O^{18}/O^{16} RATIOS IN COEXISTING MINERALS OF IGNEOUS AND METAMORPHIC ROCKS

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ABSTRACT

The fluorine extraction technique for determination of oxygen isotopic abundances has been investigated, and it has been used to obtain O^{18}/O^{16} analyses of the common rock-forming minerals. A direct comparison with an independent method of analysis, that of reduction with carbon at high temperatures, has shown that both these methods are reliable for quartz samples. Most minerals can be analyzed by the fluorine method to a precision of ± 0.2 per mil. Only olivine and magnetite, of the common igneous and metamorphic minerals, are difficult to react.

Oxygen isotopic analyses of all the major minerals of the four principal rock types of the Southern California batholith have been obtained. For comparison, the same technique has been used upon similar rock types from widely scattered localities, to test the general applicability of the results. All the main rock types of the Skaergaard intrusion have been analyzed, as well as many of the minerals. Various samples of ultramafic rocks, anorthosites, and metamorphic amphibolites have also been run.

It has been found that the crystallization history and mineral paragenesis of igneous rocks are reflected by the oxygen isotopic data. In every instance where conclusive information exists, the isotopic results are in excellent agreement with the sequence and history determined by conventional geological criteria. Most rocks analyzed fell into a consistent pattern with respect to petrologic type. The Skaergaard rocks deviated markedly from the normal isotopic trends, as a direct result of the unusual course of fractional crystallization which they have undergone.

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INTRODUCTION

Aim of the research

The aim of this research is to determine the oxygen isotopic composition of the minerals in some common igneous and metamorphic rocks. Thereby, it is hoped that a greater understanding will be obtained concerning the effects of rock-forming processes upon oxygen isotopic fractionations among minerals. The oxygen isotopic data can then be used in interpreting some of the conditions of formation of igneous and metamorphic rocks.

Specifically, an attempt will be made to evaluate: (1) the use of O^{18}/O^{16} distributions as an indicator of temperature of formation of igneous and metamorphic rocks; (2) the oxygen isotopic composition of igneous rocks as a function of petrologic type and geologic occurrence; (3) whether or not isotopic equilibrium is commonly established in rocks; (4) the effect of magmatic crystallization and differentiation upon the O^{18}/O^{16} composition of igneous rocks; and (5) the approximate equilibrium fractionation factors among minerals at high temperatures.

Previous work

The earliest work on oxygen isotopes in silicates was that of Manian, Urey, and Bleakney(1), who reacted the silicate with carbon and carbon tetrachloride at 1000° C. The carbon monoxide obtained by this reaction was decomposed to give water, and this was in turn electrolyzed to give oxygen. The oxygen was analyzed in an early form of mass spectrometer. The experimental error in O^{18}/O^{16} ratio was about 2.5%, and no variations were found among the samples studied.

Tokuda and Kashida(2) heated silicates with potassium hydrogen fluoride at 230° C., forming water. By precise density measurements upon this water they claimed to be able to determine variations of 1.4 per mil in O^{18}/O^{16} ratio. Such precision should have enabled them to discover differences between igneous and metamorphic rocks, but none were reported.

All the more recent determinations have been made on sensitive mass spectrometers which can give a precision of better than ± 0.2 per mil. Baertschi and Silverman(3) used oxidation with fluorine or chlorine trifluoride at 420° C. to release oxygen from silicates. The fluorine method gave more reproducible results and larger yields of oxygen than did the chlorine trifluoride procedure, and Silverman(4) has used this method to analyze a variety of rocks. The ratio of O^{18}/O^{16} was found to vary by as much as 3 per cent in natural silicates. Sedimentary silica in the form of chert and diatomite was discovered to be richest in O^{18}, while basalts and meteorites were the isotopically lightest rocks analyzed. Granitic rocks were found to be isotopically heavier than basaltic rocks.

Baertschi and Schwander(5) have liberated oxygen from rocks as carbon monoxide, by reduction with carbon at high temperatures. Schwander(6) has used this method to analyze a number of rocks, but Clayton and Epstein(7) demonstrated that only quartz, magnetite, and zircon, of the common rock-forming minerals, can be conveniently analyzed in this manner with any great precision. Only 60-70 per cent yields of carbon monoxide are obtained for minerals other than these three, and as isotopic fractionation occurs during extraction, unreliable analyses are obtained.

Vinogradov, Dontsova, and Chupakhin(8) have analyzed several igneous rocks and meteorites by the carbon reduction method. They report 100 per cent yields of carbon monoxide, and they found meteorites and ultramafic rocks to be isotopically lighter than basalts, and granitic rocks to be isotopically heavier. In view of the difficulties encountered by other workers in applying this method to total rock samples, it is important that further analyses be obtained by their procedure.

Clayton and Epstein(7) have used the carbon reduction method to analyze quartz and magnetite from various geologic environments. They have shown that quartz-magnetite and quartz-calcite pairs from many rocks were apparently formed in equilibrium with a large oxygen reservoir of almost constant isotopic composition. Oxygen isotopic fractionations between these coexisting minerals were found to decrease as their temperatures of formation (estimated on geological grounds) increased.

In addition, two other studies have employed the carbon reduction technique to analyze quartz samples. Engel, Clayton, and Epstein(9) have shown that chert-calcite pairs in limestones bordering a hydrothermal ore deposit have been exchanged with water during the hydrothermal episode; the observed O^{18}/O^{16} fractionations are smaller the greater the proximity to the ore body. Degens and Epstein(10) have analyzed cherts in limestones of varying ages from widely scattered localities. Their work has shown that the older the rock the greater is the likelihood that post-depositional oxygen exchange has altered its isotopic composition. Also, they were able to differentiate between fresh water and marine limestones on the basis of O^{18}/O^{16} content.

Almost all oxygen isotopic studies of igneous and metamorphic rocks, up to the time of the present research, have been mainly concerned with O^{18}/O^{16} compositions of total rock samples. The major exception has been the work of Clayton and Epstein(7) on coexisting carbonates, quartz, and magnetite. Only very limited interpretations can be made using just data on total rock samples. Much more important conclusions can be reached by determining the distribution of oxygen isotopes among the individual mineral phases of a rock. This is the principal reason for the method of approach used in the present study.

Isotope exchange reactions

For this type of study it is necessary to have an understanding of the various processes which can bring about isotopic fractionations in nature. These various mechanisms are reviewed in some detail in this section and in the sections which follow.

The thermodynamic properties of two molecules which differ only in that they contain different isotopes of the same element, are in general different. This difference in properties is a quantum effect, and has been discussed theoretically(11)(12). Following the treatment of Urey(11), consider an isotopic exchange reaction:

$$aA_1 + bB_2 \rightleftharpoons aA_2 + bB_1 \qquad (1)$$

where A and B are molecules which have some one element in common, and the subscripts 1 and 2 indicate that the molecule contains only the light or the heavy isotope, respectively. The equilibrium constant for this reaction, as for any ordinary chemical reaction, is given by:

$$K(T) = \left[\frac{Q_{A_2}}{Q_{A_1}}\right]^a \Big/ \left[\frac{Q_{B_2}}{Q_{B_1}}\right]^b \qquad (2)$$

where the Q's are the partition functions of the molecules containing the various isotopic species.

$$Q = \sum_i e^{-\epsilon_i/kT} \qquad (3)$$

sum over all quantum states

For a perfect gas, or as a first approximation for real gases, the partition functions may be factored into their translational, rotational, and vibrational parts.

$$Q = Q_{tr} \cdot Q_{rot} \cdot Q_{vib} \qquad (4)$$

The translational partition function has its classical value at all temperatures. For all isotopes except those of hydrogen, the rotational partition function also will have its classical value at ordinary temperatures and above. Therefore, only vibrational effects produce any isotope fractionation. The various partition functions are given by:

$$Q_{tr} = \frac{V(2\pi MkT)^{3/2}}{h^3} \qquad (5)$$

$$Q_{rot} = \frac{8\pi^2 IkT}{\sigma h^2} \quad \text{(linear molecules)} \qquad (6a)$$

$$\text{or} \quad \frac{\pi^{1/2}(8\pi^2 kT)^{3/2}(ABC)^{1/2}}{\sigma h^3} \quad \text{(polyatomic)} \qquad (6b)$$

$$Q_{vib} = \frac{e^{-u/2}}{1 - e^{-u}} \quad \text{(diatomic)} \tag{7a}$$

$$\text{or} \quad \prod_i \frac{e^{-u_i/2}}{1 - e^{-u_i}} \quad \text{(polyatomic)} \tag{7b}$$

where M = molecular weight of the molecule
V = volume of the gas
I = moment of inertia of a linear molecule
A, B, C = principal moments of inertia of a polyatomic molecule
σ = symmetry number
u = $h\nu/kT$, where ν is a vibrational frequency (in sec^{-1})

Anharmonicity terms have been neglected in deriving the expressions for the vibrational partition functions.

We then have:

$$\frac{Q_2}{Q_1} = \frac{\sigma_1}{\sigma_2}\frac{I_2}{I_1}\left(\frac{M_2}{M_1}\right)^{3/2}\frac{(e^{-u_2/2})(1 - e^{-u_1})}{(1 - e^{-u_2})(e^{-u_1/2})} \tag{8a}$$

for diatomic molecules, and

$$\frac{Q_2}{Q_1} = \frac{\sigma_1}{\sigma_2}\left(\frac{A_2B_2C_2}{A_1B_1C_1}\right)^{1/2}\left(\frac{M_2}{M_1}\right)^{3/2}\prod_i \frac{(e^{-u_{2i}/2})(1 - e^{-u_{1i}})}{(1 - e^{-u_{2i}})(e^{-u_{1i}/2})} \tag{8b}$$

for non-linear, polyatomic molecules.

These expressions may be simplified, and the ratios calculated without a knowledge of the moments of inertia. A theorem of Teller and Redlich$^{(13)}$ states that the expressions

$$\frac{\nu^2 m^{3n}}{M^3 I^2} \quad \text{and} \quad \prod_i \frac{\nu_i^2 m^{3n}}{M^3 ABC}$$

are invariant under isotopic substitution, where m is the atomic mass, and n is equal to the number of atoms exchanged. Application of this rule to the above equation leads to

$$\frac{\sigma_2}{\sigma_1}\left(\frac{m_1}{m_2}\right)^{3n/2}\frac{Q_2}{Q_1} = \frac{u_2}{u_1}\,\frac{(e^{-u_2/2})(1 - e^{-u_1})}{(1 - e^{-u_2})(e^{-u_1/2})} \tag{9a}$$

and

$$\frac{\sigma_2}{\sigma_1}\left(\frac{m_1}{m_2}\right)^{3n/2}\frac{Q_2}{Q_1} = \prod_i \frac{u_{2i}}{u_{1i}}\,\frac{(e^{-u_{2i}/2})(1 - e^{-u_{1i}})}{(1 - e^{-u_{2i}})(e^{-u_{1i}/2})} \tag{9b}$$

The ratios of the masses will cancel in any isotope exchange reaction, and the ratio of the symmetry numbers, no matter what its value, cannot result in any isotopic enrichment, as it represents only the relative probabilities of forming symmetrical and unsymmetrical molecules.

The only significant term, so far as isotopic fractionation is concerned, is the right-hand side of the above expressions. If $u_{1i} - u_{2i} = \Delta u_i$ is small, as it will be for everything but the isotopes of hydrogen, this term has been shown to be approximately equal to:

$$1 + \sum_i G(u_{2i})\Delta u_i$$

where

$$G(u_{2i}) = \frac{1}{2} - \frac{1}{u_{2i}} + \frac{1}{e^{u_{2i}} - 1} \tag{10}$$

This expression was derived by Bigeleisen and Mayer$^{(14)}$, and they have also demonstrated that if u_{2i} is itself small (less than two), then to a good approximation

$$G(u_{2i}) = \frac{u_{2i}}{12} \tag{11}$$

The expression for the equilibrium constant, K, which finally results is:

$$K(T) = \frac{\left[\frac{\sigma_{A_1}}{\sigma_{A_2}}\left(1 + \sum_i G(u_{2i})\Delta u_i\right)_A\right]^a}{\left[\frac{\sigma_{B_1}}{\sigma_{B_2}}\left(1 + \sum_i G(u_{2i})\Delta u_i\right)_B\right]^b} \tag{12}$$

and it can be seen that a knowledge of the vibrational frequencies, alone, is in general sufficient to calculate the equilibrium constant of an isotopic exchange reaction at a given temperature. These vibrational frequencies have been determined experimentally (usually by infra-red or Raman spectroscopy) for many substances, and Urey(11) has used these data to calculate the equilibrium constants for a large number of isotopic exchange reactions. For the few instances in which these constants have been determined directly by experiment, and for which reliable data on the vibrational frequencies exist, agreement between the theoretical and experimental results has been remarkably good.

In classical mechanics, the right-hand sides of equations 9a and 9b are equal to one, a value of one indicating no separation of isotopes. This is tantamount to saying that the function $\sum_i G(u_{2i})\Delta u_i$ is equal to zero. It should be expected, therefore, that at very high temperatures as the partition function for vibration approaches its classical value $kT/h\nu$, there should be no isotope fractionation. That this is indeed the case is easily seen, because at high temperatures or very low frequencies equation 11 becomes applicable, and $\sum_i (u_{2i}/12)\Delta u_i$ approaches zero as T approaches infinity. At very low temperatures and high frequencies, $G(u_{2i})$ approaches $\frac{1}{2}$, and $\Delta u_i/2$ approaches the difference in zero-point energies for the two isotopic species.

If equilibrium constants for reactions between materials in condensed phases are desired, they may be calculated from the exchanges between the identical materials in the vapor phase, but the respective vapor pressures and vibrational frequencies must be known. Such calculations are difficult, especially for ionic solids and for species in solution. To evaluate directly the ratio of the partition functions in the condensed phases, the effects of interaction between the internal vibrations of a molecule and the fields produced by closely adjoining molecules must be considered. Grant has made a very approximate calculation of this nature for silicon isotope exchange in silicates.(15) These are very complex problems, in general, and isotopic fractionations among condensed phases are much better measured directly by experiment.

Although at very high temperatures all isotopic exchange effects will disappear, and at low temperatures they should be most pronounced, it is not always true that the equilibrium constant of an exchange reaction is a continuously decreasing function of temperature. For certain materials, calculated equilibrium constants change with temperature from a region in which K is greater than one, to a region where it is less than one. This "cross-over" effect is certainly not a general phenomenon, however.

The equilibrium constant, K, of an isotopic exchange reaction is primarily a function only of temperature. Variations in pressure and chemical environment should not markedly modify its value. For reactions between phases of constant chemical composition, or for reactions in ideal gas mixtures, changes in chemical environment can have no effect upon K. Even for real gases, or in solutions, variations in the concentration of other constituents will have, in general, a negligible effect, as long as the chemical nature of the species in question are not altered appreciably. These considerations follow as a result of the ideality of the solutions of isotopic molecules of a compound, and because the products and reactants of an isotopic exchange reaction are nearly identical in terms of molar volumes.

Most of the variations in O^{18}/O^{16} ratio among minerals can be explained on the basis of chemical exchange effects of the type discussed above. However, other mechanisms exist whereby isotopes may be fractionated; these are mentioned below, because in rare instances they may be important in nature.

Diffusion processes

At thermal equilibrium the average velocity of a molecule in a gas is inversely proportional to the square root of its molecular weight. Because the lighter isotope travels with a higher average velocity, it should travel a given distance more rapidly than the heavy isotope in any diffusion process. This can produce an enrichment of the diffusing material in the lighter isotope. In principle, isotopic separation can occur by diffusion in solids and liquids also, but the effect will be much smaller than in gases.

Any chemical potential gradient can make a diffusion process operative, but processes also exist which tend to separate isotopes directly. In the presence of a thermal gradient in a gas, the lighter isotope will in general concentrate in one part of the system and the heavier isotope in the other. Other things being equal, the heavier isotope should become enriched with depth, at equilibrium in a gravitational field.

The importance of diffusive processes in producing significant oxygen isotopic fractionations in nature has never been evaluated in detail. Silverman(4) has called upon diffusion to explain the O^{18}/O^{16} variations he observed in a gabbro-granophyre sequence at Bayfield County, Wisconsin, but on the basis of data in this paper his results can be better interpreted in another manner.

Kinetic effects

Because a light molecule in a gas travels with a higher average velocity than does a heavy one at the same temperature, the lighter isotope will collide more often with the surface of the solid during a solid-gas chemical reaction than does the heavy one. If the rate of reaction is proportional to the collision frequency, a non-equilibrium process exists whereby the reaction products are enriched in the lighter isotope. Such an effect might also occur in reactions in condensed phases, although to a lesser degree.

The collision frequency mechanism described above is just one way in which the rate of reaction of one isotope may differ from the rate of reaction of another. Other effects can be important, although they cannot be obviously related to a simple process such as collision frequency. The problems of the kinetics of chemical reactions of different isotopic molecules have been treated by Bigeleisen(16), and considerable experimentation has been carried out on the subject by other workers.

Fractional distillation

The respective vapor pressures of two chemical species, differing only in that they contain different isotopes of one element, are in general different. Relative vapor pressures for a few volatile substances have been tabulated by Urey(11). For example, for water at its boiling point:

$$\frac{p_{H_2O^{16}}}{p_{H_2O^{18}}} = 1.0046$$

A "cross-over" phenomenon exists in such ratios of vapor pressures, and appears to be a regular feature of these relationships. At 217° C., for example, the calculated vapor pressures of H_2O^{18} and H_2O^{16} are identical, and above this temperature H_2O^{18} has the higher vapor pressure.(11)

These differences in vapor pressures provide another mechanism whereby isotopes may be separated, because through distillation one isotope is concentrated in the vapor phase relative to another. It is impossible to state, in general, whether the lighter or the heavier isotope will be concentrated in the vapor phase, as this will depend upon the temperature and upon the substances involved.

Definition of terms

All data are reported in terms of the quantity δ:

$$\delta = \left[\frac{R_{(\text{sample})}}{R_{(\text{standard})}} - 1\right] 1000$$

where $R_{(\text{sample})}$ is O^{18}/O^{16} in the sample

$R_{(\text{standard})}$ is O^{18}/O^{16} in the standard

δ is thus the deviation in per mil (parts per thousand) in the O^{18}/O^{16} ratio from that of an arbitrary standard. The standard used in this work is Hawaiian ocean water. A $\delta = +10$ means that the sample has an O^{18}/O^{16} ratio 1 per cent, or 10 per mil, greater than that of ocean water.

The principal quantities with which one is concerned in this type of work are the variations in O^{18}/O^{16} in one substance relative to another. Such variations are most simply reported as Δ, the difference between the δ-values for the two substances. For example, the quantity $\Delta_{\text{QUARTZ-MAGNETITE}}$ is identical to $\delta_{\text{QUARTZ}} - \delta_{\text{MAGNETITE}}$, and is a measure of the fractionation of oxygen isotopes between a quartz sample and a magnetite sample.

These Δ-values, or δ-differences, are related to the actual fractionation factor, α, in the following way, using quartz and magnetite as examples:

$$\alpha = \frac{(O^{18}/O^{16})_{\text{qtz}}}{(O^{18}/O^{16})_{\text{mag}}} = \frac{(O^{18}/O^{16})_{\text{std}}\,(1 + \delta_{\text{qtz}}/1000)}{(O^{18}/O^{16})_{\text{std}}\,(1 + \delta_{\text{mag}}/1000)}$$

from the definition of δ, given above.

Then we have

$$\alpha = \left[1 + \frac{\delta_{\text{qtz}}}{1000}\right] \Big/ \left[1 + \frac{\delta_{\text{mag}}}{1000}\right]$$

and, making an approximation which is valid for $\frac{\delta_{\text{mag}}}{1000} << 1$, we have

$$\alpha \cong 1 + \frac{\Delta_{qtz-mag}}{1000}$$

Taking a numerical example, suppose $\delta_{QUARTZ} = 29.7$ and $\delta_{MAGNETITE} = 10.2$. Then $\Delta_{QUARTZ-MAGNETITE} = 19.5$, and $\alpha = 1.0297/1.0102 = 1.0193$. The approximate expression relating α and Δ is

$$\alpha \cong 1 + \frac{19.5}{1000} = 1.0195$$

The fractionation factor for two substances in a given isotopic exchange reaction is related to the equilibrium constant in the following manner. If the molecules of the chemical compounds under consideration each contain only one atom of the element undergoing exchange, then the equilibrium constant and the fractionation factor are identical. An example of this would be the reaction

$$CO^{18} + H_2O^{16} \rightleftharpoons CO^{16} + H_2O^{18}$$

$$K = \frac{[H_2O^{18}]}{[H_2O^{16}]} \Big/ \frac{[CO^{18}]}{[CO^{16}]} \; ; \qquad \alpha = \left(\frac{O^{18}}{O^{16}}\right)_{H_2O} \Big/ \left(\frac{O^{18}}{O^{16}}\right)_{CO}$$

and α is seen to be equal to K.

When these conditions are not met, each individual reaction must be considered separately. An example used by Urey(11) in this connection is the exchange between carbon dioxide and water:

$$\tfrac{1}{2}CO_2{}^{16} + H_2O^{18} \rightleftharpoons \tfrac{1}{2}CO_2{}^{18} + H_2O^{16}$$

$$K = \frac{[CO_2{}^{18}]^{\frac{1}{2}}}{[CO_2{}^{16}]^{\frac{1}{2}}} \Bigg/ \frac{[H_2O^{18}]}{[H_2O^{16}]}$$

The fractionation factor for this reaction is

$$\alpha = \frac{(O^{18}/O^{16})_{CO_2}}{(O^{18}/O^{16})_{H_2O}} = \frac{2[CO_2{}^{18}] + [CO^{16}O^{18}]}{[CO^{16}O^{18}] + 2[CO_2{}^{16}]} \Bigg/ \frac{[H_2O^{18}]}{[H_2O^{16}]}$$

If the equilibrium constant for the reaction

$$CO_2{}^{18} + CO_2{}^{16} \rightleftharpoons 2CO^{16}O^{18}$$

is equal to 4, as it will be if the proportions of the isotopic species are determined by random distribution, it is easily shown that

$$\alpha = \frac{(O^{18}/O^{16})_{CO_2}}{(O^{18}/O^{16})_{H_2O}} = \frac{[CO_2{}^{18}]^{\frac{1}{2}}}{[CO_2{}^{16}]^{\frac{1}{2}}} \Bigg/ \frac{[H_2O^{18}]}{[H_2O^{16}]}$$

and $K = \alpha$, as before.

It is generally true, therefore, if the probabilities of forming the various isotopic species of a compound are determined by the symmetry numbers alone, that the fractionation factor is identical with the equilibrium constant. The equilibrium reaction must, however, be written with fractional stoichiometric coefficients so that only one atom of each molecule is exchanged. Also, this generalization is not valid for compounds in which the isotopes of hydrogen are considered, or for those in which the several atoms of a single element are not equivalent, as in N_2O where only one of the nitrogen atoms is bound to oxygen.

APPARATUS AND EXPERIMENTAL PROCEDURES

Experimental requirements

When the present work was initiated, it was known that the differences in δ for coexisting magnetite and quartz in igneous and metamorphic rocks were of the order of 7-13 per mil. Also, previous work indicated that quartz-potash feldspar fractionations of 1-2 per mil might be expected in igneous rocks. The mass spectrometer in this laboratory may be used to measure variations in the oxygen isotopic composition of carbon dioxide gas with a precision of better than 0.2 per mil. It is therefore possible to obtain analytical results of sufficient accuracy to give geologically interesting information about O^{18}/O^{16} fractionations among rock-forming minerals.

Given mass spectrometry of such accuracy, the critical problem is to extract oxygen from a mineral and convert it to carbon dioxide without introducing any errors greater than 0.2 per mil. Only very careful analytical procedures can give such precision, and the number of possible methods is limited because of the difficult chemical problem of extracting oxygen from silicates. All chemical reactions must be carried out either quantitatively or with no isotope fractionation.

Extraction of oxygen by reaction with fluorine appears to be the most reliable procedure that is applicable to a wide variety of minerals, and it is used in the present investigation. Samples analyzed by the fluorine method are, however, compared with analyses of the same samples done by reduction with carbon at high temperatures, to better check the analytical accuracy of both procedures.

Fluorine oxidation

General statement - Fluorine gas reacts with oxides and silicates, producing oxygen and metal fluorides. Three typical reactions are:

$$SiO_2 + 2F_2 \longrightarrow SiF_4 + O_2$$

$$2Fe_3O_4 + 9F_2 \longrightarrow 6FeF_3 + 4O_2$$

$$CaMgSi_2O_6 + 6F_2 \longrightarrow CaF_2 + MgF_2 + 2SiF_4 + 3O_2$$

Baertschi and Silverman(3), and Silverman(4) have used the fluorine oxidation procedure to extract oxygen from a variety of geologic materials. They reacted rocks at 420° C., using hydrogen fluoride as a catalyst. Hydrogen fluoride was found to be necessary because silicates react slowly with pure fluorine under such conditions. Higher temperatures could not be used because the nickel fluoride armoring film on the inner walls of the reaction vessels decrepitates, and fluorine rapidly attacks the vessels themselves. Sample materials were ground finer than 100 mesh, and 50 mg aliquots were loaded into the nickel reaction vessels in a "dry box" under an atmosphere of dry nitrogen. Without again exposing the inner surfaces to air, the vessels were fitted to an all-nickel vacuum line, 6 at a time, a vacuum seal being obtained by using Teflon gaskets at the junctures. The reactions with excess fluorine were carried out for at least 6 hours. Gaseous reaction products were oxygen, excess fluorine, hydrogen fluoride, and any volatile fluorides which may have been present. Hydrogen fluoride and the other volatile fluorides were removed by passing the gas mixture through a liquid nitrogen trap. Fluorine was removed by passing the remaining gas through a trap containing heated potassium bromide. The bromine liberated by this reaction was then frozen out in another liquid nitrogen trap, leaving only oxygen gas, which was collected and analyzed in a mass spectrometer. Quantitative yields of oxygen were obtained for most materials, as well as reproducible isotopic analyses, although results were less reproducible for the more mafic rocks such as basalt. The extraction procedure used by Baertschi and Silverman, with modifications to give improvements in accuracy, is the procedure which is used in the present work.

Apparatus -

(a) high vacuum system (fig. 1) - The part of the vacuum system with which fluorine comes into contact is constructed of metal that forms an armoring film of metal fluoride, protecting the metal from further attack by fluorine in much the same manner in which aluminum is protected from atmospheric oxidation by an oxide coating. Inconel or copper tubing, with copper elbows and tees, are used, and all parts are joined together with silver solder. Connections to removable parts are made by flanged joints with Teflon gaskets. Valves with Monel body, Inconel diaphragm, and Teflon gasket are used (Hoke, Inc. #413). Pressure in the line is determined by 3 Bourdon-type pressure and vacuum gauges with Monel diaphragm. An ordinary thermocouple gauge is used to determine finer vacuums and is never exposed to fluorine. Glass-to-metal transitions are made with Kovar seals.

(b) fluorine container - Fluorine gas from a commercial compressed gas cylinder, stored for safety outside the laboratory, is introduced into the vacuum line through Inconel tubing.

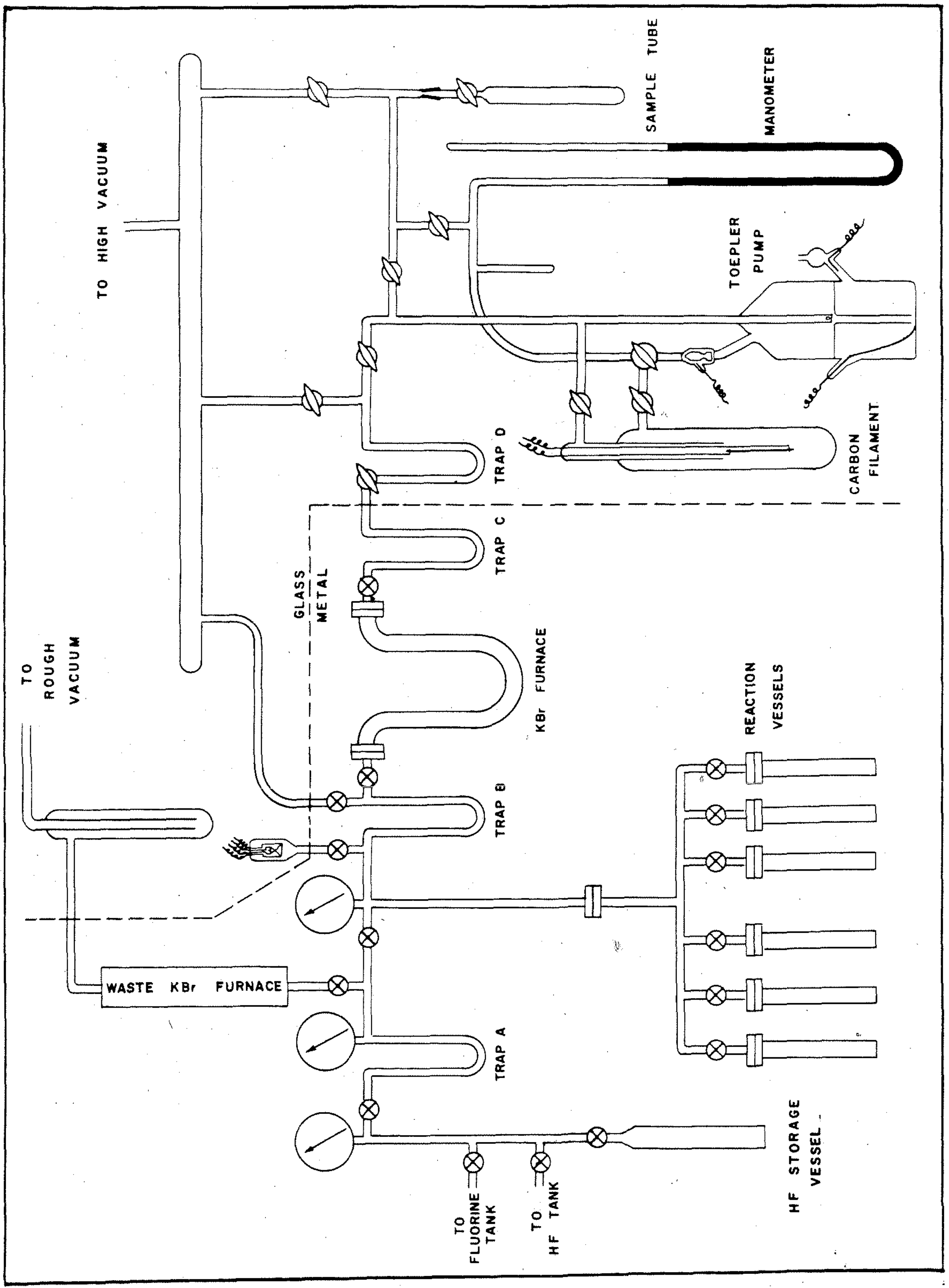


Fig. 1. Fluorine extraction and collection lines.

(c) hydrogen fluoride container - Hydrogen fluoride is stored in a nickel vessel which is part of the vacuum line, and this vessel is refilled as necessary from a commercial cylinder of hydrogen fluoride.

(d) reaction vessels - The 6 reaction vessels are connected to a removable section of the vacuum line through flanged joints with Teflon gaskets, by screwed fittings. The vessels are made of nickel tubing 7/8 in. O.D., 5/8 in. I.D., 10 in. long, with welded bottoms. They have a capacity of approximately 50 cm^3. A cooling coil of 1/4 in. copper tubing is wrapped around the top of each reaction vessel, and during heating of the reaction vessels water is circulated through this tubing to protect the Teflon gaskets. Electrical resistance heated furnaces are used to heat the reaction vessels.

(e) potassium bromide furnaces - Two heated tubes contain solid, coarsely crystalline potassium bromide. One, used for reaction of waste fluorine, is a horizontal tube of 18-8 stainless steel $1\frac{1}{2}$ in. diameter and 18 in. long. The other, used for removal of fluorine from the sample gas, is a U-tube of pure nickel, 7/8 in. O.D., 5/8 in. I.D., with a total length of 36 in. It is surrounded by an electrical resistance heated furnace, maintained at 200° C.

(f) collection line - The part of the vacuum line which does not come into contact with fluorine or hydrogen fluoride is made of pyrex glass tubing, with an Urry-type automatic toepler pump for collecting gas samples and a mercury-filled manometer tube for measuring the volume of gas collected. High-vacuum, ground-glass stopcocks, lubricated with Apiezon N stopcock grease, are used throughout.

(g) carbon filament - Oxygen is converted to carbon dioxide by reaction with a hot carbon rod. The rod is prepared from a 1/8 in.

pressed graphite spectrographic electrode, 3 in. long. The cross-sectional area of the center of the rod is reduced by a factor of four by carefully grinding it. Electrical connection is made through 1 mm platinum rods in holes drilled through the graphite rod near the ends. The platinum leads are joined with threaded couplings to No. 12 copper wires, which are in turn connected to tungsten leads which pass through the glass and out of the vacuum system. The leads pass down the central tube of a glass trap with a 40/50 ground joint, supporting the filament inside the trap near the bottom, as shown in fig. 1. The carbon of the filament is used up in the reaction, and a new rod is usually necessary after about 6 samples have been converted.

(h) vacuum pumps - For attainment of high vacuum, a conventional set-up using a 2-stage mercury diffusion pump backed by a Welch duo-seal mechanical pump is used on the main part of the line. The automatic toepler pump is operated through an electrical relay by another Welch duo-seal pump, this same pump at other times being used to produce a rough vacuum in the waste fluorine system.

(i) dry box - Samples are loaded into the reaction vessels in an atmosphere of dry nitrogen. This is done in a specially designed plastic box approximately 3 ft. x 2 ft. x 2 ft. through which are fitted shoulder-length latex rubber gloves. Materials are inserted into the dry box through a hinged flap in the side, and the flap is sealed with a waxy material. Connection is made near the bottom of the box to a cylinder of dry nitrogen, and gas is allowed to escape from the box through a small valve in the top. A humidity meter, 6 weighed samples in 10 ml beakers, 2 petri dishes filled with powdered phosphorus pentoxide drying agent, a wrench, and extra Teflon gaskets are placed inside the box along with the removable assembly of 6 reaction vessels, during a loading. Dry nitrogen is cycled through the box, a small fan on the inner wall insuring good circulation and rapid drying.

Analytical procedure - Before an extraction is made, the inner surfaces of the reaction vessels are cleaned to a high polish with steel wool, rinsed with carbon tetrachloride, and flushed with dry nitrogen. The vessels are then fastened onto the vacuum line, evacuated, and filled with fluorine and hydrogen fluoride. The vessels are isolated and heated to approximately 450° C. for a minimum of two hours. Simultaneously, the entire metal portion of the vacuum line is treated with a mixture of fluorine and hydrogen fluoride, and the line is heated at intervals with a torch. This procedure is necessary to remove extraneous oxygen compounds from parts of the line which will be exposed to fluorine during a sample extraction. All oxide films are removed, and the interior metal surfaces are covered with a fluoride film.

The system is then evacuated through the waste potassium bromide furnace, and the hydrogen fluoride and newly-formed bromine are frozen into a liquid nitrogen trap (-195.8° C.). After a rough vacuum is attained by pumping through the waste system, the line is isolated and opened to the high vacuum, mercury diffusion pumping system, which produces a vacuum of about 10^{-4} mm Hg. During this outgassing, the reaction vessels remain heated to 450° C., and the metal line is torched at intervals. If the thermocouple gauge indicates that the system is vacuum tight after an outgassing period of at least 2 hours, the reaction vessels are sealed off, and the removable assembly of 6 reaction vessels is taken from the line and placed in the dry box. Inasmuch as atmospheric oxygen and moisture are possible sources of isotopic contamination, entry of air into the reaction vessels is carefully avoided beyond this stage.

Removing water vapor from the atmosphere of the dry box, and replacing the air with nitrogen, generally takes 8-10 hours. When the humidity meter indicates zero humidity, each vessel is in turn unbolted from its Teflon gasket seal and charged with a previously weighed 30 mg or 40 mg sample. The reassembled group of reaction vessels are returned to the fluorination line. All parts of the metal line which have come into contact with air during the transfer from the line are again treated with a hot fluorine-hydrogen fluoride mixture for at least one hour. This material is removed through the waste vacuum line, and the reaction vessels are then evacuated. The valve of each reaction vessel is opened slowly to insure that none of the powdered sample is blown out of the reaction vessel by a too rapid evacuation. Also, each vessel is tested separately to make certain that a vacuum seal was maintained during the reassembly in the dry box. This insures that if a gasket leak is present in one of the vessels, all the samples are not spoiled by contact with air from this leak.

The reaction vessels are heated to about 450° C. and outgassed for one hour. The metal portion of the line is then isolated, and approximately 15 mg of hydrogen fluoride are condensed into each reaction vessel by cooling the vessels in a mixture of dry ice, chloroform, and carbon tetrachloride. About 40 cm^3 (S.T.P.) of fluorine gas are then added to each vessel, the valves closed, and the vessels heated to 450° C. for at least eight hours. Higher temperatures, up to 520° C., are used for certain mineral samples, as will be described in a later section.

With Dewar flasks of liquid nitrogen placed around U-tube traps B, C, and D (fig. 1), the valve of a reaction vessel is opened and the gaseous reaction products are allowed to stream slowly into the main potassium bromide furnace. After 10-15 minutes, the valve on the collection system side of the furnace is opened slightly, and the gas slowly streams through traps C and D and into the toepler pump, which forces it into the manometer. The collection procedure generally takes 30-45 minutes, and the reaction vessels are heated throughout this interval.

The gas sample consists only of oxygen liberated from the mineral plus the small amount of oxygen and nitrogen present as original impurities in the fluorine. Its volume is measured in the calibrated manometer, and the gas is then cycled by the toepler pump through the glass vessel containing the heated graphite filament (orange-red in the center). The entire vessel is immersed in a Dewar flask filled with liquid nitrogen.

The oxygen in the sample gas is converted to carbon dioxide, which is immediately frozen out on the sides of the glass vessel, thereby forcing the reaction to completion. This conversion is done in four stages; the reasons for so doing are outlined in a succeeding section. In the first stage, approximately half the gas is reacted to completion, the remainder being held in the manometer. In the second stage, an aliquot of 90 per cent of this remaining gas is converted. Only 5 per cent of the original sample now remains unconverted, and another 90 per cent aliquot of this is reacted during the third stage. The small amount of oxygen still remaining (about 0.5 per cent of the original volume) is then reacted to completion with the temperature of the filament just high enough so that reaction barely proceeds.

Any traces of non-convertible gas remaining are pumped away, and the carbon dioxide is frozen into the manometer and its volume measured. For most samples, 100 per cent yields are obtained, producing 10–12 cm^3 of carbon dioxide. Finally, the carbon dioxide is condensed into a sample tube and taken to the mass spectrometer, where its oxygen isotopic composition is determined.

During the conversion procedure outlined above, all the condensible material frozen into the 3 U-tube traps in the course of the collection is removed through the waste vacuum line and frozen into the waste bromine trap. The line is then opened to high vacuum and heated with a torch and outgassed for approximately one hour, the average time necessary for a comlete conversion. The line is thus ready for another collection as soon as the previous sample has been frozen into a sample tube. The contents of all 6 reaction vessels can usually be collected in one day, 14–18 hours generally being required.

As soon as the sixth sample is collected, the entire procedure outlined above is begun again with 6 more samples, and barring unforeseen circumstances, 6 samples can ordinarily be collected and converted every 4 days. The reaction vessels are usually not cleaned with steel wool after each set of runs, unless the previous set of samples gave less than 100 per cent yields. Instead, the vessels are simply filled with fluorine and hydrogen fluoride and reheated at 450° C. for at least 12 hours. After another period of outgassing they are again ready for a loading. During loading in the dry box the reaction vessels are emptied of the residual fluorides left over from the reaction of the previous sample.

Mass spectrometry

The mass spectrometer used in this work is a 60°, single-focusing, double-collecting instrument of the type described by Nier(17), with modifications as described by McKinney et al(18). Various features give this instrument a much higher sensitivity than can be obtained with commercial mass spectrometers, and measurements can be carried out with a precision of better than 0.2 per mil.

The carbon dioxide sample is introduced into the ion source of the mass spectrometer through a tiny gas leak, whereby the pressure is reduced from centimeters to less than a micron. The gas is ionized to CO_2^+, and these ions, while passing through collimating slits, are accelerated by means of an electrostatic field of about 1500 volts. They emerge from the final slit as a well-defined beam of CO_2^+ ions of nearly constant energy. The ions pass through a magnetic analyzer and are deflected into different paths, depending upon their mass.

The ion beam corresponding to mass 46, and the ion beams due to mass 45 plus mass 44, are collected simultaneously on two collectors that have been mounted at the points of best focus of the resolved beams. Upon hitting the collectors the ions are neutralized, imparting an electric current to the collectors. The positive ion current due to mass 44 plus mass 45 is 1.7×10^{-9} amps. The current due to mass 46 is about 1/250 of this, or 6.8×10^{-12} amps, corresponding to the collection of 4×10^{7} ions per second.

Simultaneous collection of the beams is important, because the ratio of the intensities of two ion beams can be measured with much greater accuracy than can the absolute intensities of the beams. Fluctuations in total beam intensity due to instabilities in the source are nullified by measuring an isotopic ratio. The currents from the collectors pass through high-value resistors, across which are developed voltages proportional to the ion intensities striking the collectors. The voltages developed by the two signals are balanced and compared with one another in a bridge circuit. The output of the circuit gives a null point which is recorded on a sensitive potentiometer.

The isotopic ratio in the sample gas is compared with the ratio in a standard gas. This is done with the aid of a magnetically operated valve in the gas feed system, which permits the switchover from a standard gas to the unknown in a matter of seconds. This allows rapid comparison of the O^{18}/O^{16} ratios of the gases at a time when conditions in the mass spectrometer source are essentially the same for both gases. In this way, long-term drifts in electronics are cancelled out, as are the effects of any fractionation or mass discrimination in the spectrometer itself. The effect of gas background impurities is also common for the two samples.

The experimentally determined quantity is, therefore, the relative difference in an isotopic ratio between the sample gas and the standard gas. This quantity must then be corrected in the manner outlined by Craig(19), in order to obtain the pure difference in O^{18}/O^{16} ratios between the two gases. A correction is necessary because of the minor amounts of O^{17} and C^{13} which enter into the uncorrected isotopic ratio.

At least two separate mass spectrometric determinations were done upon each carbon dioxide sample analyzed in this work.

SPECIFIC PROBLEMS

Sample preparation

Mineral samples used in this work are prepared from the least altered rock samples available. Only a few samples contained more than 1 per cent hydrothermal alteration, and these are described in discussions of the respective suites of rocks in a subsequent section. None of the rocks analyzed had been weathered to any noticeable degree.

Where hand-picking is used to separate minerals, or where separation is easily accomplished with heavy liquids and magnetic separator, 95-100 per cent pure samples are readily obtained. If minerals are too fine-grained for convenient hand-picking, and if their densities and magnetic susceptibilities are similar, greater than 90 per cent purity is difficult to obtain. Accurate oxygen isotopic results can be obtained even for such impure mineral separates, however, because a correction can be made for the isotopic composition of the impurity. Generally, the impurity has very nearly the same O^{18}/O^{16} ratio as the sample, so a correction of the analytical result is usually 0.1 per mil or less, within the experimental error. Inasmuch as all minerals from a given rock are analyzed, such corrections are always possible.

A principal concern of any type of analytical work is whether the final experimental results are representative of the mass one is attempting to sample. In the present study, an attempt has been made to make representative samples of the various minerals in a "large hand specimen". It is probable that isotopic analyses of such samples will also very nearly represent the large mass of rock from which the sample was collected, if the body of rock is fairly uniform. This has not been checked in detail, but isotopic variations within a given rock type appear to be small enough to make this a reasonable assumption.

In picking grains by hand, large, single grains of a mineral are favored over the smaller, binary grains. One is discriminating in the sample in favor of the large grains, and also in favor of the central parts of those grains. Similarly, in heavy liquid separations or in magnetic separations, only the purest concentrates are accepted, and binary grains and grains whose chemical compositions vary from the average are discarded. For example, some discrimination against the outer-most, lower specific gravity zone of a zoned plagioclase might result. A bias enters the results if the O^{18}/O^{16} ratio of the outer zone is different from that of the inner zone. Unfortunately, these sampling errors are not easy to evaluate, but in all likelihood they are minor, and within the experimental error.

The grinding of samples in air with an agate mortar and pestle conceivably could affect the oxygen isotopic analyses of a sample. The agate mortar may contribute isotopically heavier silica to the sample, or water vapor may be adsorbed onto the surface of the mineral powder during grinding. In the grinding of magnetite in moisture-laden air, oxidation of the iron may occur under the heat developed by grinding.

To evaluate these several possibilities, a magnetite sample was treated in three distinct ways. One split, from crushing in a diamond mortar, was analyzed directly. Another split was ground in air, and still another was ground in the dry box under an atmosphere of dry nitrogen. All samples were passed through 200 mesh screen and analyzed, with results as shown in Table I.

Table I

Analyses of U.B. 157 magnetite under differing conditions of preparation

Run	Reaction yield (%)	$\delta O^{18}/O^{16}$ (‰)	Procedure
161	98	4.4	Ground in air
162	98	3.9	Crushed in air
163	97	3.9	Ground in dry box
165	101	4.1	Ground in air
166	103	4.0	Ground in dry box
205	96	3.8	Ground in air
211	101	3.9	Ground in air

The analyses are in relatively good agreement, and there is no evidence of a significant isotopic effect dependent upon the method of grinding a sample.

Reaction with fluorine

Quantitative yields of oxygen are easily obtained from most rock-forming minerals by the fluorine extraction process. Quartz, plagioclase, potash feldspar, muscovite, biotite, hornblende, clinopyroxene, orthopyroxene, spodumene, apatite, and ilmenite have been analyzed without undue difficulty. Yields are measured to only ± 2 per cent, but there is little doubt that essentially all the oxygen contained in these minerals is released by reaction with fluorine and hydrogen fluoride.

On the other hand, problems have been encountered in attempting to analyze certain other minerals — olivine, magnetite, epidote, and garnet. Quantitative yields of oxygen are difficult to obtain from these minerals, and oxygen isotopic analyses of these are less precise than for those minerals which are more easily reacted. Even were the isotopic data reproducible, doubts would be cast upon its validity so long as 100 per cent of the oxygen in a sample is not extracted.

If olivine and magnetite are simply ground to minus 100 mesh, reaction yields are very low, between 20-40 per cent. If these minerals are ground to minus 200 mesh, yields are larger — 60-85 per cent. Maximum yields are obtained when the materials are ground finer than 200 mesh and reacted with $1\frac{1}{2}$ times the normal amount of fluorine and twice the normal amount of hydrogen fluoride,,at the highest possible temperatures, 490-520° C., for 2-3 days. At higher temperatures the nickel fluoride armor film in the reaction vessels decrepitates. If the above procedure is followed, yields of 85-100 per cent are recorded.

In Table II are tabulated all pertinent data on reaction yields and oxygen isotopic analyses of the four minerals so far investigated that react slowly with fluorine. The difficulties in obtaining complete reaction yields are a reaction rate effect, because the reactions are all thermodynamically favorable. Forsteritic olivine, for example, is almost identical chemically to enstatite, yet the latter quickly reacts with fluorine to give complete oxygen yields. As the data in Table II indicate, the finer a material is ground, and the higher the temperature of reaction, the larger is the reaction yield.

None of the highly polymerized silicates, with single-chain, double-chain, sheet, or three-dimensional network structures, are difficult to react. Only the independent tetrahedral silicates olivine, garnet, and epidote, of those which have been studied, are difficult of

Table II

Isotopic analyses of minerals that are difficult to react with fluorine

				Reaction procedure		
Run	Sample	$\delta O^{18}/O^{16}$ (‰)	Yield (%)	Mesh size	Temp. °C.	Time (hrs.)
	Olivines					
96	Gila River	6.3	29	-100	450	30
158	" "	5.1	95	-200	490	150
160	" "	5.1	85	-200	450	160
164	" "	5.1	93	-200	510	25
95	Union Bay	4.5	19	-100	450	25
156	Union Bay	5.8	80	-200	460	250
159	Union Bay	5.7	82	-200	480	200
380	Union Bay	6.2	53	-200	470	50
171	I-37-2 Duke I.	4.9	71	-200	500	100
379	" "	5.3	62	-200	470	70
377	I-40-2 Duke I.	6.0	62	-200	470	75
378	H-4-4 Duke I.	5.7	11	-100	500	30
408	Skaergaard	4.5	77	-200	480	35
	Magnetites					
129	A.L. II	5.5	23	-100	450	10
132	" "	4.7	35	-100	450	70
130	HJ-23-55	3.4	85	-200	450	25
133	HJ-23-55	2.7	74	-200	450	75
161	U. B. 157	4.4	98	-200	450	100
162	" "	3.9	98	-200	470	55
163	" "	3.9	97	-200	470	50
165	" "	4.1	101	-200	480	50
166	" "	4.0	103	-200	480	25
205	" "	3.8	96	-200	470	20
211	" "	3.9	101	-200	470	25
217	San Marcos	2.3	102	-200	450	200
223	San Marcos	2.8	91	-200	440	50
239	San Marcos	2.9	75	-200	420	30
245	San Marcos	3.0	75	-200	420	20
330	San Marcos	4.0	54	-200	400	20
402	Skaergaard	4.6	87	-200	520	120
	Others					
270	Bonsall epidote	6.2	48	-200	430	100
281	A-9A garnet	6.6	75	-200	430	20
420	" "	7.3	81	-200	450	40

reaction. This suggests that crystal structural type may have a bearing upon this problem.

When quartz is reacted with fluorine, the only fluoride formed is SiF_4, a gas. With most other materials, some non-volatile fluorides such as CaF_2, NaF, and MgF_2 are formed, and these may provide an armor coating on the mineral grains, slowing further reaction. One might therefore expect that the higher the ratio of volatile fluorides to refractive fluorides formed during a reaction, the greater would be the reaction rate. The minerals with independent silica tetrahedra are lowest in SiO_2 content among the silicates, and the data of Table II are thus compatible with the above reasoning. Single analyses have been carried out upon two other independent tetrahedral silicates, sphene and zircon, with oxygen yields of 103 per cent and 95 per cent, respectively. These minerals are perhaps more easily reacted because the fluorides of zirconium and titanium are volatile at the temperatures of reaction. The same reasoning may explain why ilmenite reacts so much more easily with fluorine than does magnetite, even though the structures of the two minerals are not markedly dissimilar.

Samples of the same mineral type from various localities present varying degrees of resistance to fluorine attack. One olivine sample (Union Bay) has never yielded over 85 per cent of its oxygen in any analysis, although another olivine (Gila River) consistently gave 85-95 per cent yields under the identical reaction procedure. Such variations among samples of the same mineral may be caused by the degree to which minute fractures or other physical imperfections are present. This may be the explanation why the magnetite U.B. 157 is more easily reacted than the other magnetites shown in Table II, but its relatively high TiO_2 content (about 5 per cent) may be a factor.

Probably few oxygen-bearing minerals exist for which it is impossible to obtain quantitative yields of oxygen by the fluorine extraction procedure. Slowness of reaction rates is a factor for only a few materials, and even these should present only minor difficulties, if special precautions are taken with respect to fineness of grain size, and temperature and duration of reaction. Crystal structural type, relative amounts of volatile and non-volatile fluorides formed during reaction, perfection and degree of cleavage, and presence or absence of minute fractures, may all be important in determining the ease with which quantitative yields of oxygen may be obtained from a given mineral.

Contamination

Oxygen in fluorine - The commercial cylinder of fluorine used in these studies contains oxygen and nitrogen as impurities. A chemical analysis of the gas contained in this cylinder is given below:

Substance	Weight per cent
fluorine	98.64
oxygen	0.36
nitrogen	1.00

The oxygen impurity has been analyzed by running blanks of fluorine through the extraction and collection procedure, just as if a sample were being collected. Reaction vessels are filled with approximately the amount of fluorine used during an ordinary sample extraction, with or without hydrogen fluoride. All 6 vessels are heated and their contents collected, thus giving 6 times the amount of contamination of any given mineral analysis. The results of these procedures are listed in Table III.

Table III

Analyses of oxygen from commercial cylinder of fluorine

Run	$\delta O^{18}/O^{16}$ (‰)	Type	Volumes (S.T.P.) oxygen (cm^3)	Volumes (S.T.P.) nitrogen (cm^3)
46	11.8	with HF	1.0	0.6
47	9.5	with HF	1.0	0.7
67	12.8	with HF	1.6	1.2
194	10.5	no HF	0.8	1.2
195	10.9	no HF	0.9	1.2
320	11.2	with HF	0.9	1.0

Reproducibility is good, considering that: (1) such small samples are being analyzed that other contamination effects and errors are magnified; and (2) where blanks are run with hydrogen fluoride, oxygen from any water in the HF is added to the samples.

Corrections of each sample analyzed in these studies are therefore done on the basis of 0.2 cm^3 of oxygen of isotopic composition $\delta = 11.5$ per mil. Fortunately, this δ-value is very near the values of most of the samples analyzed, so the correction ordinarily amounts to no more than 0.1 per mil.

<u>Water in the hydrogen fluoride</u> - Hydrogen fluoride has a great affinity for water, and should any water be present during a reaction it is decomposed by the fluorine, thereby adding extraneous oxygen to the sample gas. To prevent this, the hydrogen fluoride is made anhy-

drous by prolonged exposure to fluorine gas before it is used. This is carried out several times on each new aliquot added to the storage vessel from the commercial cylinder.

Necessity for using dry box - The use of the dry box during sample loading was shown to be necessary by the following experiment. All reaction vessels were filled with dry nitrogen, and each vessel was opened and charged with a sample while still on the vacuum line. The interior of each vessel was exposed to the atmosphere no longer than 30 seconds, and as soon as the vessel was tightly sealed it was evacuated. The interior walls of the reaction vessels were thus exposed to moisture for no longer than 3 minutes. The results of this experiment are shown in Table IV, along with the most probably correct isotopic analysis of each sample, obtained from runs in which the dry box was used.

Table IV

Run	Sample	$\delta O^{18}/O^{16}$ (‰)	Most accurate value $\delta O^{18}/O^{16}$ (‰)
333	Potsdam sandstone	15.2	15.5
334	Olivine - Union Bay	3.7	5.8
335	Olivine - Union Bay	4.2	5.8
336	Magnetite - San Marcos	2.7	3.0
337	Olivine - Gila River	4.2	5.1
338	Potsdam sandstone	14.8	15.5

The analyses are all consistently deficient in O^{18}, probably indicating that adsorbed water on the interior walls of the reaction vessels is the principal source of contamination, inasmuch as

δ-water vapor is approximately -20 per mil. It is encouraging that the contaminating effects are as small as is indicated by Table IV, but even given favorable circumstances the dry box step cannot be eliminated.

<u>F_2 or HF reaction with glass of vacuum line</u> - Theoretically, no fluorine should get past the potassium bromide trap into the glass section of the line, and no hydrogen fluoride should get past U-trap B (fig. 1). When this work was initiated, U-trap C was constructed of glass, and even though every possible precaution was taken, hydrogen fluoride reached this part of the line. It was therefore replaced with the nickel U-trap now indicated in fig. 1. Hydrogen fluoride definitely gets no further than U-trap C, so there is no longer any possibility of reaction with the glass portion of the line. If fluorine is allowed to diffuse slowly into the potassium bromide trap, and bromine allowed to slowly diffuse out, no fluorine gets as far as U-trap C.

<u>Air in potassium bromide furnace</u> - Whenever the potassium bromide furnace is opened to the atmosphere the following 6-12 analyses deviate from the correct values in a consistent fashion. This contamination effect gradually disappears as more samples are analyzed. In the cases where a Potsdam sandstone sample is run concurrently with the 5 other samples, and where deviations from the correct analyses are small, a correction is made for this contamination effect. Otherwise, the analyses are discarded. Because of this problem, care is taken that air never comes into contact with the potassium bromide furnace unless absolutely necessary. The principal contaminant is undoubtedly mois-

ture from the air.

Impure mercury in the toepler pump - During the course of the research, the toepler pump had to be replaced and new mercury added. The new mercury was apparently not absolutely pure, and the first few analyses upon samples collected with it were found to be spurious. This is an unimportant effect, but the discarding of the analyses is justified.

Leaks in the vacuum line - Air leaks occur in the metal portion of the vacuum line occasionally, but these are an unimportant contaminating factor because their presence is clearly indicated by the quantity of nitrogen remaining at the end of a carbon dioxide conversion. Any analyses of samples containing larger than normal amounts of nitrogen are discarded, and the leak is traced and repaired.

Conversion of oxygen to carbon dioxide

As described in an earlier section, oxygen samples are converted to carbon dioxide before being analyzed in the mass spectrometer. The principal reason for doing this is that the mass spectrometer is specially equipped to handle carbon dioxide, and analyses of this gas are done routinely in these laboratories. Carbon dioxide is easier to handle than is oxygen, and is a better gas to analyze because it lies in a region of the mass spectrum less contaminated with background impurities. In addition, oxygen is more reactive than is carbon dioxide, and were an oxygen sample to come inadvertantly into contact with an easily oxidizable substance, isotopic fractionation might result. The conversion allows an estimate to be made of the amount of air contamination, as was pointed out above. Finally, gases which have appreciable vapor pressures at the temperatures of liquid nitrogen can be easily removed from the sample.

If each newly-replaced carbon filament is heated and out-gassed before it is used, contamination of the samples during a conversion, from gas adsorbed on the filament, is negligible. As a precautionary measure, this heating and outgassing is also done before each conversion.

The presence of small amounts of nitrogen impurities in the sample does not affect the conversion in any way, except that it makes it more difficult to ascertain exactly when the oxygen has been completely converted to carbon dioxide. Because of this, the gas sample is kept cycling past the heated filament for at least 10 minutes after all noticeable reaction has stopped.

If the temperature of the carbon rod is raised too high during conversion, the copper leads may conceivably become oxidized, with an accompanying isotopic fractionation. This process is considered to be a negligible source of error, because all conversions are carried out at sufficiently low temperatures that such oxidation does not occur.

A more serious problem is the formation of carbon monoxide in the course of a conversion, should the filament temperature be too high. This process is a source of error if the carbon monoxide that is formed has a different $0^{18}/0^{16}$ composition than the sample gas. In the early stages of this research, it was found that small amounts of carbon monoxide did form in a few instances and did affect the oxygen isotopic composition of the sample. Several experiments were carried out to study this effect, using aliquots of oxygen from a commercial cylinder under different conditions of conversion. Results are tabulated in Table V.

Table V

Analyses of oxygen samples by different conversion procedures

Run	Procedure	Vol. of CO_2 (cm^3)	$\delta O^{18}/O^{16}$ (‰)
87	Entire sample of O_2 converted to CO_2, in a single stage	14.4	24.9
88	First 40 per cent of a sample of O_2 converted to CO_2	5.8	2.5
89	Remaining 60 per cent of above sample converted to CO_2	8.3	42.4
97	First 85 per cent of a sample of O_2 converted to CO_2	11.5	13.4
98	Remaining 15 per cent of above sample converted to CO_2	2.2	90.1
99	Purposely made some CO by using high filament temperature; converted most of this CO to CO_2 by adding another aliquot of oxygen and lowering filament temperature to normal	13.3	22.8
100	Purposely converted a sample so that 60 per cent CO was formed; the 40 per cent CO_2 was then analyzed	3.6	17.8
101	All these samples were converted in 4 stages, in the manner outlined in the section on experimental procedure	10.4	25.3
102		11.5	25.2
103		12.9	24.9

The results of runs 88, 89, 97, and 98 indicate that a major isotopic fractionation occurs during the conversion, with the early-formed carbon dioxide enriched in O^{16}. The final 15 per cent of a sample is enriched in O^{18} over the original sample by 60–70 per mil. Run 99 demonstrates that any carbon monoxide formed early in a conversion probably reacts quickly with the excess oxygen that is present to form carbon dioxide. This is true only if the carbon monoxide is formed at not too rapid a rate, because a large amount of carbon monoxide can form if the temperature of the carbon filament is very high, as shown by the results of run 100.

Therefore, if a conversion is carefully done, only the carbon monoxide formed in the very end-stages of conversion should be a source of analytical error. In the oxygen-deficient environment of this stage, some carbon monoxide may form permanently. Inasmuch as this CO forms from oxygen greatly enriched in O^{18}, even the formation of a very small amount could cause an appreciable lowering of the O^{18}/O^{16} ratio of the sample gas.

To minimize any such effect, all conversions done after run 100 were carried out in 4 stages, in the manner outlined in the section on experimental procedure. By this method, any carbon monoxide that might be formed at the very end of a conversion is formed from material whose oxygen isotopic composition is approximately the same as that of the original sample gas. Oxygen removed in any carbon monoxide fraction will therefore not noticeably affect the O^{18}/O^{16} analysis of the sample.

The most reasonable explanation for the large isotopic fractionations produced during a conversion is as follows. If the rate of conversion of oxygen to carbon dioxide is proportional to the number of oxygen molecules striking the heated carbon filament per unit time, O^{16} should react more rapidly than O^{18}. Reactions which depend upon the collision frequency of gaseous molecules are known to cause isotopic fractionation in certain instances, as briefly discussed earlier.

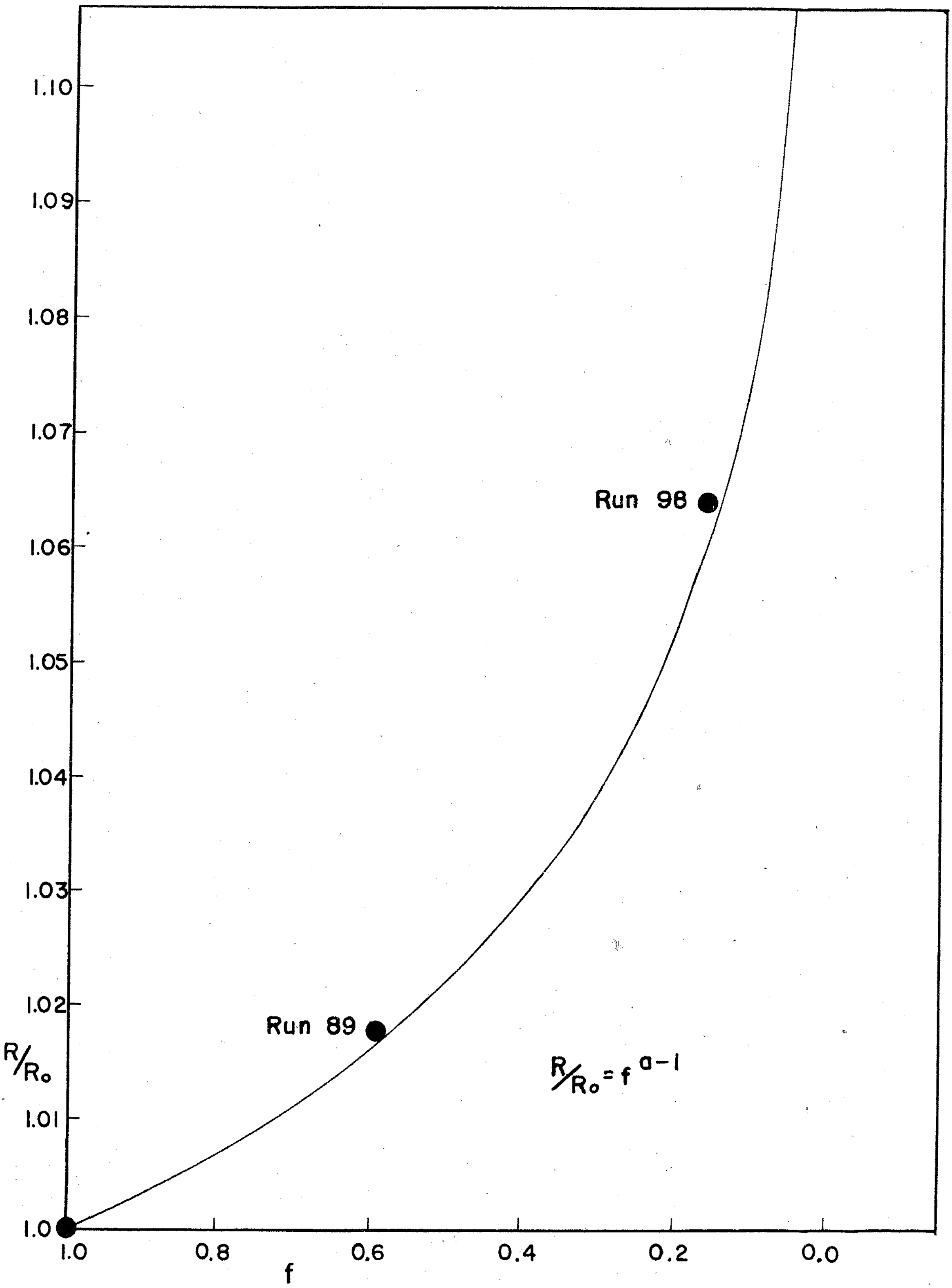


Fig. 2. Comparison of a theoretical conversion of oxygen to carbon dioxide with experimental results of runs 89 and 98.

Because the oxygen-32 molecule and the oxygen-34 molecule travel with velocities which are in the inverse ratio of the square roots of their masses, the relative rates at which each collides with the carbon filament should also be given by this ratio. The increase in O^{18} in the residual gas at any stage of the conversion procedure is then predicted by the Rayleigh distillation formula:

$$R/R_o = f^{(a-1)}$$

where f = fraction of oxygen gas remaining at any stage
a = fractionation factor given by relative reaction rates of oxygen-32 and oxygen-34
R = O^{18}/O^{16} ratio of residual oxygen gas at any stage
R_o = O^{18}/O^{16} ratio of original oxygen sample

This relationship is shown on the graph of fig. 2, and experimentally determined points from runs 89 and 98 are also plotted. The theory based upon collision frequencies appears to fit the data very well.

ANALYTICAL ACCURACY

Isotopic standards

The zero for the oxygen isotopic scale used in this report is the O^{18}/O^{16} ratio of Hawaiian ocean water. This is the scale that was used by Silverman, and it was also adopted by Clayton and Epstein.(4)(7) Hawaiian sea water is 0.2 per mil heavier than mean ocean water.(20)

The working standard for this research is, however, the Potsdam sandstone material analyzed by Silverman(4); hence the data are accurate relative to the ocean water standard only insofar as Silverman's results are accurate. An independent determination of the zero of this scale has been made by Clayton and Epstein(7), and they obtained essentially the same result (to within 0.2 per mil) as was obtained by Silverman.

The data in this paper are therefore in all likelihood accurate relative to ocean water at least to within 0.5 per mil. The analytical error among the individual silicate minerals themselves is much smaller, ± 0.2 per mil, as will be discussed below.

Isotopic corrections

It was necessary to apply various corrections to the raw oxygen isotopic data obtained in this research, before the results could be presented in the final form in which they now appear. All data have therefore been subjected to the following corrections, some of which are discussed in greater detail elsewhere in this report.

(1) Mixing of standard and sample gases in the mass spectrometer due to slight imperfections in the valve system, and mass spectrometer background; this correction factor is 1.04 for the mass spectrometer in these laboratories, and the individual δ-values were all multiplied by this factor.

(2) Extraneous oxygen in the commercial fluorine cylinder. This correction varies with the amount of oxygen released during reaction relative to the amount of fluorine used, and it also depends upon the δ-value of the sample oxygen relative to that of the contaminant. In general the correction is 0.1–0.2 per mil.

(3) Potsdam sandstone is the working standard and is generally run at least once in each set of 6 samples analyzed. These other samples are then corrected by the difference in δ-values between this

Potsdam sandstone analysis and the mean value of all Potsdam sandstone analyses which have been done. The reason for doing this is that the mass spectrometer standards are changed periodically, and also this partially corrects for secular drifts in the mass spectrometer analyses and for contamination in the fluorine extraction procedure. The corrections made in this way are generally 0.2 per mil or less.

(4) The quantity measured by the mass spectrometer is the ratio of mass-46 carbon dioxide to combined mass-45 plus mass-44 carbon dioxide. A small correction must be made to reduce these results to an O^{18}/O^{16} ratio. This has been done in the manner outlined by Craig(19).

(5) A few of the mineral samples analyzed were not 100 per cent pure, so a correction was made for the δ-value of the impurity. This correction never amounts to more than 0.1 per mil.

Precision of analytical method

The isotopic reproducibility of the analytical method is indicated in Table VI. The mean of the Potsdam sandstone analyses has been arbitrarily established at 15.5, and all other analyses have been adjusted to this standard. Even though the Potsdam sandstone analyses were carried out over a period of almost two years and through several mass spectrometer standard changes, a precision of better than 0.2 per mil has been obtained.

Table VI

Isotopic reproducibility of the analytical method

Sample	Run no.	Date	Yield(%)	$\delta O^{18}/O^{16}$ (‰)
Potsdam sandstone	30	3/1/57	90	15.3
	34	3/11/57	97	15.5
	37	3/12/57	99	15.5
	40	4/1/57	98	15.2
	43	4/2/57	95	15.8
	61	6/8/57	104	15.3
	64	6/8/57	102	15.5
	69	6/12/57	100	15.3
	73	6/13/57	99	15.2
	76	6/18/57	100	15.3
	80	6/19/57	101	15.5
	82	6/23/57	98	15.5
	85	6/24/57	104	15.3
	104	7/9/57	101	15.7
	106	7/9/57	101	15.6
	107	7/10/57	100	15.6
	108	7/10/57	100	15.6
	109	7/10/57	100	15.4
	117	7/22/57	95	15.3
	123	7/26/57	101	15.7
	149	10/29/57	101	15.4
	150	10/30/57	101	15.5
	151	10/31/57	102	15.6
	152	10/31/57	100	15.5
	153	11/1/57	101	15.4

Sample	Run no.	Date	Yield(%)	$\delta O^{18}/O^{16}$ (‰)
Potsdam sandstone	175	12/18/57	98	15.9
	177	12/19/57	98	15.8
	181	1/4/58	98	15.6
	214	3/11/58	99	15.5
	220	3/16/58	98	15.4
	242	5/22/58	100	15.7
	265	6/12/58	96	15.3
	269	6/15/58	96	15.4
	282	6/22/58	103	15.9
	307	7/11/58	101	16.0
	363	8/20/58	100	15.3
	375	9/28/58	100	15.2
	429	11/15/58	98	15.8
	434	11/16/58	94	15.8
	435	12/5/58	98	15.1
40 analyses		av. dev. = 0.18		Mean = 15.5
St. Peter sandstone	38	3/12/57	98	11.2
	42	4/1/57	97	11.3
	45	4/2/57	97	10.9
	59	6/8/57	105	11.3
	72	6/13/57	100	11.2
	79	6/19/57	99	10.9
	114	7/16/57	102	10.6
	118	7/23/57	89	11.0

Sample	Run no.	Date	Yield(%)	$\delta O^{18}/O^{16}$ (‰)
St. Peter sandstone	124	7/26/57	97	11.8
9 analyses		av. dev. = 0.2		Mean = 11.1
Randville pegmatite orthoclase	71	6/13/57	101	9.4
	75	6/17/57	102	8.9
	78	6/18/57	102	8.7
	121	7/23/57	102	9.3
	127	7/28/57	98	9.3
5 analyses		av. dev. = 0.2		Mean = 9.1
Randville pegmatite quartz	35	3/11/57	99	10.0
	120	7/23/57	102	10.4
	126	7/27/57	92	10.1
3 analyses		av. dev. = 0.2		Mean = 10.2
Dover flint	29	3/1/57	95	32.0
	31	3/1/57	95	32.5
	36	3/12/57	96	32.0
	41	4/1/57	87	32.9
	44	4/2/57	94	32.1
	119	7/23/57	101	32.0
	125	7/27/57	97	32.3
7 analyses		av. dev. = 0.3		Mean = 32.2

Sample	Run no.	Date	Yield(%)	$\delta O^{18}/O^{16}$ (‰)
Herkimer, N. Y. quartz "diamond"	65	6/8/57	96	22.6
	70	6/13/57	99	22.9
	77	6/18/57	101	23.2
	81	6/23/57	101	22.2
	86	6/24/57	98	23.5
5 analyses		av. dev. = 0.3		Mean = 22.9
Diatomite	39	3/12/57	90	35.2
	116	7/22/57	78	33.1
	122	7/26/57	94	35.0
3 analyses		av. dev. = 0.9		Mean = 34.5

Experiments were carried out to see if there were any "memory effect", that is, if an analysis of one sample contaminated the apparatus in any way, so as to give an incorrect analysis of the following samples. Table VII shows the results of several analyses of Potsdam sandstone, with the analysis of the previously collected sample for comparison.

Table VII

Test for "memory effect" on isotopic analysis

Run	Sample	$\delta O^{18}/O^{16}$ (‰)	Potsdam sandstone Run	Potsdam sandstone $\delta O^{18}/O^{16}$ (‰)
29	Dover flint	32.0	30	15.3
36	Dover flint	32.0	37	15.5

			Potsdam sandstone	
Run	Sample	$\delta O^{18}/O^{16}$ (‰)	Run	$\delta O^{18}/O^{16}$ (‰)
39	Diatomite	35.2	40	15.2
42	St. Peter sandstone	11.3	43	15.8
72	St. Peter sandstone	11.2	73	15.2
75	Randville orthoclase	8.9	76	15.3
79	St. Peter sandstone	10.9	80	15.5
81	Quartz, Herkimer, N. Y.	22.2	82	15.5
122	Diatomite	35.0	123	15.7
306	Apatite	3.9	307	16.0
433	Potash feldspar	9.2	434	15.8

No evidence of a significant "memory effect" exists.

Comparison with previous work

Up to the time of the present research there has been no absolute comparison of oxygen isotopic analyses of minerals by two different methods of extraction. Clayton and Epstein(7) were able to make relative comparisons of analytical results on quartz samples done by the carbon reduction method with results obtained by Silverman(4) upon the same sample materials. Only relative comparisons were possible because the primary mass spectrometer standards used in the two investigations were not identical. These relative comparisons agreed within the experimental error of 0.2 per mil. The oxygen isotopic results obtained by Schwander(6) could not be compared with data from either of the above investigations, because no common samples were analyzed.

The Potsdam sandstone standard and other sample materials that have been analyzed by Silverman(4) and by Clayton and Epstein(7) have been analyzed many times during the present investigation, in order to compare in detail the various methods that have been used to extract oxygen for isotopic analysis. These relative comparisons are shown in Table VIII.

Table VIII

Comparison of analyses of identical samples by various workers

Sample	Clayton & Epstein δ (‰)	Silverman δ (‰)	This work δ (‰)
Randville orthoclase		8.8±0.2 (4)	9.1±0.2 (5)
Randville quartz	10.3±0.2 (5)	10.3±0.2 (4)	10.2±0.2 (3)
St. Peter s.s.	11.0±0.2 (4)	10.9±0.2 (2)	11.1±0.2 (9)
Potsdam s.s.	15.5±0.2 (19)	15.5±0.0 (2)	15.5±0.2 (40)
Dover flint		29.3±0.5 (2)	32.2±0.3 (7)
Diatomite		30.3±0.0 (2)	34.5±0.9 (3)

Analytical error shown is average deviation from the mean.
Numbers in parentheses indicate the number of separate determinations.

Analyses of the flint and of the diatomite are poorly reproducible, probably because of their water content. Differing amounts of water of possibly different isotopic composition are lost by such samples unless preliminary heating and dessicating treatments are ~~exactly~~ identical for each run. This might in part explain the discrepancies between Silverman's data and that of the present work for these two materials. The results for the diatomite in the present work are considered to be more reliable than the data of Silverman because this material has been checked by the carbon reduction method. Analyses of the other quartz samples indicate that all 3 analytical procedures produce relatively similar oxygen isotopic results.

Comparison with an independent analytical method

It is very important to obtain an absolute comparison of oxygen isotopic results by two independent methods in which the nature of the sources of error will be different. This is most conveniently done when samples extracted by different procedures are measured in the same mass spectrometer. In the laboratories where the present study was carried out it was possible to do this.

A comparison between the two methods is established by analyses of identical quartz samples. Determinations by Clayton(21), by Degens(22), and by Irvine(23), all by the carbon reduction method, are compared with analyses done by the fluorine procedure in Table IX.

Table IX

Comparison of O^{18}/O^{16} analyses of quartz by different methods

	Carbon reduction procedure			Fluorine method
Sample	Clayton δ	Degens δ	Irvine δ	This work δ
Potsdam s.s.	15.9 ± 0.2		15.9 ± 0.2	15.5 ± 0.2
St. Peter s.s.	11.4 ± 0.2			11.1 ± 0.2
Randville quartz	10.7 ± 0.2			10.2 ± 0.2
Dover flint	33.3 ± 0.2			32.2 ± 0.3
Diatomite	35.8 ± 1.0	35.0 ± 0.6		34.5 ± 0.9
Quartz, Duke I.			8.7 ± 0.1	8.3 ± 0.1
Chert		34.8 ± 0.0		34.6 ± 0.1

Analytical error shown is average deviation from the mean.

The analytical data presented in Table IX indicate that determinations of O^{18}/O^{16} ratios of quartz by the carbon reduction method are consistently about 0.4 per mil enriched in O^{18} relative to analyses carried out by fluorine extraction. Because the former procedure gives carbon dioxide yields of only about 95 per cent from quartz samples, while the fluorine extraction gives yields of 100 per cent, it is thought that the latter method is the more reliable of the two. Also, more reproducible results are ordinarily obtained by the fluorine procedure.

When minerals other than quartz, magnetite, and zircon are analyzed by carbon reduction, yields of only 50-70 per cent are obtained(7), with resultant O^{18}/O^{16} ratios that are considerably too high. Perhaps the consistently slightly higher O^{18}/O^{16} ratios observed for the quartz samples shown in Table IX are a result of the same error-producing processes. In any event, both extraction procedures clearly can give accurate analyses relative to a given quartz standard, within the experimental error of ± 0.2 per mil; hence both methods represent valid techniques for extracting oxygen from quartz samples. When comparing δ-values of one method with those from another, 0.4 per mil should be subtracted from the values obtained by carbon reduction.

The fluorine method produces oxygen yields of 100 per cent of the stoichiometric amount for most common minerals, as well as for quartz; thus there is good reason to believe that these analyses should also be accurate to ± 0.2 per mil, even though no comparison with an independent extraction method has been made. This is, however, not true for magnetites and for some independent tetrahedral silicates. These minerals do not generally give 100 per cent yields in a fluorine extraction, nor do they give as reproducible O^{18}/O^{16} data as are obtained from the more easily reacted minerals.

The oxygen isotopic composition of magnetite can be measured by the carbon reduction method, and Table X shows how the results of this procedure compare with results of the fluorine method upon identical samples of magnetite.

Table X

Comparison of O^{18}/O^{16} analyses of magnetite by two methods

Sample	Carbon reduction procedure Clayton δ	Carbon reduction procedure Irvine δ	Fluorine method This work δ
U.B. 157		2.3 ± 0.1 (2)	4.0 ± 0.2 (7)
San Marcos gabbro	1.5 ± 0.1 (4)	1.7 ± 0.1 (2)	3.0 ± 0.4 (5)
HJ-23-55	1.0 ± 0.1 (2)		3.0 ± 0.3 (2)
A.L. II	3.3 ± 0.1 (2)		5.0 ± 0.4 (2)

Analytical error shown is average deviation from the mean.
Numbers in parentheses indicate the number of separate determinations.

The magnetite data indicate larger discrepancies between the two methods than do the quartz data, and the deviations are in the opposite direction. An almost constant difference of about 1.5 per mil appears to exist between the two sets of data, although too few analyses have been obtained to be certain of this value. Inasmuch as approximately 100 per cent yields are obtained from magnetite samples by the carbon reduction method, whereas great difficulties are met with in the fluorine extraction process, data by the former procedure are assumed to be more nearly correct — at least until further experimental comparisons can be made.

These discrepancies, though large, should make no difference in the interpretations which are set forth in subsequent sections, because by either extraction process magnetite is the most O^{18}-deficient mineral of any that have been analyzed. The discrepancies are not particularly surprising for those magnetite samples upon which the fluorine method gives less than 100 per cent yields. It is not known why a discrepancy of similar magnitude exists for sample U.B. 157, for which approximately 100 per cent yields are obtained by both methods.

Oxygen isotopic data obtained by fluorine extraction, for minerals which are difficult to react completely with fluorine, must remain in question until these types of materials are further checked. For this reason, data by Silverman(4) upon ultramafic and mafic rocks may be inaccurate by 0.5 per mil. This also applies to data upon these rock types in this paper.

Evaluation of data of Schwander

Three rocks of the Skaergaard intrusion were analyzed by Schwander(6), and these have also been analyzed in the present study. Although identical specimens were not used, the samples should be comparable. Relevant data are presented in Table XI.

Table XI

Comparison of data of Schwander(6) with that of the present work

	Schwander		This work	
Sample	Specimen	δ (‰)	Specimen	δ (‰)
Hypersthene olivine gabbro	E.G.4067	-8.3	E.G.4077	6.0
Fayalite ferrogabbro	E.G.1974	-10.2	E.G.4328	4.3
Transgressive hedenbergite granophyre	E.G.3046	-15.9	E.G.4489	1.0

Inasmuch as spurious O^{18}/O^{16} ratios commonly result with the carbon reduction procedure for minerals that contain significant quantities of the relatively volatile metals — Mg, Na, K, etc.(7), it is perhaps surprising that relative O^{18}/O^{16} analyses of the Skaergaard rocks listed in Table XI should be so consistent with data from a fluorine extraction. The agreement may be partly a result of the unusually high Fe/Mg ratio of these rocks, or it may be because isotopic fractionation during carbon reduction is approximately constant for each. If any such fractionation is small, the analyses listed in Table XI provide a means of tying together the data of Schwander and that of the present work. It would appear that the standard carbon monoxide sample used by Schwander is about 15 per mil richer in O^{18} than is ocean water, the standard used in the present work. This value, 15 per mil, should therefore be added to all the δ-values reported by Schwander, to convert them to the scale commonly in use. If one applies the 15 per mil correction factor, Schwander's quartz analyses fall near the isotopic results obtained upon geologically similar types during the present investigation. A detailed comparison is shown in Table XII.

These quartz analyses cannot, of course, be compared in any direct manner, but it is apparent that the range of O^{18}/O^{16} ratios is about the same for the two sets of data. For materials other than quartz, similarities are lacking. This is indicated in Table XIII, which confirms the conclusion of Clayton and Epstein(7) that the carbon reduction method gives unreliable results for such rocks.

The most significant discrepancies between the two sets of data

Table XII

Comparison of O^{18}/O^{16} analyses of quartz samples from geologically similar environments by Schwander and by the present work

Schwander		This work	
Sample	$\delta O^{18}/O^{16}$ (‰)	Sample	$\delta O^{18}/O^{16}$ (‰)
Quartz from miarolitic cavity - Baveno granite	10.4	Quartz from Rubidoux granite	9.9
Quartz from Bergell pegmatite	9.7	Quartz from Randville pegmatite	10.2
Quartz phenocrysts in a dacite	8.1	Quartz from San Jose tonalite	9.7
Quartzite, Switzerland	12.4	St. Peter s.s.	11.1
Quartz sand, Switzerland	13.3	Potsdam sandstone	15.5
Diatomite, Scotland	33.4	Diatomite	34.5
Radiolarian earth	37.3	Chert	34.6

Table XIII

Comparison of O^{18}/O^{16} analyses of similar types of rock samples by Schwander and by the present work

Schwander		This work	
Sample	$\delta O^{18}/O^{16}$ (‰)	Sample	$\delta O^{18}/O^{16}$ (‰)
Basalt	15.7	Steens basalt	6.6
Gabbro	10.4	San Marcos gabbro	7.0
Granodiorite	5.8	Woodson granodiorite	8.6
Adamellite	5.5	Elberton adamellite	8.8
Baveno granite	11.5	Rubidoux granite	9.2
Biotite from Baveno granite	11.5	Biotite from Woodson granodiorite	4.4
Light minerals from Baveno granite	10.4	Light minerals from Woodson granodiorite	8.9

are the reversals in trend of the O^{18}/O^{16} variation through the series of igneous rock types from gabbro to granite. The present work and the work of Silverman(4) are in agreement that granitic rocks are generally enriched in O^{18} relative to basic rocks, whereas the data of Schwander indicate the reverse. Schwander also found a much larger isotopic variation within a given rock type than was found in either the work of Silverman or in the present work. In this research, biotite was always found to be deficient in O^{18} relative to quartz and feldspar, while Schwander observed the inverse relationship in the one rock he investigated.

It is therefore probable that many of the O^{18}/O^{16} analyses presented by Schwander may be in error by as much as 3-5 per mil, although the quartz determinations may be reasonably accurate. It is certainly of interest that the lowest O^{18}/O^{16} ratio of any of the rocks analyzed by Schwander is given by the hedenbergite granophyre of the Skaergaard intrusion, because this is also the isotopically lightest rock analyzed in the present investigation. Highest O^{18}/O^{16} ratios in either work are given by silica precipitated from ocean water, so the total range of oxygen isotopic composition is approximately the same for both sets of data.

EXPERIMENTAL RESULTS

General statement

In isotopic studies of the nature of the present work, one is primarily interested in the distribution of isotopes among coexisting mineral phases. Only the fractionation factors give any information about the physicochemical conditions of formation of a particular mineral assemblage, but determinations of total rock isotopic compositions may indicate genetic relationships between rock types or give information concerning source.

As Clayton and Epstein have pointed out(7), the determination of relative O^{18}/O^{16} ratios for three or more coexisting minerals can provide the following information: (1) whether or not oxygen isotopic equilibrium was attained at the time of their formation; (2) the temperature at which equilibrium was attained; and (3) possible processes that have affected the minerals, should equilibrium not have been established. These statements are predicated on the basis that the equilibrium fractionation factors between the minerals as a function of temperature are known. Experimentally determined fractionation factors do not at present exist, but a qualitative understanding of these subjects can be obtained by a study of naturally occurring mineral assemblages.

Clayton and Epstein(7) have demonstrated that the mineral pairs calcite-quartz and quartz-magnetite have apparently been commonly formed in equilibrium with an oxygen reservoir of almost constant oxygen isotopic composition, over wide ranges of temperature and in different geologic environments. This oxygen reservoir is postulated to be juvenile water, and this serves as the third phase referred to above, necessary for unequivocal determinations of temperature or degree of attainment of equilibrium. They have shown that the quantities $\Delta_{\text{QUARTZ-MAGNETITE}}$ and $\Delta_{\text{QUARTZ-CALCITE}}$ decrease with increasing temperature of formation, if equilibration with a large quantity of hydrothermal fluid has occurred.

These findings are in line with the theoretical discussion of isotopic exchange reactions presented in the introduction to this paper. At isotopic equilibrium at a given temperature the fractionation factor between two minerals is constant. If it were certain that two coexisting mineral phases formed under equilibrium conditions, the measured fractionation between just these two minerals should determine their temperature of formation. It is usually not obvious whether or not equilibrium actually has been attained; hence it is necessary to determine the O^{18}/O^{16} ratio of a third coexisting phase.

Occurrence of oxygen isotopic equilibrium between minerals is, in general, an excellent indication that chemical equilibrium probably also exists. This is because any processes which are pervasive enough to bring about an interchange and re-assembling of all the oxygen atoms into a new equilibrium distribution probably also would allow complete cation exchange to occur.

O^{18}/O^{16} fractionations among minerals

The present study has been primarily concerned with minerals in igneous rocks, although a few determinations of hornblende and plagioclase from metamorphic amphibolites have been made. The variations of mineral fractionation factors with temperature in the range of magmatic temperatures is small. As a result, metamorphic rocks must be included if it is desired to establish relationships of the type discussed by Clayton and Epstein(7) for magnetite, quartz, and calcite. Hornblende and plagioclase are therefore the only minerals studied which formed over a sufficient range of temperatures to enable one to do this.

The experimental results for all analyzed hornblende-plagioclase pairs have been plotted in fig. 3. The 45° line through the origin is the locus of points where $\delta_{\text{PLAGIOCLASE}} = \delta_{\text{HORNBLENDE}}$, and points lying closest to this line should represent highest temperatures of formation, providing isotopic equilibrium has been attained. The experimental points lie not far from a straight line, and this is evidence that many of these hornblende-plagioclase pairs were formed in approximate equilibrium. They also must have been in near equilibrium with a large oxygen reservoir of almost constant isotopic composition.

By extrapolation of their quartz-calcite data to very high temperatures, Clayton and Epstein(7) calculated that this water-rich solution would have $\delta_{\text{WATER}} = 2$ per mil. An approximate $\delta_{\text{WATER}} = 3\text{–}5$ per mil can be estimated from the hornblende-plagioclase data of this work. It is of interest that such similar results are obtained from different minerals and from unrelated rock types.

It is clear from the scatter of points in fig. 3 that these assumptions of equilibrium are only a gross approximation. This may be the reason for the slight discrepancy in the values of δ_{WATER} as calculated by Clayton and Epstein and by this work. Fig. 3 is intended mainly to demonstrate the general temperature dependence of the O^{18}/O^{16} fractionations for a typical pair of rock-forming silicates. The highest temperatures of formation indicated by the isotopic evidence agree with the generally accepted relationships based on geological grounds. The pairs from metamorphic rocks show larger fractionations than the pairs from igneous rocks, in keeping with their lower temperature origin. The largest fractionation shown is given by a point near the top

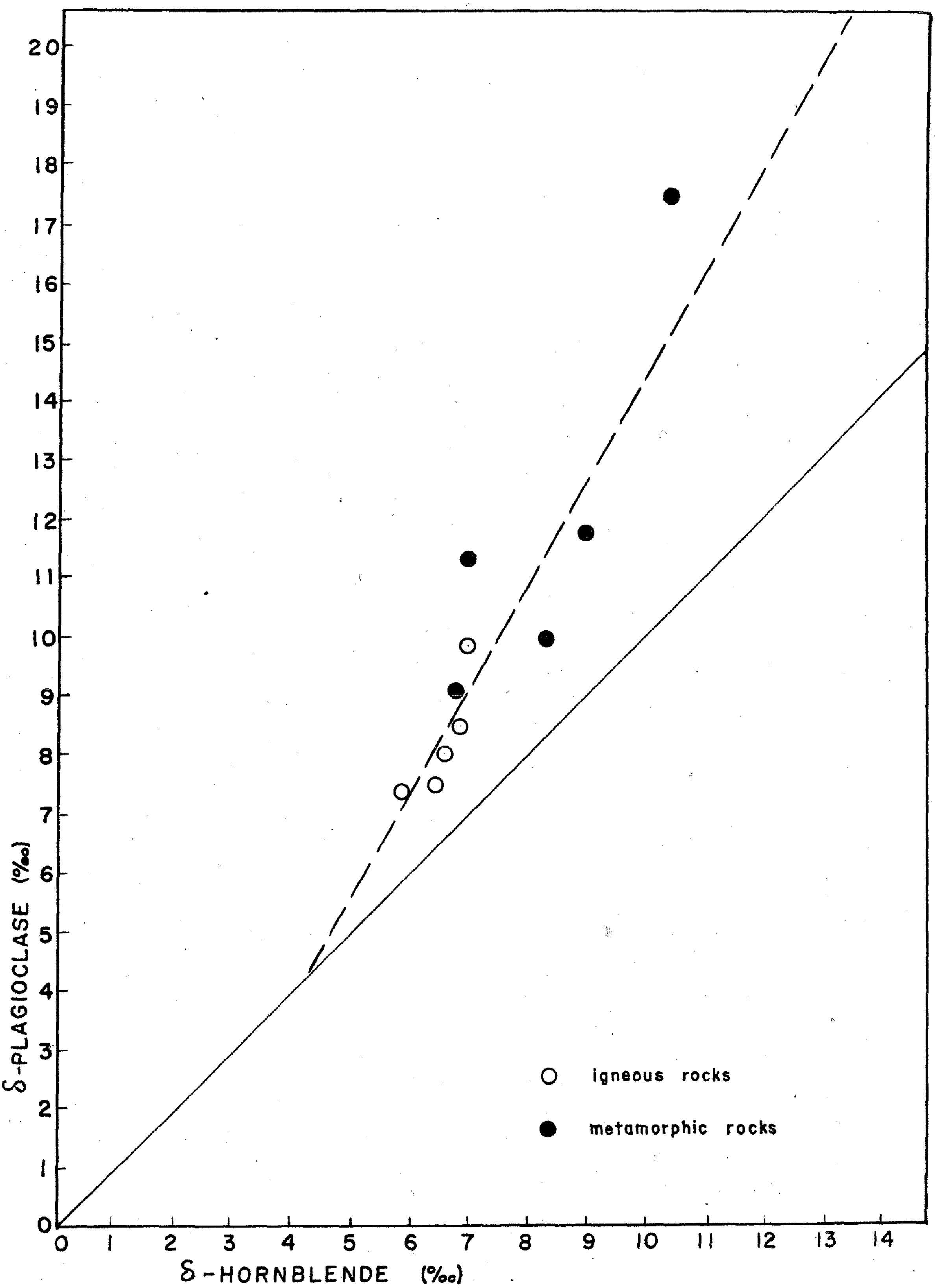


Fig. 3. Isotopic analyses of all plagioclase-hornblende pairs.

of fig. 3, and this represents hornblende and plagioclase from an amphibolite that has undergone a post-metamorphism episode of hydrothermal alteration.

Certain complicating factors have been ignored in noting the above relationships. Hornblende and plagioclase are not constant in chemical composition throughout the range of rock types analyzed. The ratio of albite/anorthite is variable, as is the cation content of the hornblende. The isotopic data which exist, however, tend to indicate that even fairly large variations in cation composition will produce little change in the oxygen isotopic properties of a given mineral. The measured fractionations demonstrate that these isotopic properties depend primarily upon silicate structural type rather than upon the particular cations that enter the structure. One might ascertain from this that it is the Si-O bonds in the silicate structure which are the most important determining factors. Even substitution of aluminum for silicon, which occurs in most of the silicates, should produce no major change in oxygen isotopic properties, inasmuch as the atomic masses of these two elements are similar.

The consistency of O^{18}/O^{16} fractionations among various minerals coexisting with plagioclase is shown in fig. 4, on which are also repeated the hornblende data discussed above. On this diagram have been plotted $\delta_{\mathrm{BIOTITE}}$, δ_{QUARTZ}, $\delta_{\mathrm{MAGNETITE}}$, $\delta_{\mathrm{HORNBLENDE}}$, and $\delta_{\mathrm{PYROXENE}}$ as a function of $\delta_{\mathrm{PLAGIOCLASE}}$, for all mineral-plagioclase pairs for which analyses have been obtained. The data are from a wide variety of igneous rock types, as well as from the metamorphic amphibolites already discussed. All points for a given mineral are joined by a solid line on the diagram, only to make more apparent the

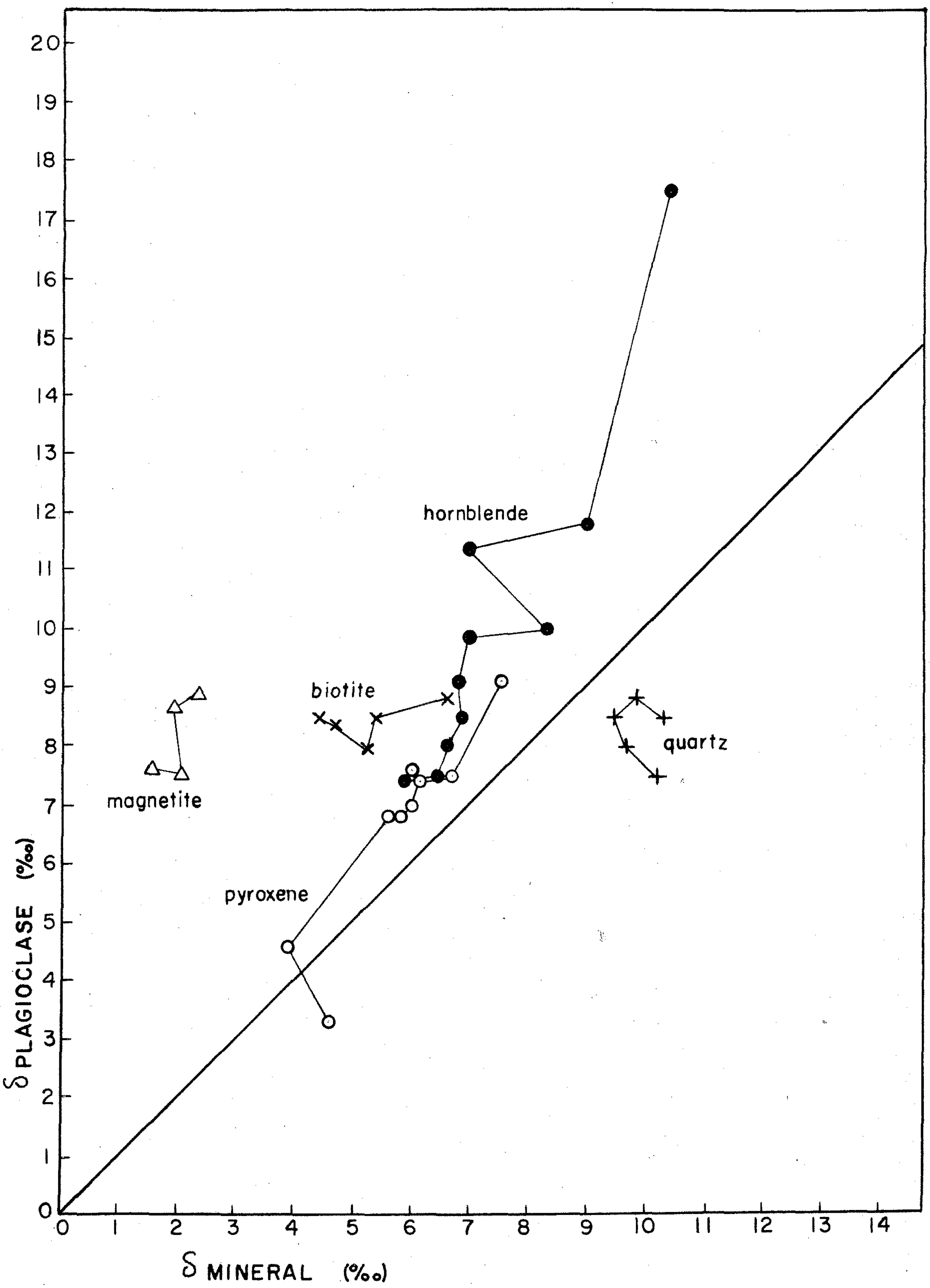


Fig. 4. Isotopic analyses of all quartz, pyroxene, hornblende, biotite, and magnetite that coexist with plagioclase.

degree of consistency in the data. Quartz is invariably richer in O^{18} than is coexisting plagioclase. Plagioclase is more enriched in O^{18} than is coexisting hornblende or biotite, and the fractionation between biotite and plagioclase is consistently larger than the fractionation between hornblende and plagioclase. Pyroxene-plagioclase fractionations lie very near the values for hornblende-plagioclase pairs but are in general somewhat smaller. Magnetite is invariably the isotopically lightest of any of these minerals.

The degree of scatter in the experimental points makes it appear unlikely that these pairs of minerals represent attainment of complete isotopic equilibrium. However, the consistency of the gross relationships can only be explained on the basis that isotopic equilibrium is closely approximated in almost all cases. Otherwise, for example, there is no reason why quartz with lower O^{18}/O^{16} ratios than coexisting plagioclase should not occur, or biotite and hornblende with higher.

Isotopic disequilibrium is most clearly indicated when the fractionation commonly observed for a mineral pair is reversed in sign. Only 3 instances of such a phenomenon have been observed in the rocks that have been studied, and these particular discrepancies are all reasonable on the basis of independent geological evidence. One such instance of marked disequilibrium in indicated at the lower left of fig. 4, in which a pyroxene shows a higher O^{18}/O^{16} ratio than coexisting plagioclase. This peculiar mineral pair is from the Skaergaard intrusion, and the reversal is discussed in detail in a later section.

Many different graphs could be shown, using all permutations and combinations of the oxygen isotopic data, but no further useful generalizations would result. The preliminary statements outlined above are useful in that they demonstrate the following features: (1) oxygen isotopic fractionations among rock-forming minerals indicate that, in general, approximate isotopic equilibrium is established in rocks; (2) unsystematic variations in these fractionation factors are common, and are best interpreted as representing slight deviations from complete isotopic equilibrium; (3) oxygen isotopic data concerning the relative temperatures at which gross equilibrium is attained are in agreement with the geological evidence; and (4) if quartz, plagioclase, pyroxene, hornblende, and biotite were to coexist in isotopic equilibrium at temperatures of the order of 700-1000° C., their relative $0^{18}/0^{16}$ ratios in all likelihood would be in the above-named order, quartz isotopically heaviest, and biotite lightest. The only uncertain relationship within the above sequence is the relative fractionation between pyroxene and hornblende.

$0^{18}/0^{16}$ compositions of total rocks

Fig. 5 shows all oxygen isotopic data that have been gathered, up to the time of the present writing, upon total igneous and metamorphic rocks. Included are data by Silverman(4), as well as results of the present study. The data of Schwander(6) and the data of Vinogradov, Dontsova, and Chupakhin(8) are not used for reasons previously discussed.

The most striking feature of the data is the correlation of the oxygen isotopic data with the chemical composition of the rocks. The more mafic igneous rocks are consistently deficient in 0^{18} relative to the more sialic rocks, even though rocks of widely varying ages and

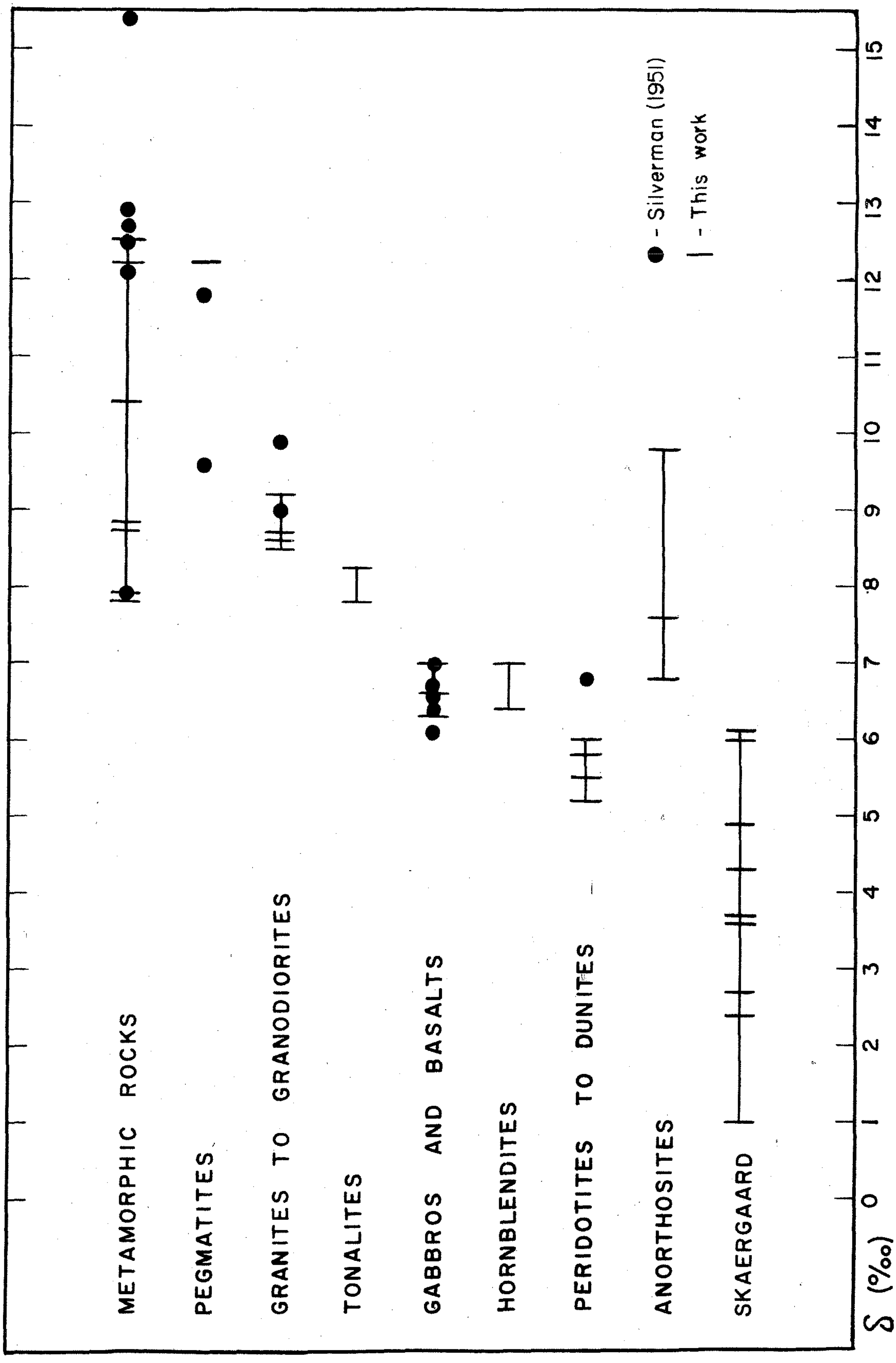


Fig. 5. All reliable oxygen isotopic analyses of total rock samples.

geographic distribution are represented. In this respect, the rocks parallel the individual minerals, as mafic minerals almost invariably show lower O^{18}/O^{16} ratios than coexisting sialic minerals. The narrow range of oxygen isotopic composition shown by each rock type probably indicates that igneous rocks of a given type must originate by fairly similar physical and chemical processes from sources of similar isotopic composition, irrespective of geologic age or location. The only group of igneous rocks yet analyzed that deviate markedly from the normal trends are rocks of the Skaergaard intrusion, and these have therefore been plotted separately in fig. 5.

As can be understood from theoretical grounds, and as Silverman(4) has demonstrated, sedimentary processes ordinarily tend to enrich rocks in O^{18}; hence metamorphic rocks derived from sediments show a much wider range of oxygen isotopic composition than do igneous rocks, and they are usually isotopically heavier. Metamorphosed igneous rocks also show a wide range in O^{18}/O^{16} composition and are commonly enriched in O^{18} relative to unaltered igneous rocks. This can in general be attributed to oxygen isotopic exchange with hydrothermal water at lower than magmatic temperatures during the metamorphic recrystallization.

O^{18}/O^{16} variations during magmatic crystallization

The liquid portion of a magma will in general change in O^{18}/O^{16} composition as crystallization proceeds, whether or not the magma is a completely closed system. This is because the total crystalline material forming at any one instant ordinarily will have an oxygen isotopic composition different from that of the liquid. Obviously, if the bulk of the material crystallizing is isotopically lighter than the magma, the liquid will become enriched in O^{18} during the course of crystallization. This is the normal trend one would expect, inasmuch as the more mafic minerals of a rock (which are deficient in O^{18} relative to the magma as a whole) usually crystallize early.

Any attempt to relate the measured δ-values of minerals to the crystallization effects outlined above must take into account two fundamentally distinct processes: (A) the outer portions of a crystallizing mineral grain may act as an armor, protecting the earlier-formed inner portions from further exchange or reaction with the magma — hence portions of a crystal would be in isotopic equilibrium with the magma only at the instant of their precipitation; and (B) conversely, complete and continuous oxygen isotopic exchange between crystals and liquid may occur throughout the interval of crystallization, with an equilibrium oxygen isotopic distribution not being permanently "frozen in" until some sub-solidus temperature is reached. Actual crystallization processes in nature undoubtedly vary somewhat between these two extremes, but the present oxygen isotopic evidence indicates that process (A) is dominant.

As will be discussed in detail in later sections, the minerals of igneous rocks show slight oxygen isotopic disequilibrium features; these are readily explained on the basis of crystallization with incomplete reaction. At present, it is impossible to tell whether or not process (A) commonly operates in nature in its ideal form, because there is no way of estimating exactly how much oxygen isotopic exchange occurs between already-formed crystals in a magma and the liquid itself. For almost every rock studied, however, the crystallization history is reflected by the O^{18}/O^{16} data. The data are generally in good agreement with the sequence of crystallization as determined by conventional geologic criteria.

These observations imply that most of the minerals in igneous rocks should be isotopically zoned, just as many are zoned in chemical composition. Each mineral δ-value determined in this work therefore represents a composite of the δ-values of the various zones.

During the crystallization of most of the rocks studied in this work, the liquid portion of the magma apparently became enriched in O^{18}. This is shown by the abnormally large δ-values of the late-crystallizing constituents, such as the quartz in the San Marcos gabbro. However, for certain rocks, it appears that crystallization has produced a reversal of this isotopic trend. The Skaergaard intrusion has undergone an unusual type of fractional crystallization, accompanied by a marked depletion of the late-crystallizing fractions in O^{18}. Also, granitic magmas that are deficient in mafic constituents may become isotopically either lighter or heavier during crystallization, depending upon the relative periods of crystallization of the quartz and feldspars; the minor amounts of mafic minerals will not control the O^{18}/O^{16} changes in such a magma.

Justification for the above statements will be found in detailed discussions of the various rock types in the following sections. Although the gross trends in oxygen isotopic composition can be evaluated fairly easily, the detailed changes during magmatic crystallization are very complicated. These are dependent upon: (1) the types of minerals crystallizing; (2) the relative amounts of each relative to the amount of liquid; and (3) the O^{18}/O^{16} fractionations between each mineral and the liquid. Factors (1) and (2) are continuously changing throughout the course of crystallization. In addition, (3) is complicated by the following considerations: (a) the oxygen isotopic properties of liquid magma change as the chemical composition of the magma changes; (b) the oxygen isotopic properties of the individual minerals change as their chemical composition changes, although changes in cation composition are apparently of little importance in this respect; (c) all fractionations are functions of temperature and change over the temperature interval of crystallization; (d) most magmas are not completely closed systems, although many can probably be considered so as a first approximation — loss of volatiles (especially water) would change the oxygen isotopic composition of the magma; and (e) the extent of oxygen isotopic exchange between already-solidified crystals and remaining liquid cannot be easily ascertained, and may be greater for some minerals than for others.

Fortunately, most of the complicating features listed above are of minor importance. They should not greatly interfere with any of the major interpretations made in this study. It is only in quantitative discussions of crystallization that they must be carefully considered, and this must remain an intractable problem until extensive experimental data are available upon oxygen isotopic fractionation factors among minerals.

Theoretical O^{18}/O^{16} variations in a simple binary system

It is desirable to illustrate in a more detailed fashion the variations that can take place during crystallization of a magma. By making certain assumptions, a calculation of the O^{18}/O^{16} effects of crystallization in a simple two-component system can be easily carried out. The simple examples that will be given will indicate the relationships between the equilibrium fractionation factor for two minerals and the actual fractionation brought about by the crystallization process. The examples should therefore serve to illustrate the types of changes involved and the magnitude of the variations which can be expected during the crystallization of a magma in nature.

The assumptions are: (1) equilibrium fractionation factors between crystals and between crystals and liquid are constant throughout the period of crystallization; (2) portions of crystals are effectively removed from the magma the moment they precipitate, by the armoring effect of the later-crystallizing portions — in otherwords process (A) outlined above operates in its ideal form; (3) when both minerals are crystallizing simultaneously, each forms at a fixed rate relative to the other; and (4) both minerals contain identical oxygen percentages.

Calculations are based upon the Rayleigh distillation equation already mentioned in another connection; this equation was given on p. 43. Three different conditions of crystallization are illustrated by figs. 6, 7, and 8. For any value of the ordinate (per cent liquid crystallized) the curves on each diagram give the δ-value of the liquid that exists at that stage of crystallization, as well as giving the δ-values of the minerals precipitating from that liquid. The average δ-value for each mineral, shown on the figures by vertical dashed lines, represents a composite of all the zones of the mineral;

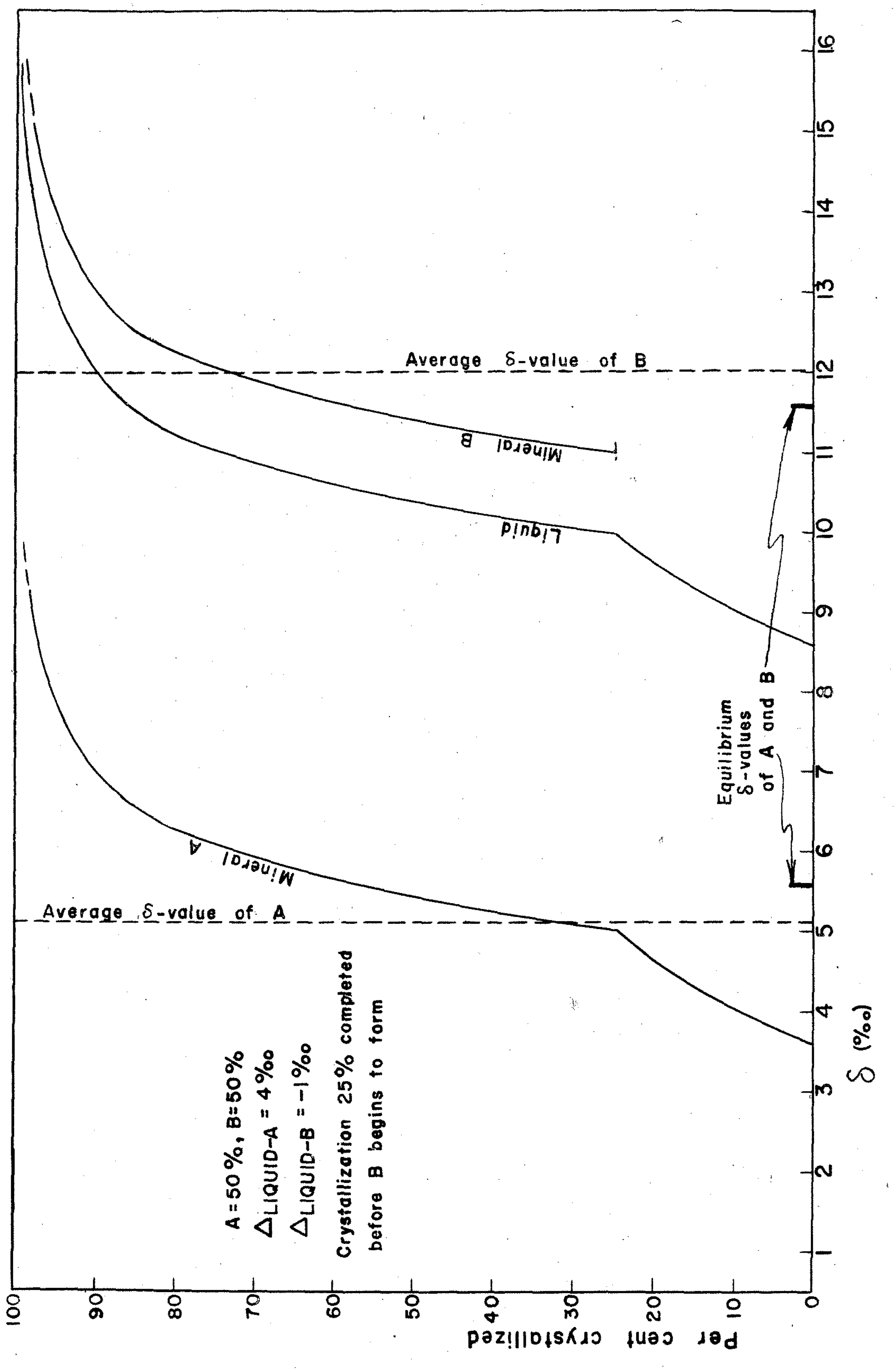


Fig. 6. Theoretical $0^{18}/0^{16}$ variations during crystallization - no. 1.

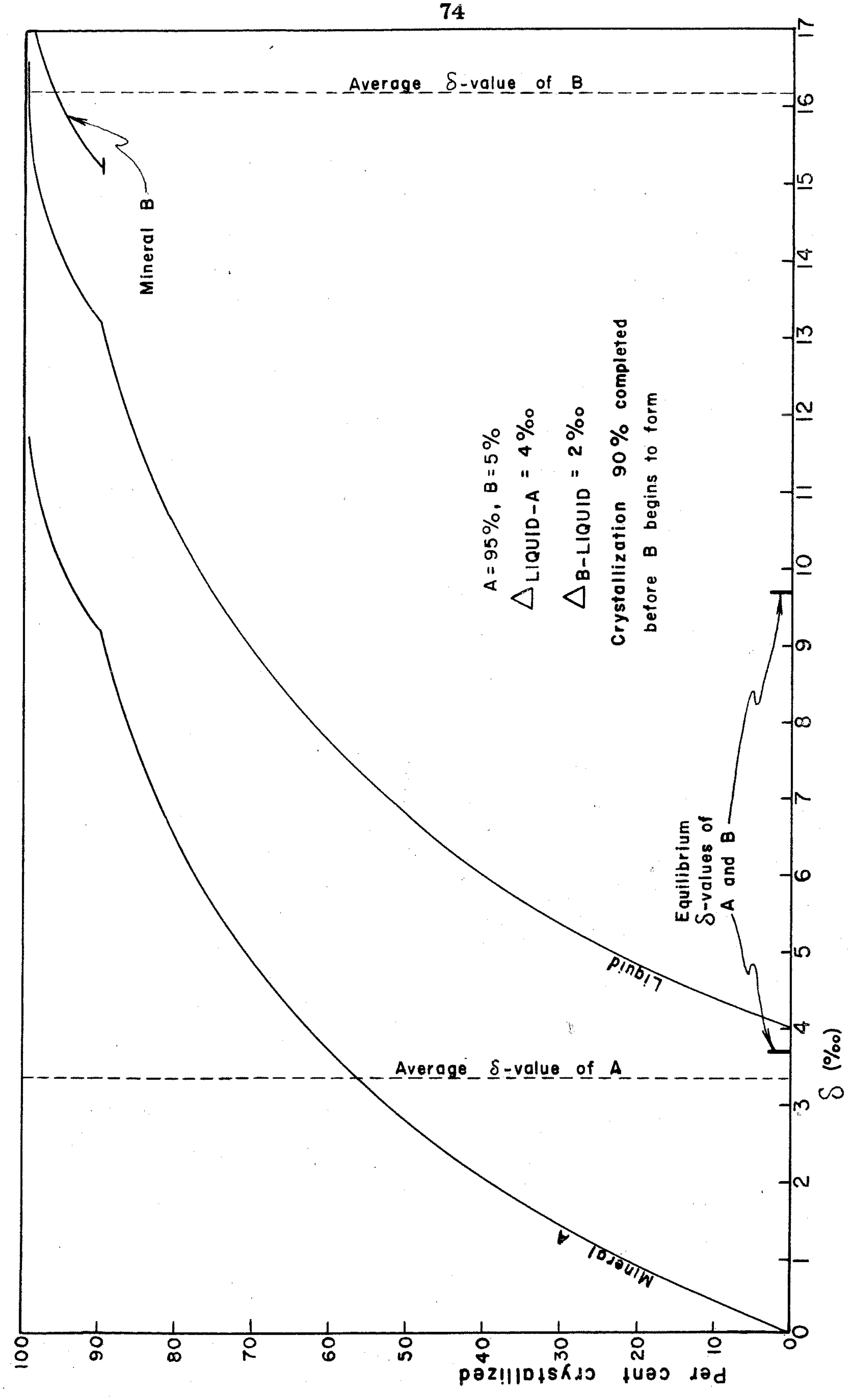


Fig. 7. Theoretical O^{18}/O^{16} variations during crystallization - no. 2.

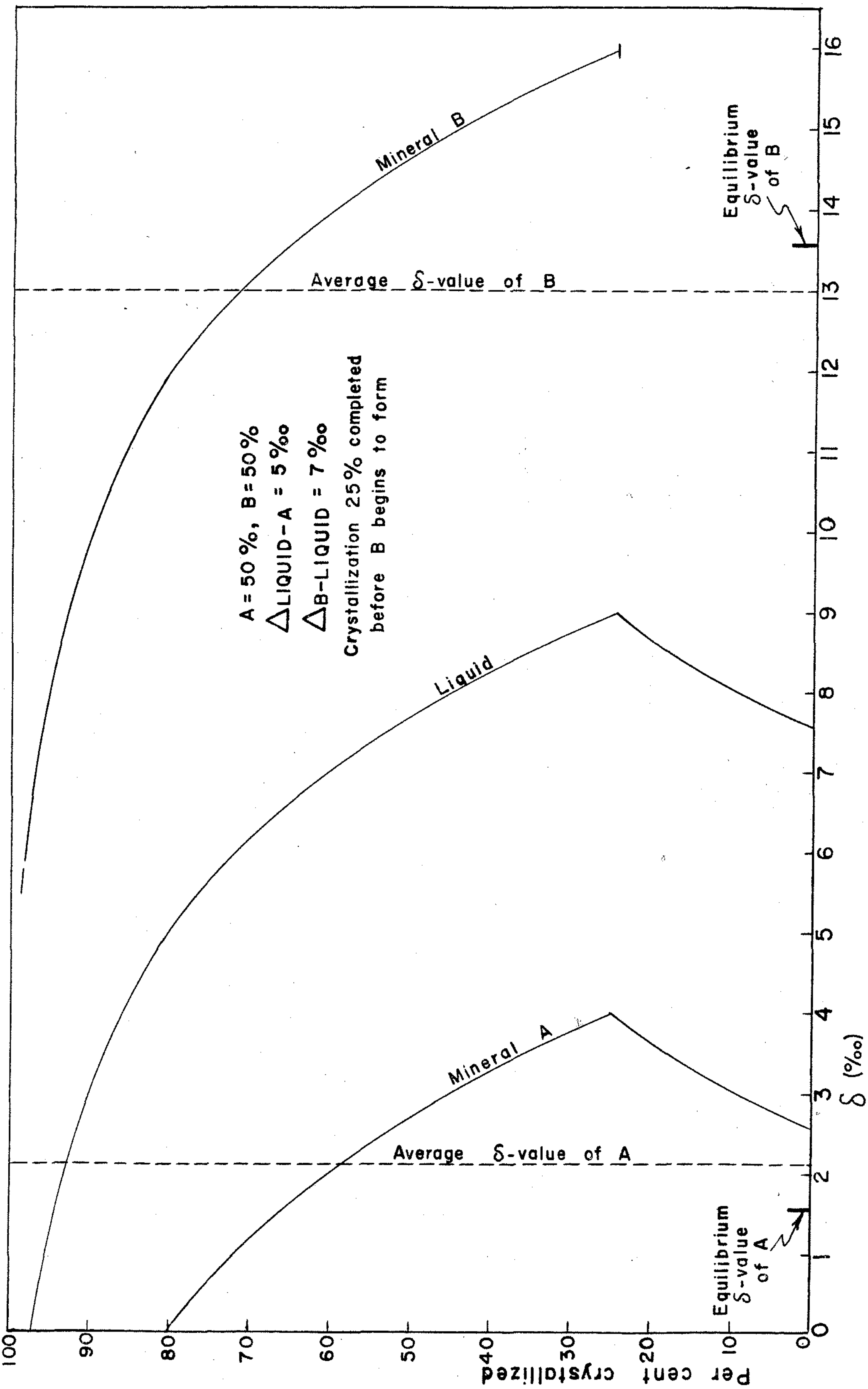


Fig. 8. Theoretical O^{18}/O^{16} variations during crystallization – no. 3.

these are the values that would be measured if the minerals were separated from the final, completely crystalline mass and analyzed by the methods used in this research. The equilibrium δ-values for each of the minerals, shown on the abscissa of each figure, are the values that would be obtained if the crystals had continuously re-equilibrated with the liquid throughout the course of crystallization — or in otherwords, if process (B) outlined previously had operated in its ideal form.

In the example of fig. 6, the liquid originally is composed of equal amounts of constituents A and B, but half of the O^{18}-deficient mineral A crystallizes before any of mineral B forms. By the time mineral B starts to form the magma liquid is about 1.5 per mil heavier than it was initially. After mineral B has begun to crystallize along with mineral A the liquid does not change in O^{18}/O^{16} ratio at so fast a rate as it had been, but it still becomes progressively enriched in O^{18}. This is because the total crystalline material forming at any stage is isotopically lighter than the magma. The final fractionation between the average δ-values of the two minerals is about 0.8 per mil greater than the equilibrium fractionation.

An important feature of these crystallization curves is that the isotopic changes become much more marked in the very late stages of crystallization. Late-forming minerals should therefore show more pronounced variations than do the early-formed ones. Such a case is illustrated by fig. 7. A liquid originally composed of 95 per cent of A and only 5 per cent of B crystallizes only mineral A until 10 per cent of the liquid is all that remains. Then both A and B crystallize in equal amounts to the end. For the fractionations assumed for this example, the final measured difference in average δ-values between A and B will be 6.8 per mil greater than the equilibrium fractionation for these two minerals. The final δ-value for mineral B is 12.2 per mil larger than the original δ-value of the liquid, whereas the equilibrium fractionation between mineral B and liquid is only 2 per mil.

In both the examples discussed above the final difference in the average δ-values for minerals A and B is greater than the equilibrium fractionation. That this is not necessarily the case is shown in fig. 8. In this situation a liquid composed of equal amounts of A and B crystallizes only A until 25 per cent of the liquid has crystallized. Then both minerals, 2 parts of B to 1 part of A, crystallize until no liquid remains. In this example the liquid-crystal equilibrium fractionation factors were so chosen that the liquid initially becomes enriched in O^{18}, but as soon as mineral B begins to form this trend is reversed. By the stage half the liquid has crystallized, the liquid is isotopically lighter than it was originally. It continues to become progressively more depleted in O^{18} throughout its crystallization. The final measured fractionation between A and B is 1.2 per mil smaller than the equilibrium fractionation.

On the basis of the above hypothetical examples of crystallization, it is clear that measured δ-values of actual minerals can give information about sequence of crystallization in natural magmas, if disequilibrium effects of isotopic zoning prevail, and if the magma changes significantly in O^{18}/O^{16} composition during solidification. These crystallization models should therefore be kept in mind when examining the oxygen isotopic data presented in the following sections.

SOUTHERN CALIFORNIA BATHOLITH

General statement

The granitic batholith of Southern and Baja California, of Cretaceous age, is exposed continuously from near Riverside, California, southward for a distance of about 350 miles. The northern part has been studied in detail by Larsen(24), and the chief rock types of this portion appear to be representative of the entire plutonic mass. A major zonation is present, with mainly gabbros and granodiorites forming the western portion of the main mass and tonalites the eastern portion. Scattered bodies of similar age in the desert ranges to the east are chiefly granodiorite. The relative ages of the individual units, as determined by Larsen from the field relationships, are those commonly found in batholiths; the gabbros were intruded first, then the tonalites, the granodiorites, and finally the granites.

The percentage of exposed area of the batholith that is underlain by the various rock units is given in Table XIV, as determined by Larsen for the Corona, Elsinore, and San Luis Rey quadrangles.

Table XIV
(after Larsen)

Percentages of the different rock types which make up the batholith

Rock type	Area (sq.mi.)	Per cent of total
San Marcos gabbro	120	14
Bonsall tonalite	325	38
Other tonalites	106	12
Woodson Mt. granodiorite	220	25.5
Other granodiorites	70	8.5
Rubidoux Mt. leucogranite	1	0.1
Other granites	18	2.4

In most places the contacts of the intrusive bodies are megascopically sharp, but locally complete gradations between rock types exist. Larsen(24) interprets these to mean that the invaded rock was not completely crystalline when new magma was injected. Only very few dikes or apophyses cut the bordering rocks, but the more granitic types commonly show a gneissic foliation near contacts with older units. In only a few places are the rocks finer-grained near contacts with these older units, although some bodies of Woodson Mt. granodiorite of relatively small size are finer-grained than the larger bodies.

The Bonsall tonalite contains abundant inclusions of a more mafic rock that have been almost completely reworked by the magma and have been softened and stretched into thin discs. These inclusions are usually oriented parallel to contacts with older rocks. Hurlbut(25) has interpreted the inclusions to be principally fragments of San Marcos gabbro which have been incorporated into the tonalite magma.

Larsen(24) believes the batholithic rocks to have been emplaced by magmatic stoping and not by forceful intrusion, citing the evidence of the abundant inclusions that occur to a greater or lesser degree in almost all the granitic rock types. Because the chemical analyses of rocks from the batholith fall near smooth variation curves, and because the amounts of the different minerals in the rocks also range systematically from the gabbros to the granites, the dominant process which brought about the variations in the rocks had to be, in the opinion of Larsen, both systematic and relatively simple. He called upon differentiation of a primary magma of gabbroic composition at depth, from which in succession were produced large bodies of tonalite and granodiorite, as well as the smaller amounts of late granite and quartz monzonite.

Such a postulated mechanism of origin cannot be proved. Any one, or all, of processes such as melting of the crust and sub-crust, crystal fractionation or other types of magmatic differentiation, assimilation of wall-rock or of earlier-crystallized material, or even local granitization, may have been operative at one time or another during emplacement of a batholith. Nevertheless, there is certainly good evidence for a magmatic origin for these rocks, and there can be little doubt but that the various rock types are genetically related.

This discussion is intended merely to indicate that this is an intrusive complex which has been well studied, which is composed of uniform and distinctive rock types, and which is probably typical of the great granodiorite-tonalite batholiths of the earth's crust. These features indicate that the Southern California batholith should be a promising area in which to initiate studies of the oxygen isotopic composition of coexisting minerals in igneous rocks.

San Marcos gabbro

The specimen of San Marcos gabbro used in these studies was collected from the Emil Johnson & Son quarry 3 miles northeast of Pala, California by L. T. Silver, who also provided a norm and mode for this rock, as shown below.

Mode		Norm	
Mineral	wt. %	Mineral	wt. %
quartz	0.24	quartz	3.7
plagioclase (An$_{55}$)	59.4	plagioclase (An$_{65}$)	63.2
biotite	0.21	orthoclase	1.7
hornblende	17.2	diopside (Di$_{58}$Hd$_{42}$)	7.4
hypersthene	10.75	hypersthene (En$_{58}$Fs$_{42}$)	17.9

Mineral	wt. %	Mineral	wt. %
augite	6.93	apatite	0.4
apatite	0.29	magnetite	3.5
chlorite	0.03	ilmenite	2.0
opaques	4.98		

This specimen is a noritic hornblende gabbro, compositionally intermediate between a true norite and a quartz-biotite-hornblende gabbro, all gradations of which exist in the batholith. The San Marcos gabbro as a unit is extremely variable in both composition and texture, with rock types ranging from troctolite and olivine gabbro to quartz gabbro. The most abundant rock type and the one which represents approximately the average of the entire group is a medium-grained dark grey norite, locally grading to hypersthene gabbro.(26) The most widespread and marked type of gradation results from abrupt changes in the amount and character of the hornblende.

This particular sample is thus in no way representative of the entire mass of what has been mapped as San Marcos gabbro by Larsen(24), but its content of quartz and hornblende make it amenable to comparison with other rock types of the batholith which contain these minerals. The specimen is medium-grained and equigranular, with zoned, markedly subhedral laths of plagioclase of average composition An_{55}. The larger grains are most strongly zoned, smaller ones are sharply zoned only near borders. The two pyroxenes appear both as separate grains and together in finer-grained clusters, always with abundant included magnetite grains. Hornblende is deep green, and is in obvious reaction relationship to the pyroxenes, which are enclosed by it. Both pyroxenes are replaced by the hornblende, but the augite preferentially so.

Quartz and biotite occur as rare, tiny, anhedral grains interstitial to plagioclase and hornblende. Apatite occurs in euhedral grains scattered uniformly through the rock, and more is probably present than is listed in the mode, on the basis of quantities obtained during mineral separations.(27) A slight amount of chlorite occurs as an alteration of the hornblende. A photomicrograph showing the texture of this rock is given in plate I.

Almost pure concentrates of plagioclase, apatite, and hypersthene were prepared, using heavy liquids. Augite and hornblende concentrates contained about 10 per cent of one another as impurities, and the quartz concentrate contained 10 per cent plagioclase. Isotopic corrections were made for the impurity in each case. Oxygen isotopic results for the minerals of this rock are presented in Table XV.

Table XV

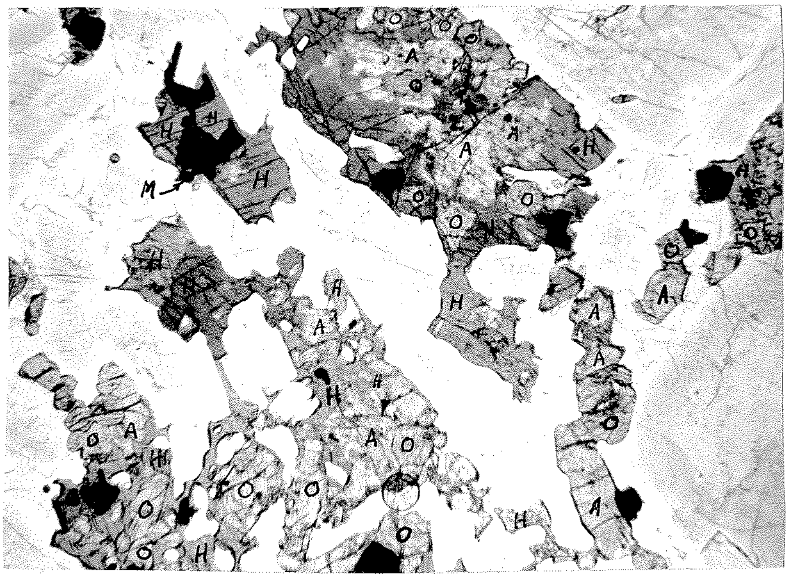
Oxygen isotopic analyses of minerals of San Marcos gabbro

Mineral	$\delta O^{18}/O^{16}$ (‰)	av. dev.	no. of runs
quartz	10.2	0.2	4
plagioclase (An_{55})	7.5	0.2	5
hornblende	6.5	0.2	3
clinopyroxene	5.9	0.1	2
orthopyroxene	6.6	0.1	3
apatite	4.1	0.3	2
magnetite	3.0	0.3	6
entire rock	7.1	0.2	2

Ia - Photomicrograph of a thin section of San Marcos gabbro (plane light, x 26). Note the marked reaction rims of hornblende that enclose both the pyroxenes and magnetite. The augite is apparently more completely replaced by this hornblende than is the orthopyroxene, as shown by the very irregular outlines of the augite residuals as compared with the smaller, more equant hypersthene grains. The zoning in the plagioclase can be seen even in the photograph taken in plane light because of the finely disseminated dark inclusions in the central portions of the plagioclase grains. A = augite, O = orthopyroxene, h = hornblende, M = magnetite.

Ib - Photomicrograph of a thin section of San Marcos gabbro (crossed nicols, x 24). Note the markedly subhedral plagioclase grains which form an interlocking network of laths. In the interstices of these laths are minor amounts of quartz which apparently form a connected intergrowth, as shown by their being in near optical orientation with one another. Atypically large amounts of quartz are shown in this photograph because it was chosen especially to demonstrate the interstitial nature of the quartz. Q = quartz, P = plagioclase, H = hornblende.

PLATE I



Ia

Ib

The O^{18}/O^{16} ratio of the entire rock, as calculated from the mode and the individual δ-values of the minerals, gives $\delta_{ROCK} = 7.0$, in good agreement with the measured value of 7.1.

Bonsall tonalite

The specimen of Bonsall tonalite was collected 2 miles west of Val Verde, California by L. T. Silver, who provided a norm and mode for the sample, as shown below.

Mode

Mineral	wt. %
quartz	25.2
plagioclase (An_{40})	48.3
orthoclase	0.5
biotite	14.2
hornblende	10.0
apatite	0.25
opaques	0.14
accessories	0.78
epidote	0.65

Norm

Mineral	wt. %
quartz	18.6
plagioclase (An_{46})	53.5
orthoclase	10.0
diopside ($Di_{49}Hd_{51}$)	2.2
hypersthene ($En_{49}Fs_{51}$)	12.4
apatite	0.3
magnetite	1.6
ilmenite	1.4

The Bonsall tonalite is a fairly uniform rock, as contrasted with the San Marcos gabbro, and this specimen is fairly typical of its occurrence throughout the batholith. The ubiquitous mafic inclusions are finer-grained than the host rock, and are made up of the same minerals, but in different proportions. Hornblende is generally much more abundant in the inclusion than in the host, and biotite is somewhat more abundant. Pyroxenes are only locally present, and quartz and orthoclase are rare. Biotite and hornblende are usually more iron-rich in the inclusions than in the host, and some of the plagioclase grains have cores of calcic bytownite.(25)

This particular sample of the host rock is medium to coarse-grained and inequigranular, with strongly zoned, subhedral, well-twinned laths of plagioclase 0.5–5 mm in length, averaging An_{40} in composition. Hornblende is subhedral, commonly twinned, deep green, and zoned. Biotite averages 2 mm in size, as does the hornblende, and occurs in independent grains with ragged borders. Although biotite and hornblende are sometimes seen to be clustered together, the two minerals are not in any apparent reaction relationship. Quartz grains average 2–3 mm in size, show pronounced strain shadows, are anhedral, and are markedly interstitial to the plagioclase laths. Rare potash feldspar is interstitial to the quartz and plagioclase. A photomicrograph showing the texture of this specimen is given in plate II.

Quartz and plagioclase were separated by hand-picking. Pure biotite and hornblende concentrates were prepared by magnetic separation. Epidote and apatite separates, prepared with heavy liquids, were provided by L. T. Silver. The oxygen isotopic analyses of these minerals are tabulated in Table XVI.

Table XVI

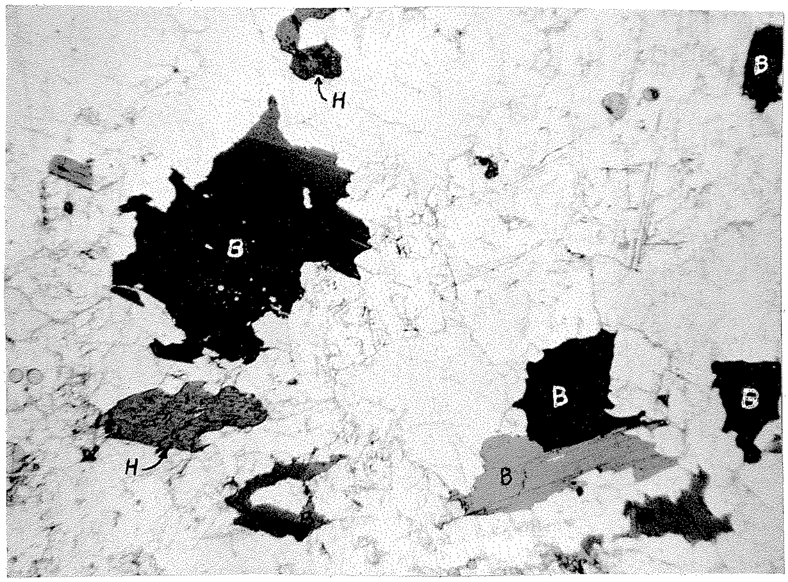
Oxygen isotopic analyses of minerals of Bonsall tonalite

Mineral	$\delta O^{18}/O^{16}$ (‰)	av. dev.	no. of runs
quartz	10.3	0.1	3
plagioclase (An_{40})	8.5	0.1	4
hornblende	6.9	0.1	5
biotite	5.4	0.0	3
apatite	6.7	0.1	2
epidote	6.2		1
entire rock	8.0		1

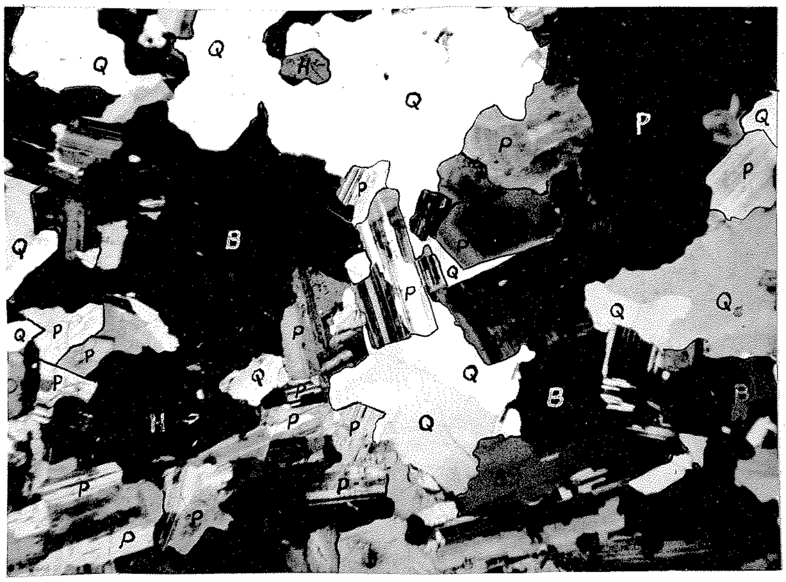
IIa - Photomicrograph of a thin section of Bonsall tonalite (plane light, x 9). Note the large, individual biotite and hornblende grains which are subhedral to euhedral. Hornblende tends to show better crystal development than does biotite. B = biotite, H = hornblende.

IIb - Same field as above, (crossed nicols, x 9). Note that the mafic minerals in this rock are as large as the sialic minerals. The plagioclase is markedly subhedral and is strongly zoned. The interstitial nature of the quartz relative to the plagioclase is well shown. Q = quartz, P = plagioclase, B = biotite, H = hornblende.

PLATE II



IIa



IIb

The oxygen isotopic composition of the total rock, calculated from the mode and the individual δ-values of the minerals, is $\delta_{ROCK} =$ 8.3. This is probably a more accurate value than that obtained by the single analysis of the entire rock listed in Table XVI. No minerals from the inclusions associated with this rock have been analyzed.

Woodson Mt. granodiorite

The specimen of Woodson Mt. granodiorite was collected 3 miles south of Temecula, California, by L. T. Silver, who also supplied the following norm and mode for this rock.

Mode		Norm	
Mineral	wt. %	Mineral	wt. %
quartz	36.80	quartz	35.3
plagioclase (An_{25})	39.48	plagioclase (An_{20})	44.2
potash feldspar	15.24	orthoclase	16.5
myrmekite	1.80	corundum	0.28
biotite	5.78	hypersthene ($En_{36}Fs_{64}$)	2.52
hornblende	0.17	apatite	0.16
opaques	0.17	ilmenite	0.44
accessories	0.52	magnetite	0.77
alteration	0.02		

This specimen is considered to be fairly representative of the Woodson Mt. granodiorite throughout its outcrop area. It is moderately coarse-grained, almost equigranular, and contains subhedral plagioclase grains that are zoned, well-twinned, and average An_{25} in composition. Plagioclase grains average about 3 mm in length. Microcline microperthite and quartz occur as slightly smaller grains and are anhedral. A few of the potash feldspar grains are larger than 4 mm. Much of the quartz occurs in clusters of grains, and in small amounts as myrmekitic intergrowths. Biotite averages 3 mm in length, and occurs in irregular, ragged grains, some of which are interstitial to the plagioclase. A photomicrograph of this rock is shown in plate III.

Minerals were separated into relatively pure fractions with heavy liquids and magnetic separator. Oxygen isotopic analyses of the various minerals are listed in Table XVII.

Table XVII

Oxygen isotopic analyses of minerals of Woodson Mt. granodiorite

Mineral	$\delta O^{18}/O^{16}$ (‰)	av. dev.	no. of runs
quartz	9.5	0.1	4
plagioclase	8.5	0.2	3
potash feldspar	7.9	0.1	3
biotite	4.4	0.3	2
entire rock	8.9		1

The calculated $\delta_{ROCK} = 8.6$, which is probably a more accurate value than that given by the single analysis listed in Table XVII.

Rubidoux Mt. leucogranite

The specimen of Rubidoux Mt. leucogranite was collected from Mt. Rubidoux near Riverside, California, by L. T. Silver, who supplied a norm and mode for the rock, as shown below.

Mode

Mineral	wt. %
quartz	34.42
plagioclase (An_{20})	30.28
microperthite	27.91
biotite	3.03
hornblende	1.39
myrmekite	2.50
hypersthene	0.05
accessories	0.32
opaques	0.10

Norm

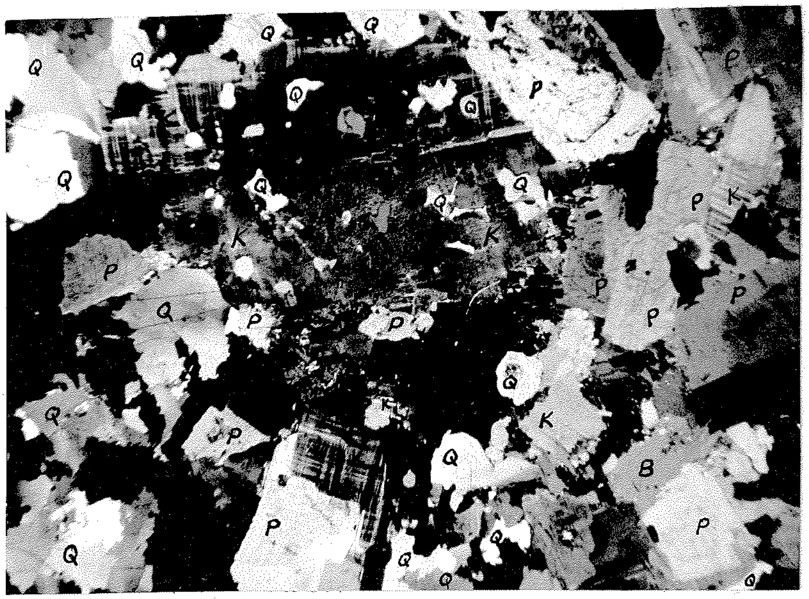
Mineral	wt. %
quartz	32.7
plagioclase (An_{15})	31.8
orthoclase	26.2
diopside ($Di_{19}Hd_{81}$)	0.6
hypersthene ($En_{19}Fs_{81}$)	1.7
apatite	0.2
ilmenite	0.4
magnetite	0.7

IIIa - Photomicrograph of a thin section of Woodson Mt. granodiorite (plane light, x 9). Note the ragged borders of the biotite grains and their relatively small size as compared with the other minerals of this rock. B = biotite.

IIIb - Same field as above (crossed nicols, x 9). Note the large potash feldspar crystal with its many inclusions of quartz (replacement residuals?), as well as the smaller grains of microcline. Quartz occurs in clusters of grains which show sutured boundaries and a considerable range in size. The plagioclase grains are zoned and exhibit the most euhedral form of any of the minerals in this rock. Q = quartz, K = potash feldspar, P = plagioclase, B = biotite.

PLATE III

IIIa



IIIb

This specimen is typical of the coarse-grained leucogranite, and it is pale greenish-grey in hand specimen, with grains averaging about 8 mm in length. Microperthite contains stringers of albite that carry blebs of quartz. Quartz grains are large and anhedral. Plagioclase (An_{20}) is unzoned and contains blebs of quartz near grain borders. Minor biotite, dark green hornblende, and iron-rich hypersthene are finer-grained and tend to be interstitial to the major minerals.

This rock type should be properly called a leuco-quartz monzonite, and it occurs in only the limited area near Riverside, California. By far the majority of granites in the batholith are leucocratic, and the Rubidoux Mt. leucogranite is considered to be typical of these rocks, which represent the very last stages of intrusion of major rock bodies in the batholith. Many small dikes of aplite, mafic rocks, and pegmatite were probably even later to form but make up no large bodies. A photomicrograph of this rock is shown in plate IV.

Owing to the coarseness of the grains, separation of the individual minerals by hand-picking was easily accomplished. Results of analytical determinations of O^{18}/O^{16} ratios are presented in Table XVIII.

Table XVIII

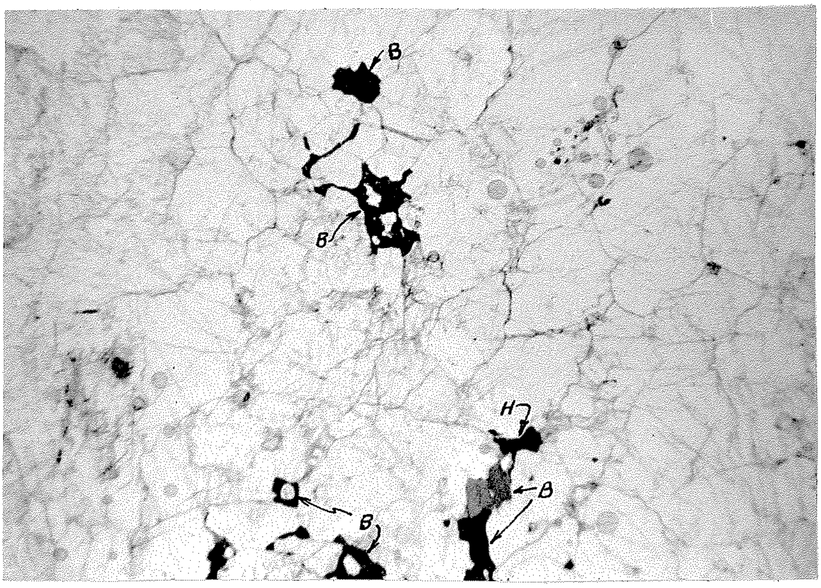
Oxygen isotopic analyses of minerals of Rubidoux Mt. leucogranite

Mineral	$\delta O^{18}/O^{16}$ (‰)	av. dev.	no. of runs
quartz	9.9	0.0	2
plagioclase (An_{20})	8.8	0.0	2
microperthite	9.1	0.1	2
biotite	6.6	0.1	2

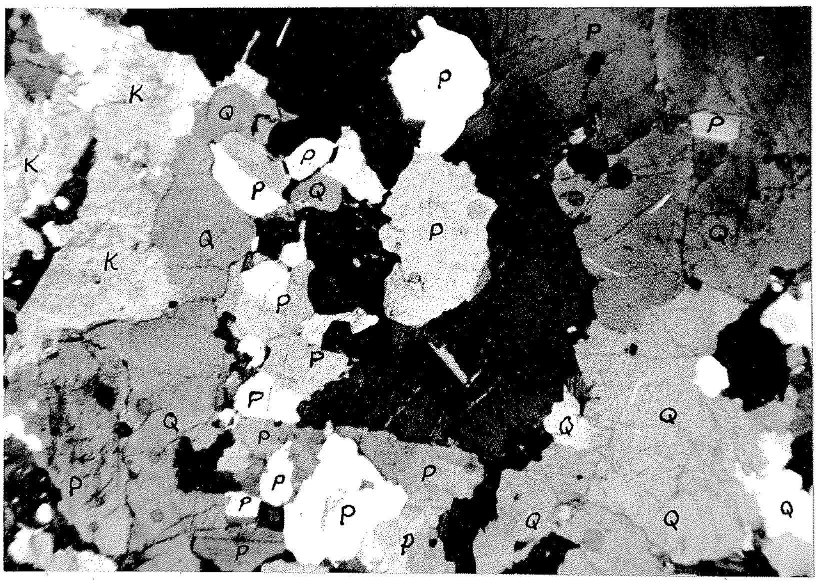
IVa - Photomicrograph of a thin section of Rubidoux Mt. leucogranite (plane light, x 9). Note that the biotite and hornblende are markedly interstitial to the quartz and feldspar, and they occur in smaller grains. B = biotite, H = hornblende.

IVb - Same field as above (crossed nicols, x 9). Note the large range in size of the major minerals of this rock. Note also that grains of a given mineral occur in clusters, and that all the minerals generally show anhedral forms. Q = quartz, P = plagioclase, K = potash feldspar.

PLATE IV



IVa



IVb

The calculated value for $\delta_{ROCK} = 9.2$, no analysis of a total rock sample having been done.

Interpretation of O^{18}/O^{16} data from the batholithic rocks

Oxygen isotopic data obtained for the minerals of the four distinctive rock types of the Southern California batholith are presented in the graph of fig. 9. The δ-values for each mineral have been joined by dashed lines only to make the variations among the various rocks more obvious. Magnetite data are from the work of Clayton and Epstein, corrected to the present standard.(7)

A certain degree of order exists in the data, as has already been pointed out in a previous section. Quartz has the highest O^{18}/O^{16} ratio of any of the minerals of a given rock, and a generalized sequence of minerals progressively more enriched in O^{16} are, in order, quartz, feldspar, hornblende, biotite, and magnetite. It appears, however, that complete oxygen isotopic equilibrium was not attained in these rocks. The fractionation factors for the different mineral pairs do not vary in a simple manner from one rock to another. For example, $\Delta_{QUARTZ-PLAGIOCLASE}$ changes from 2.7 per mil in the gabbro to 1.8 per mil in the tonalite, and it is as low as 1 per mil in the granodiorite and leucogranite. In turn, $\Delta_{PLAGIOCLASE-BIOTITE}$ shows a variation from 3.1 per mil in the tonalite to 4.1 in the granodiorite, and is 2.2 in the leucogranite.

These complex changes in the fractionation factors among the minerals of these rocks must be a result of minor disequilibrium among the minerals. As was mentioned in an earlier section, evidence exists that the equilibrium fractionation factors for mineral pairs such as quartz-magnetite and hornblende-plagioclase decrease continuously with

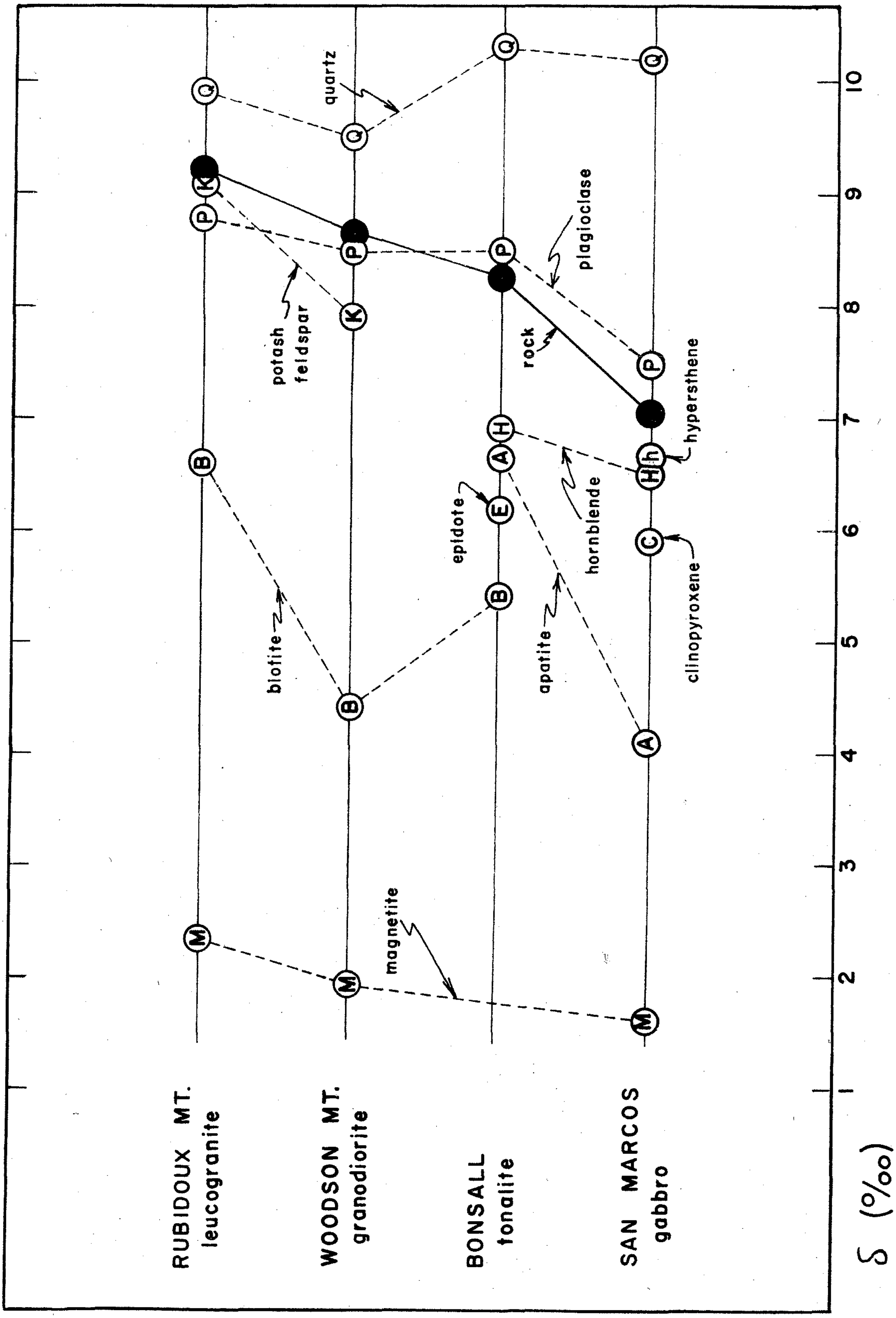


Fig. 9. Isotopic analyses of minerals in rocks of the Southern California batholith.

temperature, and at magmatic temperatures this rate of decrease is much smaller than at lower temperatures. In direct opposition to such relationships, $\Delta_{\text{QUARTZ-PLAGIOCLASE}}$ increases markedly from the lower temperature rocks (the granodiorite and leucogranite) to the higher temperature rocks (the tonalite and gabbro). Other observations make the presence of disequilibrium even more obvious. The value of $\Delta_{\text{PLAGIOCLASE-POTASH FELDSPAR}}$ changes from +0.6 per mil in the granodiorite to -0.3 per mil in the leucogranite, and $\Delta_{\text{QUARTZ-APATITE}}$ changes from 6.1 per mil in the gabbro to only 3.6 per mil in the tonalite.

These arguments result in an interpretation of the formation of these rocks based upon a near approach to equilibrium, but with superposition of minor disequilibrium features. This hypothesis is reached by a consideration of the isotopic evidence alone, but resort to the petrographic data for these rock types lends support to such an interpretation. The mineralogical compositions and textures of these rocks indicate that each has attained a state of gross equilibrium. Minor textural features also clearly imply the existence of departures from equilibrium. Included among such features are zoning in plagioclases and hornblendes, and reaction rims of hornblende enclosing pyroxene. Because these obvious textural features of disequilibrium are most easily explained on the basis of magmatic crystallization with incomplete reaction, it is only natural to turn to such a mechanism to explain the features of the oxygen isotopic data.

The San Marcos gabbro, from textural evidence and from a consideration of experimental phase equilibria studies of appropriate systems, probably began crystallizing calcic plagioclase, two pyroxenes, and magnetite relatively early. When the water content of the magma had reached a high enough value, almost certainly not before at least half the rock had crystallized, hornblende began to develop and replace the pyroxenes. Only after about 98 per cent of the rock had crystallized did the minor amounts of quartz and biotite form, along with the outermost rims of the plagioclase grains, which by this stage had become as sodic as An_{40}.

If it is assumed that the O^{18}/O^{16} ratio of the total rock as now analyzed is approximately the same as that of the original magma from which the rock crystallized, a qualitative crystallization model can be set up in the same manner as was discussed for the 3 hypothetical examples mentioned in a previous section. Throughout the early stages of crystallization of the San Marcos gabbro, mafic minerals isotopically much lighter than the magma were forming, along with plagioclase of about the same isotopic composition as the magma. Hence the magma should have become progressively enriched in O^{18}. In support of this reasoning is the large value of $\Delta_{\text{QUARTZ-ROCK}}$. This Δ-value, abnormally large compared with the values for the other batholithic rocks, is evidence that this quartz formed from an isotopically heavier magma than did the other minerals of the gabbro.

Evidence will be presented in discussing metamorphic amphibolites to show that at isotopic equilibrium clinopyroxene is richer in O^{18} than is hornblende. Because hornblende is a late-crystallizing mineral in the gabbro, the fact that $\Delta_{\text{HORNBLENDE-CLINOPYROXENE}}$ is positive in this rock is further proof that the magma became progressively heavier. The equilibrium fractionation factor between orthopyroxene and clinopyroxene is probably small; hence the 0.7 per mil enrichment in O^{18} shown by the hypersthene relative to the augite is indicative that the hypersthene began crystallizing later than did the augite. However, the small fractionation between hypersthene and hornblende shows that hornblende crystallized still later, in agreement with the textural evidence. $\Delta_{\text{PLAGIOCLASE-HORNBLENDE}}$ is 0.6 per mil smaller in the gabbro than in the tonalite, and inasmuch as the tonalite hornblende is an early-crystallizing mineral, this is still another indication that the postulated trend of O^{18} enrichment in the gabbro magma is correct.

Hornblende and plagioclase were in all likelihood the earliest minerals to form in the Bonsall tonalite magma. Biotite, too, began to crystallize relatively early, but only after about half the rock had crystallized did the quartz begin to form in appreciable quantities. These four minerals then crystallized together to the end, except that hornblende may have stopped forming during the very end stages and been replaced by biotite. That the Bonsall tonalite magma also became progressively enriched in O^{18} is indicated by the relatively large value of $\Delta_{\text{QUARTZ-ROCK}}$, showing that quartz crystallized over most of its range from a more O^{18}-rich magma than that represented by the O^{18}/O^{16} ratio of the present rock. This Δ-value is, however, not as large for the tonalite as for the gabbro — in keeping with the much later crystallization of quartz in the gabbro than in the tonalite.

$\Delta_{\text{ROCK-APATITE}}$ varies from 3 per mil in the gabbro to 1.5 per mil in the tonalite; hence apatite probably began crystallizing earlier in the gabbro than in the tonalite. This is not unreasonable in view of the higher content of CaO and P_2O_5 in the gabbro, as the solubility of apatite may well have been exceeded earlier in this magma. This, of course, tells nothing about the crystallization period of apatite relative to the major minerals of the rock, and in fact nothing can be said in this regard until an approximate equilibrium fractionation factor between apatite and one of the major minerals is known.

The tonalite and gabbro magmas both became enriched in O^{18} as crystallization proceeded, as evidenced by the high O^{18}/O^{16} ratios of their late-crystallizing minerals. Both rocks contain large quantities of mafic minerals whose early formation would have made the magmas become progressively enriched in O^{18}. The Woodson Mt. granodiorite contains only 6 per cent biotite and 0.2 per cent magnetite, so these mafic minerals could have only a minor effect upon the oxygen isotopic trend of this magma. Inasmuch as potash feldspar and biotite in the granodiorite are abnormally deficient in O^{18}, compared with the other batholithic rocks, this magma evidently became isotopically lighter as crystallization progressed.

The earliest minerals to form in the granodiorite magma were in all likelihood plagioclase and quartz. The plagioclase would have had an oxygen isotopic composition close to that of the magma, but the quartz would have been about 1 per mil heavier. Therefore the liquid would have become more and more enriched in O^{16}, at least until biotite and potash feldspar were forming in significant amounts. The small quantity of magnetite in the granodiorite probably was not formed early, as it was in the San Marcos gabbro, inasmuch as $\Delta_{\text{ROCK-MAGNETITE}}$ is 7.0 in the granodiorite and only 5.6 in the gabbro. Also,

$\Delta_{\text{ROCK-BIOTITE}}$ is 2.9 per mil in the tonalite and 4.2 in the granodiorite; this is compatible with a progressive decrease in O^{18} in the granodiorite magma, as biotite undoubtedly formed relatively later in this magma than in the tonalite magma. By the stage that potash feldspar was forming along with these other minerals the magma may have reached approximate balance; its O^{18}/O^{16} ratio may not have changed markedly after this stage had been reached.

Oligoclase may have been the earliest mineral to form in the Rubidoux Mt. leucogranite magma, but it would have been almost immediately joined by quartz. Potash feldspar would have formed earlier in this rock than in the granodiorite, but biotite would probably have formed relatively later. This magma either remained about constant in its oxygen isotopic composition as solidification proceeded, or it became slightly enriched in O^{18}, inasmuch as the biotite and potash feldspar are both markedly richer in O^{18} in this rock than in the granodiorite. $\Delta_{\text{ROCK-BIOTITE}} = 2.6$ per mil for this rock, whereas a value of 4.2 is obtained for the granodiorite and a value of 2.9 for the tonalite. Therefore the leucogranite magma apparently paralleled the tonalite magma more closely in its oxygen isotopic history, even though it is chemically more similar to the granodiorite. The most compelling evidence is shown by the reversal in $\Delta_{\text{PLAGIOCLASE-MICROCLINE}}$ between the granodiorite and the leucogranite. This is easily explained if the former magma became isotopically lighter during crystallization while the latter remained constant or became slightly heavier, but is difficult to explain on any other basis.

There is, a priori, no reason to believe that quartz precipitating from a tonalite magma should give the same $\Delta_{QUARTZ-MAGMA}$ as quartz forming in a granitic magma. There is even less reason to believe that bytownite or labradorite from a gabbroic magma should give a $\Delta_{MAGMA-PLAGIOCLASE}$ similar to that of the oligoclase from a granitic magma. Irrespective of the changes in the fractionation factors because of temperature effects alone, in the first case the chemical composition of one of the phases, the magma, has changed; in the latter case both phases, the plagioclase and the magma, have changed in composition. Available data indicate that these fractionations do, in fact, change as a result of such changes in chemical composition. Oligoclase from the leucogranite is estimated to have been about 0.4 per mil lighter than the liquid from which it precipitated, whereas the initial plagioclase to develop from the gabbroic magma probably was 0.2-0.3 per mil heavier than the magma. Fractionations in the granodiorite and tonalite magmas would lie between these extremes.

Magmas at their liquidus have an internal structure, and this structure changes from a chain and independent tetrahedral intergrowth in a gabbro to a more highly polymerized 3-dimensional network in the viscous granitic types. As was pointed out in a previous section, it is changes of structural type which should play the dominant role in changing fractionation factors between silicate phases. Variations in cation composition, without concomitant changes in structural type, should produce little effect. Such a theory fits the observed facts very well, as at equilibrium the more highly polymerized silicate minerals are richest in O^{18}; hence plagioclase might well be isotopically heavier than a gabbroic magma, but lighter than a granitic magma. Even though such marked changes of $\Delta_{MAGMA-MINERAL}$ can occur, there should be little change in fractionation factors between individual minerals over wide ranges of chemical composition. For example, at equilibrium at a given temperature the value of $\Delta_{\text{QUARTZ-PLAGIOCLASE}}$ should be very nearly the same whether the plagioclase is calcic or sodic.

An assumption throughout much of the foregoing discussion has been that the magma crystallizes as a closed system, so that the O^{18}/O^{16} ratio of the original magma would be identical with that of the total rock as now analyzed. This is only an approximation because loss of water and other volatiles from a crystallizing magma may change the oxygen isotopic composition of the magma. Clayton and Epstein(7) have presented evidence showing that the fractionation of oxygen isotopes between magnetite and water, and between magnetite and an aqueous hydrothermal fluid, is practically zero over a wide range of temperatures. If this were true, a maximum difference of about 8 per mil could exist between the δ-value of the magma and that of the water in equilibrium with it. If the magma originally contained 4 per cent water and it was all lost during crystallization, a change of about 0.6 per mil would occur in the δ-value of the magma. This is a significant change, but inasmuch as the rock probably crystallizes under essentially closed conditions at least until 95-99 per cent crystalline, only those minerals which form extremely late should be affected by such a loss of volatiles. The late quartz of the San Marcos gabbro may have been influenced in this manner, and the relatively large value of δ_{QUARTZ} in this rock could be partially explained on this basis.

The original magmas, therefore, may have been slightly lighter, in general, than the rocks as now analyzed. Because the amounts of water that have been lost by a given magma cannot be easily determined, the extent of isotopic change cannot be calculated. It is presumed that ordinarily it would never be larger than 0.2-0.4 per mil. Continuous loss of water by diffusion from the magma during the entire course of crystallization could be an added factor, the magnitude of whose effect is difficult to evaluate.

The rock types of the batholith have up till now been discussed without making reference to any possible genetic relationships between them. All four rocks might well have come from widely different localities, for none of the interpretations outlined above would be changed thereby. A gabbro of identical chemical composition as the San Marcos gabbro, crystallized under the same physical conditions, presumably would give exactly the same relative isotopic results, even were the total oxygen isotopic composition of the two magmas different.

A formidable problem exists in attempting to relate these four batholithic rocks genetically through their oxygen isotopic compositions. Any attempt to extrapolate to bodies of the size of a batholith from data on four randomly collected specimens must certainly be a gross over-interpretation of the data. Nevertheless, suggestive results are obtained when the O^{18}/O^{16} ratios of the entire rocks are plotted on the variation diagram shown in fig. 10, as a function of weight per cent $1/3\ SiO_2 + K_2O - CaO - MgO - FeO$.

The analyses form nearly a straight line on the variation diagram, each succeedingly younger rock being more enriched in O^{18}. Such a consistent sequence could be a result of magmatic differentiation of gabbroic magma at depth, as postulated by Larsen$^{(24)}$, inasmuch as

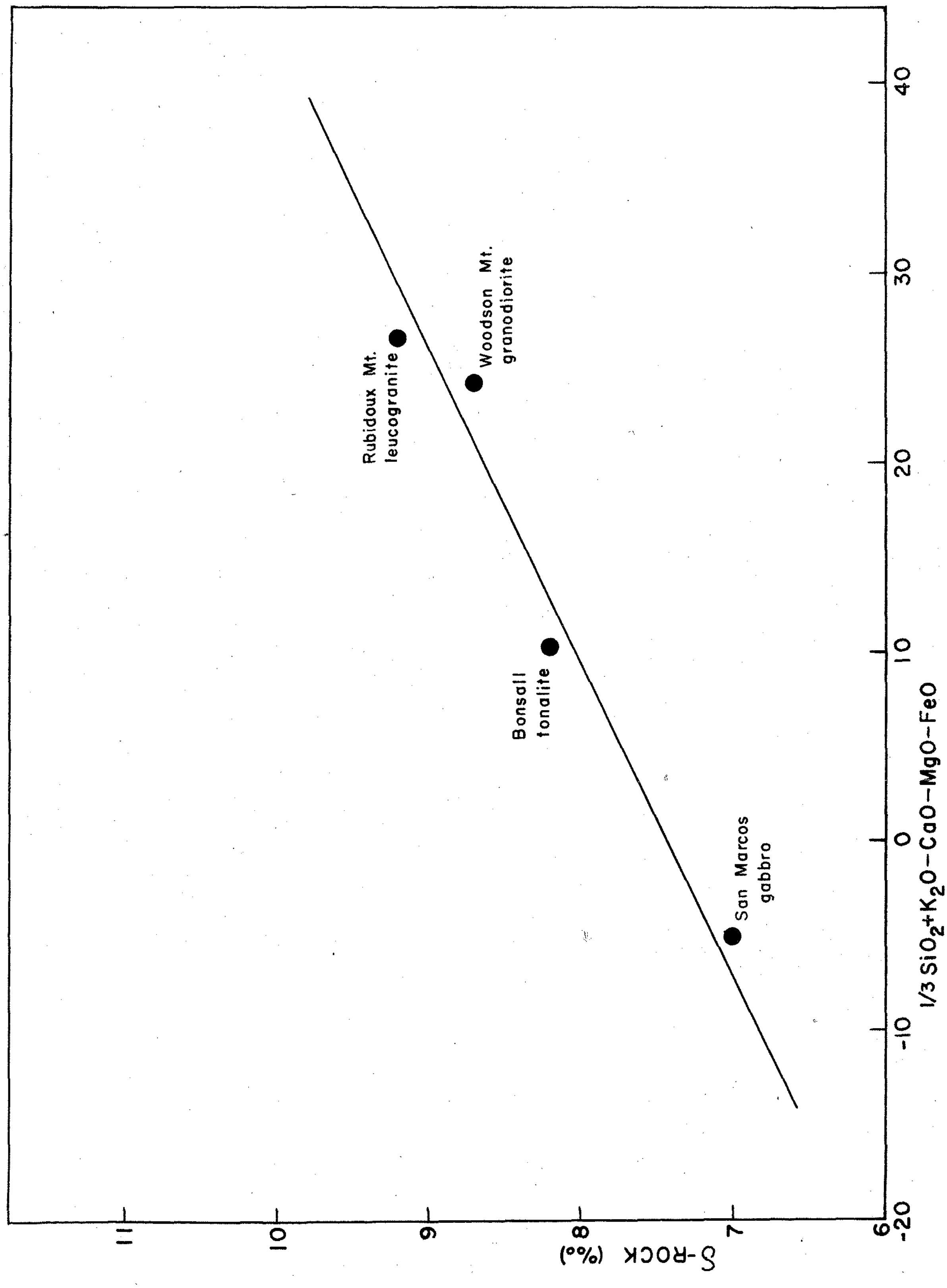


Fig. 10. Variation diagram showing isotopic analyses of total rocks of the Southern California batholith.

the San Marcos gabbro magma became isotopically heavier during crystallization. Additional enrichment in O^{18} could have occurred by the gravitational settling of early-formed mafic minerals. It appears certain, however, that while all these magma types could probably have been derived from the gabbro, the leucogranite could not have formed by fractional crystallization of the granodiorite magma, as represented by the two specimens collected. This is because the granodiorite magma became progressively lighter during crystallization, and by the time a magma of quartz monzonite composition were tapped off it would have had a δ-value at least 1 per mil lighter than that of the present leucogranite.

While the oxygen isotopic evidence is compatible with the mechanism of fractional crystallization as postulated by Larsen(24), the mechanism cannot be proved by such evidence as is now available. Other ways probably exist whereby these variations might arise. However, the isotopic evidence does add to the growing accumulation of data which indicate that these various rock types of the batholith are genetically related in some manner.(24)(28)

ROCK TYPES FROM OTHER LOCALITIES COMPARED WITH THOSE OF THE SOUTHERN CALIFORNIA BATHOLITH

General statement

An important and as yet unanswered question is how generally applicable are the O^{18}/O^{16} relationships determined for the four rocks of the Southern California batholith. This problem may be partially answered by a comparison with analytical data obtained upon rocks from various geographical localities.

Four rocks have been studied in this connection, a quartz monzonite from Georgia, the Elberton granite; a tonalite from the Baja California portion of the Southern California batholith, the San Jose tonalite; a gabbro from Duke Island in southeastern Alaska, here termed N-36-8; and a Tertiary basalt from eastern Oregon, the Steens basalt. The rocks are discussed in detail and $0^{18}/0^{16}$ analyses of their minerals are compared with data from their counterparts in the Southern California batholith.

San Jose tonalite

The specimen of San Jose tonalite was collected from near the center of the San Jose pluton of the Sierra de San Pedro Martir, 25 miles east of San Telmo, Baja California by L. T. Silver, who has provided a norm and mode for this sample, shown below.

Mode		Norm	
Mineral	wt. %	Mineral	wt. %
quartz	17.1	quartz	16.0
plagioclase (An_{35})	62.3	plagioclase (An_{37})	65.4
hornblende	9.59	orthoclase	4.8
biotite	5.95	diopside ($Di_{87}Hd_{13}$)	3.2
orthoclase	0.02	hypersthene ($En_{87}Fs_{13}$)	5.3
magnetite	2.6	apatite	0.5
accessories	0.24	magnetite	3.5
		ilmenite	1.3

The San Jose tonalite has been described by Woodford and Harriss (29) and is similar to the Bonsall tonalite of the northern portion of the batholith. It contains similar, but less abundant, disc-shaped inclusions of a more mafic rock, elongate parallel to the foliation. This particular specimen is not so mafic as the specimen of Bonsall tonalite previously described; the plagioclase content is higher and quartz, hornblende, and biotite are less abundant. In keeping with the less mafic character, plagioclase averages An_{35} in composition, whereas the average in the Bonsall is An_{40}.

The plagioclase of the San Jose tonalite is slightly more strongly zoned, and the rock as a whole is more strongly foliated and is finer-grained than is the Bonsall tonalite. Biotite and hornblende, especially, occur in smaller grains, and are commonly clustered together. These minerals are more clearly interstitial to the plagioclase in this rock than in the Bonsall, and it is probable that some biotite has formed by late stage reaction with hornblende. Both minerals show ragged borders, and plagioclase laths are not so markedly subhedral as in the Bonsall tonalite. Quartz in both rocks is clearly interstitial to the plagioclase. A photomicrograph of this rock is shown in plate V.

The four major minerals of the San Jose tonalite have been picked by hand from the crushed rock. Their oxygen isotopic compositions are presented in Table XIX.

Table XIX

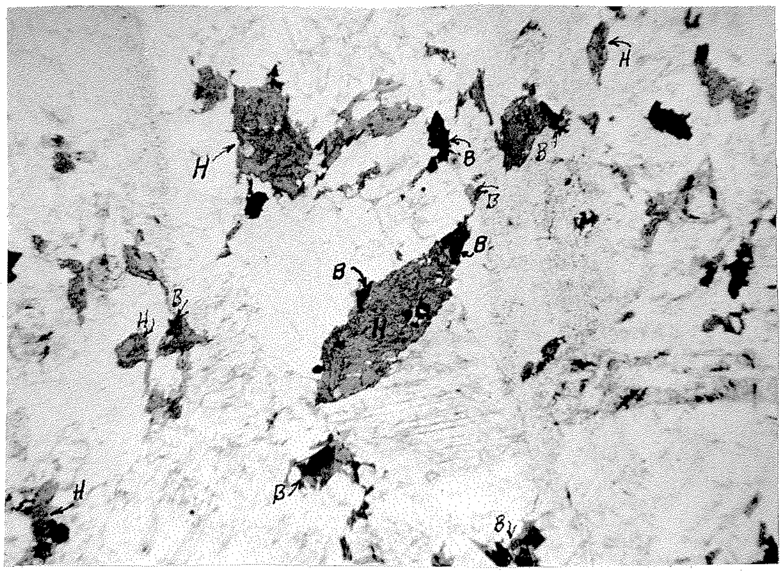
Oxygen isotopic analyses of minerals from the San Jose tonalite

Mineral	$\delta O^{18}/O^{16}$ (‰)	av. dev.	no. of runs
quartz	9.7	0.2	3
plagioclase (An_{35})	8.0	0.0	2
hornblende	6.6	0.3	3
biotite	5.2	0.0	2
sphene	6.3		1

Va - Photomicrograph of a thin section of San Jose tonalite (plane light, x 9). Note the imperfect foliation shown by the hornblende and biotite grains, as well as the ragged borders that are shown by these grains. Biotite tends to occur as smaller grains than does the hornblende, and it commonly occurs clustered at the borders of the hornblende grains. B=biotite, H=hornblende.

Vb - Photomicrograph of a thin section of San Jose tonalite (crossed nicols, x 31). Note the subhedral, strongly zoned plagioclase laths, and the relationship of these to the quartz grains, which occur interstitially to the plagioclase. Dark crystal in center of photograph is a subhedral hornblende grain. Note how smaller biotite grains cluster at lower extremity of this grain. Q=quartz, P=plagioclase, H=hornblende, B=biotite.

PLATE V



Va

Vb

The single sphene analysis was carried out on a mineral separate provided by L. T. Silver from a border phase of this same San Jose pluton — hence this mineral was not coexisting with the analyzed major minerals. A calculated $\delta_{ROCK} = 7.8$, but the entire rock has not been analyzed directly.

The oxygen isotopic compositions of the minerals from the Bonsall tonalite are compared with the analytical results obtained for the San Jose tonalite in fig. 11. Remarkably similar results have been obtained for these two rocks, insofar as relative δ-values are concerned. Except for δ_{ROCK} being 0.5 per mil greater for the Bonsall than for the San Jose, the only differences between the rocks are that $\Delta_{ROCK-HORNBLENDE}$ and $\Delta_{ROCK-BIOTITE}$ are both slightly smaller in the latter. These small differences are even what might be predicted from textural and chemical features, which indicate that the mafic minerals probably crystallized relatively later in the San Jose tonalite than in the Bonsall.

Both tonalite magmas evidently became progressively enriched in O^{18} during the course of crystallization; hence it is expected that $\Delta_{HORNBLENDE-BIOTITE}$ would be slightly larger in the Bonsall than in the San Jose, because the hornblende should have formed, on the whole, earlier relative to the biotite in the latter than in the former. Similarities between the two rocks are clearly indicated by comparing Δ-values for mineral pairs:

Mineral pair	San Jose tonalite	Bonsall tonalite
$\Delta_{QUARTZ-PLAGIOCLASE}$	1.7	1.8
$\Delta_{PLAGIOCLASE-HORNBLENDE}$	1.4	1.6
$\Delta_{HORNBLENDE-BIOTITE}$	1.4	1.5

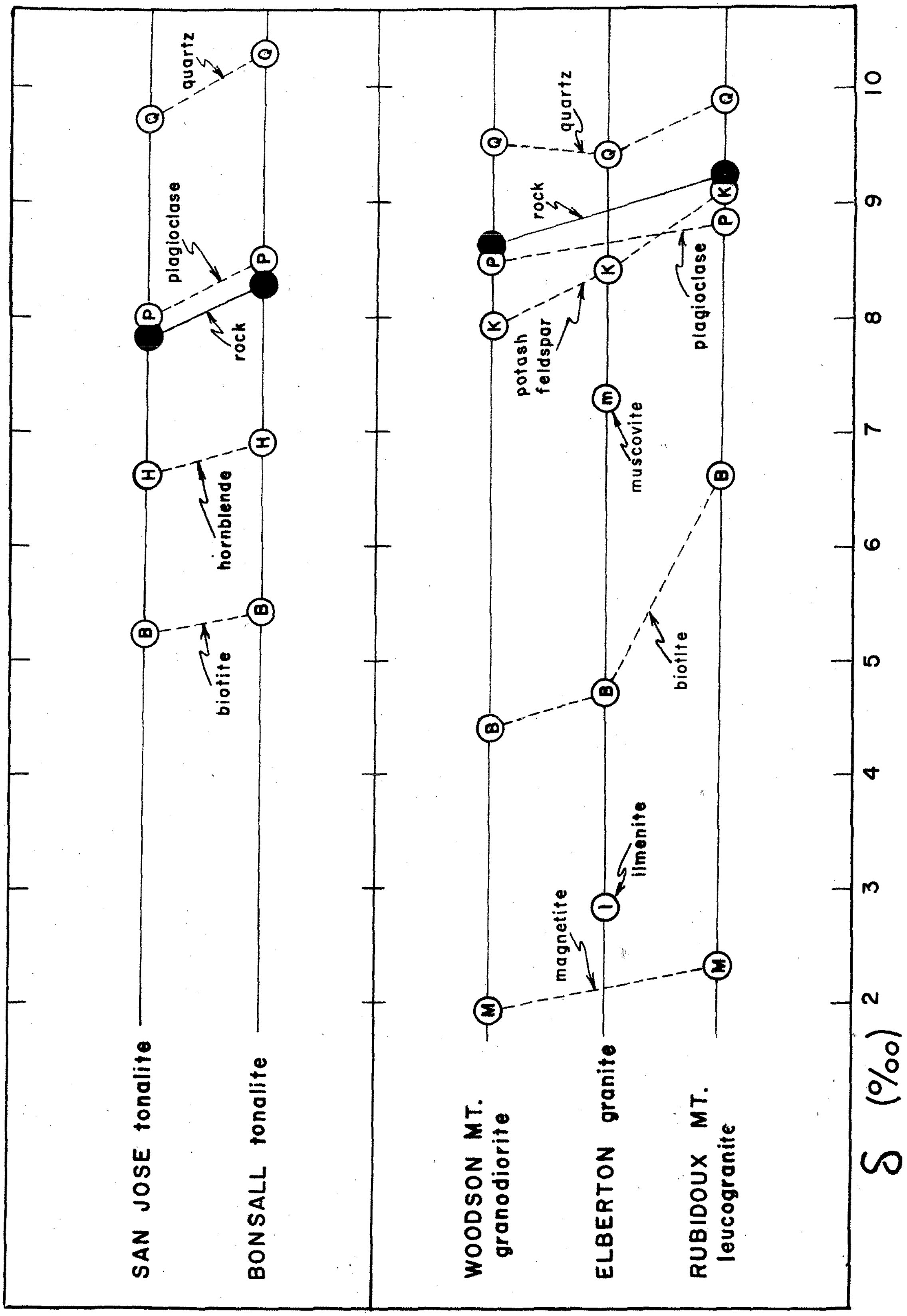


Fig. 11. Isotopic analyses of minerals of two granitic rocks compared with their counterparts in Southern California batholith.

Just why the rocks should be 0.5 per mil different in total oxygen isotopic composition cannot be ascertained without further analytical data from batholithic rocks. If both tonalites had differentiated from the same primary magma one would expect the San Jose to be richer in O^{18} than the Bonsall, because it is farther along the liquid line of descent. The reverse is actually true, and in all probability the source magma was isotopically different for the two rocks, or else some other mechanism has been important in their formation.

The data presented above make it appear likely that batholithic tonalites in general will probably contain minerals with relative δ-values that are similar to those obtained for the Bonsall and San Jose tonalites. Also, it is interesting to speculate whether or not individual bodies of granitic rock might be distinguished on the basis of total oxygen isotopic composition, even though petrographically and chemically they were nearly identical.

<u>N-36-8 gabbro</u>

This gabbro specimen was collected on Duke Island, southeastern Alaska, by T. N. Irvine, who has supplied the following norm and mode for this rock.

Mode		Norm	
Mineral	vol.%	Mineral	wt. %
plagioclase (An_{58})	49.0	plagioclase (An_{58})	55.2
clinopyroxene	22.4	clinopyroxene ($Di_{68}Hd_{32}$)	12.8
hornblende	13.3	olivine ($Fo_{68}Fa_{32}$)	2.8
orthopyroxene	1.5	orthopyroxene ($En_{68}Fs_{32}$)	15.0
opaques	13.7	magnetite	9.6
apatite	0.1	ilmenite	4.6

This specimen is from a body of gabbro that almost completely envelops an ultramafic body, and it was collected about 800 feet from the contact between the gabbro and an olivine pyroxenite unit. Oxygen isotopic data for rocks from this ultramafic complex are described in a subsequent section. This rock is considerably more mafic than the San Marcos gabbro specimen described above, and it has a remarkably high iron content, reflected mainly in the amounts of titaniferous magnetite which it contains. Relative to the San Marcos gabbro N-36-8 also contains less plagioclase, no quartz whatsoever, and much less hypersthene. The plagioclase is compositionally identical in both rocks.

Hornblende forms even more marked reaction rims about pyroxene in N-36-8 than in the San Marcos gabbro, and in addition all magnetite grains have pronounced reaction borders of this hornblende, much of which is uralitic. Plagioclase is finely twinned, zoned, slightly saussuritized, and shows slight strain effects. Magnetite forms large irregular intergrowths of the same size as the other minerals in the rock, all of which average about 4 mm in diameter. N-36-8 is thus coarser than the San Marcos gabbro. A photomicrograph of this rock is shown in plate VI. Only clinopyroxene, plagioclase, and magnetite have been analyzed, and the oxygen isotopic results are given in Table XX.

Table XX

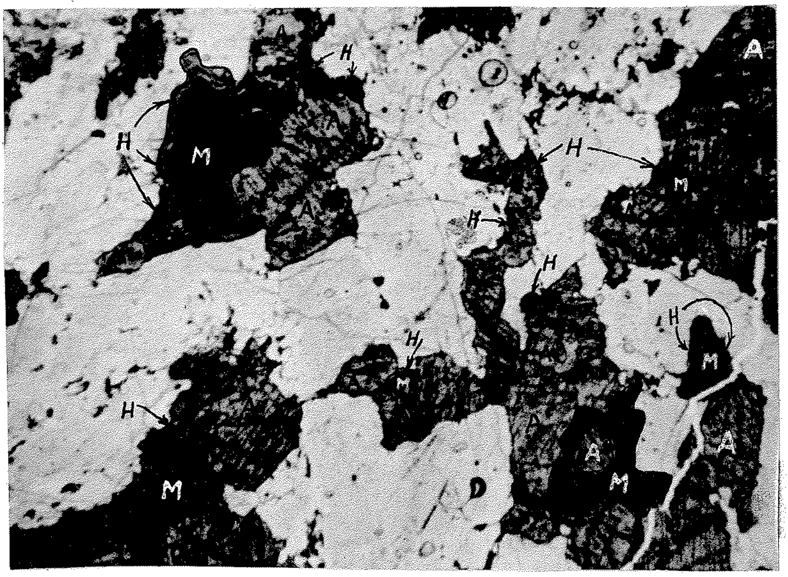
Oxygen isotopic analyses of minerals from N-36-8 gabbro

Mineral	$\delta O^{18}/O^{16}$ (‰)	av. dev.	no. of runs
plagioclase (An_{58})	7.4	0.1	2
clinopyroxene	5.9	0.7	4
magnetite	2.1	0.0	2

VIa - Photomicrograph of a thin section of N-36-8 gabbro (plane light, x 9). These photographs are very dark and the critical relationships are not well shown. However, note the reaction border of uralitic hornblende that is invariably present surrounding all magnetite grains. The magnetite grains are as large as any of the major minerals in this rock. The reaction border of hornblende is also commonly seen enclosing the pyroxene grains. The light-colored portion of this photograph is entirely plagioclase. H = hornblende, A = augite, M = magnetite.

VIb - Same field as above (crossed nicols, x 10). Note the strain effects shown by the plagioclase laths.

PLATE VI



VIa

VIb

The magnetite analyses were obtained by T. N. Irvine by the carbon reduction method. The total rock has not been analyzed, but a calculated value, which can only be very approximate because $\delta_{\text{HORNBLENDE}}$ is unknown, gives $\delta_{\text{ROCK}} = 6.3$.

The mineral fractionations observed for the San Marcos gabbro and for N-36-8 gabbro are compared below.

Mineral pairs	San Marcos gabbro	N-36-8 gabbro
$\Delta_{\text{PLAGIOCLASE-CLINOPYROXENE}}$	1.6	1.5
$\Delta_{\text{PLAGIOCLASE-MAGNETITE}}$	5.8	5.3

Even though the total oxygen isotopic composition for the two rocks is different, $\Delta_{\text{PLAGIOCLASE-CLINOPYROXENE}}$ and even the individual δ-values of the minerals are very similar, indicating that the respective crystallization histories of the two rocks could not have been markedly different. The isotopic evidence indicates that the bulk of N-36-8 magnetite crystallized later relative to plagioclase than did the major portion of magnetite in the San Marcos gabbro, assuming that both rocks became progressively enriched in O^{18} as they crystallized. Another possibility, however, is that magnetite recrystallized or was partially introduced into N-36-8 after solidification was well under way, thereby allowing isotopic exchange with a more O^{18}-rich magma. This is suggested by the texture and also by relationships in other occurrences of the Duke Island gabbro, in which magnetite appears to have replaced olivine.(30)

Inasmuch as the hornblende has not been analyzed, it is fruitless to try to speculate in detail about the O^{18}/O^{16} crystallization trends that are indicated by the minerals of N-36-8. Hornblende is clearly the latest mineral to form in this rock, and most of it very likely was formed during the very end stages of crystallization as a deuteric phenomenon. Therefore, it is not possible to be certain that both gabbro magmas became isotopically heavier during crystallization. The similarity of O^{18}/O^{16} results for the two rocks suggests this, however.

Steens basalt

The specimen of Steens basalt, of probable Miocene age, was collected by J. E. Conel in Alvord Creek on Steens Mt., in southeastern Oregon. This unit is a distinctive series of basalt flows forming an aggregate thickness of 3000 feet in the vicinity of Steens Mt. Individual flows average approximately 10 feet in thickness and extend laterally over large distances without significant change in character. These rocks are discussed and described by Fuller(31).

This specimen contains coarse plates of clear, glassy labradorite that average 1-2 cm in length and are essentially unzoned. They occur both as separate individuals roughly oriented with flat faces sub-parallel, and as rosettelike aggregates with the crystal plates radiating in all directions from a common nucleus. The rock has a holocrystalline groundmass which shows diktytaxitic texture. This is an unusual textural feature wherein open cavities exist locally between the grains of the groundmass, with delicate laths of plagioclase projecting into them. Olivine and clinopyroxene occur in tiny phenocrysts, 0.5-2 mm in length, and the groundmass itself is made up almost entirely of a plagioclase more sodic than the large phenocrysts, along with clinopyroxene and minor olivine.

Fairly representative samples of the groundmass and of the plagioclase phenocrysts have been analyzed, and the results are indicated in

Table XXI.

Table XXI

Oxygen isotopic analyses of minerals of Steens basalt

Mineral	$\delta O^{18}/O^{16}$ (‰)	av. dev.	no. of runs
plagioclase	6.6		1
groundmass	6.6	0.1	2

No significant oxygen isotopic fractionation exists between the groundmass and the plagioclase. This is slightly different from what is surmised to be the plagioclase-magma relationship for a material such as the San Marcos gabbro, but the total oxygen isotopic composition of this rock falls well within the average range for gabbros and basalts. A comparison with the two analyzed gabbros is shown below.

Rock	$\delta_{PLAGIOCLASE}$	δ_{ROCK}
San Marcos gabbro	7.5	7.0
N-36-8 gabbro	7.4	6.3*
Steens basalt	6.6	6.6

*- only approximate

These phenocrysts of labradorite had nucleated at the moment of extrusion, but they almost certainly were not so large as they now appear. Extremely rapid growth must have occurred in the short interval just subsequent to extrusion, the separation of a gas phase perhaps catalyzing this rate of growth. The diktytaxitic texture is striking evidence for a higher than normal volatile content. If all the phenocrysts had formed before the rock was extruded it is difficult to explain how the magma could have crystallized 95 per cent plagioclase and only 5 per cent mafic minerals, and also why there should be such a discrepancy in size between the mafic minerals and the plagioclase. Finally, the platelike nature of the plagioclase and the radiating rosettelike structures indicate that the phenocrysts probably could not have undergone significant violent flowage, for otherwise they would have been largely broken up.

This digression is important only in that it indicates that these phenocrysts may not have crystallized under the same conditions as did the plagioclase in the two gabbros which were analyzed. This rock probably formed at a much higher temperature than did the gabbros, and this may have been a factor in reducing the plagioclase-magma fractionation as compared with those rocks.

Elberton granite

The specimen of Elberton granite was collected from the New Comolli quarry 1½ miles northwest of Elberton, Georgia, by L. T. Silver, who has provided the following norm and mode for this rock.

Mode		Norm	
Mineral	wt. %	Mineral	wt. %
quartz	30.70	quartz	19.9
plagioclase	29.70	plagioclase (An$_5$)	36.8
potash feldspar	30.69	orthoclase	37.8
biotite	5.78	hypersthene (En53Fs47)	2.6
muscovite	1.27	diopside (Di$_{53}$Hd$_{47}$)	1.4
myrmekite	1.04	apatite	0.3
opaques	0.23	magnetite	0.5
accessories	0.58	ilmenite	0.7

This specimen bears some of the characteristics of both the Rubidoux Mt. leucogranite and of the Woodson Mt. granodiorite. The content of quartz, plagioclase, and microcline is similar to the former, but the biotite content is similar to the latter. The content of SiO$_2$ in this rock is about 5 per cent less than in either of the other granitic rocks, and an added factor is the presence of muscovite in significant quantities.

The Elberton granite shows field relationships which are most easily interpreted as being the result of magmatic emplacement. However, the rock also bears considerable petrographic similarity to the adjoining Lithonia gneiss, which some workers have interpreted as having formed by a process of granitization.(27)

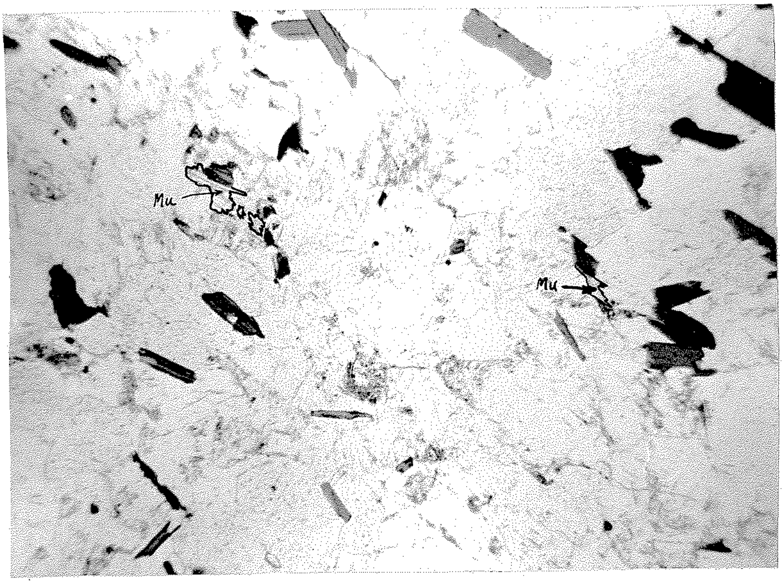
This specimen should be properly termed a quartz monzonite, and it is medium-grained and inequigranular, with an average grain size of 1 mm. Quartz grains are commonly clustered together in aggregates, and range in size from 0.2-2 mm. They are anhedral and show strain shadows. Microcline ranges from 0.2-2 mm, and larger grains contain tiny inclusions. Twinning is poorly developed in the plagioclase, and although most is oligoclase, some finer-grained albite is present. Minor myrmekite has developed, and some plagioclase has apparently been replaced by microcline. Biotite and muscovite exhibit a marked parallelism, giving the rock a gneissic foliation. The two micas are commonly clustered together in grains averaging 0.5 mm in length, with muscovite generally in replacement relationship to the biotite. Both minerals also occur as separate grains. Very fine-grained muscovite has apparently replaced plagioclase along grain borders. In plate VII is shown a photomicrograph of this rock.

Minerals were separated with the aid of heavy liquids, and a 98 per cent pure microcline concentrate and a 90 per cent pure quartz concentrate were obtained. Almost 100 per cent pure separates of biotite and muscovite, as well as an ilmenite concentrate, were provided by L. T. Silver. Corrected oxygen isotopic analyses of these

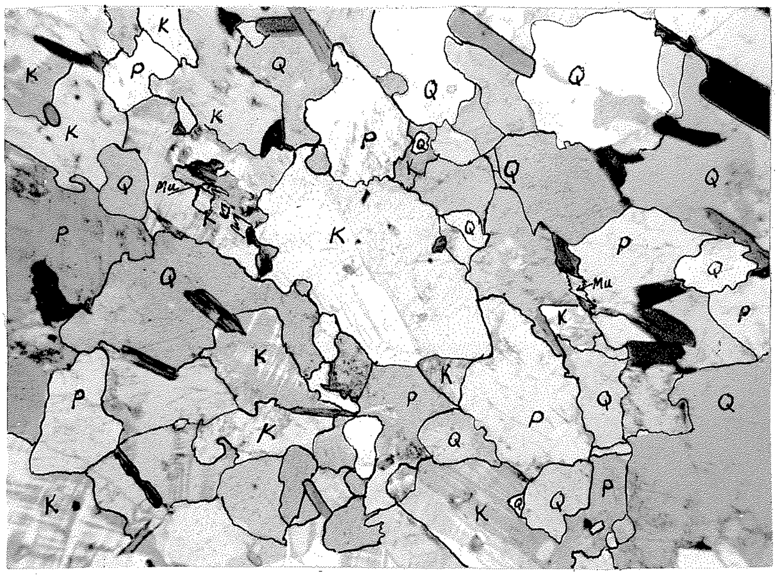
VIIa - Photomicrograph of a thin section of Elberton granite (plane light, x 24). Note the gneissic foliation displayed by the biotite and muscovite. Muscovite grains are extremely ragged in shape and are associated with biotite grains of identical optical orientation as the muscovite. Biotite grains are subhedral and have much smoother crystal outlines than do the muscovite grains. Mu = muscovite, all the dark-colored grains in the photograph are biotite.

VIIb - Same field as above (crossed nicols x 24). Note that the feldspars show a preferred orientation parallel to the mica foliation. All the major minerals show anhedral forms and are commonly gathered together as crystal aggregates of a single mineral - especially quartz. Q = quartz, P = plagioclase, K = potash feldspar, Mu = muscovite.

PLATE VII



VIIa



VIIb

mineral separates are indicated below in Table XXII.

Table XXII

Oxygen isotopic analyses of minerals from the Elberton granite

Mineral	$\delta O^{18}/O^{16}$ (‰)	av. dev.	no. of runs
quartz	9.4	0.0	2
microcline	8.4	0.1	2
muscovite	7.3	0.3	5
biotite	4.7	0.3	4
ilmenite	2.8		1

Unfortunately, no plagioclase analysis has been carried out, but its δ-value would almost certainly lie between 8.0 and 8.8, from experience with other rocks. Until its isotopic composition is determined, δ_{ROCK} cannot be accurately calculated. An approximate estimate, if $\delta_{PLAGIOCLASE}$ is arbitrarily established as 8.4, is $\delta_{ROCK} =$ 8.5.

Inasmuch as $\delta_{PLAGIOCLASE}$ is not known, it is probably fruitless to try to resolve the isotopic changes that have occurred during the crystallization of this rock. Similarities between the Elberton granite and the two rocks from the Southern California batholith which most resemble it are indicated in fig. 11, and are tabulated below:

Mineral pair	Woodson Mt.	Elberton	Rubidoux Mt.
$\Delta_{QUARTZ-MICROCLINE}$	1.6	1.0	0.8
$\Delta_{QUARTZ-BIOTITE}$	5.1	4.7	3.3
$\Delta_{MICROCLINE-BIOTITE}$	3.5	3.7	2.5

Note that isotopically, the Elberton granite appears to fall between the other two rocks, especially as shown by $\delta_{\text{MICROCLINE}}$ and δ_{BIOTITE}. This is an indication that the plagioclase and microcline of the Elberton granite might have very similar δ-values, and also it is evidence that the Elberton magma in all likelihood varied only very slightly in its oxygen isotopic composition throughout crystallization. The measured fractionations may therefore be very close to the actual equilibrium fractionations for the temperature interval over which crystallization occurred. This would also apply even had this rock formed by granitization in place.

Fractionations between muscovite and the other minerals of the rock might be an exception. Inasmuch as this is the only O^{18}/O^{16} analysis of a muscovite that has ever been done, it is impossible to tell, even approximately, what its equilibrium fractionation with any other mineral would be. A priori, it might be expected to be isotopically similar to biotite because it has almost the same structure; if this were so, the muscovite in this rock would definitely have formed out of equilibrium with the other minerals. On textural grounds this is reasonable, because of the evidence of replacement of other minerals by the muscovite. Judgment should be reserved until further O^{18}/O^{16} analyses of muscovite from other rocks are done.

Even though the Elberton granite is of a different age, and is from a different section of the earth's crust, O^{18}/O^{16} analyses of the total rock and of its individual minerals are nearly identical to those obtained for the corresponding rocks of the Southern California batholith. This is further evidence that gross equilibrium is generally attained, and it also indicates that the oxygen isotopic results are of general applicability.

SKAERGAARD INTRUSION

General statement

In order to check more fully the foregoing hypotheses regarding oxygen isotopic distributions in a crystallizing magma, samples of the Skaergaard intrusion of east Greenland were obtained from L. R. Wager. Wager and Deer(32) have presented detailed petrographic and chemical descriptions of this intrusive complex, Wager and Mitchell(33) have discussed trace element distributions within the body, and Wager, Vincent, and Smales(34) have described the sulfides that are present. These studies probably represent some of the most intensive work which has been done on an intrusive body of such a size, and the Skaergaard intrusion is certainly one of the best-documented instances of fractional crystallization of basaltic magma.

The Skaergaard intrusion, of middle Eocene age, is an inverted cone-shaped mass of gabbro about 300 km^3 in volume, with an exposed area of 60 km^2. During cooling and crystallization of this magma crystals accumulated from the bottom of the magma chamber upwards, being carried down by convection currents which produced gravitationally stratified rhythmic layers. Crystals were thus continuously being removed from the magma, and after they were removed they had no further opportunity to react with it. This process has produced a marked and unusual trend of fractional crystallization, leading to progressive iron-enrichment in the later stages of the differentiation process. Little or no selective gravitational sinking of mafic minerals relative to plagioclase has taken place, because <u>all</u> minerals formed at a given stage were swept to the bottom of the magma chamber to add to the accumulating pile.

Fig. 12 shows the succession of rock types and indicates how the amounts of the minerals change throughout the sequence. The lowest layered rocks exposed are hypersthene-olivine gabbros, and these grade successively upwards through rocks containing more sodic-rich plagioclase and more iron-rich olivines and pyroxenes. The upper units in the layered series are ferrogabbros containing fayalite, hedenbergite, and quartz. Individual layers throughout the sequence are composed of 80 per cent primary crystals that have accumulated as a sediment on the floor of the magma chamber, and 20 per cent interprecipitate material which necessarily had the composition of the liquid existing at the time a given layer was formed. The interprecipitate liquid crystallized around the primary crystals, adding to them outer borders of lower melting point solid solution material, and in certain instances producing additional mineral phases such as apatite and quartz.

The composition of any one rock type in the layered series therefore does not represent the composition of the magma from which it formed, an important point to consider when comparing these rocks with other types that have crystallized essentially in place. From the observed compositional trends of the layered series, and from the composition of the chilled marginal olivine gabbro, Wager and Deer(32) have estimated that 60 per cent of the volume of the intrusive lies below the lowermost exposed hypersthene-olivine gabbro, arbitrarily taken as the zero for the scale in meters shown in fig. 12.

Above the main part of the layered series is a section about 200 meters thick which, although retaining the gradually changing compositional layering, lacks both the rhythmic layering and the lamination

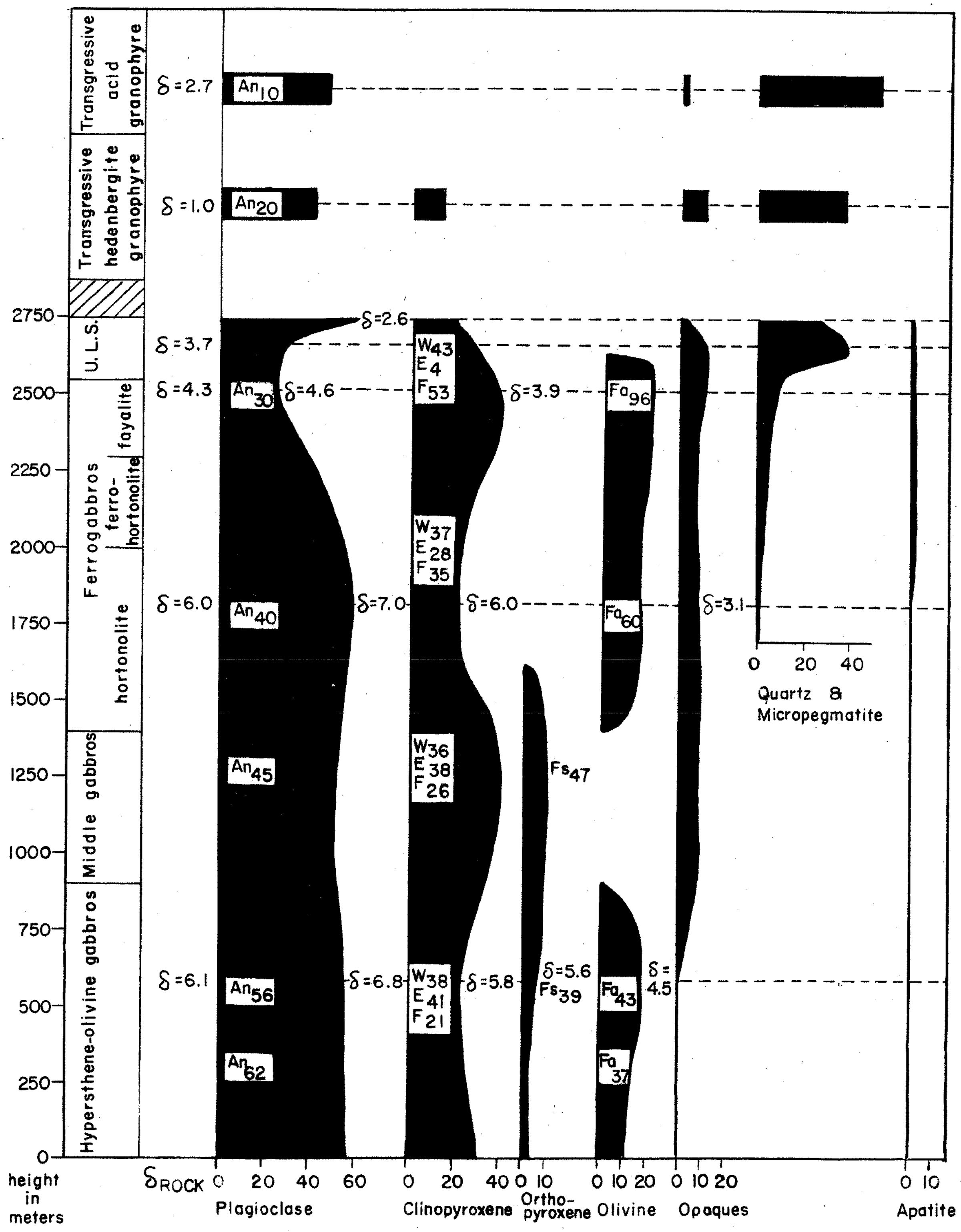


Fig. 12. Mineralogical variations in Skaergaard intrusion (after Wager and Deer[32]), showing isotopic analyses of minerals and total rocks. Height in intrusion is measured from the lowermost exposed hypersthene-olivine gabbro.

(parallelism of the platy minerals) so characteristic of the lower rocks. These rocks are termed the unlaminated layered series, and they grade upward through fayalite ferrogabbro into basic hedenbergite granophyre. These were the latest rocks to form in the layered part of the intrusion, and they apparently accumulated within a sheet of liquid so shallow that convection currents could no longer operate.

Above, and on all sides, the layered series is surrounded by a border series of rocks. The upper border group is composed largely of quartz gabbros that have been contaminated with gneiss inclusions derived from the country rock gneiss complex. In the northern marginal border group a number of blocks of gabbro picrite occur, probably formed by an early gravitational concentration of olivine crystals. Also contained in the outer part of the border group are olivine eucrites which are thought to be fairly similar in composition to the hidden, lower part of the layered series.

In the very final stages of solidification, perhaps by filter press action, indefinite sill-like bodies of transgressive hedenbergite granophyre were produced, and later still a large sill of transgressive acid granophyre developed, along with irregular veins and dikelets of the same material. The hedenbergite granophyre is certainly a product of the differentiation process, but it is believed that the acid granophyre was formed partially by assimilation of acid gneiss inclusions. Necessarily, these transgressive bodies crystallized from magmas of their own composition, in contrast to the layered rocks.

The original Skaergaard magma was of a relatively normal olivine basalt composition, except that it was lower in K_2O, and had a somewhat higher ratio of FeO/Fe_2O_3. Apparently its water content was extremely low, as even the immense removal of anhydrous minerals until at least 99 per cent of the magma had crystallized was not sufficient to raise the concentration of water to a high enough value for a hydrous mineral such as hornblende to crystallize instead of hedenbergite. It has been suggested that this low content of water was the cause of the high FeO/Fe_2O_3 ratio, and was the factor which brought about the extreme iron-enrichment in the later stages of differentiation.(45) Lack of water may have allowed only very little oxidation of the ferrous iron, which in turn would prevent early magnetite from crystallizing and depleting the system in iron — enough so that an ordinary calc-alkaline trend of differentiation could not occur. Wager and Deer, however, believe that the Skaergaard trend of differentiation is the normal course any basaltic magma would take, if conditions were favorable for strong fractionation.

Analyses of the rock types

The O^{18}/O^{16} ratios of the various minerals and rocks from the Skaergaard series are listed in fig. 12, but a more detailed description of the rocks is given below. All minerals were separated from small pieces of a given rock sample by crushing and carefully hand-picking, and all rock samples used were almost completely unaltered. The collection numbers of each specimen are those used in the Department of Geology and Mineralogy, Oxford, and all specimens are keyed either to the paper of Wager and Deer(32), or to the paper of Wager, Vincent, and Smales(34), so that the oxygen isotopic results may be easily compared with existing petrographic and chemical information. Chemical compositions and volume percentages given in the following tables are only approximate.

Hypersthene-olivine gabbro (E.G. 5112) Height in intrusion 580 meters. East side of Uttentals Sound. Should be almost equivalent to E.G. 4077 (Table X, p. 92)$^{(32)}$.

Mineral	vol.%	$\delta O^{18}/O^{16}$ (‰)	av. dev.	no. of runs
plagioclase (An_{55})	55	6.8	0.2	2
clinopyroxene ($W_{45}E_{34}F_{21}$)	21	5.8	0.1	2
orthopyroxene (Fs_{47})	5	5.6	0.1	2
olivine (Fa_{39})	18	4.5		1
entire rock		5.6		1

δ_{ROCK} is calculated to be 6.1, probably a much more accurate value than the single analysis listed above.

Hortonolite ferrogabbro (E.G. 5181) Height in intrusion 1800 meters. Basishusene, east side of Uttentals Sound. (Table I, p. 867)$^{(34)}$. Should be equivalent to E.G. 1907 (Table XIII, p. 102)$^{(32)}$.

Mineral	vol.%	$\delta O^{18}/O^{16}$ (‰)	av. dev.	no. of runs
plagioclase (An_{40})	54	7.0	0.1	2
clinopyroxene ($W_{27}E_{23}F_{50}$)	23	6.0	0.2	2
magnetite		3.1		1
entire rock		6.0	0.2	2

The calculated δ_{ROCK} is 6.1, in good agreement with the measured value of 6.0 listed above. No olivine analysis has been carried out, but a value of 4.5, used in making the material balance calculation, seems not too unreasonable, and is in agreement with the O^{18}/O^{16} value obtained for olivine of the hypersthene-olivine gabbro.

Fayalite ferrogabbro (E.G. 4328) Upper purple band. Height in intrusion 2500 meters. West face of Basistoppen. (Table I, p. 861)(34). Should be equivalent to E.G. 1907 (Table XIII, p. 102)(32).

Mineral	vol.%	$\delta O^{18}/O^{16}$ (‰)	av. dev.	no. of runs
plagioclase (An_{30})	24	4.6		1
clinopyroxene ($W_{30}E_2F_{68}$)	37	3.9	0.4	2
entire rock		4.3	0.1	2

Neither quartz, olivine, magnetite, nor apatite have been analyzed, but if the above analyses are correct, and if reasonable assumptions are made about the δ-values of olivine and magnetite, δ_{QUARTZ} must be at least 6.0 or larger.

Basic hedenbergite granophyre (E.G. 4332) Height in intrusion 2600 meters. West face of Basistoppen in the unlaminated layered series. (p. 869)(34). Should be about equivalent to E.G. 4137 (p. 113, Pl. 18, fig. 2, Table XV)(32).

Mineral	$\delta O^{18}/O^{16}$ (‰)	av. dev.	no. of runs
entire rock	3.7	0.3	2

Individual minerals were not analyzed because they are too fine-grained to be separately concentrated for analysis. This is true for all the granophyres that have been studied from this intrusion.

Hedenbergite andesinite (E.G. 5264) Late differentiates, Brodretoppen. Should be approximately equivalent to E.G. 3047 (p. 210, Table XXXIV)(32).

Mineral	$\delta O^{18}/O^{16}$ (‰)	av. dev.	no. of runs
plagioclase	2.6		1

This is a coarse-grained rock containing about 70 per cent plagioclase, and minerals could be separated by hand-picking.

Transgressive hedenbergite granophyre (E.G. 4489) Sill, southeast of Copper Rognon. This should be roughly equivalent to E.G. 3047 (p. 210, Table XXXIV)(32), but is apparently more clearly transgressive and is considered to represent a later stage than does E.G. 5264, above.

Mineral	$\delta O^{18}/O^{16}$ (‰)	av. dev.	no. of runs
entire rock	1.0	0.4	2

Transgressive acid granophyre (E.G. 5259) Sill on west ridge of Tinden. Should be equivalent to E.G. 3058 (p. 204, Table XXXIII)(32).

Mineral	$\delta O^{18}/O^{16}$ (‰)	av. dev.	no. of runs
entire rock	2.7	0.2	2

Chilled marginal olivine gabbro (E.G. 4507) Collected 3 feet from southern margin, east side of Skaergaard Bay. (p. 873)(34). Should be roughly equivalent to E.G. 1724 (p. 138, Table XVII)(32).

Mineral	vol.%	$\delta O^{18}/O^{16}$ (‰)	av. dev.	no. of runs
plagioclase (An_{60})	55	3.3	0.0	2
clinopyroxene	30	4.6	0.2	2
entire rock		3.6	0.2	2

This rock contains about 5 per cent hypersthene and only about 10 per cent olivine, hence its mineralogical composition is not quite identical with E.G. 1724. A calculated δ_{ROCK} is in agreement with the analyzed result listed above.

Gabbro picrite (E.G. 4526) Northern border group, 40 meters from margin. North of Uttentals Sound. Should be equivalent to E.G. 1682 (p. 160, Table XXIII)(32).

Mineral	vol.%	$\delta O^{18}/O^{16}$ (‰)	av. dev.	no. of runs
plagioclase	20	5.3	0.3	2
entire rock		4.9		1

Inasmuch as this rock is about 65 per cent olivine, a calculation of δ_{OLIVINE} from the above analyses gives, very approximately, a value of 4.7. The 15 per cent of pyroxene has not been analyzed.

Fused inclusion of acid gneiss (E.G. 1841) Western border group of Mellemo. (p. 187, fig. 36, Table XXX)(32).

Mineral	$\delta O^{18}/O^{16}$ (‰)	av. dev.	no. of runs
plagioclase (phenocrysts)	8.6		1
entire rock	7.9		1

Grey gneiss - average material (E.G. 1867) Mellemo, 100 meters west of contact with the intrusion. (p. 10, Table I, p. 196, Table XXX)(32).

Mineral	$\delta O^{18}/O^{16}$ (‰)	av. dev.	no. of runs
entire rock	8.0		1

Grey gneiss - country rock (E.G. 4209) Collected 2 km N.N.W. of Bagnaesset, Kangerdlugssuag.

Mineral	$\delta O^{18}/O^{16}$ (‰)	av. dev.	no. of runs
entire rock	8.6		1

Interpretation of oxygen isotopic analyses

Determinations of δ-values of minerals and rocks of the Skaergaard intrusion are listed in both fig. 12, and graphically in fig. 13. These rocks are the most O^{18}-deficient of any for which analyses have been obtained, and these extremes of oxygen isotopic composition are readily explained as being a result of the fractional crystallization processes that have produced the peculiar trend of chemical differentiation shown by this intrusive complex.

If the O^{18}/O^{16} ratio of the original Skaergaard magma was approximately that of a normal olivine basalt, δ_{MAGMA} would have been about

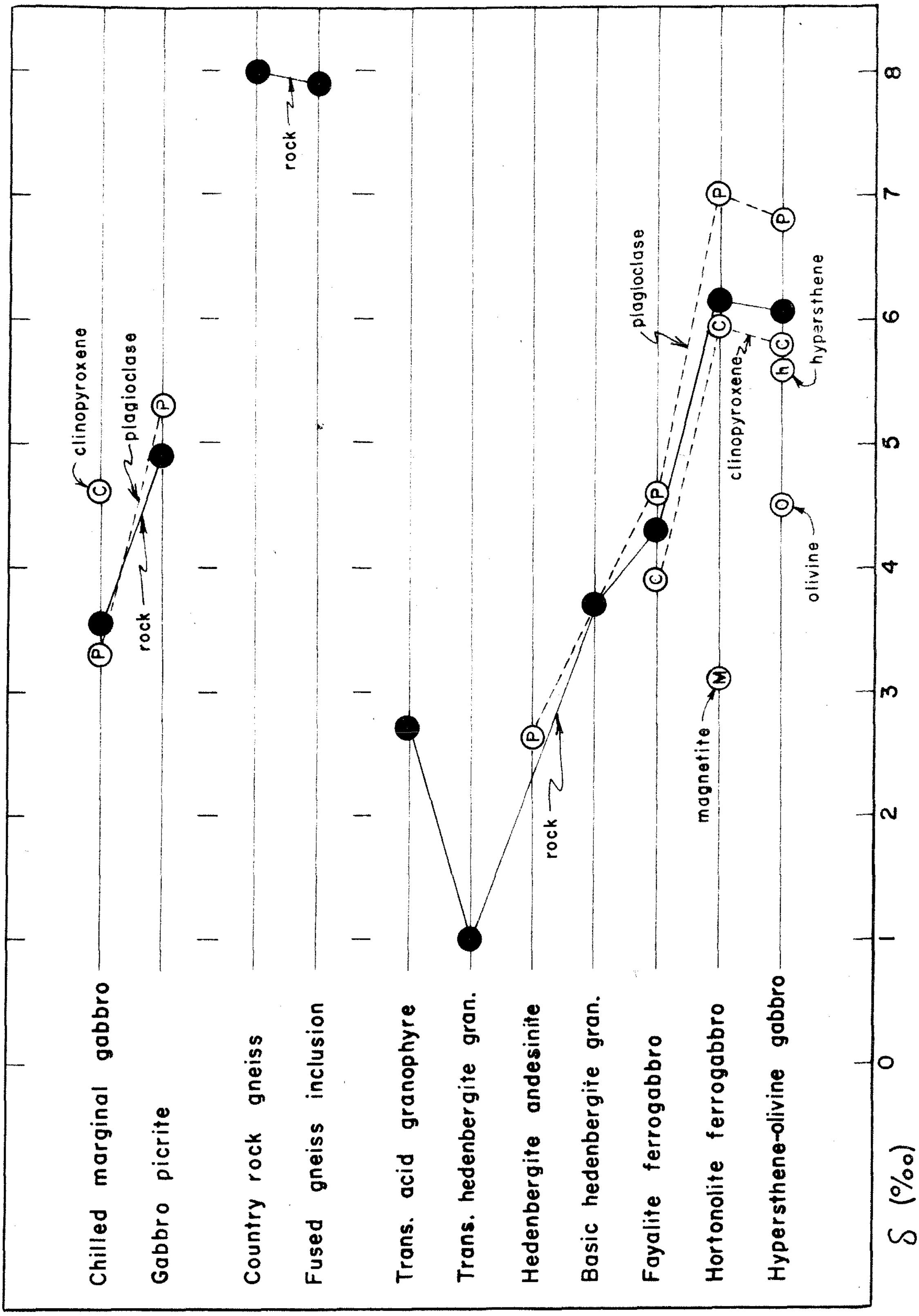


Fig. 13. Isotopic analyses of minerals and total rocks of the Skaergaard intrusion.

6.0 per mil. Only two analyses exist for rocks in the lower 2000 meters of exposed section of the layered series, but both of these give similar δ-values of about 6 per mil. The hypersthene-olivine gabbro at 580 meters and the hortonolite ferrogabbro at 1800 meters are the two rocks analyzed, and although the data are meager, it would appear that little isotopic change has occurred throughout the crystallization of 90 per cent of the magma. More analyses of intervening rocks would undoubtedly show slight differences from these values, and they might show that at certain intervals the magma was becoming isotopically heavier as crystallization proceeded, while at other times it was being depleted in O^{18}. The available evidence, however, indicates that the bulk of the crystalline material forming at any one stage must have had about the same O^{18}/O^{16} composition as the liquid. The oxygen isotopic composition of the chilled marginal gabbro is of no help in answering this problem because, as will be later discussed in detail, this rock very likely has been altered from its original O^{18}/O^{16} value.

The minerals of the hypersthene-olivine gabbro and of the hortonolite ferrogabbro show very nearly identical O^{18}/O^{16} relationships. The observed δ-values are also similar to results from the ultramafic rocks and the more normal gabbros that have been studied. Plagioclase is richer in O^{18} than coexisting pyroxene, and pyroxene is heavier than olivine. From the petrologic evidence presented by Wager and Deer, it is concluded that the measured Δ-values for the various mineral pairs in these two rocks are those that would be obtained were the coexisting minerals to be found in approximate isotopic equilibrium at their crystallization temperatures. These equilibrium δ-values probably would have been "frozen in" at the time the minerals were formed. This conclusion must be modified in that 20 per cent of magma was added to the primary crystals by crystallization of interprecipitate liquid. The oxygen isotopic composition of this magma is not accurately known, but for the reasons outlined above it must have been approximately the same as that of the total rock as now analyzed — hence its effect on the mineral fractionations was probably negligible.

A comparison of Δ-values for various mineral pairs from these layered series rocks with those determined for the more normal gabbros is given below:

Mineral pair	Skaergaard rocks		Normal gabbros	
	Hypersthene olivine gabbro	Hortonolite ferro-gabbro	San Marcos gabbro	N-36-8 gabbro
$\Delta_{\text{PLAGIOCLASE-AUGITE}}$	1.0	1.0	1.6	1.5
$\Delta_{\text{PLAGIOCLASE-HYPERSTHENE}}$	1.2		0.9	
$\Delta_{\text{PLAGIOCLASE-MAGNETITE}}$		3.9	5.9	5.3
$\Delta_{\text{ROCK-AUGITE}}$	0.3	0.1	1.1	0.4
$\Delta_{\text{PLAGIOCLASE-ROCK}}$	0.7	0.9	0.5	1.1

The magnetite-plagioclase fractionation shown for the hortonolite ferrogabbro is in question because only one analysis of the magnetite was attempted, and because of the inherent difficulty involved in analyzing this mineral. Therefore, the 1.4-2.0 per mil discrepancy between this value and the values for the normal gabbros may not be real. If it is real, it might be explained on the basis that magnetite is an early mineral to crystallize from the normal gabbros; hence $\Delta_{\text{PLAGIOCLASE-MAGNETITE}}$ for such rocks would be larger than for the ferrogabbro, in which all minerals crystallized contemporaneously.

This same interpretation may explain the differences between the Skaergaard gabbros and the normal gabbros as regards the fractionation between plagioclase and clinopyroxene. The value of this fractionation in both Skaergaard rocks is 1.0 per mil, and this should closely represent the equilibrium fractionation. The identical quantity is 0.5-0.6 per mil larger in the normal gabbros because these rocks became progressively enriched in O^{18}, thereby causing a greater spread in O^{18}/O^{16} ratios between the augite, which stopped precipitating early, and the plagioclase, which crystallized over the entire range.

An additional factor that may have contributed to the smaller Δ-values in the Skaergaard rocks is the probable higher temperature origin of these rocks. The Skaergaard magma was certainly more water-deficient than a normal gabbroic magma. Estimates of the crystallization range of a very "dry" basaltic magma might be 1050-1150° C., while a rock such as the San Marcos gabbro, which contains a hydrous mineral — hornblende, might well have crystallized at temperatures 150-200° C. lower. Until experimental data exist on the equilibrium fractionation factors between minerals, there is no possibility of an evaluation of the relative importance of these two effects.

Analyses from the hypersthene-olivine gabbro indicate that orthopyroxene and clinopyroxene have practically identical oxygen isotopic properties. The gabbro from southeastern Alaska, N-36-8, shows oxygen isotopic relationships that are very similar to the Skaergaard rocks, in contrast to the San Marcos gabbro, perhaps reflecting the fact that it is also more similar chemically. The gross agreement of δ-values among all four rock types is further evidence of the general applicability of the oxygen isotopic data.

A marked change in O^{18}/O^{16} ratio occurs between the hortonolite ferrogabbro horizon and the fayalite ferrogabbro at 2500 meters elevation in the intrusion. The latter rock is 1.7 per mil lighter than the hortonolite ferrogabbro. This change is compatible with the calculations made previously for the 3 hypothetical crystallization models of figs. 6, 7, and 8, whereby it was shown that the most pronounced variations in O^{18}/O^{16} ratio should occur in the latest crystallizing fractions. The change actually observed is so marked, however, that it appears likely that some newly operative process has brought it about. The most reasonable ways that such a change might be produced are: (1) for a new O^{18}-rich phase to begin crystallizing; (2) by selective removal of a phase richer in O^{18} than the magma; or (3) for a subtle change in mineral-magma fractionation factors to occur such that the balance of minerals crystallizing becomes isotopically heavier than the magma.

A significant change that does occur, beginning at the hortonolite ferrogabbro horizon and continuing through to the final stages of crystallization, is the precipitation of quartz as a primary mineral. Quartz is known, from data on other rocks, to be invariably the most O^{18}-rich mineral present in any mineralogical assemblage. Although no direct determination of δ_{QUARTZ} has been done for the fayalite ferrogabbro, this quartz very likely has a δ-value in excess of 6.0. It would also be expected that quartz crystallizing from a slightly polymerized magma, such as the ferrogabbro magma must have been, would show a much larger $\Delta_{\text{QUARTZ-MAGMA}}$ than is shown by a granitic magma. The crystallization of quartz, therefore, may have been the change which upset the delicate balance that had brought about such little evidence of change in the δ-value of the magma throughout most of its crystallization history.

Quartz began to accumulate in the layers at the bottom of the magma chamber during formation of the hortonolite ferrogabbro, and it became increasingly more abundant as crystallization proceeded. Quartz makes up about 10 per cent of the fayalite ferrogabbro unit, and a rough calculation indicates that with $\Delta_{QUARTZ-MAGMA} = 2-3$ per mil, the magnitude of the change in $0^{18}/0^{16}$ ratio of the rocks between the hortonolite ferrogabbro and the fayalite ferrogabbro horizons can be accounted for.

It may be that the crystallization of quartz is not the only factor that has produced the observed shift towards more 0^{18}-deficient rock types. At the level of the purple band, the liquid from which the extremely iron-rich olivines and pyroxenes were precipitating was evidently such a shallow sheet that the convective circulation was no longer able to operate. It is known that andesine crystals float in this magma, because accumulates of these crystals are found underneath a large, raft-shaped, gabbro inclusion. Quartz, with almost the same density as andesine, must also float. Any removal of either of these minerals by such a flotation process would accentuate still further the observed trend of 0^{18} depletion, inasmuch as both minerals are isotopically heavier than the magma from which they precipitate.

The possibility also exists that the magma was becoming progressively enriched in 0^{16} throughout crystallization, but that the change only became significant in the very end stages — as predicted by the Rayleigh equation. The effects of changes in magma-mineral fractionation factors resulting from the iron enrichment of the minerals and magma cannot be evaluated, and it is possible that these may have influenced the O^{18}/O^{16} changes to some extent.

About 100 meters above the fayalite ferrogabbro is the basic hedenbergite granophyre, which shows a $\delta_{ROCK} = 3.7$, evidently indicating that the magma was still becoming isotopically lighter. This rock contains 30–40 per cent quartz and micropegmatite, fitting the hypothesis that the formation of quartz is the principal process bringing about the striking changes in oxygen isotopic composition. From a different part of the intrusion, on Brodretoppen (instead of on Basistoppen where the fayalite ferrogabbro and hedenbergite granophyre were collected), but clearly even later in forming than the rocks just discussed, is a hedenbergite andesinite. Plagioclase from this rock gives a δ-value of 2.6, probably indicating that the total rock would show $\delta_{ROCK} = 2.0$–2.3 per mil; hence this andesinite falls along the oxygen isotopic sequence as well as along the sequence determined from age relationships and by bulk chemistry and mineralogy.

Resembling the andesinite in chemical composition is the transgressive hedenbergite granophyre, which probably crystallized from a magma of its own composition. This is not only the isotopically lightest rock in the Skaergaard sequence, with $\delta_{ROCK} = 1.0$, but it has the lowest O^{18}/O^{16} ratio of any rock that has been analyzed. The magma from which it crystallized probably was squeezed off from the very latest crystallizing material of the entire series.

The transgressive acid granophyre, with $\delta_{ROCK} = 2.7$, forms a large sill and was probably the last of the Skaergaard magmas to crystallize. It is almost devoid of mafic minerals and must also have solidified essentially in place from a magma of its own composition. Wager and Deer(32) believed this to be one of the differentiates of the main Skaergaard magma, but they decided that its highly sialic composition had been produced by assimilation of acid gneiss. Thus it may have been derived by contamination of a magma of about the chemical composition of the transgressive hedenbergite granophyre. The observed oxygen isotopic composition, 1.7 per mil heavier than the hedenbergite granophyre, might be a result of gravitational settling of the dense, mafic, 0^{18}-deficient minerals from that type of magma, or it could be a product of the accumulation of quartz and plagioclase crystals by flotation. These processes may have occurred, but the best explanation of the isotopic data is probably that some gneiss, with $\delta_{ROCK} = 8.0$, was assimilated by the hedenbergite granophyre magma, just as postulated by Wager and Deer(32).

There is little doubt, on the basis of field relations and chemical and petrological data, that the acid inclusions in the border group rocks are blocks of the country rock "grey gneiss" complex that have been incorporated by the gabbroic magma. It is reassuring, however, that the oxygen isotopic evidence completely bears out such a hypothesis. The fused inclusion from Mellemo has $\delta_{ROCK} = 7.9$. The δ-value of this inclusion is in remarkable agreement with that of the country rock gneiss 100 meters west of the contact on Mellemo, as this gneiss has $\delta_{ROCK} = 8.0$. The inclusion was definitely fused to a liquid, from which plagioclase phenocrysts could form, as shown by the perfectly spherical drusy cavities that exist in the rock. Apparently, no significant oxygen isotopic exchange has occurred between the gneiss inclusion and the gabbroic magma, even though the inclusion was completely fused. This is further evidence against there having been much water in the Skaergaard magma, because had there been, marked chemical and isotopic exchange undoubtedly would have occurred.

The chilled marginal gabbro and gabbro picrite of the marginal border groups represent separate problems from those so far discussed. The 2 specimens analyzed come from opposite sides of the intrusion, the gabbro picrite from the northern border group, and the chilled marginal gabbro from the southern border group. Although the two rocks are not directly comparable, they must both have formed in similar environments.

The chilled marginal olivine gabbro is one of the most peculiar rocks encountered in these isotopic studies. In this rock the relative δ-values of clinopyroxene and plagioclase are reversed from what has been established for all other analyses of this mineral pair. There is little doubt that this rock represents marked oxygen isotopic disequilibrium; with $\delta_{PLAGIOCLASE} = 3.3$ and $\delta_{CLINOPYROXENE} = 4.6$, one has $\Delta_{PLAGIOCLASE-CLINOPYROXENE} = -1.3$, which is 2-3 per mil different from the normal fractionation and reversed in sign.

Not only are there indications of isotopic disequilibrium, but $\delta_{ROCK} = 3.6$, almost 3 per mil lighter than a normal olivine basalt. This is an enormous discrepancy, and inasmuch as the chilled gabbro is chemically a normal basalt, and because most of the layered series of rocks apparently crystallized from basaltic magma with a normal O^{18}/O^{16} ratio, there must have been a profound alteration of the oxygen isotopic composition of the chilled gabbro. Any hypothesis that the original

Skaergaard magma had the same O^{18}/O^{16} ratio as is now given by the marginal gabbro would imply that the hidden layered series be composed principally of rocks even more O^{18}-deficient than this rock, in order that a material balance of oxygen be retained for the entire intrusive. Although some early gravitational accumulations of olivine crystals have formed, it is unlikely that sufficient quantities of these exist to have enriched the magma in O^{18} to the degree that a normal basaltic O^{18}/O^{16} composition was attained by the stage that the lowermost exposed hypersthene-olivine gabbros crystallized. In addition, such a hypothesis leaves unexplained just how such a large amount of basaltic magma so extremely deficient in O^{18} could have developed in the first place.

The preferred explanation for the oxygen isotopic features shown by the chilled marginal gabbro is outlined below. Because the chemical composition of the chilled gabbro is almost constant along the entire intrusive contact, and because it fits all chemical and spatial criteria for being a chilled remnant of the original Skaergaard magma, the alteration process that brought about the disequilibrium must have been one which could bring about oxygen isotopic exchange without significant chemical exchange. Exchange with water that is diffusing through the marginal gabbro magma as it crystallizes is a process that most likely fits this requirement. To produce the observed effects, the water would have to have been isotopically lighter than water in isotopic equilibrium with normal basaltic magma.

The water could have become deficient in O^{18} relative to magmatic water either because of the diffusion process, which itself tends to enrich the diffusing material in O^{16}, or it may have originated by a non-equilibrium process of some sort in which kinetics favored formation of H_2O^{16}. The possibility also exists that the exchange between the gabbro and the diffusing water was a disequilibrium process dependent upon the collision frequency of the water molecule. The most reasonable explanation is, however, that the water was at least partially derived from fresh meteoric waters, as these are known to be isotopically light(35).

In any event, exchange occurred to a greater degree with the plagioclase than with the pyroxene. In this connection, it may be significant that the chilled gabbro shows a distinct "patchy" appearance, 3/4 of the plagioclase being fine-grained and the remainder markedly coarser, with pyroxene enclosing olivine and plagioclase in coarse ophitic masses. The finer grain size of the plagioclase might have insured a more rapid exchange with any water diffusing along grain boundaries through the rock, especially if the process occurred during or just subsequent to the crystallization of the fine-grained material. The pyroxene has a slightly lower than normal δ-value, but it has probably been altered by no more than 1 per mil, whereas the plagioclase has undergone a change of at least 3 per mil.

Other evidence bears upon this problem. A 10-inch thick apophysis from the Skaergaard intrusion, described by Wager and Deer(32) as being of identical original mineralogy and texture to the chilled gabbro, now shows marked alteration. Orthopyroxene is completely replaced by a bastite pseudomorph, and olivine is largely replaced by serpentine. In addition, 3 chemical analyses of specimens of the chilled marginal gabbro collected at varying distances from the contact with the country rock gneiss show different amounts of water, as follows:

Specimen no.		wt. % H_2O
E.G. 1724	(25 meters from contact)	0.27
E.G. 1825	(3 meters fron contact)	0.55
E.G. 4507	(1 meter from contact)	0.83

The data listed above are taken from Wager and Deer(32) and from Wager, Vincent, and Smales(34). The water is most likely bound up in minor amounts of hydrous alteration products, such as those which occur so abundantly in the 10-inch thick apophysis. The data suggest that the farther the chilled gabbro was from the contact when it crystallized, the smaller the amount of hydrous alteration it contains. The specimen upon which the oxygen isotopic studies have been carried out is E.G. 4507, and because of its proximity to the contact this rock presumably should show the most marked isotopic disequilibrium of any of the above 3 specimens. None of the specimens more distant from the contact have yet been obtained for analyses.

The country rock gneiss has been converted to a pyroxene granulite for 2-3 meters from the contact. This process has noticeably dehydrated the gneiss, and Wager and Deer(32) postulate that the water made mobile by such a process was expelled into the surrounding rocks. During metamorphism at the margins of a normal magma this is probably what takes place, but a "dry" magma of the Skaergaard type may very well act as a "sink" for any mobile water in its immediate environment. Although water commonly diffuses from a high temperature region to a low temperature region during metamorphism, the thermal gradient is not the driving mechanism. Instead, it is simply that water is liberated from hydrous minerals when a more anhydrous assemblage becomes stable. The water becomes mobile and must diffuse out of the system. The most convenient direction for it to move at the contact with a magma that is undersaturated with water is into the magma, not away from it, and it is this water, along with any meteoric water that may have been present in the rocks, which very likely brought about the postulated oxygen isotopic exchange.

Oxygen isotopic data from the gabbro picrite, although meager, provide further evidence that the original Skaergaard magma could not have been as deficient in 0^{18} as the analyzed chilled marginal olivine gabbro. The gabbro picrite was formed by crystallization of border group magma along with an early-crystallized concentrate of olivine crystals. This rock contains plagioclase of a much more normal oxygen isotopic composition than the plagioclase of the chilled gabbro. Perhaps it has been affected to only a slight degree by the exchange processes that modified the chilled marginal gabbro.

ULTRAMAFIC ROCKS

Gila River dunite "bomb"

This dunite nodule was collected from a basalt flow near Peridot, Arizona, and it is of Pleistocene to Recent age. The rock is described by Ross, Foster, and Myers(36), who also present analyses of the minerals. This particular specimen is totally unaltered, has an average grain size of 2-3 mm, and is composed of olivine (95 per cent) and enstatite (5 per cent), with accessory chromian spinel and diopside. Both the olivine and the enstatite are magnesian-rich, approximately $Fo_{90}Fa_{10}$ and $En_{90}Fs_{10}$, respectively. By hand-picking, enstatite and olivine were separated for analysis. Results are indicated in Table XXIII.

Table XXIII

Oxygen isotopic analyses of minerals from the Gila River dunite "bomb"

Mineral	$\delta O^{18}/O^{16}$ (‰)	av. dev.	no. of runs
olivine (Fo_{90})	5.1	0.0	3
enstatite (En_{90})	6.4	0.3	4

A calculated $\delta_{ROCK} = 5.2$.

Duke Island ultramafic complex

The ultramafic complex at Duke Island, southeastern Alaska, is one of a series of zoned ultramafic bodies exposed along a north trending linear belt that are thought to have a common origin. This particular body has been studied in detail by Irvine(37), who has provided the specimens which have been analyzed. The zonation consists of a series of rock types ranging from almost pure dunite through peridotite, olivine pyroxenite, and hornblende pyroxenite, grading outwards from the center of the body. The entire complex is intrusive into a gabbro body, a specimen of which has already been described — N-36-8. The chief minerals of the complex are olivine, diopside, and magnetite; no orthopyroxene occurs, and plagioclase appears only in the late-stage hornblende-plagioclase dikes. Analyses of the rocks are presented in Table XXIV, and the rock types are described below.

Table XXIV

Oxygen isotopic analyses of minerals from Duke Island ultramafic body

Mineral	$\delta O^{18}/O^{16}$ (‰)	av. dev.	no. of runs
R-37-1a hornblende-plagioclase dike			
hornblende	5.9	0.0	2
plagioclase (An_{90})	7.4	0.0	2
I-37-2 olivine pyroxenite			
olivine	5.1	0.2	2
entire rock	6.0	0.2	2
I-40-1 pyroxene veinlet			
diopside	5.5	0.1	3

R-37-1a hornblende-plagioclase dike - This rock, made up of about equal amounts of pegmatitic hornblende and anorthite, was collected from the border gabbro zone which it markedly transects; this material is thought to be a differentiation product of the ultramafic magma. A calculated $\delta_{ROCK} = 6.6$.

I-37-2 olivine pyroxenite - This rock is made up of 25 per cent olivine (Fo_{80}), 70 per cent diopside, and minor hornblende and magnetite. It is typical of much of the olivine pyroxenite in the ultramafic complex. The olivine is slightly serpentinized. A calculated diopside analysis gives $\delta_{DIOPSIDE} = 6.3$, but is only approximate.

I-40-1 pyroxene veinlet - This rock is a very coarse-grained diopside veinlet which transects peridotite in the central portions of the ultramafic complex. Most probably it did not crystallize from a magma of its own composition, but was formed by replacement.

Other ultramafic bodies of southeastern Alaska

Two other ultramafic rock types from southeastern Alaska have been analyzed, and results are listed in Table XXV.

Table XXV

Oxygen isotopic analyses of minerals from southeastern Alaska ultramafics

Mineral	$\delta O^{18}/O^{16}$ (‰)	av. dev.	no. of runs
Union Bay dunite	5.8	0.2	3
entire rock			
Pt. Frederick hornblendite			
hornblende	6.9	0.3	2
biotite	7.1	0.1	2

Union Bay dunite - This rock is from the core of the Union Bay ultramafic body(38), located some 80 miles north of Duke Island. This body is a zoned intrusive very similar to the complex on that island. The rock is completely unaltered and is composed of 98 per cent olivine (Fo_{90}) with accessory diopside and chromite.

Pt. Frederick hornblendite - This rock is collected from a small hornblendite intrusive near Petersburg, Alaska. The specimen is a pegmatitic biotite-diopside hornblendite, biotite having clearly formed later than either the pyroxene or hornblende, both of which it replaces. An approximate mineralogical composition is 60 per cent hornblende, 30 per cent biotite, and 10 per cent clinopyroxene, with minor amounts of magnetite.

Interpretation of data from ultramafic rocks

The oxygen isotopic data obtained from the ultramafic rocks are plotted on the graph of fig. 14. The pyroxene-olivine fractionation for these ultramafic rocks is very nearly the same as is shown by the hypersthene-olivine gabbro of the Skaergaard intrusion, which certainly establishes the result that $\Delta_{\text{PYROXENE-OLIVINE}}$ is positive at isotopic equilibrium. The indication is that clinopyroxene and orthopyroxene are very similar in their oxygen isotopic properties, as was also shown by the rocks of the Skaergaard intrusion. It is of interest that $\Delta_{\text{PYROXENE-OLIVINE}}$ is the same for both the Gila River "bomb" and for the olivine pyroxenite, even though the pyroxene is enstatite in the former and diopside in the latter.

The oxygen isotopic composition of the hornblende-plagioclase dike is compatible with an origin by differentiation of the olivine pyroxenite magma, inasmuch as such a magma would almost certainly have become enriched in O^{18} during progressive crystallization. The value of $\Delta_{\text{PLAGIOCLASE-HORNBLENDE}}$ is almost identical for this rock and for the Bonsall tonalite; evidently very little change occurs in this fractionation factor over a wide range of plagioclase compositions, as plagioclase is An_{40} in the Bonsall tonalite and is An_{90} for this rock. Hornblende and plagioclase probably crystallized almost simultaneously in both rocks — hence these Δ-values probably closely represent equilibrium fractionations for both pairs.

It is not known why the diopside veinlet should be isotopically lighter than the diopside from the olivine pyroxenite. Many conceivable mechanisms exist whereby such a variation could be brought about.

The Pt. Frederick hornblendite body shows evidence of oxygen isotopic disequilibrium in that biotite is richer in O^{18} than is the hornblende — the only known example of a reversal from the normal

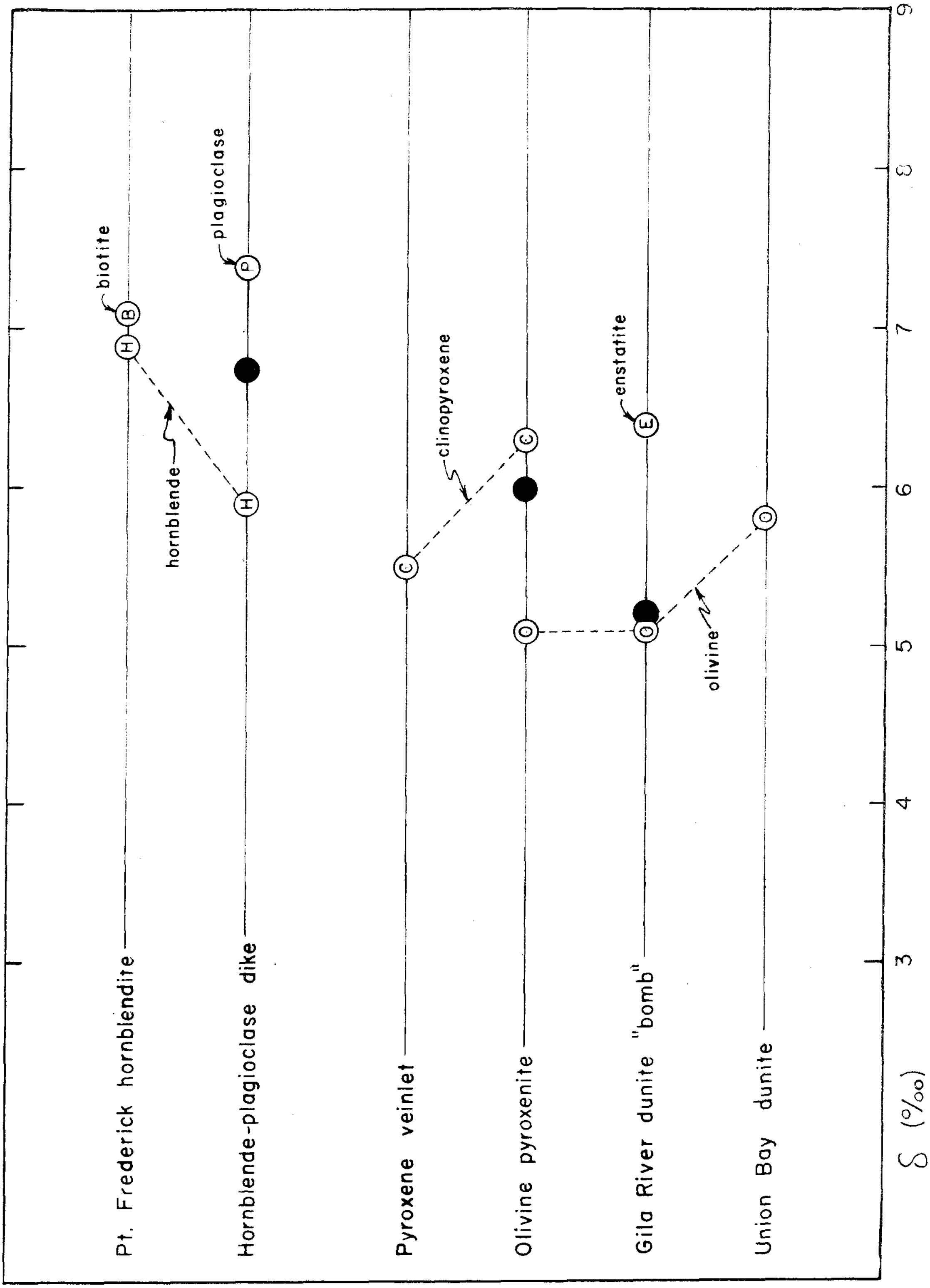


Fig. 14. Isotopic analyses of minerals in ultramafic rocks.

fractionation between these minerals. The oxygen isotopic evidence is thus compatible with the textural evidence that suggests that the biotite crystallized very late and deuterically replaced the hornblende, if it is assumed that the magma was being progressively enriched in O^{18}, which seems reasonable.

No overall trends can be definitely inferred on the basis of these few analyses, except that the hornblendite and the hornblende-plagioclase dike lie in the gabbroic range of O^{18}/O^{16} composition, whereas the olivine-bearing rocks are somewhat lighter, in general. The hornblende-bearing rocks are also chemically similar to gabbros, and their O^{18}/O^{16} compositions are compatible with an origin by fractional crystallization from the olivine pyroxenites. These ultramafic rocks conceivably may have formed at higher temperatures than any of the other rocks analyzed in the present study. It is of importance that large fractionations exist between the minerals of these rocks, and it appears likely that these fractionations change quite slowly as a function of temperature in this high temperature range.

ANORTHOSITES

San Gabriel anorthosite

This anorthosite specimen was collected from near the center of the large anorthosite massif in the San Gabriel Mts., California. The body has been described by Higgs(39), and it is a noritic anorthosite complex with norites at the borders grading through more plagioclase-rich material towards the central portions, finally becoming a monomineralic rock containing plagioclase of andesine composition. The giant crystals of andesine have been pervasively shattered. One analysis has been made of a part of one of these large crystals. giving $\delta_{\text{PLAGIOCLASE}} = 7.6$.

Adirondack anorthosite

This specimen is collected from the large anorthosite complex of the Adirondack Mts., New York. The body is described by Buddington(40), and it is similar to the San Gabriel Mts. body in that it is a complex of gabbroic anorthosite containing pervasively shattered calcic andesine crystals of giant size. Two analyses of this pure plagioclase rock give a mean $\delta_{\text{PLAGIOCLASE}} = 9.8$, with average deviation of 0.2 per mil. The body has undergone a major metamorphic episode subsequent to intrusion.

Plagioclase "bomb" - Hawaii

This specimen of a plagioclase nodule was collected from an olivine basalt flow on Hawaii that also contained dunite nodules. The plagioclase is a bytownite, and two analyses of this sample give a mean $\delta_{\text{PLAGIOCLASE}} = 6.8$, with average deviation 0.0 per mil.

Interpretation of results

The Hawaiian "bomb" and the San Gabriel Mts. andesine show δ-values that are reasonable in that such plagioclase have normal O^{18}/O^{16} ratios for the types of rocks they are associated with. The Hawaiian "bomb" bytownite is similar to the plagioclase phenocrysts of the Steens basalt, and the San Gabriel Mts. andesine is similar to the plagioclase of the San Marcos gabbro. The δ-value for the Adirondack anorthosite is more unusual, and this rock has either developed from a source of different oxygen isotopic composition, or more probably, the metamorphism which it has undergone has allowed oxygen exchange to occur.

AMPHIBOLITES

General statement

To further demonstrate the general applicability of the oxygen isotopic results, and to better understand the manner in which the equilibrium fractionation factors of some common igneous minerals change with temperature, it seemed advisable to investigate a few metamorphic rocks. This study was also intended to produce data upon whether or not isotopic equilibrium is commonly established during metamorphic recrystallization, and hence whether a practicable oxygen isotopic temperature scale might be used in studies of these rocks. Five specimens of amphibolite of varying metamorphic grade were selected for this study.

Adirondack Mts.

Three amphibolites from the Grenville series of the northwest Adirondack Mts. have been provided for these studies by A. E. J. Engel. The general distribution of rock types in the area and a short discussion of the amphibolites is given by Engel and Engel(41)(42). A forthcoming paper by the same authors will describe the amphibolites of the region in detail, including the specimens used in the present study.

A-9A - This specimen was collected 2 miles northeast of Colton, New York, less than a mile from the contact between the Grenville series and the granitic massif of the Adirondack Mts. According to Engel and Engel(42), the temperature at which metamorphism occurred was approximately 600° C. The rock is made up of approximately 30 per cent andesine, 25 per cent hornblende, 25 per cent clinopyroxene, 10 per cent orthopyroxene, and 10 per cent garnet. Almost pure mineral separates have been analyzed, and the results are shown in Table XXVI.

Table XXVI

Oxygen isotopic analyses of minerals in A-9A amphibolite

Mineral	$\delta O^{18}/O^{16}$ (‰)	av. dev.	no. of runs
andesine	9.1	0.0	2
hornblende	6.8	0.1	3
clinopyroxene	7.5	0.3	3
garnet	7.0	0.4	2

A total rock oxygen isotopic composition can be calculated, and gives approximately $\delta_{ROCK} = 7.8$.

A-104 - This specimen was collected from the same locality as A-9A, and is identical except that it contains no garnet. Very approximately, this rock contains 35 per cent andesine, 25 per cent hornblende, 30 per cent clinopyroxene, and 5 per cent orthopyroxene. Pure mineral separates of hornblende and plagioclase have been provided by A. E. J. Engel, and these have been analyzed with results as given in Table XXVII.

Table XXVII

Oxygen isotopic analyses of minerals in A-104 amphibolite

Mineral	$\delta O^{18}/O^{16}$ (‰)	av. dev.	no. of runs
andesine	11.4		1
hornblende	7.0		1

A-3A - This specimen was collected about 1 mile north of Emeryville, New York, more than 10 miles from the nearest exposed contact between the Grenville series and the Adirondack granitic massif.

According to Engel and Engel(42) this rock was metamorphosed at about 500° C. The rock is free of alteration, and contains 70 per cent hornblende, 27 per cent andesine, and 3 per cent quartz. Pure separates of the plagioclase and hornblende were provided by A. E. J. Engel, and the analyses of these minerals are listed in Table XXVIII.

Table XXVIII

Oxygen isotopic analyses of minerals in A-3A amphibolite

Mineral	$\delta O^{18}/O^{16}$ (‰)	av. dev.	no. of runs
andesine	10.0	0.2	3
hornblende	8.3	0.1	2

A calculated value of δ_{ROCK} is 8.8.

Black Hills

Two amphibolite specimens, collected from the vicinity of Lead, South Dakota by B. Raychaudhuri, have been provided for analysis. One is from the staurolite zone of regional metamorphism, and one is from the upper part of the biotite zone. The amphibolites of the Black Hills are described by Dodge(43) and the metamorphism of the area by Noble and Harder(44).

Both of these rocks are of lower metamorphic grade than any of the Adirondack amphibolites, but unfortunately they are not so unaltered. The specimen from the staurolite zone contains large amounts of hydrothermal carbonate and chlorite. The minerals of both appear not to be in complete chemical equilibrium, as the hornblende and plagioclase are somewhat zoned. Pure separates of hornblende and plagioclase, provided by B. Raychaudhuri, have been analyzed with results as shown in Table XXIX. Only one analysis of each has been done.

Table XXIX

Oxygen isotopic analyses of minerals in Black Hills amphibolites

Mineral	δ(‰) Staurolite zone	δ(‰) Biotite zone
plagioclase	17.5	11.8
hornblende	10.4	9.0
entire rock (calculated)	12.5	10.4

Interpretation of amphibolite data

The results of the oxygen isotopic analyses of the five amphibolite specimens are plotted graphically in fig. 15, roughly in the order of their supposed isotopic equilibration temperatures. It is clear that if these rocks were originally gabbros or basalts, they have in every case been modified in their total oxygen isotopic composition, because none now show a δ_{ROCK} in the basaltic range. This is exactly what would be expected if the rocks had been exchanged with large amounts of water during metamorphism, because oxygen isotopic exchange with a reservoir of water at lower than magmatic temperatures should produce an increase in the δ-value of the rock.

All the specimens may not have been derived from original mafic igneous rock, but it would be unlikely that none were. Some may even be metasomatized limestone. Even so, the consistency of the isotopic data indicates that gross equilibrium has been attained. The minor variations, however, do not fit the geological evidence unless slight disequilibrium effects are assumed. Isotopically, A-3A indicates the highest equilibration temperature, with $\Delta_{PLAGIOCLASE-HORNBLENDE}=1.7$ per mil, a larger fractionation than any found in the igneous rocks which have been studied. A-9A and A-104, which were supposedly meta-

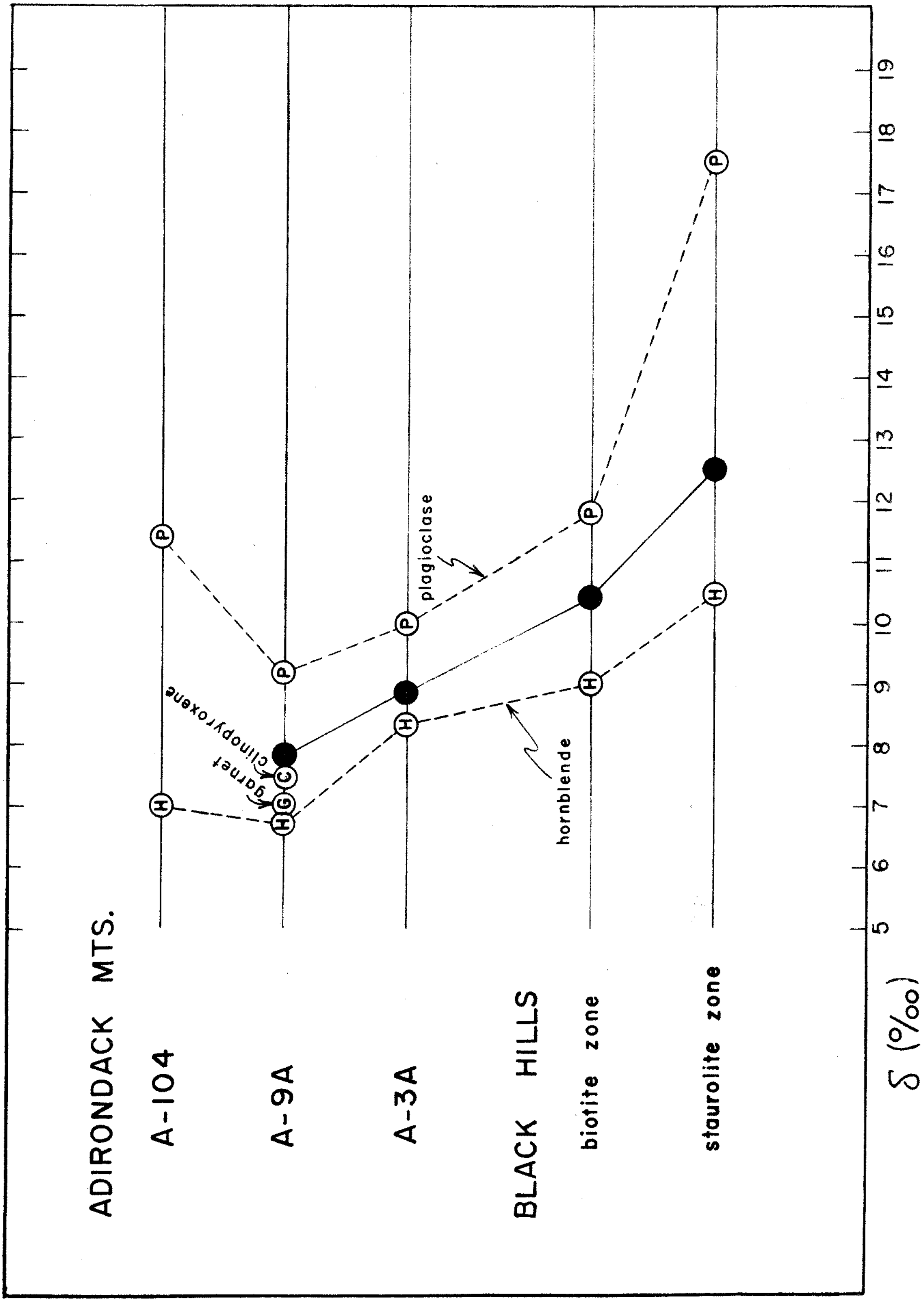


Fig. 15. Isotopic analyses of minerals in metamorphic amphibolites; black circles are calculated δ-values of total rocks.

morphosed under higher temperature conditions than was A-3A, both show larger plagioclase-hornblende fractionations than does A-3A. The most reasonable interpretation of such discrepancies is that complete oxygen isotopic equilibrium was not attained during the metamorphism of these rocks. The data from A-9A do, however, indicate that in all likelihood $\Delta_{\text{CLINOPYROXENE-HORNBLENDE}}$ is positive at oxygen isotopic equilibrium, the best evidence presently available concerning this fractionation. This conclusion can be reached because the minerals in A-9A could not have been formed very far out of equilibrium.

It may be significant that $\delta_{\text{HORNBLENDE}}$ is nearly the same in A-9A and in A-104, perhaps indicating that only the plagioclase in A-104 has been affected by the disequilibrium processes to any noticeable extent. A-104 definitely appears to represent a more marked disequilibrium than do the others. It is impossible to decide which of these other two represents a closer attainment of equilibrium for their respective temperatures of metamorphism. More data upon amphibolites, or preferably, experimental data on the equilibrium fractionation between hornblende and plagioclase, are necessary before an answer can be given.

$\Delta_{\text{PLAGIOCLASE-HORNBLENDE}}$ for the specimens from the Black Hills is larger than for the near-equilibrium A-3A and A-9A from the Adirondack Mts. This is consistent with the geological evidence for their lower temperature origin. However, the fractionations are reversed in that the supposedly higher temperature rock of the staurolite zone shows an extremely large Δ-value that is only consistent with quite low temperatures of equilibration. This apparent discrepancy can be readily explained as being a result of low temperature exchange with the hydrothermal solutions which altered the rock and produced the carbonate and chlorite. Amphibolites from the Black Hills show evidence for chemical disequilibrium and for hydrothermal alteration in many localities(43).

The data outlined above demonstrate that the fractionation factor between hornblende and plagioclase increases with a decrease in the temperature of their equilibration. The data also indicate that it is possible to have oxygen isotopic disequilibrium in rocks which are in apparent chemical equilibrium. Oxygen isotopic exchange evidently can occur by subtle processes that may leave little or no chemical imprint upon a rock. This is the same conclusion that was reached by a consideration of the oxygen isotopic data for the chilled marginal gabbro of the Skaergaard intrusion. Any such natural processes almost certainly occur through the medium of exchange with a hydrothermal fluid. It appears doubtful that complete oxygen isotopic equilibrium is commonly established during a metamorphic recrystallization, and application of an oxygen isotopic geothermometer to these types of rocks must be done with caution.

CONCLUSIONS

Experimental technique

O^{18}/O^{16} ratios of most of the common rock-forming minerals have been measured with a precision of ± 0.2 per mil by the fluorine extraction procedure. Principal exceptions are magnetite and some of the independent tetrahedral silicates. Even these minerals can probably be analyzed if highest possible reaction temperatures are used and if samples are ground extremely fine, inasmuch as the principal problem is one of rate of reaction.

The carbon reduction procedure gives quartz analyses that are about 0.4 per mil heavier than results obtained by the fluorine extraction method, but relative to a given quartz standard both methods represent valid techniques for determining O^{18}/O^{16} ratios in quartz. Preliminary work shows that magnetite analyses obtained by carbon reduction are about 1.5 per mil lighter than analyses done by a fluorine extraction. The former method gives 100 per cent yields of oxygen for magnetite samples, and is probably the more accurate of the two methods for this mineral.

O^{18}/O^{16} fractionations among minerals

Approximate oxygen isotopic equilibrium is ordinarily established among coexisting minerals during the formation of igneous and metamorphic rocks. Minor variations from complete equilibrium, however, have been found in almost every rock studied. In the range of magmatic temperatures the equilibrium fractionation factors between minerals change only slightly as a function of temperature, and for all mineral pairs for which conclusive data exist, equilibrium fractionation factors apparently decrease continuously with temperature. Significant and easily measured fractionations exist in even the highest-temperature rocks.

The more highly polymerized silicates generally show the largest O^{18}/O^{16} ratios, and oxygen isotopic properties of minerals are apparently primarily dependent upon crystal structure and are almost insensitive to variations in cation composition. In other words, end members of isomorphous series appear to be nearly identical in their oxygen isotopic properties. On the basis of oxygen isotopic results obtained in this work, an approximate estimate of the relative equilibrium δ-values of the common rock-forming minerals at magmatic temperatures can be given. These are indicated below, to within ± 0.5 per mil.

Mineral	$\delta O^{18}/O^{16}$ (‰)
quartz	9.5
plagioclase	8.5
potash feldspar	8.5
clinopyroxene	7.5
orthopyroxene	7.5
hornblende	7.0
olivine	6.0
biotite	5.5
magnetite	2.0

The anhydrous silicates give δ-values that increase as the number of shared silica tetrahedra in the mineral structure increase. The hydroxyl-bearing silicates, hornblende and biotite, fall out of this sequence in that they are abnormally deficient in O^{18}. This is probably explicable on the basis that the hydroxyl oxygen in these minerals is isotopically lighter than the ordinary silicate oxygen. Hence biotite is lighter than hornblende because 1/6 of its oxygen occurs in hydroxyl groups whereas only 1/12 of the oxygen in hornblende is so bound. A very rough calculation, assuming that the silicate oxygen in each would be about $\delta = 8.0$ on the above scale, gives a δ-value of about -4 for the hydroxyl oxygen in these minerals. This hydroxyl oxygen thus would be at least 6 per mil lighter than the oxygen of any water that might be in equilibrium with the hornblende or the biotite.

Not much of significance can be attached to the calculation given above, but it might imply that an amphibole or mica in which a halogen has partially replaced the hydroxyl group would show oxygen isotopic properties significantly different from normal. Therefore, micas from pegmatites or greisen probably would not be isotopically comparable with the micas of normal rocks. Determination of the isotopic properties of fluorine-bearing micas or amphiboles should enable one to establish more exactly the fractionation between silicate oxygen and hydroxyl oxygen.

Igneous and metamorphic petrology

Ordinarily, a magma will change in oxygen isotopic composition as it crystallizes, and it may become isotopically lighter or heavier depending upon the types of minerals crystallizing and their relative amounts. A mineral is probably in isotopic equilibrium with its magma only at the instant of crystallization; hence most minerals will be isotopically zoned, because continuous and complete isotopic exchange between crystals and liquid does not commonly occur. If the magma becomes enriched in O^{18} as it crystallizes, the outer zones of the minerals should be isotopically heavier than the inner zones, and the late-crystallizing minerals should be heavy relative to the early-formed ones. Therefore, the crystallization history and paragenetic sequence of minerals in an igneous rock are reflected by the relative

δ-values of the minerals. Application of this isotopic technique should be especially useful in unraveling the crystallization history of the accessory minerals of igneous rocks, as conventional methods have thrown very little light upon this problem.

Coexisting minerals of an igneous rock will ordinarily not be in complete oxygen isotopic equilibrium because of these crystallization phenomena. Therefore, determinations of O^{18}/O^{16} ratios of total minerals probably cannot be used as a practicable geothermometer for igneous rocks, inasmuch as the temperature effect generally will be outweighed by the crystallization effects. The oxygen isotopic properties of a magma change as its chemical composition changes. This is a result of changes in degree of polymerization that accompany the change in composition; for example, granitic magma apparently is slightly heavier than coexisting plagioclase, whereas gabbroic magma is lighter.

It should be possible in certain instances to obtain definitive evidence whether or not a given rock type has formed by magmatic differentiation from another rock type. Even though chemical, petrological, and field evidence may be compatible with a process of magmatic differentiation, the oxygen isotopic data may not fit such a mechanism. It is impossible, for instance, for most granitic rocks to have formed by fractional crystallization of the type which produced the Skaergaard granophyres.

Oxygen isotopic determinations should be very valuable in the study of temperatures of recrystallization of metamorphic rocks, even though complete oxygen isotopic equilibrium may not always have been established in such rocks. An important question in metamorphic petrology is whether or not a sequence of rocks was open to water during metamorphism. If the rocks are truly open so that isotopic exchange can occur with a large quantity of hydrothermal fluid the rock will become lighter with increasing grade of metamorphism. This is what has happened to the amphibolites studied in this report. If the rock is not truly open, but if water is simply removed from the system by the dehydration reactions which accompany increasing grade of metamorphism, the rock should become isotopically heavier.

Subtle oxygen exchange processes, probably through the medium of a hydrothermal solution, apparently can occur in rocks and leave little or no chemical imprint. For instance, a low temperature hydrothermal event which has affected a rock may be clearly shown by the oxygen isotopic data, even though essentially no chemical reconstitution has occurred. Even so, it is highly unlikely that exchange could occur to such a degree that complete isotopic equilibrium is attained without almost complete chemical equilibrium also being established.

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