0° to 500°C). Experiments were also done with CdCO<sub>3</sub>, MnCO<sub>3</sub> and PbCO<sub>3</sub> and a comparison of the permil O<sup>18</sup> fractionations between these minerals and water at 25°C and 240°C is shown in Table 2, together with ionic radii and atomic masses. The isotope effects correlate well with cationic mass, the dependence on cationic size being more complicated. Size appears more important to the internal vibrational contribution of the carbonate ion and mass seems more important to the lattice vibrational contribution. For example, Ca<sup>2+</sup> and Cd<sup>2+</sup> have similar size, and the isotopic differences between these two carbonates must arise almost entirely from the lattice vibrational contribution. PbCO<sub>3</sub> departs slightly from the general trend with mass. Adler and Kerr (1963) point out that PbCO<sub>3</sub> is anomalous also in its internal

**Table 2.** Permil O<sup>18</sup> fractionation between MCO<sub>3</sub> and H<sub>2</sub>O

M	$\Delta O^{18}(25^\circ C)^a$	$\Delta O^{18}(240^\circ C)^a$	Radius (M <sup>2+</sup> )	Mass (M <sup>2+</sup> )
Mg	31.2	—	0.72	24.3
Ca (aragonite)	28.7	—	1.18	40.1
Ca (calcite)	28.0	7.2	1.00	40.1
Mn	—	6.8	0.83	54.9
Sr	26.8	6.2	1.16	87.6
Cd	26.1	6.0	0.95	112.4
Ba	24.5	4.7	1.36	137.4
Pb	—	4.5	1.18	207.2

Data from O'Neil et al. (1969) except for hydromagnesite (O'Neil and Barnes, 1971) and aragonite (Tarutani et al., 1969)

<sup>a</sup>  $\Delta O^{18} = 10^3 \ln \alpha(MCO_3-H_2O)$

vibrational frequencies, which are lower than would be predicted on the basis of the ionic radius of Pb<sup>2+</sup>.

Suzuoki and Epstein (1976) found that the chemical composition of the octahedral site in hydrous minerals is the dominant factor controlling their relative hydrogen isotope compositions. These authors conducted experiments from 450° to 800 °C and found the following relationship for micas and amphiboles:

$$\Delta D(\text{mineral-water}) = -22.4(10^6 T^{-2}) + 28.2 + (2X_{Al} - 4X_{Mg} - 68X_{Fe})$$

where  $\Delta D$  is the per mil fractionation of deuterium between the mineral and water, and  $X$  is the mole fraction of the cations in six-fold coordination. Again, the heavy isotope concentrates in the bond to the element of smaller mass. Muscovite always concentrates deuterium relative to biotite or amphibole in natural equilibrium assemblages (Taylor and Epstein, 1966). The most unusual aspect of the above expression is the implication that all mineral-water fractionations (and thereby all mineral-mineral fractionations) have the same temperature coefficient. That is, hydrogen isotope fractionations among coexisting minerals apparently cannot be used for geothermometry.

In this section several examples were discussed of the influence of chemical bonding on the isotopic characteristics of the mineral. It is clear that a given element should have different isotopic compositions in different structural or bonding sites in a mineral. For example, on the basis of associated vibrational frequencies, the difference between the O<sup>18</sup> content of OH groups and aluminosilicate oxygen in a hydrous mineral should be large enough to provide an excellent internal geothermometer providing certain conditions are met. Savin (1967) concluded from preliminary experiments that selective extraction and analysis of oxygen from different structural sites in kaolinite was possible, and that differences of up to 18‰ exist between aluminosilicate oxygen and hydroxyl oxygen in kaolinite formed at low temperatures. Hamza and Epstein (per. commun.) are testing the systematics of such internal thermometers at present. If this technique proves successful, it will be a very powerful petrologic and mineralogic tool.

### *Crystal Structure*

The crystal structures of minerals can influence their isotopic properties to an extent depending on how different the interatomic interactions are between the various structural forms. Structural effects are secondary in importance to those arising from the primary chemical bonding discussed in the previous section, but are surprisingly large in some cases. On the basis of limited experiments and calculations, the heavy isotope apparently concentrates in the more closely packed or well-ordered structures: The  $O^{18}$  and  $D$  permil fractions between ice I and liquid water at  $0^\circ C$  are 3.0 and 19.5, respectively, and arise chiefly from differences in the degree of hydrogen bonding (order) and lattice vibrational effects (e.g., O'Neil, 1968). The  $O^{18}$  fractionation between  $D_2O$  and  $H_2O$  is over 15‰ at  $25^\circ C$  (Staschewski, 1965) implying a more ordered structure for  $D_2O$ , and this implication is in agreement with many other lines of evidence concerning the structure of liquid  $D_2O$ . Because these are fairly large isotope effects relative to experimental error, an isotope fractionation technique could be used to study bonding characteristics in the various polymorphs of ice.

The  $O^{18}$  and  $C^{13}$  permil fractionations between aragonite and calcite at  $25^\circ C$  are rather small at 0.6 and 1.8, respectively (Tarutani et al., 1969; Rubinson and Clayton, 1969). It is noteworthy that the carbon atom exhibits the greater isotope effect. Enrichments of the heavy isotopes in the denser aragonite relative to calcite have also been observed in marine and fresh water pelecypods (Keith et al., 1974). In the series of alkaline earth carbonates examined by O'Neil et al. (1969) no consistent differences between the isotopic behavior of hexagonal carbonates and that of orthorhombic carbonates were observed.

Several observations indicate that crystal structure or even the presence of structural water is not important to the oxygen isotope properties of silica species. Preliminary experiments indicate that there is no measureable fractionation between cristobalite and quartz at  $500^\circ C$  (O'Neil, unpublished data). Even at very low temperatures no significant structural effect is present. For example, radiolaria and authigenic quartz formed at relatively low temperatures from ocean water have  $\delta O^{18}$  values in the narrow range of 36–38 (Mopper and Garlick, 1971; Savin, 1970). Although possibly fortuitous, the oxygen isotope fractionation curve for the diatom-water (Labeyrie, 1974) and quartz-water (Clayton et al., 1972) systems coincide at low temperatures. Also the isotopic relations among the diagenetic silica minerals biogenic opal, disordered and ordered cristobalite and microcrystalline quartz determined by Murata et al. (1977) indicate similar isotopic characteristics for all these forms (see below). Shiro and Sakai (1972) calculate that at the transition temperature ( $573^\circ C$ ), the reduced partition function ratio of  $\beta$ -quartz is about 0.8‰ smaller than that of  $\alpha$ -quartz, the more dense crystal structure, but this difference has not been observed in the laboratory experiments of Clayton et al. (1972).

One of the largest isotopic effects associated with structure is found in the carbon system. The calculated permil fractionation between diamond and graphite ranges from a large value of 11.5 at  $0^\circ C$  to the still measureable value of 0.4 at  $1000^\circ C$  (Bottinga, 1969). As was the case with  $CaCO_3$ , the heavy isotope concentrates in the more dense phase.

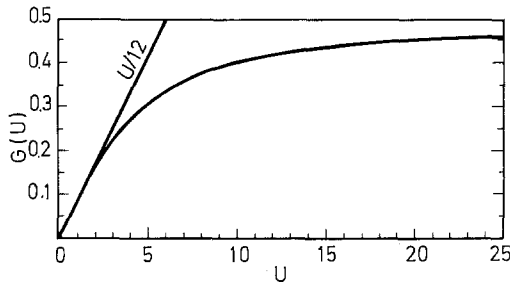


Fig. 1. A plot of the Bigeleisen-Mayer function  $G(U)$  against  $U$ . See text for explanation

### Temperature

The extent to which temperature affects the vibrational energy of a mineral (or its partition function) is a prime factor in determining the isotopic characteristics of the mineral. Details of the theory of isotopic fractionation between ideal gases can be found in Urey (1947) and Bigeleisen and Mayer (1947). Only a brief discussion of the theoretically predicted temperature dependence of isotopic fractionation between minerals will be presented here. As mentioned in a previous section, the fractionation factor between minerals  $a$  and  $b$  can be written in terms of partition function ratios,  $Q$ :

$$\alpha_{a-b} = \frac{(Q_2/Q_1)_a}{(Q_2/Q_1)_b}$$

where the subscripts 2 and 1 refer to molecules or crystals substituted by the heavy and light isotopes of an element, respectively. For a diatomic molecule, the Bigeleisen-Mayer treatment yields the following expression for the partition function ratio

$$Q_2/Q_1 = 1 + \left( 1/2 - \frac{1}{U_2} + \frac{1}{e^{U_2} - 1} \right) \Delta U = 1 + G\Delta U$$

where  $U_1 = \frac{hc\omega_1}{kT}$  for the molecule containing the light isotope,  $\Delta U = U_1 - U_2$ , and  $G$  is the expression in parentheses.

The above expression can be generalized to the polyatomic case

$$U_{2i} = \frac{hc\omega_{2i}}{kT}$$

where  $\omega_{2i}$  are the frequencies of the normal modes of vibration for the molecule containing the heavy isotope.

If  $G\Delta U \ll 1$ , then

$$\ln Q_2/Q_1 \cong G\Delta U.$$

Figure 1 is a plot of the function  $G(U)$  against  $U$  from Bigeleisen and Mayer (1947). Recalling the  $1/T$  factor in the expression for  $U$  and using the approximate



equation above, the following temperature dependence is predicted: (1) At  $U > 20$  (high frequencies and/or low temperatures), the function  $G(U)$  approaches the value  $1/2$  and  $\ln Q_2/Q_1$  is proportional to  $1/T$ . (2) At  $U < 5$  (low frequencies and/or high temperatures), the function  $G(U)$  has a slope  $U/12$  and  $\ln Q_2/Q_1$  is proportional to  $1/T^2$ . At room temperature  $hc/kT = 5 \times 10^{-3}$  erg-cm and the highest frequencies for minerals not containing hydroxyl groups are approximately  $1000 \text{ cm}^{-1}$ . Therefore  $U < 5$  for all temperatures above room temperature and temperature dependence (2) is predicted. O—H stretching frequencies are quite large ( $\sim 3000 \text{ cm}^{-1}$ ) and therefore minerals containing this group are expected to show complicated temperature dependence, with the  $1/T^2$  proportionality coming in only at very high temperatures. At infinite temperature the fractionation factors between all pairs of minerals become unity ( $\ln \alpha_{a-b} = 0$ ).

It must be emphasized that the theoretical considerations presented here were developed for perfect gases and extension of them to condensed phases is fraught with uncertainties. However, this theory serves as an excellent guide, and the  $1/T^2$  dependence for fractionation factors between minerals has been observed in both laboratory and natural systems.

### *Oxidation State*

Under equilibrium conditions, heavy isotopes tend to concentrate in the minerals that contain the isotopic element in its higher oxidation state. Of the elements under consideration here, only C and S occur in more than one oxidation state in minerals and it is normally observed in nature and in the laboratory that carbonates are more  $\text{C}^{13}$ -rich than coexisting graphites, sulfates are more  $\text{S}^{34}$ -rich than coexisting sulfides, etc. This generalization is also predicted from theoretical considerations (Sakai, 1968; Bottinga, 1969; Ohmoto, 1972). A similar effect is expected for oxygen that is bonded to ions in different oxidation states. That is, bonds to elements in higher oxidation states are more  $\text{O}^{18}$ -rich than bonds to the same elements in lower oxidation states (e.g.,  $\text{S(VI)}-\text{O} > \text{S(IV)}-\text{O}$ ;  $\text{Fe(III)}-\text{O} > \text{Fe(II)}-\text{O}$ , etc.). Inasmuch as ions in higher oxidation states are smaller and have larger ionic potentials than ions in lower oxidation states, these effects are inseparable from other chemical effects already discussed.

### *Pressure*

Because the change in molar volumes of solids on isotopic substitution is small, it has generally been assumed that the effect of pressure on isotopic fractionation between minerals is negligible. However, Joy and Libby (1960) suggested that the oxygen isotope fractionation between  $\text{CaCO}_3$  and  $\text{H}_2\text{O}$  might be measureably pressure dependent at low temperatures. This system, or any mineral-water system, would be particularly sensitive to pressure effects because isotopic substitution of the centrally symmetric oxygen atom in  $\text{H}_2\text{O}$  should not produce a volume change sufficient to offset the volume change of the carbonate. From another point of view, pressure effects might be expected for mineral-gas or melt-gas systems because the

isotopic properties of the gas might change drastically with big density changes while those of the melts or minerals remain unaffected.

The pressure effects calculated by Joy and Libby (1960) were not observed in the experiments of Clayton et al. (1975). These latter authors measured the oxygen isotope fractionation between  $\text{CaCO}_3$  and  $\text{H}_2\text{O}$  at  $500^\circ\text{C}$  from 1 to 20 kbar and at  $700^\circ\text{C}$  at pressures of 0.5 and 1 kbar and did not detect a pressure effect. Clayton et al. point out that root-mean-square values of C—O bond lengths (depending on vibrational amplitudes) were used in the calculations of Joy and Libby, and if mean values of the C—O distance (depending on anharmonicity of the vibrational potential) are used, the calculated pressure effects are markedly less, in agreement with experiment.

Pressure effects have been invoked to explain unusual oxygen isotope compositions of some kimberlitic eclogites (Garlick et al., 1971) and olivine from a suite of ultramafic rocks (Pinus and Dontsova, 1971). From the experiments of Clayton et al. (1975) and from some theoretical considerations, it would appear at this time that factors other than pressure are probably responsible for these unusual oxygen isotope compositions.

Insufficient knowledge of the pressure that prevailed during geological processes often places severe constraints on the applicability of the chemical and physical thermometers used by petrologists. In this respect, stable isotope fractionations between cogenetic minerals are particularly useful in geothermometry because of the apparent lack of dependence on pressure (and activity of other phases as well).

## Provenance

The origin or derivation of a mineral can often be inferred by stable isotope analysis. In recent years, this “tracer” aspect of stable isotope geochemistry has become more important than the “thermometry” aspect, particularly in identifying the origins of the various aqueous fluids that have participated in so many geologic processes. In this latter respect, if a mineral is depleted in  $\text{O}^{18}$  or D to an extent far beyond that normally encountered, it is almost a certainty that the mineral (or its source material) has precipitated from or undergone isotopic exchange with meteoric water. This is so because meteoric waters are the only large reservoirs of  $\text{O}^{18}$ - and D-depleted material that can logically enter into mineralogical reactions. Such  $\text{O}^{18}$ -poor minerals were first observed in rocks from the Skaergaard intrusion (Taylor and Epstein, 1963). Garlick and Epstein (1966) then recognized the role of groundwater in the formation of isotopically similar rocks which were formed during hydrothermal mineralization at Butte, Montana.

If minerals that have interacted with ground water are excluded as special cases, it is generally true that the  $\text{O}^{18}$  content of minerals decreases with an increase in the temperature of formation. This follows logically from the fact that isotopic fractionations decrease with increasing temperature. As a consequence of this, the  $\text{O}^{18}/\text{O}^{16}$  ratios of authigenic minerals are from 10–30% greater than those of detrital minerals of high temperature origin and therefore oxygen isotope analyses

can be used to distinguish the origin of minerals in ocean sediments (Savin and Epstein, 1970). Oxygen isotope ratios in minerals from the granitoid rocks of southeastern Australia have been used to distinguish source materials that had previously been through a weathering cycle (and which consequently had become relatively enriched in  $O^{18}$ ) from those of a primitive or deep-seated origin (O'Neil and Chappell, 1977). Taylor and Turi (1976) found extremely high  $O^{18}$ -contents in volcanic rocks from the Tuscan Magmatic Province in Italy which indicates that these magmas formed by melting or large-scale assimilation of high- $O^{18}$  argillaceous sedimentary rocks.

Through oxygen isotope analysis Clayton et al. (1973) made the remarkable discovery of an extremely primitive component in carbonaceous meteorites. The anhydrous high temperature minerals in these meteorites are unusually depleted in  $O^{17}$  and  $O^{18}$  and the oxygen isotope systematics indicate an admixture of a component that is essentially pure  $O^{16}$  and which probably predates the solar system. On the basis of the oxygen isotope composition of pyroxenes and whole rocks, Taylor et al. (1965) were able to classify stony meteorites into several groups and to make inferences about possible genetic relationships between these groups. Many investigations have been made of the oxygen isotope compositions of lunar minerals (e.g., Taylor and Epstein, 1970; Onuma et al., 1970; O'Neil and Adami, 1970) and an important conclusion concerning provenance is that the moon, earth, and ordinary chondrites have essentially identical  $O^{18}/O^{16}$  ratios, implying a common source material.

Among many other studies, stable isotope ratios of minerals have been used to identify the eolian origin of quartz in soils (Rex et al., 1968), to correlate tuffs (Cerling et al., 1975), to trace the origin of chert nodules used by primitive man (Stiles et al., 1974), to identify the localities from which archeological specimens of Greek marble were quarried (Craig and Craig, 1972), to realign Neolithic trade routes (Shackleton and Renfrew, 1970), to distinguish sulfide ore deposits of biogenic origin from those of magmatic origin (Jensen, 1967), and to distinguish marine from fresh-water sediments (Clayton and Degens, 1959).

### **Mineralogical Reaction Mechanisms**

Stable isotopes are excellent tracer materials for elucidating reaction paths of mineralogical reactions that occur both in nature and in the laboratory. Oxygen isotope studies are most useful in this connection because of the ubiquity of this element in the common rock-forming minerals and fluids. On the basis of several experimental studies (e.g., O'Neil et al., 1969; Clayton et al., 1972), it would appear that a solution-redeposition step is involved when oxygen isotope exchange between minerals and aqueous fluids takes place. Certainly all metal-oxygen bonds are broken and reformed to affect this exchange, and recrystallization has occurred. This effect has been exploited in the study of mineralogical reactions which occur in the presence of aqueous fluids.

O'Neil and Taylor (1967) observed a one-to-one correspondence between cation and oxygen isotope exchange in experiments in which albite was reacted

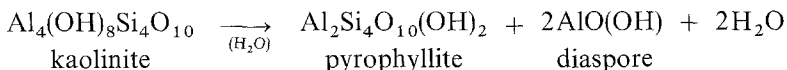
with KCl solutions to form sanidine. The results of detailed studies made during the course of this work suggest that the mechanism of oxygen isotope and cation exchange in these reactions involves fine-scale solution and redeposition in a fluid film at the interface between exchanged and unexchanged feldspar. A mechanism involving simple solid-state diffusion cannot explain the observed communication between the oxygen at the interfacial boundary and the solution. This postulated reaction mechanism has implications regarding the importance of solid-state diffusion during alkali metasomatism in nature. These experimental results indicate that large scale ionic replacements cannot take place without reconstitution of the aluminosilicate framework. In addition, cation exchange may well be the driving force which promotes oxygen isotope exchange between feldspars and aqueous fluids during deuteric, hydrothermal, or metamorphic processes in nature. In the absence of net sodium and potassium exchange, oxygen isotope exchange between alkali feldspar and water occurs by diffusion of an oxygen bearing species, either hydroxyl ion or water (Yund and Anderson, 1974).

Schwarcz (1966) attempted to distinguish models of exsolution phenomena by analysis of the  $O^{18}$  contents of host and exsolved phases of perthites. The results are compatible with a process of alkali ion diffusion alone, but the experimental precision was insufficient to rule out reconstruction of the feldspar lattice and oxygen isotope equilibration between Na-rich and K-rich phases during exsolution.

Stable isotope techniques are particularly well-suited to the study of possible inheritance of structural units of precursor minerals during mineralogical reactions. On the basis of rate studies and X-ray measurements, Velde (1965) suggested that muscovite that is produced by reaction of kaolinite with  $K^+$  inherits intact portions of the crystal structure of kaolinite. Inasmuch as kaolinite and muscovite have identical Al/Si ratios, the transformation involves only addition of potassium ion and removal of hydrogen ion and water,



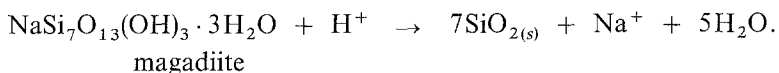
and the inheritance proposal seemed very reasonable. However, the oxygen isotope exchange accompanying the reaction proves that essentially every bond to oxygen in the kaolinite is broken and reformed in constructing the muscovite lattice (O'Neil and Taylor, 1969). That is, all parts of the kaolinite structure are completely broken down in the transformation. In a different series of experiments, O'Neil and Kharaka (1976) heated kaolinite in water at 350° to produce pyrophyllite and diaspore.



With so profound a change in mineralogy it is not surprising that hydrogen isotope exchange went essentially to completion. However, only 33% of possible exchange of  $O^{18}$  took place concomitantly and perhaps the disparity in D and  $O^{18}$  exchange rates would have been greater had the bomb run been terminated sooner. A logical conclusion is that pyrophyllite inherited oxygen from the kaolinite. Because of chemical and structural similarities to kaolinite, the pyrophyllite could inherit

intact units from the precursor, but the diaspore would undoubtedly undergo isotopic exchange with the water during its formation. This is the first published isotopic evidence of structural inheritance during a mineralogical reaction.

Arguments by Eugster (1969) and Hay (1968) point to the sodium silicates magadiite and kenyaite as chemically precipitated precursor minerals to certain cherts. The chemistry of such conversions is illustrated for magadiite in the following reaction:



Oxygen isotope analyses were used by O'Neil and Hay (1973) to aid in distinguishing between the following two proposed mechanisms for these reactions: (1) percolating ground waters leach sodium from the precursor and form amorphous silica which is altered to quartz with time, and (2) the precursor goes directly to quartz in a moderately or highly saline solution of low  $a_{\text{SiO}_2}$  and high pH. The saline brines which would be present in the second process are significantly enriched in  $\text{O}^{18}$  relative to normal ground waters. The cherts analyzed ranged widely in  $\text{O}^{18}$  content but were, in general, relatively  $\text{O}^{18}$ -rich. The degree of enrichment correlated well with the salinity of the lake as inferred from geologic evidence. The data suggest that the precursors were transformed to chert in fluids of widely varying salinity and  $a_{\text{Na}^+}/a_{\text{H}^+}$  ratio, and indicate that most of this chert was formed from precursor in contact with lake water trapped at the time of deposition.

Murata et al. (1977) determined the oxygen isotope composition of silica polymorphs in three diagenetic zones (1) biogenic opal, (2) disordered and ordered cristobalite, and (3) microcrystalline quartz, in two areas of California. They found that the  $\text{O}^{18}$  content remains fairly constant in each zone and changes substantially at zone boundaries. The authors suggest that the phase transformations at these boundaries proceed by a solution-deposition mechanism in which the isotopic composition of the new phase reflects the ambient temperature and the isotopic composition of the interstitial water. On this basis, the progressive structural ordering of cristobalite within zone 2 must proceed by a solid-state reaction not involving water.

Degens and Epstein (1964) found very similar  $\text{O}^{18}/\text{O}^{16}$  and  $\text{C}^{13}/\text{C}^{12}$  ratios for coexisting sedimentary dolomites and calcium carbonates of a variety of environments, modes of formation, and geologic ages. On the assumption that the equilibrium oxygen isotope fractionation between dolomite and calcite is at least several permil, the authors concluded that the sedimentary dolomites they studied formed by metasomatic replacement of calcite or aragonite by a straightforward solid-state diffusion mechanism. This interpretation of the data is widely disputed.

To date little attention has been given to combining stable isotope and radiogenic isotope measurements in a single system. Such studies can provide very powerful petrologic and mineralogic tools. In their study of the Idaho batholith, Taylor and Magaritz (1976) showed that there is an excellent correspondence between areas of reset K-Ar ages and areas of flow deuterium content. It seems clear that the loss of Ar was caused by widespread meteoric-hydrothermal activity. On the basis of oxygen isotope measurements, Frey et al. (1976) suggested that

radiogenic isotopes in biotite from a regionally metamorphosed terrane in the Alps may have been mobilized without recrystallization, that is, without breaking Al—O or Si—O bonds. These same authors presented evidence that deuterium exchange between minerals and aqueous fluids may have taken place in nature without  $O^{18}$  exchange (without recrystallization). Such an effect has been observed in laboratory systems as well, where the water/mineral ratios were very large. O'Neil and Kharaka (1976) measured appreciable hydrogen isotope exchange rates between clay minerals and water at temperatures as low as  $100^{\circ}\text{C}$ ; the oxygen isotope exchange rates in these experiments were almost negligible. The great disparity in D and  $O^{18}$  exchange rates observed in all their experiments demonstrates that hydrogen isotope exchange occurred by a mechanism of proton exchange independent of the slower process of  $O^{18}$  exchange.

The application of stable isotope techniques to the study of reaction mechanisms is virtually limitless. Some diffusion studies have been made (e.g., Anderson, 1972; Giletti and Anderson, 1975) and others are in progress. There is a severe lack of information on the relative rates of stable isotope exchange reactions in mineralogic systems.

### Crystal Structures

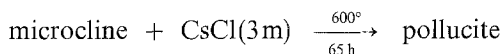
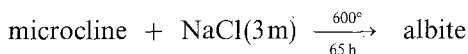
Inasmuch as stable isotope properties of minerals depend ultimately on fundamental interatomic interactions, it is conceivable that stable isotope studies could provide information on details of crystal structure. Mentioned earlier were the relatively large oxygen and hydrogen isotope effects observed in the ice-water system. As we have seen, fractionation factors should be relatively independent of pressure and a study of structural details among the various polymorphic forms of ice should be possible using stable isotope techniques.

In their studies of the relative exchange rates of oxygen and hydrogen isotopes between clay minerals and water, O'Neil and Kharaka (1976) found the exchange rates for montmorillonite markedly greater than for either illite or kaolinite. This effect, which is probably related to the presence of interlayer water in smectite minerals, was first observed in natural samples by Savin and Epstein (1970). Savin and Epstein (1970) found that interlayer water of clay minerals exchanges almost completely with either liquid water or atmospheric water vapor at room temperature in minutes to a few hours. They also demonstrated that when this interlayer water is removed by heating *in vacuo* at  $200^{\circ}\text{C}$ , no hydrogen isotope exchange takes place with the hydroxyl hydrogen of the clay. Hydrogen isotope exchange between hydroxyl groups and water is greatly facilitated by the presence of interlayer water but except for halloysite (Lawrence and Taylor, 1972), the exchange rates are still relatively low. If the mechanism of this exchange can be worked-out through the use of both hydrogen and oxygen measurements, it may be possible to elucidate structural details of interlayer water in certain minerals. Lawrence and Taylor (1972) demonstrated that interlayer water readily exchanges hydrogen isotopes with hydroxyl groups in halloysite even at room temperature. They suggested that this results from the fact that the interlayer water in halloysite is in direct contact with 75% of the hydroxyl groups. The generally accepted structure for the smectite minerals follows the original suggestion of Hofmann et al. (1933), in which the interlayer water is separated from the structural OH groups

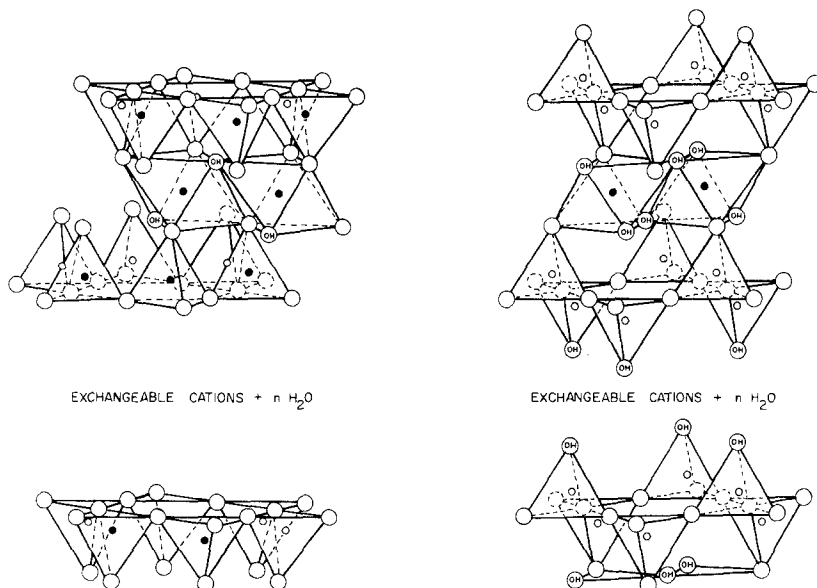
by a sheet of silica tetrahedra. In alternative structures proposed by Edelman and Favejee (1940) and McConnell (1950) various fractions of the available OH groups (50% for the Edelman and Favejee structure) are adjacent to the interlayer water (and exchangeable cations). The proposed structures are shown in Figure 2. Inasmuch as isotopic exchange between OH groups and interlayer water should be greatly facilitated by their intimate association, these initial experiments are more compatible with structures like those proposed by Edelman and Favejee and by McConnell than with that of Hofmann et al. (1933).

On the basis of hydrogen isotope measurements of water released from  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  below and above  $50^\circ\text{C}$ , Heinzinger (1969) identified two kinds of water which differ in their bonding characteristics in the crystal. The oxygen of four water molecules is bonded to the copper ion, that of the fifth molecule is hydrogen bonded. He showed that the water which is hydrogen bonded is enriched in deuterium by 57‰ relative to the water that is coordinated to the copper ion. Heinzinger presents a detailed picture of the bonding in  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , derived not only from the isotope data but from X-ray and neutron diffraction measurements as well.

In heretofore unpublished work, the author has conducted experiments bearing on pollucite, a cesium alumino-silicate. In the following reactions

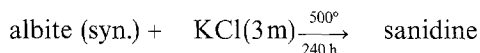
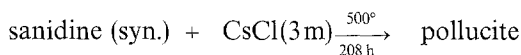
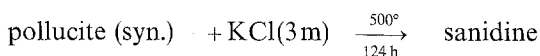


the products are pseudomorphs after microcline and have cores of unreacted microcline. The X-ray pattern of synthetic pollucite formed in this way is identical



**Fig. 2.** Proposed crystal structures for montmorillonite. On the left is the classical structure of Hofmann et al. (1933) and on the right is the structure proposed by Edelman and Favejee (1940)

with that of natural pollucite. The mechanism of such reactions involves fine-scale solution and redeposition as described by O'Neil and Taylor (1967). In another set of experiments, synthetic (syn.) starting materials were allowed to react to completion with alkali chloride solutions:



The permil fractionation of  $\text{O}^{18}$  between the product minerals and water was +1.5 in each case. As part of the extraction procedure for oxygen isotope analysis the oxygen content of the synthetic pollucites were determined to be 10.79 micromoles of  $\text{O}_2/\text{mg}$ . Emission spectrographic analysis indicated 7% Al and 22% Si for these materials. In Table 3 the oxygen, aluminum and silicon contents of the synthetic pollucite are compared with theoretical amounts for the various chemical formulas that have been proposed by several investigators. The chemical data are most compatible with the formula  $\text{CsAlSi}_3\text{O}_8$ , like that of a normal alkali feldspar. Synthetic pollucite behaves like alkali feldspars in reactions with alkali chloride solutions and has identical oxygen isotopic properties to alkali feldspars. From these data it is concluded that despite the fact that pollucite does not have the X-ray diffraction pattern of an alkali feldspar, there are other characteristics which imply a closer similarity to alkali feldspars than had previously been thought.

## Conclusion

The factors that bear on the isotopic properties of minerals as well as some of the uses of stable isotopes in mineralogical studies have been discussed. I have chosen examples chiefly from my own work and that of my coworkers and by no means consider this article an exhaustive review of the subject. Stable isotope techniques are normally applied to the solution of petrologic problems, but it is clear that there is widespread applicability to purely mineralogic problems. The applications to problems of crystal structure are limited, but the use of stable isotopes as tracer materials in mineralogical reactions is a rich field relatively unexploited.

**Table 3.** Oxygen, Aluminum, and Silicon contents of synthetic pollucite and various proposed structural formulas

Mineral	Oxygen	Aluminum	Silicon
Synthetic Pollucite	10.79	7	22
$\text{CsAlSi}_3\text{O}_8$	10.75	7.2	22.6
$\text{CsAl}_2\text{Si}_9\text{O}_{26} \cdot \text{H}_2\text{O}$	10.17	8.1	19.0
$\text{CsAlSi}_2\text{O}_6$	9.61	8.6	17.9
$\text{CsAlSi}_2\text{O}_6 \cdot 1/2\text{H}_2\text{O}$	10.12	8.4	17.4

The oxygen contents are expressed in micromoles of  $\text{O}_2/\text{mg}$ , and the aluminum and silicon in percent



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