VARIATIONS IN OXYGEN ISOTOPE ABUNDANCES
IN ROCK MINERALS

Thesis by

Robert Norman Clayton

In Partial Fulfillment of the Requirements

for the Degree of

Doctor of Philosophy

California Institute of Technology

Pasadena, California

1955

ACKNOWLEDGEMENTS

I wish to thank Dr. Samuel Epstein, at whose suggestion this work was done, for encouragement and guidance throughout the course of the research.

None of this work would have been possible without the cooperation of the geologists who supplied the specimens for analysis, and contributed greatly to my geological education: Drs. L. T. Silver, A. E. J. Engel, H. L. James, C. W. Burnham, R. H. Jahns, M. L. Keith and others.

The assistance of C. R. McKinney, E. V. Nenow and C. Bauman in the construction of some of the apparatus is much appreciated.

The Stanolind Foundation provided a fellowship under which part of the work was done.

ABSTRACT

Analytical techniques for determination of oxygen isotope abundances in silicates and oxides have been investigated. The reduction of compounds with carbon at high temperatures gives reliable results only from a few important minerals, including quartz and iron oxides. Liberation of oxygen from compounds using fluorine has more wide-spread application, but is more susceptible to errors by contamination.

Oxygen isotope analyses have been made on nineteen natural samples of quartz and associated carbonates, and on seventeen samples of quartz and associated iron oxides. It has been found that, for suitable samples, the isotopic fractionation measured between two associated minerals can be used to fix the temperature at which the minerals crystallized.

Several geological problems are discussed on the basis of the oxygen isotope data. In cases where the geological evidence is clear-cut, the conclusions from the isotope analyses are in complete agreement with those from geological reasoning.

TABLE OF CONTENTS

INTRODUCTION

In studying the rocks of the earth one is concerned with the materials from which the rocks are built, and with the processes these materials have undergone in order to reach their present condition. The problem is one of very great complexity, and can be successfully attacked only by the concerted effort of many independent approaches. From astronomy and geophysics we get some of the physical properties of the earth; from geological investigation of rocks in the field and under the microscope we can deduce many facts concerning the processes of formation of rocks; from analytical chemistry we learn the chemical composition of rocks, both for major constituents and for trace elements; from physical chemical principles and laboratory experiments we can predict the behaviour of a natural system under known conditions, or conversely, reconstruct the natural conditions by observation of the results of the processes in rocks. In the last few years, a new method of attack has been through the measurement of the abundances of stable isotopes of the light elements to determine the variations resulting from natural processes.

The thermodynamic properties of two molecules which differ only in that they contain different isotopes of one element, are in general different. This difference in properties is a quantum effect and has been discussed theoretically.(1)(2) Following Urey's treatment consider an isotope exchange reaction:

$$aA_1 + bB_2 \rightleftharpoons aA_2 + bB_1$$

where A and B are molecules containing one element in common, and the subscripts 1 and 2 indicate that the molecule contains the light or heavy isotope of this element. Then the equilibrium constant for this reaction can be written in terms of the partition function for the molecules:

$$K = \left(\frac{Q_{A_2}}{Q_{A_1}}\right)^a \Bigg/ \left(\frac{Q_{B_2}}{Q_{B_1}}\right)^b$$

The partition function for a molecule can be written as the product of the translational, rotational, and vibrational partition functions. For ordinary temperatures the translational and rotational partition function can be considered classical (except for the hydrogen isotopes), and the vibrational anharmonicity is usually neglected.

$$Q = Q_{tr} \cdot Q_{rot} \cdot Q_{vib}$$

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

$$Q_{rot} = \frac{8\pi^2 IkT}{\sigma h^2} \qquad \text{or} \qquad Q_{rot} = \frac{\pi^{1/2}}{\sigma} \frac{(8\pi^2 kT)^{3/2}}{h^3} \cdot (ABC)^{1/2}$$

$$Q_{vib} = \frac{e^{-\frac{u}{2}}}{1-e^{-u}} \qquad \text{or} \qquad Q_{vib} = \prod_i \frac{e^{-\frac{u_i}{2}}}{1-e^{-u_i}}$$

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

$u = \frac{h\nu}{kT}$ where ν is a vibrational frequency (in $\sec^{-1}$)

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

for diatomic molecules, and

$$\frac{Q_2}{Q_1} = \frac{\sigma_1}{\sigma_2} \left(\frac{A_2 B_2 C_2}{A_1 B_1 C_1}\right)^{1/2} \left(\frac{M_2}{M_1}\right)^{3/2} \prod_i \frac{e^{-\frac{u_{2i}}{2}}}{1-e^{-u_{2i}}} \cdot \frac{1-e^{-u_{1i}}}{e^{-\frac{u_{1i}}{2}}}$$

for polyatomic molecules.

The moments of inertia can be eliminated from these expressions by application of the theorem of Teller and Redlich(3)

$$\frac{I_2}{I_1}\left(\frac{M_2}{M_1}\right)^{3/2}\left(\frac{m_1}{m_2}\right)^{3n/2}\frac{u_1}{u_2} = \left(\frac{A_2 B_2 C_2}{A_1 B_1 C_1}\right)^{1/2}\left(\frac{M_2}{M_1}\right)^{3/2}\left(\frac{m_1}{m_2}\right)^{3n/2}\prod_i \frac{u_{1i}}{u_{2i}} = 1$$

where n is the number of isotopic atoms exchanged, and m_1, m_2 are the masses of the atoms exchanged.

Then

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

and

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

It is therefore possible to calculate the equilibrium constant in terms of the frequencies of vibration of the normal and isotopically substituted molecules. Such constants at several temperatures have been calculated by Urey for isotope exchange reactions involving most of the light elements. Experiments have confirmed many of the predicted equilibrium constants for exchange between gas molecules.

The above calculations are least reliable where the reactions involve condensed phases, since the calculations are based on perfect gas partition functions. This has been demonstrated in the case of the relative vapor pressures of $B^{10}Cl_3$ and $B^{11}Cl_3$, where Urey's calculations predict an enrichment of $B^{10}Cl_3$ in the vapor of 1.5% at 0°C, but careful experiments by Green and Martin(4) show that $B^{11}Cl_3$ is enriched in the vapor phase by 0.18%. At present the most fruitful approach to the study of isotope fractionation between condensed phases is, therefore, through experimental measurement. Some attempts have been made to estimate theoretically the fractionation in isotopic exchange reactions involving solids.(5) (6) McCrea calculated fractionation factors for exchange of carbon and oxygen atoms between crystalline calcium carbonate and aqueous carbonate ion, and also for exchange of oxygen between calcium carbonate and liquid water. In calculating the ratio of partition functions for the solid phase, two types of vibration were considered: internal vibrations of the carbonate ion and lattice vibrations of the whole ion in the crystal. The internal vibration frequencies are known from the infra-red and Raman spectra. To calculate the fractionation effect due to lattice vibrations, McCrea used the Einstein and Debye relationships to estimate the distribution of energy. Both the value of the calculated isotope fractionation, and its gradient with temperature are in reasonable agreement with experimental data.

In his theoretical treatment of the fractionation of silicon isotopes, Grant assumes that the interaction of SiO_4 tetrahedra with the rest of the structure can be neglected, and calculates the fractionation on the basis of observed vibration frequencies within the SiO_4 group. This method gives fractionation factors in the right direction and of the right order of magnitude to agree with the experimental results of Reynolds and Verhoogen(7) and Allenby.(8) For similar geological samples, the fractionations found by Allenby are about five times as great as those found by Reynolds and Verhoogen, although both sets of data are internally consistent. The reason for this discrepancy is not known.

The equilibrium constants for isotopic exchange reactions are generally of the order of 1.01 at room temperature for elements of the first row of the periodic table (and is smaller for heavier elements). The constants approach 1.000 at high temperatures, and 0 or infinity at 0°K. Since the value of K is so near unity at ordinary temperatures, the amount of isotopic fractionation is small, and can be measured with accuracy only be very sensitive mass spectrometry. The most extreme samples of oxygen found in natural compounds differ in atomic weight by only .001%. This corresponds to a variation of 6% in the ratio of O^{18}/O^{16} and amounts to 500 times the experimental error in the best mass spectrometers.

The spectrometer used in this work is a 60° single-focusing instrument of the type described by Nier(9), with modifications as described by McKinney et al.(10) Several important factors are responsible for the high precision attainable with this mass spectrometer:

(a) Ion Source

In order to achieve reliable electronic amplification of the ion beam, the intensity of the beam itself must be constant. This can be done only with ion sources in which the sample is admitted as a gas, and is ionized by electron bombardment.

The intensity of the ion beam must also be several times greater than that in commercial spectrometers. In order to provide the intense ion beam, a very stable source of ionizing electrons is necessary. In our instrument, the positive ion current due to mass 44 ($C^{12}O^{16}O^{16}$) is 1.7×10^{-9} amps. The current due to mass 46 ($C^{12}O^{16}O^{18}$) is 1/250 of this, or 6.8×10^{-12} amps, corresponding to the collection of 4×10^{7} ions per second. Statistical variations in this number will be of the order of its square root, 6.4×10^{3}, which is about .02% of the total mass 46 beam. These variations are integrated electronically to some extent, since the time constants for the measuring circuits are of the order of seconds, but the statistical fluctuations still remain one of the ultimate limitations of the mass spectrometer.

(b) Double Collection

The ratio of the intensities of two ion beams can be measured with much greater accuracy than the absolute intensities of the beams. Fluctuations in total beam intensity are nullified by measuring an isotope ratio. In a double collecting mass spectrometer, two ion beams, corresponding to two different values of $\frac{m}{e}$, are collected simultaneously on two collectors. The ion currents are amplified and the isotope ratio determined by a bridge circuit.

(c) Relative Measurements

A further factor of ten in long range precision can be realized if the isotope ratio in a sample gas is compared with the ratio in a standard gas. 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 is also common for the two samples. With such an arrangement the actual value of the ratio of isotope abundances, R, is not determined to high precision. Rather, the potential of the "null point" of the bridge circuit mentioned in (b) is measured relative to ground. Then a small change in the ratio of the ion beams will change this potential, by an amount which is exactly proportional to the change in ion beam ratio. The experimentally determined quantity is, therefore, the relative difference in isotope ratio between the sample gas and the standard gas. This quantity is called δ, and is:

$$\delta = \frac{R}{R_{std}} - 1 \qquad 1000$$

where R is O^{18}/O^{16} for the sample gas

R_{std} is O^{18}/O^{16} for the standard gas

δ is the difference expressed in permil (‰).

Variations in the isotopic composition of oxygen from natural sources have been studied by many people using analytical methods of varying sensitivity (Table I). An asterisk indicates that the experimental errors are probably 0.1 - 0.2‰. Others are greater.

Table I

Previous Oxygen Isotope Studies

Investigators	Source of oxygen	Method of isotopic analysis
Dole(11)(12)	Atmospheric O_2	Density of water
Swartout and Dole(13)	Atmospheric O_2	
Dole, Lane, Rudd and Zaukelies(14)	Atmospheric O_2	Mass spectrometer*
Kirshenbaum(15)	Water	Density of water
Epstein and Mayeda(16)	Water	Mass spectrometer*
Dansgaard(17)(18)(19)	Water	Mass spectrometer
Dole and Slobod(20)	Water	Density of water
McCrea(4)	Carbonates	Mass spectrometer*
Urey, Lowenstam, Epstein and McKinney(21)	Carbonates	Mass spectrometer*
Epstein, Buchsbaum, Lowenstam and Urey(22)(23)	Carbonates	Mass spectrometer*
Epstein and Lowenstam(24)	Carbonates	Mass spectrometer*
Baertschi(25)	Carbonates	Mass spectrometer*
Manian, Urey and Bleakney(26)	Silicates	Mass spectrometer
Tokuda and Koshida(27)	Silicates	Density of water
Baertschi and Silverman(28)	Silicates	Mass spectrometer*
Silverman(29)	Silicates	Mass spectrometer*
Baertschi and Schwander(30)	Silicates	Mass spectrometer

Investigators	Source of oxygen	Method of isotopic analysis
Schwander(31)	Silicates	Mass spectrometer
Adams(32)	Silicates	Mass spectrometer
Dole and Slobod(17)	Iron oxides	Density of water
Donstova(33)	Iron oxides	Density of water

The earliest work on oxygen isotopes in silicates was that of Manian, Urey and Bleakney.(26) They heated the silicate with carbon and carbon tetrachloride at 1000°C, obtaining carbon monoxide. This was decomposed by hydrogen to give water, which was 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 analyzed.

Tokuda and Koshida(27) heated the silicate with potassium hydrogen fluoride at 230°C, forming water. They measured its density, and claimed to be able to determine variations of 1.4‰ in the O^{18}/O^{16} ratio, but could not find significant differences between igneous and metamorphic rocks.

Adams reduced quartz with carbon in an induction furnace at high temperature, producing carbon monoxide. This was oxidized with cupric oxide to carbon dioxide and analyzed mass spectrometrically. The oxidation over cupric oxide is almost certain to invalidate the results, since isotopic exchange between carbon dioxide and cupric oxide has been shown to take place at 430°C.(34)

In the analytical method of Baertschi and Silverman(28) and Silverman(29), oxygen was released from its compounds by oxidation with fluorine or chlorine trifluoride, and analyzed as oxygen by means of a sensitive mass spectrometer. Their results indicated that the ratio of

O^{18}/O^{16} may vary as much as 3% in natural silicate rocks. Some of the data taken from Silverman's paper are shown in Table II.

Table II

Oxygen Isotopic Composition in Silicate Rocks

Sample	O^{18}/O^{16} ‰	Av. deviation	No. of runs
Hawaii sea water	0.0	0.2	2
Columbia river basalt	6.4	0.2	3
Disco basalt	6.6	0.7	3
Mt. Etna lava	6.7	0.2	4
Olivine basalt	7.0	0.1	3
Yellowstone obsidian	7.7	0.8	2
Gneissic granite	7.9	0.2	2
Nepheline syenite	8.3	0.0	2
Quartz vein	14.0	0.2	4
Potsdam sandstone	15.5	0.0	2
Atmospheric oxygen	19.2	0.9	2
Diatomite	30.3	0.0	2

Several groups can be seen which are correlated with the geological histories of the samples. Basalts and basic rocks have δ's from 6.4 to 7.0, granite rocks from 7.5 to 8.5, vein quartz from 13 to 16, sedimentary silica around 30‰.

Further work in this field has been done by Baertschi and Schwander(30) and by Schwander.(31) They liberated oxygen from rocks as carbon monoxide by reduction with carbon at high temperatures (2000°C). For reasons to be discussed later, the results of these analyses may be very much in error. But here too it was found that the O^{18}/O^{16} ratio is much higher in sediments than in igneous rocks.

Schwander analyzed several suites of geologically well-chosen samples in an effort to show what happens to the overall isotopic composition of rocks formed by crystallization from magmas, or by metamorphism of previously existing sediments. Even if the analytical data are correct (something which is not possible to evaluate by reading his publication), measurement of the isotopic composition of a whole rock cannot be expected to yield much information.

The last two pieces of work indicate that there do exist variations in the isotopic composition of oxygen in silicate rocks which are large in terms of present day mass spectrometry. This work was exploratory and much more must be done in order that any extensive conclusions may be drawn from isotopic abundance data. Real physical chemical conclusions can be drawn only from the measurements of fractionation among phases within a rock. As described above, the fractionation between two phases at equilibrium depends on (1) the chemical nature of the phases and (2) the temperature. Then the fractionation between a given mineral pair will be a function only of temperature.

Ultimately, it should be possible to use the inter-mineral isotope fractionation as a measure of the temperatures of geological events, and to use the absolute isotopic composition of the phases as an indication of the source of material in the geological process.

APPARATUS AND EXPERIMENTAL PROCEDURES

Experimental Requirements

The value of the ratio of O^{18}/O^{16} in samples found in nature varies over a range of about 6%. However, for a given chemical species, the variations so far observed are of the order of 3%. It has been found in the past(21)(23)(29) that analytical precision of the order of 0.1 - 0.2‰ is satisfactory for most geological problems, and is attainable by careful chemistry and precision mass spectroscopy.

Oxygen isotopes have been studied using oxygen(28)(29), carbon monoxide(30)(31), and carbon dioxide(21)(23)(24) as the sample gas. Of these, carbon dioxide has proved the most satisfactory, since its mass falls in a region of the mass spectrum not contaminated with the background effects of nitrogen and oxygen of the air.

The analytical problem is, therefore, to prepare from a mineral a carbon dioxide sample of identical oxygen isotope composition within an experimental error of ±0.2‰.

In order that the isotopic composition of the sample gas be the same as that in the original material, all chemical reactions must be done (a) quantitatively, or (b) with no isotope fractionation. In general any incomplete chemical reaction will result in isotopic fractionation if a mechanism exists for exchange of the atoms of the element in question. The amount of fractionation decreases as the temperature of reaction increases, but as yet it has not been demonstrated at what temperature isotopic fractionations become negligible. Evidence from geological specimens given in this thesis indicates that there can be considerable fractionation of oxygen isotopes at temperatures over 1000°C.

The most important chemical procedures used for extraction of oxygen from minerals have been (a) oxidation with fluorine, chlorine trifluoride or bromine trifluoride, liberating oxygen, and (b) reduction with carbon, liberating carbon monoxide. In the method (a), quantitative yields of oxygen have been obtained, but the operation is fairly difficult, and the problem of contamination of the sample with foreign oxygen is great. In method (b) yields of 60 - 70% have been reported, with no explanation why higher yields were not obtained.

Analytical Methods

A. Fluorine Oxidation:

(a) Principle

The reaction of fluorine with oxides and silicates gives oxygen and metal fluorides:

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

$$2MSiO_3 + 6F_2 \longrightarrow 2SiF_4 + 2MF_2 + 3O_2$$

The reactions are thermodynamically favorable at all temperatures. Silverman and Baertschi carried out the reaction at 430°C, and used hydrogen fluoride as a catalyst. Gaseous reaction products are: oxygen, excess fluorine, hydrogen fluoride (from catalyst and from the mineral if it contains hydrogen), and volatile fluorides (silicon tetrafluoride, boron trifluoride). The removal of hydrogen fluoride and silicon tetrafluoride can be achieved by passing the gas through a liquid nitrogen trap. The removal of fluorine from the oxygen sample is not so simple. It was accomplished by Baertschi and Silverman by passing the gas mixture through heated potassium bromide, which is oxidized by fluorine to give bromine, which can be frozen out. This process was considered to be a major source of contamination.

The product gas is oxygen, which can be mass analyzed as such, with the inherent difficulties involved in the use of oxygen in the mass spectrometer.

(b) Apparatus

1) High Vacuum System (Fig. 1)

The part of the vacuum system with which fluorine comes in contact is constructed of metal resistant to fluorine attack:

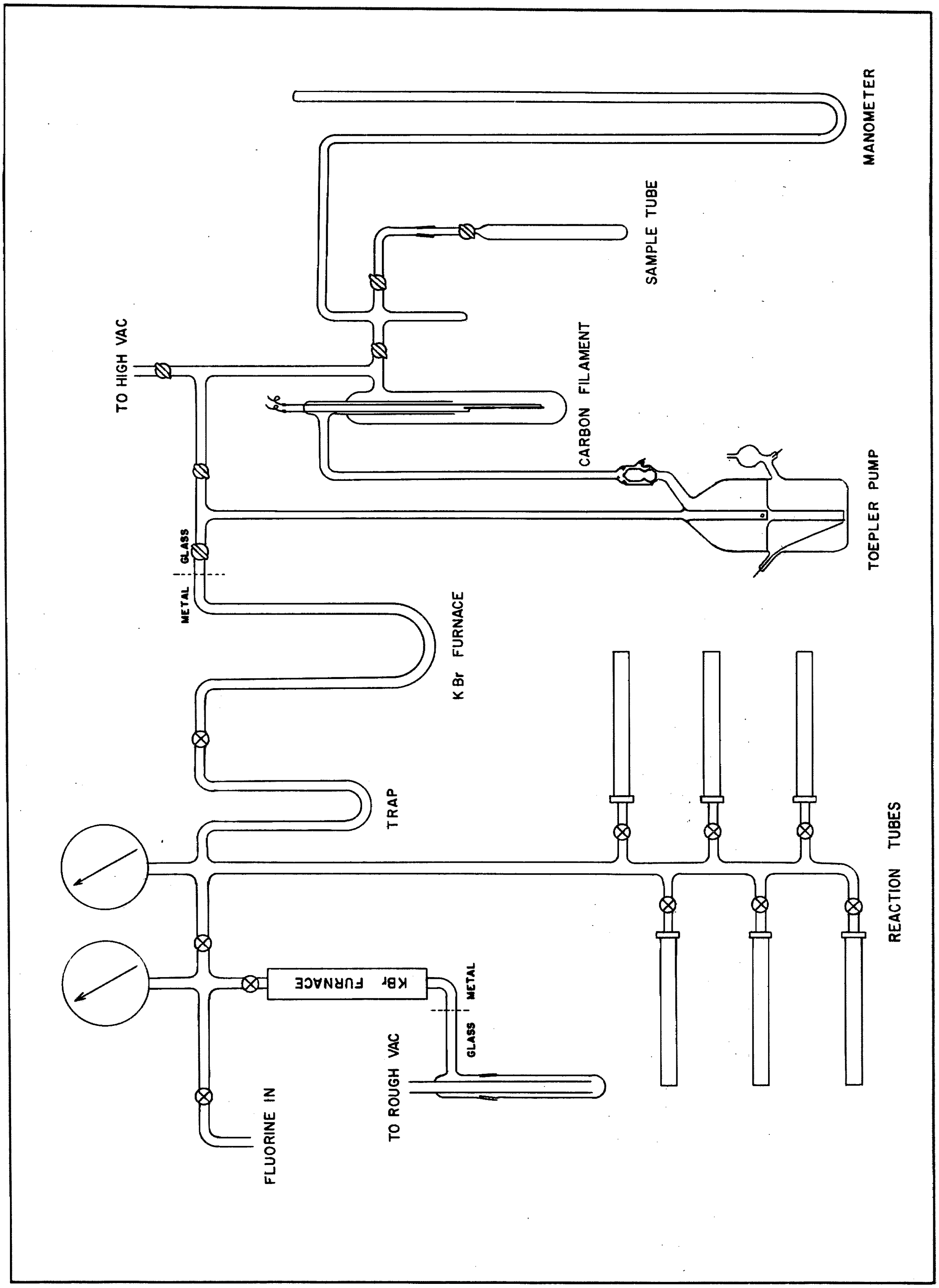


Fig. 1. Fluorine System.

Inconel tubing with copper elbows and tees, joined by silver solder. Connections to removable parts are made using flanged joints with Teflon gaskets. Valves with Monel body, Inconel diaphragm and Teflon gasket are used (Hoke Incorporated, #413T). Pressure in the line is determined by Bourdon-type pressure and vacuum gauges with Monel diaphragm. Metal to glass transitions are made with Kovar seals.

2) Reaction Tubes

Six reaction tubes are connected to the vacuum line by screwed fittings with Teflon gaskets. The reaction tubes are made of nickel tubing 7/8 in. O.D., 5/8 in. I.D., 10 in. long, and have a capacity of 50 c.c.

3) Potassium Bromide Furnaces

There are two heated tubes containing solid coarsely granular potassium bromide. One furnace, 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 furnace, 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, capable of heating the tube to 1000°C, although such high temperatures are not used for this purpose.

4) Carbon Filament

Oxygen is converted to carbon dioxide by reaction with a hot carbon rod. The rod is prepared from a 1/8 in. graphite spectrograph electrode, 3 in. long. The cross-sectional area of the center of rod is reduced by a factor of about five by careful sandpapering. Electrical connection is made through 1 m.m. platinum rods in holes drilled through the carbon rod near the ends. The platinum leads are joined with threaded couplings to No. 12 copper wires, which in turn are connected to tungsten leads which pass through the glass and out of the vacuum system. The rod is heated by a current of 15 amps (A.C.) at 5 volts. 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. The carbon of the filament is used up in the reaction, and a new rod is necessary after one or two samples have been converted.

(c) Analytical Procedure

Before the apparatus is used for preparation of oxygen from mineral samples, all extraneous oxygen compounds must be removed from the parts of the system which will be exposed to fluorine. Likely to provide the biggest sources of contamination are certain of the soldered connections from which the flux cannot be removed by water washing. The metal system was filled with fluorine at a pressure of half an atmosphere for several days to remove oxide films, or cover them with a fluoride coating.

The sample, 10 or 20 mg. of finely ground material, is weighed into the reaction tube, the tube remounted on the vacuum line and evacuated. With the reaction tubes cold, a charge of fluorine at half an atmosphere pressure is admitted for fifteen minutes then pumped away. Again the tubes are filled with fluorine to half an atmosphere, then closed off and heated to 500°C for two hours.

After the sample tube is cool, the gas, a mixture of oxygen, fluorine and silicon tetrafluoride in the case of a silicate mineral, is passed through a trap cooled in liquid nitrogen to remove the silicon tetrafluoride. In the potassium bromide furnace, fluorine is removed and bromine formed, which is then removed from the oxygen by passing the mixture through another liquid nitrogen trap. Oxygen is collected by the Toepler pump.

The conversion of oxygen to carbon dioxide is accomplished by cycling the oxygen over the hot carbon filament (orange-red heat at the center), freezing out the carbon dioxide as it is formed. This reaction is quantitative and takes 10 or 15 minutes for a 5 c.c. gas sample. If the carbon rod is heated too hot, two difficulties arise: (1) some carbon monoxide is formed, which remains unchanged and represents a loss of oxygen of the sample, and (2) the copper wires may become hot enough to be oxidized and remove some of the sample gas.

The carbon dioxide is transferred to a calibrated manometer where its amount is determined then to a sample tube for the mass spectrometer.

(d) Development of Fluorine Oxidation Method

Only preliminary experiments have been done using this apparatus. No reliable isotopic data have been obtained.

1) Conversion of Oxygen to Carbon Dioxide

The procedure for burning oxygen over a carbon filament was developed in connection with a problem involving atmospheric oxygen, not described in this thesis. It was found that using a pure carbon rod, connected to leads which did not get hot enough to oxidize, gave results of good isotopic reproducibility. The results of isotopic analysis of five samples of atmospheric oxygen are given in Table III. The nitrogen in the samples acts only as a diluent, but makes it difficult to tell when all the oxygen has reacted.

Table III

Isotopic Reproducibility in Oxygen ⟶ Carbon Dioxide Reaction

Sample #	Ratio of CO_2 volume to air volume	δ ‰
1	.200	+21.7
2	.196	22.1

Sample #	Ratio of CO_2 volume to air volume	δ ‰
3	.204	21.5
4	.202	21.8
5	.206	21.8
Av.	.202	21.8 ± .14

2) Reaction of Fluorine with Minerals

The minerals tried were quartz, magnetite, orthoclase and calcite. All appeared to react with the fluorine under the conditions of the experiment. In one set of six samples, hydrogen fluoride was added to the sample tube as well as fluorine, and caused no observable change in the reaction. (Baertschi and Silverman(28) used hydrogen fluoride for all their reactions.) There is no solid residue after the reaction of quartz with fluorine. The reaction of orthoclase and calcite leaves a residue of solid fluorides. It is interesting that the action of fluorine on calcite gives all the carbon as carbon dioxide in the reaction tube; fluorine does not react with carbon dioxide under these conditions.

The case of the reaction with magnetite requires some attention. The solid residue after reaction is red, not green as expected for ferric fluoride. X-ray diffraction identification shows the product to be ferric oxide (Fe_2O_3). This is compatible with the statement from Sidgwick(35): "If heated in air or in steam ferric fluoride is converted into ferric oxide." It is therefore not possible to get quantitative oxygen yields by this method from compounds containing iron. This was not recognized by Baertschi and Silverman, but Silverman does report that the yields of oxygen were consistently lower in basic rocks (FeO + Fe_2O_3 about 10 - 12%) than in acid rocks (FeO + Fe_2O_3 about 3%). It is not yet known whether this loss of oxygen involves any isotopic fractionation.

3) Potassium Bromide Furnace

At room temperature a large amount of fluorine passes through the potassium bromide tube unreacted. At high temperature the sample oxygen will react with the metal of the tube. A temperature of about 200°C (that used by Baertschi and Silverman) appears to be the best.

4) Contamination

In the preliminary experiments which have been carried out, it has not been possible to get consistent yields of oxygen from the samples. Even using quartz, where the absence of a solid residue indicates that all oxygen has been liberated, the measured yields range from 25% to 200% of the stoichiometric amount. Clearly there are problems both of removal of the sample gas and addition of contamination. The isotopic analyses of the gas collected in fifty experiments gives no apparent information concerning the nature or location of the contamination. Work with the fluorine apparatus was suspended at this point.

B. Carbon Reduction:

(a) Principle

All solid oxides can be reduced by carbon in a vacuum system at sufficiently high temperature. The reaction products are metal or metal carbide, and carbon monoxide or carbon dioxide, depending on the temperature of the reaction (see discussion of carbon monoxide - carbon dioxide equilibria below). Thermodynamic data for the reduction of a few oxides are shown below. Thermochemical data are from K. K. Kelley(36), and Rossini et al(37), and the free energy change has been calculated as a function of temperature as described by Lewis and Randall.(38) The thermochemical data are generally valid up to 1000°K, but the equations have also been used to estimate ΔF at 2000°K.

(1) $SiO_2 + 3C \longrightarrow SiC + 2CO$

$$\Delta F_T = 128{,}360 + 1.01T\ln T + 3.15 \times 10^{-3}T^2 - 2.86 \times 10^{5}T^{-1} - 88.0T$$

T(°K)	ΔF(cal)	ΔH(cal)	ΔS(e.u)	Pco(atm)
298	+100,680	+125,860	+80.61	10^{-37}
1000	+ 50,180	+123,630	+73.5	3×10^{-6}
2000	- 19,840	+112,450	+66.1	46

(2) $MgO + C \longrightarrow Mg + CO$

$$\Delta F_T = 118{,}730 + 1.35T\ln T + 0.14 \times 10^{-3}T^2 - 1.35 \times 10^{5}T^{-1} - 57.9T$$

T	ΔF	ΔH	ΔS	Pco
298	+103,320	+117,420	+47.3	10^{-75}
1000	+ 70,150	+116,970	+46.8	10^{-15}
2000	+ 23,840	+115,340	+45.7	2.5×10^{-3}

(3) $Al_2O_3 + 3C \longrightarrow 2Al + 3CO$

$$\Delta F_T = 327{,}390 + 9.48T\ln T - 1.37 \times 10^{-3}T^2 - 7.22 \times 10^{5}T^{-1} - 209.9T$$

T	ΔF	ΔH	ΔS	Pco
298	+278,340	+319,830	+132.4	10^{-68}
1000	+180,700	+318,560	+137.9	10^{-13}
2000	+ 45,750	+323,550	+138.9	2.2×10^{-2}

(4) $Fe_3O_4 + 4C \longrightarrow 3Fe + 4CO$

$$F_T = 174{,}370 + 19.05T\ln T - 1.14 \times 10^{-3}T^2 - 9.63 \times 10^{5}T^{-1} - 307.4T$$

T	ΔF	ΔH	ΔS	Pco
298	+111,160	+161,320	+168.5	10^{-20}
1000	- 4,430	+154,530	+159.0	1.7

It is seen that temperatures of the order of 2000°K are necessary for reduction of silica and silicates.

In the work of Schwander high temperatures were obtained by use of a carbon resistance furnace. This presents the problem of the thorough outgassing of a large piece of carbon which must be exposed to air between runs.

In the present work, the sample was placed in a graphite crucible heated by a radio-frequency induction furnace. By this method, only the crucible itself (about 2 grams of carbon) is heated, and heating of the glass vessel surrounding it can be kept to a minimum. It is important that the gas sample not come in contact with any hot oxygen-containing compound or any reducing compound. In the former case, isotopic exchange is possible, resulting in an improper value of the O^{18}/O^{16} ratio in the gas. In the latter case, some of the gas may react with the reducing agent, giving uncontrollable isotope fractionation.

For most compounds of geological interest, high temperatures are required, and the gaseous product is almost pure carbon monoxide. In Schwander's work, this gas was analyzed in the mass spectrometer. In the present work, it was considered desirable to convert the carbon monoxide to carbon dioxide for reasons discussed above. Adams(32) oxidized carbon monoxide to carbon dioxide for isotopic analysis by passing it over hot copper oxide. Besides diluting the sample oxygen, this process is almost certain to give incorrect results because of exchange with the copper oxide.(34)

Carbon monoxide at low temperatures is unstable with respect to decomposition to carbon and carbon dioxide:

$$2CO \rightarrow C + CO_2$$

$$\Delta F_T = -42{,}150 - 1.07T\ln T - 0.66 \times 10^{-3}T^2 - 11.76 \times 10^5T^{-1} + 66.8T$$

$$\Delta F_{298} = -28{,}640 \text{ cal.}$$

$$\Delta F_{1000} = +15{,}400 \text{ cal.}$$

The reaction is negligibly slow at room temperature, but does proceed at temperatures of about 400°C in the presence of a catalyst.

(b) Apparatus

1) Induction Heater

The radio-frequency induction heater used in this work has a maximum power output of 10,000 watts (manufactured by Allis-Chalmers, Inc., type EI-10-A). The work coil used with the heater consists of thirteen turns of 3/8 in. O.D. copper tubing, covered with 3/8 in. I.D. Tygon tubing for electrical insulation, and wrapped in two layers. Inside diameter of the coil is 2 in., height is $3\frac{1}{2}$ in.

2) Vacuum Furnace

The assembly of the vacuum furnace is shown in Fig. 2. At the center of the work coil is the reaction crucible, machined from spectrographically pure graphite bar stock. Its design is intended to make the temperature of the walls, roof and floor of the crucible as uniform as possible.

Surrounding the crucible is a cylinder of .010 in. sheet platinum, 3 cm. in diameter, 4.5 cm. high, to shield the glass jacket from the heat radiated from the crucible. The cylinder is made by rolling a piece of flat sheet into a cylinder so that the ends overlap but do not touch. There is therefore no electrical circuit in the shield in the plane of the work coil. If such a circuit existed, the shield would be heated in the radio-frequency field.

The crucible and shield are supported on 1/8 in. graphite rods which stand on the bottom of the glass reaction vessel. The main body

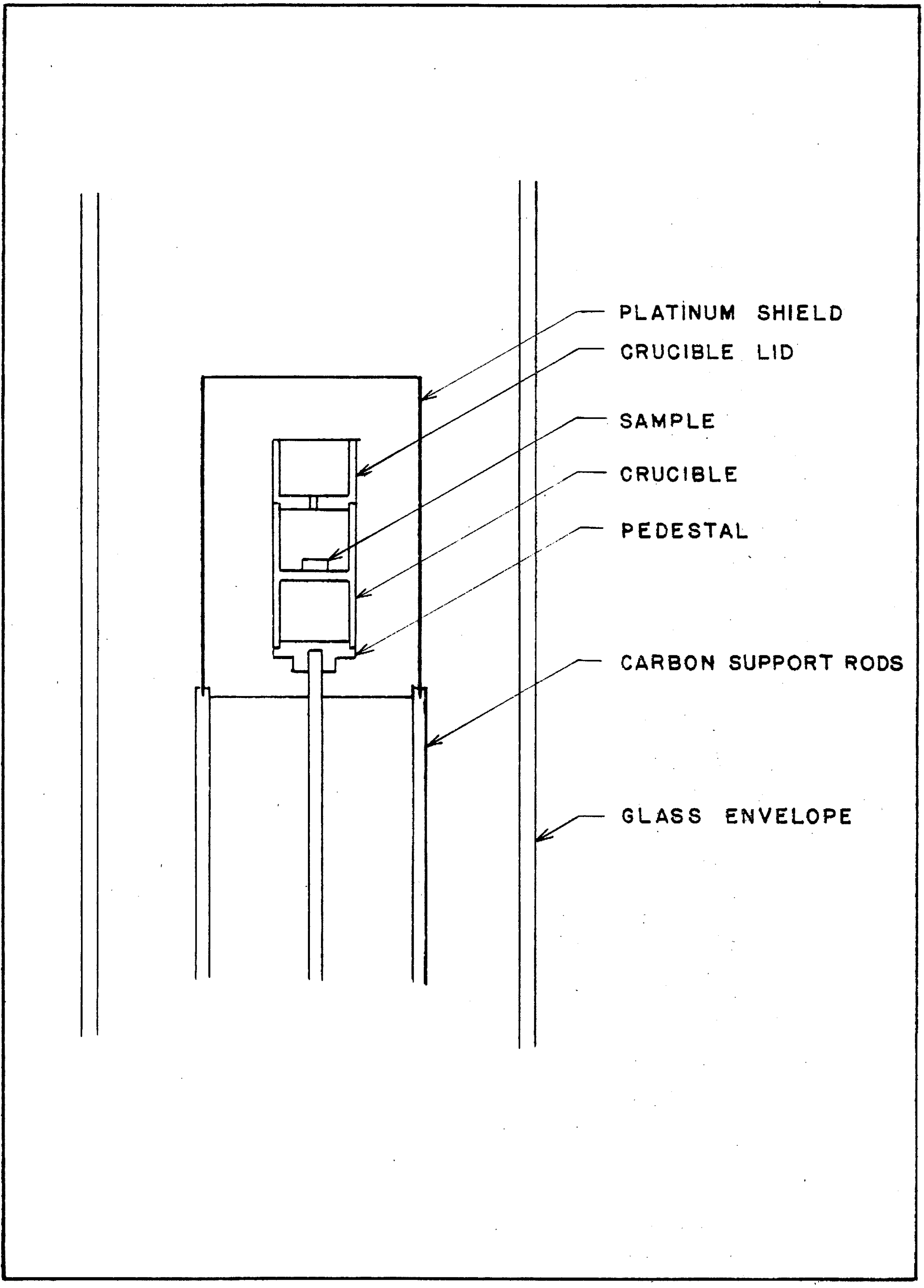


Fig. 2. Reaction Chamber.

of the reaction vessel is of 40 mm. Pyrex tubing, drawn down at the top to connect with the 12 mm. tubing of the vacuum line. Below the furnace coil, the bottom of the reaction vessel is joined to the main cylinder by a 65/40 hemispherical ground joint.

The vacuum system proper (Fig. 3) is of conventional construction, using a two stage mercury diffusion pump backed by a Welch Duo-Seal mechanical pump. Non-condensible gases are pumped by means of an automatic Toepler pump.

The furnace for conversion of carbon monoxide to carbon dioxide is a horizontal nickel tube, 3/4 in. I.D. heated in a tube furnace (Fig. 4). The tube is connected to the glass line through Kovar metal and graded glass seals. The powdered nickel catalyst is held in a cylindrical container made of nichrome sheet. It is about an inch long, diameter big enough to fit snugly into the nickel tube. Capacity of the cylinder is about two grams of nickel.

(c) Analytical Procedure

1) Preparation of Carbon Monoxide

The pure mineral ground to pass 200 mesh is mixed with finely powdered spectroscopically pure graphite, with an excess of the latter of about ten times over that required to reduce the mineral. The mixture is then formed into pellets in a $\frac{1}{4}$ in. diameter briquetting press. The purpose of this operation is to bring the two reactants into close contact, for the reductions generally take place between the two solids (i.e., below the melting point of the mineral). A pellet is then weighed into the reaction crucible. An average sample contains about 10 milligrams of mineral, and will react to give about 6 c.c. (NTP) of carbon monoxide.

The crucible and shield are then mounted in the reaction vessel

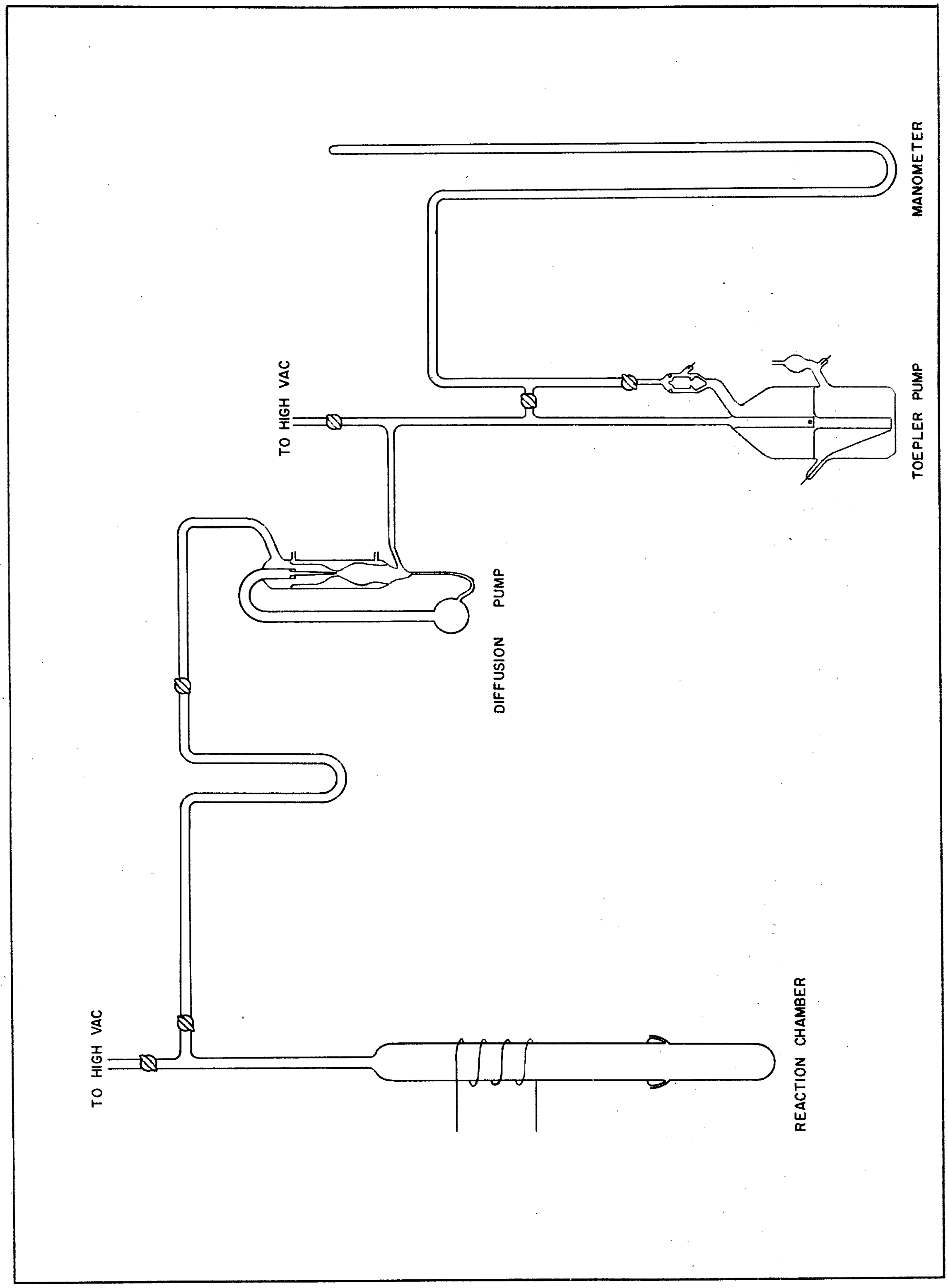


Fig. 3. Carbon Reduction System.

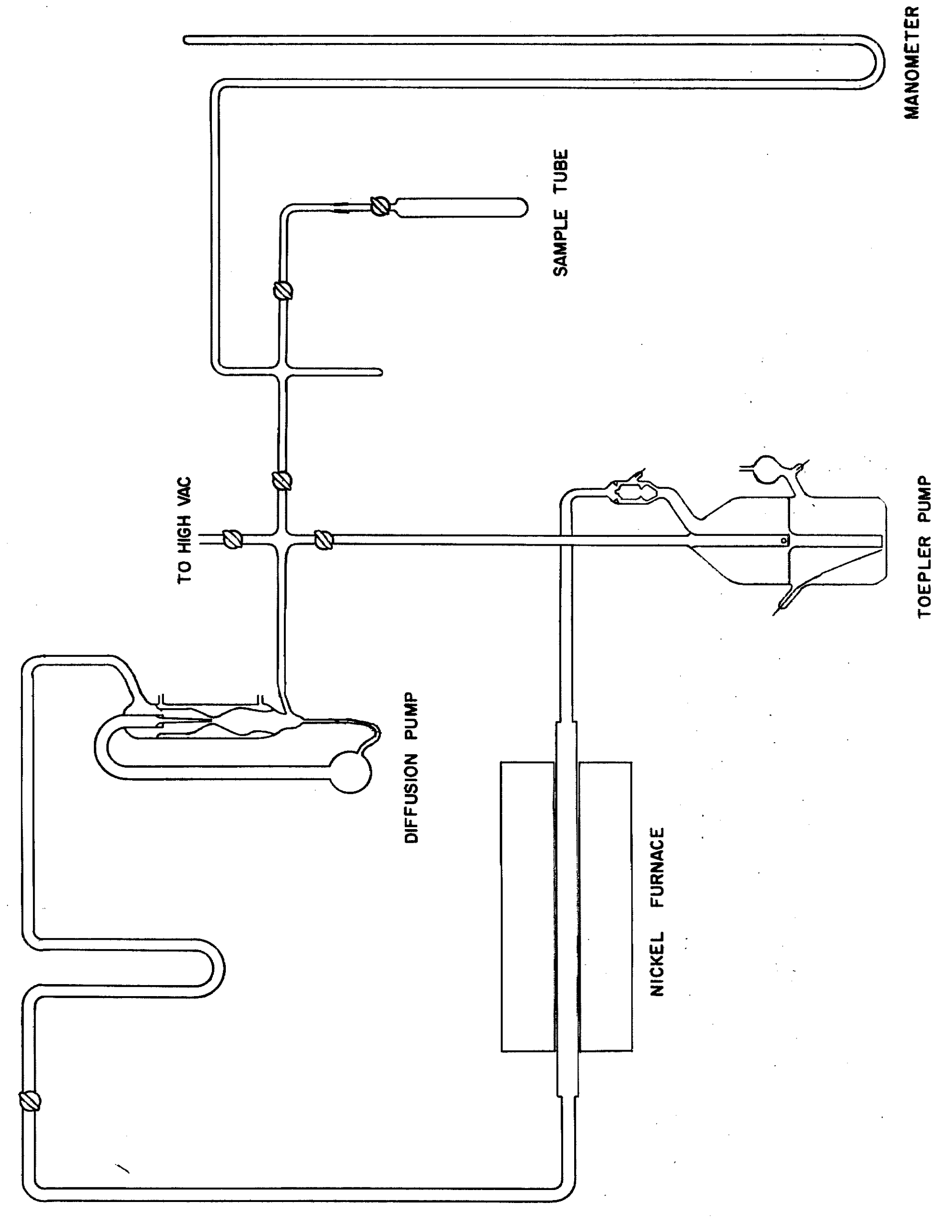


Fig. 4. System for Decomposition of Carbon Monoxide.

and the system is evacuated. Cooling water is run over the outside of the glass jacket. The induction furnace is then turned on and the sample and crucible are outgassed for one hour. The temperature of outgassing is about 200° below the temperature at which the particular mineral begins to be reduced (see results of experiments on page 34). An outgassing temperature of 1250°C is used for quartz, and 1000°C for magnetite.

After the outgassing period is over, the connection to the vacuum pumps is closed off, and the temperature of the crucible is raised until a rapid evolution of gas is observed from the thermocouple vacuum gauge. The maximum pressure of carbon monoxide is about 1 or 2 mm. of mercury. The reaction chamber is pumped on continuously by a mercury diffusion pump, backed up by an automatic Toepler pump. Between the reaction chamber and the pumps is a trap cooled in dry ice, to remove any water present. The reaction is continued until the gas evolution ceases, and the temperature is raised to insure completion. In a typical quartz reduction, gas evolution is strong at about 1550°, and the temperature is raised to 1800° at the end of the reaction. The reduction takes ten or fifteen minutes.

The carbon monoxide is pumped by the Toepler pump into a calibrated mercury manometer, where the volume of gas is measured in order to determine the reaction yield.

2) Conversion of Carbon Monoxide to Carbon Dioxide

The carbon monoxide sample is admitted to the nickel furnace. The volume of the system of furnace, traps, pumps, tubing is such that the initial gas pressure is about 1 cm. The gas is cycled through the furnace, pumped by the same diffusion pump and Toepler pump used previously. As the gas leaves the furnace, it passes through a trap cooled in liquid nitrogen, which freezes out the carbon dioxide formed in the furnace. The gas is cycled until the carbon monoxide pressure falls to .01 mm. or less. The carbon dioxide is then transferred to a calibrated manometer where its volume is determined, then to a sample tube which is taken to the mass spectrometer. The nickel catalyst is reused until it becomes too inefficient due to the carbon deposited on its surface. The amount of carbon monoxide which can be converted with one two-gram batch of catalyst varies from batch to batch from 60 c.c. to 300 c.c., the latter corresponding to deposition of about 150 milligrams of carbon.

(d) Development of Carbon Reduction Method

1) Design of Reaction Crucible and Chamber

In order to reduce silica with carbon, temperatures up to 1800°C are required. For a crucible with 8 sq. cm. surface area, this corresponds to a power loss by radiation of about one kilowatt. The induction furnace has a rated output of 10 kilowatts, but restrictions on the design make efficient transmission of the power difficult. The work coil must be outside the glass reaction vessel, which in turn must be sufficiently far from the hot crucible that the glass itself may be kept cool. This then puts a gap of at least two centimeters between the coil and the crucible. This reduces the inductive coupling between the coil and the crucible to such an extent that it was found difficult to design a crucible which would heat to high enough temperatures. The best design found, after eight attempts (using four different work coils), reached a maximum temperature of 2000°C. Under these conditions, the <u>input</u> power to the induction heater is fifteen kilowatts. Highest temperatures are attained with crucibles with a wall thickness of about one millimeter.

When an irregular shape is heated in an induction furnace, its temperature will not be uniform. The energy received by each part depends on its distance from the R-F coil, whereas the energy it radiates does not. If the thermal conductivity is low enough, as it is in graphite, this results in temperature differences that may amount to one or two hundred degrees. This is not desirable since some of the reactants in the crucible may distill to the cooler parts and cease to react. The crucible is therefore designed to give as uniform a temperature as possible.

An important device which increases the temperature of the crucible, and keeps the glass cool, is the radiation shield. For the early reactions this was made of tantalum (the anode from an 8020 vacuum tube). Later this was replaced by a shield of sheet platinum. The sheet must be thick enough for mechanical strength, but not so thick that it is heated by the R-F field. Both these metals are subject to some discoloration and etching by carbon monoxide, iron or some other product of the reactions. Any effect this may have on the isotopic composition of the carbon monoxide has not been detected. Samples analyzed with (a) the tantalum shield, (b) the platinum shield, or (c) no shield agree within the experimental error of about 0.2‰.

2) Reactions of Silicates

Preliminary experiments with the carbon reduction method were made using quartz, simplest mineral of the silicate type. The reaction:

$$SiO_2 + 3C \longrightarrow SiC + 2CO$$

is found to proceed with yields of carbon monoxide which range from 85 - 95% of the stoichiometric quantity. The solid remaining after reaction has been X-rayed, and lines of graphite and silicon carbide are the only lines observed. Examples of the other major rock-forming minerals were analyzed by the same procedure.

Yields and reaction products from various minerals are shown in Table IV.

Table IV

Yields and Reaction Products from Various Minerals

Mineral	Formula	CO yield %	Solid products (X-ray)
Quartz	SiO_2	85-95	SiC
Feldspars	$KAlSi_3O_8$	75-80	SiC
	$NaAlSi_3O_8$	70-75	SiC
Olivine	Mg_2SiO_4	50	SiC
Pyroxenes	$MgSiO_3$	65	SiC
	$CaMg(SiO_3)_2$	60	SiC
Hornblende	$Ca_2(Mg,Fe,Al)_5(SiAl)_8O_{22}(OH)_2$	70	SiC
Biotite	$K(Mg,Fe,Al)_3(Si,Al)_4O_{10}(OH)_2$	75	SiC
Periclase	MgO	30	-
Magnetite	Fe_3O_4	100	Fe
Zircon	$ZrSiO_4$	90	SiC,ZrC

In all cases of reduction of compounds containing alkali metals, alkaline earths, aluminum and zinc, no compounds of these elements have been detected by X-ray diffraction in the solid residue after reaction. These elements do not have carbides stable at the reaction temperature. Furthermore, the metals have large vapor pressures at this temperature. The reduced metals distill from the crucible forming a metallic mirror on the glass vessel which is observed early in the reaction. This mirror of active metal then acts as a getter, reacting with the carbon monoxide to give the oxides; the coating on the glass becomes a dull grey. This reaction accounts for the reduction of carbon monoxide yields, which correspond closely to an overall reaction:

$$MSiO_3 + 3C \longrightarrow MO + SiC + 2CO.$$

If there is any isotopic fractionation in the process, the gas analyzed will not be representative of the oxygen in the mineral. Experiments described below indicate that such a fractionation does occur, making the carbon reduction method in this form unusable for all compounds of the above-mentioned elements.

3) Conversion of Carbon Monoxide to Carbon Dioxide

The decomposition of carbon monoxide to give carbon dioxide and carbon is the simplest part of the gas sample preparation. A standard procedure for this reaction is to pass the gas over a catalyst of nickel or iron at a temperature low enough that the reaction is thermodynamically favorable, but high enough that the reaction rate is reasonably fast. In using this technique in oxygen isotope work, care must be taken that no contamination is introduced by the catalyst, either from an oxide coating on the metal, or from adsorbed gas from a previous sample.

The first material used was pure nickel sponge (Johnson, Mathey and Co.), which was found to be inadequate in increasing the reaction rate, probably due to too small a surface. Then nickel was prepared by ignition of nickel nitrate ($Ni(NO_3)_2\ 6H_2O$) at 1000°C, followed by hydrogen reduction of the oxide. A catalyst prepared in this way contaminates the carbon dioxide with small amounts of nitrogen dioxide (NO_2), which has a molecular weight of 46, the same as $C^{12}O^{16}O^{18}$, and is, therefore, a very serious contaminant.

The most successful catalyst found is made by reduction of nickelous oxide (NiO) (Baker Chemical Co., green powder) in hydrogen at one atmosphere pressure and 300°C. Higher temperatures give a less active product.

In all cases, in opening the tube furnace to remove an old catalyst and charge a new one, a film of oxide is formed on the catalyst and furnace walls. The catalyst also contains adsorbed hydrogen, which must be removed. The tube furnace is evacuated and heated to 450°C overnight, then several cubic centimeters of carbon monoxide are cycled through the catalyst to reduce the oxide. The furnace is then ready for use.

The isotopic reproducibility of the reaction is indicated by the results in Table V. A group of sample tubes were filled simultaneously with carbon monoxide prepared by the action of concentrated sulphuric acid on solid sodium formate in a vacuum system. Then each sample was converted to carbon dioxide and mass analyzed.

Table V

Isotopic Reproducibility in Decomposition of Carbon Monoxide

Sample #	δ ‰
1	+12.7
2	12.5
3	12.7
4	12.7
5	12.5
6	12.3
Av.	12.6 ± 0.1‰

4) Reproducibility under Fixed Conditions

Quartz samples obtained from Dr. S. R. Silverman were analyzed several times each to determine the reporducibility of the overall analytical method. The results are assembled in Table VI.

Table VI

Isotopic Reproducibility of Analytical Method

Sample	Run #	Date	δ‰
Potsdam sandstone	162	5/17/54	15.6
	163	5/17/54	15.8
	172	5/21/54	15.7
	173	5/21/54	15.5
	174	5/21/54	15.4
	175	5/21/54	16.0
	176	5/21/54	15.3
	211	6/11/54	16.1
	351	11/11/54	15.6
	475	1/10/55	15.7
	476	1/10/55	15.1
	514	1/28/55	15.6
	535	2/12/55	15.5
			15.6 ± 0.2‰
St. Peter sandstone	181	5/24/54	11.0
	182	5/24/54	11.4
	183	5/24/54	11.0
	184	5/25/54	11.1
	349	11/11/54	11.2
	350	11/11/54	11.0
			+11.1 ± 0.1‰
Randville pegmatite quartz	177	5/22/54	9.6
	178	5/22/54	10.0
	179	5/22/54	10.4
	180	5/22/54	9.7
			+ 9.9 ± 0.3‰

The isotopic reproducibility on magnetite has not been tested so thoroughly. One of the magnetite samples has been analyzed four times, the rest in duplicate (Table VII).

Table VII

Isotopic Reproducibility for Magnetite

Sample	Run #	Date	δ ‰
Mt. Everts magnetite	335	10/28/54	0.5
	338	10/29/54	0.7
	392	11/25/54	1.1
	453	12/27/54	0.2
			+0.6 ± 0.3‰

Experiments were done to see if there was any "memory" effect, that is, if analysis of one sample contaminated the apparatus in any way, so as to give an incorrect analysis of the following samples. Table VIII shows the results of several analyses of the Potsdam sandstone, with the analysis of the previous sample for comparison. There is no evidence of a significant "memory" effect.

Table VIII

Test for "Memory" Effect on Isotope Analysis

Run #	Sample	δ ‰	Run #	Potsdam sandstone
122	chert	+27.7	123	+15.9
131	chert	+28.1	132	+15.5
210	diatomite	+36.8	211	+16.1
350	sandstone	+11.0	351	+15.6
474	quartz	+15.0	475	+15.7
513	magnetite	+ 2.9	514	+15.6
534	quartz	+23.6	535	+15.5
				15.5 ± 0.2‰

5) Outgassing of Crucible and Sample

Removal of adsorbed gas from the graphite crucible and powdered graphite in the sample pellet was found to be a critical step. If the crucible is not preheated before the reaction is started, a quantity of gas is formed several times the stoichiometric quantity from the oxide. Experiments conducted with quartz show that, even if the outgassing temperature is so high that a large amount of the sample reacts and the gas is lost, the isotopic composition of the gas collected after outgassing is constant. The sample was the Potsdam sandstone (Table IX).

Table IX

Effect of Outgassing Temperature on Isotope Analysis

Run #	Outgas Temp. °C.	Outgas Time (min.)	CO collected after outgas % of stoichiometric	δ ‰
154	1150	45	87	15.9
155	1150	60	90	15.7
160	1200	60	91	15.5
162	1250	60	83	15.6
163	1250	60	85	15.8
164	1250 1370	20 10	84	16.4
165	1250 1370	20 10	82	15.8
166	1450	15	75	16.7
167	1200 1500	30 15	54	16.7
168	1200 1520	30 10	44	16.1
169	1200 1520	30 10	64	15.6

Run #	Outgas Temp. °C.	Outgas Time (min.)	CO collected after outgas % of stoichiometric	δ ‰
170	1200 1520	30 5	55	15.8
171	1200 1520	30 15	53	15.2

At high outgassing temperatures, the average analysis is unchanged, but the spread is greater. Standard procedure for quartz samples is, therefore, a one hour preheating at 1250°C, with the gas being pumped away. This results in some loss of sample gas, giving yields which range from 78 - 93%, but from the above data it may be concluded that no appreciable fractionation takes place in this process.

In using the carbon reduction method for iron oxides, the details of the procedure must be modified. Iron oxides are reduced rapidly at 1300°C, and therefore a lower outgassing temperature (1000°C) is used. This is probably the reason for a somewhat poorer reproducibility in the isotopic analyses of iron oxide samples.

6) Comparison with Silverman's Results

There is available no direct measurement which gives the difference in isotopic composition between Hawaiian sea water (Silverman's standard), and the carbonate standard used in these laboratories and in all the other work done at the University of Chicago. Determinations made routinely in these laboratories of variations in the isotopic composition of oxygen in waters do not help in this problem, since the procedure involves the mass analysis of carbon dioxide which is equilibrated with the water with a constant but quite large isotope fractionation.

It was found that the internal variations among the quartz samples analyzed by the carbon reduction method agreed with the data of Silverman's fluorine method, and the two scales were therefore tied together in this way (Table X).

Table X

Comparison of Quartz Analyses with Silverman's Results

Sample	Silverman's δ	This work δ
Postdam sandstone	15.5	15.6
St. Peter sandstone	10.9	11.1
Randville pegmatite quartz	10.3	9.9

This establishes the value of δ for Hawaiian ocean water relative to our carbonate standard. The isotopic composition of atmospheric oxygen has been measured by a method described briefly on page 16, and found to be +21.8‰ relative to ocean water. Epstein and Mayeda(16) have analyzed water prepared by Dr. Malcolm Dole from atmospheric oxygen, and found it to be +22.1‰ relative to mean ocean water. This constitutes an independent check on the zero of our scale. Carbon dioxide in equilibrium with ocean water at 25°C has $\delta = +38.4$‰, in excellent agreement with the value of +39‰ calculated theoretically by Urey(1).

When samples other than quartz are analyzed, those containing the elements which result in loss of oxygen are not in agreement with Silverman's results. For the Randville pegmatite orthoclase, Silverman reports $\delta = +8.8 \pm 0.2$‰, whereas the carbon reduction method on the same sample gave $\delta = +12.0 \pm 0.1$ on three runs, with oxygen yields of about 73%. For Silverman's "garnet schist No. 19", the fluorine method gives $\delta = +12.7$, and the carbon method gives $\delta = +20.9$, with an oxygen yield estimated at 70%.

Clearly the removal of oxygen from the sample gas by reaction with metals on the walls of the reaction chamber is a process which involves considerable fractionation, with the lighter isotope preferentially removed. Under favorable circumstances the amount of fractionation can be reproduced for a given sample from one run to another, so that the isotopic reproducibility of the results is not an adequate test of their validity when the oxygen yields are low. It is not seen how the experimental procedure of Schwander(31) avoids this difficulty in any way, and it can be concluded that his results are probably all incorrect with the exception of the data on pure silica samples. Schwander made no attempt to correlate any of his results with the previously published work by Silverman, and has analyzed no samples in common with Silverman or with us, so the isotopic composition of his standard relative to others is not known.

C. Carbon Tetrachloride Reaction:

Another possible reaction is one of the type:

$$2MO + CCl_4 \longrightarrow 2MCl_2 + CO_2$$

The reaction is thermodynamically favorable at room temperature for oxides of the alkalies, alkaline earths, and silica, and since ΔS_{298} is positive, the values of ΔF become more negative at higher temperatures.

$$2MgO + CCl_4 \longrightarrow 2MgCl_2 + CO_2 \qquad \Delta F_{298} = -89,840 \text{ cal.}$$

$$2CaO + CCl_4 \longrightarrow 2CaCl_2 + CO_2 \qquad \Delta F_{298} = -48,800 \text{ cal.}$$

$$SiO_2 + CCl_4 \longrightarrow SiCl_4 + CO_2 \qquad \Delta F_{298} = -22,700 \text{ cal.}$$

The oxide sample was contained in an open crucible made of sheet platinum. The crucible was heated to about 700°C by means of the induction furnace, in an atmosphere of approximately 100 mm. pressure of carbon tetrachloride. After heating for half an hour, the gasses were pumped away, and the extent of reaction determined by the change in weight of the sample. No attempt was made to isolate the carbon dioxide produced. Since these experiments were conducted before there was a mass spectrometer in the laboratory, no isotopic analyses could be made.

The reaction with carbon tetrachloride was attempted with oxides of calcium, magnesium and silicon, with the following yields:

$MgO \longrightarrow MgCl_2$ 100%

$CaO \longrightarrow CaCl_2$ 85%

$SiO_2 \longrightarrow SiCl_4$ no detectable reaction

Since no reaction could be observed with silicon dioxide, this process was abandoned as a method for silicates (higher temperatures cannot be used because of pyrolysis of the carbon tetrachloride. However, this method may prove satisfactory for removal of oxygen from the oxides of some of the more active metals.

D. Isotopic Analysis of Carbonates

The procedure developed by McCrea(5) was used for preparation of carbon dioxide from carbonates. The sample is mixed in an evacuated tube with 100% phosphoric acid, liberating carbon dioxide which is mass analyzed. This process gives only two-thirds of the oxygen present, and causes a reproducible fractionation, the extent of which had not previously been measured. It is necessary therefore to extract oxygen from a carbonate by a method which removes all the oxygen and to compare this oxygen with that formed by acid extraction. It was hoped that this would be done by the action of fluorine on calcite, but this has not yet been successful. However, iron and manganese carbonates can be handled by the carbon reduction method, and one sample of rhodocrocite ($MnCO_3$) has been analyzed this way. The difference in δ for carbon dioxide prepared by the two methods was 10‰, with the O^{18}/O^{16} ratio greater in the acid-prepared carbon dioxide. This value has been used as the amount by which all carbonate analyses must be corrected in order that they be compared to the same zero as the quartz and magnetite analyses. It is not considered to be reliable to better than ±0.5‰.

EXPERIMENTAL RESULTS

Introduction:

There are several possible approaches in the investigation of isotopic fractionation among mineral phases in a rock. If a single mineral pair is chosen, the equilibrium isotopic fractionation can be determined as a function of temperature by appropriate laboratory experiments; then the analyses of natural samples of the same minerals can be interpreted on the basis of the experimentally determined temperature scale. Any approach which omits the study of equilibrium fractionation in the laboratory can yield only qualitative results. At this stage even qualitative results are very desirable if they show whether or not it is feasible to use oxygen isotope fractionation as a geological tool for processes taking place at high temperatures. Thus one could choose three minerals, A, B, and C, which occur together in many rocks formed under a large variety of conditions. Then comparison of the fractionation between A and B, B and C, C and A, would show whether the results were internally consistent, and in agreement with other geological evidence. The requirement of three such minerals which could be analyzed by the techniques available in this laboratory was too stringent and a variation of this attack was used. One pair of minerals was chosen, which were formed in the presence of a third phase, an aqueous solution which we are not able to sample. Isotope analyses of such samples will yield information if (a) the isotopic composition of the water in equilibrium with all the minerals is constant, and

(b) the amount of water is so great that its isotopic composition is not changed appreciably by exchange with the solid phases. Then the two pieces of experimental evidence for each rock, the isotopic compositions of the two minerals, should determine the two unknown quantities, the isotopic composition of the water, and the temperature of equilibration. In this work two mineral pairs of this nature were studied: (a) quartz and calcite, (b) quartz and magnetite. The choice was made for the following reasons:

(a) quartz, calcite and magnetite can be analyzed isotopically with a precision of 0.2‰ or better;

(b) these minerals are formed under a wide range of geological conditions and should, therefore, show a broad range in temperature of formation;

(c) there exists an isotopic fractionation among these minerals which is many times the error of analysis.

Selection of natural samples for this problem is an important and fairly difficult job. It is generally not easy to demonstrate from geological evidence that the two mineral phases were crystallized at equilibrium. Indeed, several samples have been analyzed in which it is obvious that the quartz and calcite have been formed in two distinct generations under different conditions.

Quartz and magnetite were analyzed isotopically by the carbon reduction method described earlier. Calcite and dolomite were analyzed by liberating carbon dioxide with 100% phosphoric acid as described by McCrea.(5)

Analytical Results

A. Quartz-calcite

All samples are described in the Appendix. The isotopic compositions of oxygen in quartz and calcite crystallized over a wide range of temperature are given in Table XI.

Table XI

Isotopic Analyses of Quart-Calcite Pairs from Aqueous Environments

Sample #	δ-Quartz	δ-Calcite
1	33.7	26.0
2	28.9	22.0
3	23.6	17.9
4	22.0	17.1
5	18.5	14.8
6	23.6	19.0
7	17.0	12.1
8	11.3	8.2
9	12.0	9.5

Consider the system $SiO_2 - H_2O$ with an excess of water such that isotopic exchange with silica does not change appreciably the O^{18}/O^{16} ratio in the water. Let the value of δ for the water be arbitrarily given the value zero. Then at infinite temperature quartz in equilibrium with this water also has $\delta_Q = 0$. At ordinary temperatures, the value of δ_Q is positive, becoming very large at very low temperatures. An entirely analgous situation exists in the system $CaCO_3 - H_2O$. Therefore in a system $SiO_2 - CaCO_3 - H_2O$, the value of δ for both SiO_2 and $CaCO_3$ will be large for low temperature and small for high temperature. Hence, a smooth curve relationship can be expected if δSiO_2 is plotted against $\delta CaCO_3$, providing that the two minerals are formed at equilibrium with a large amount of water of constant isotopic composition. Such a graph for the natural samples analyzed is shown in Fig. 5.

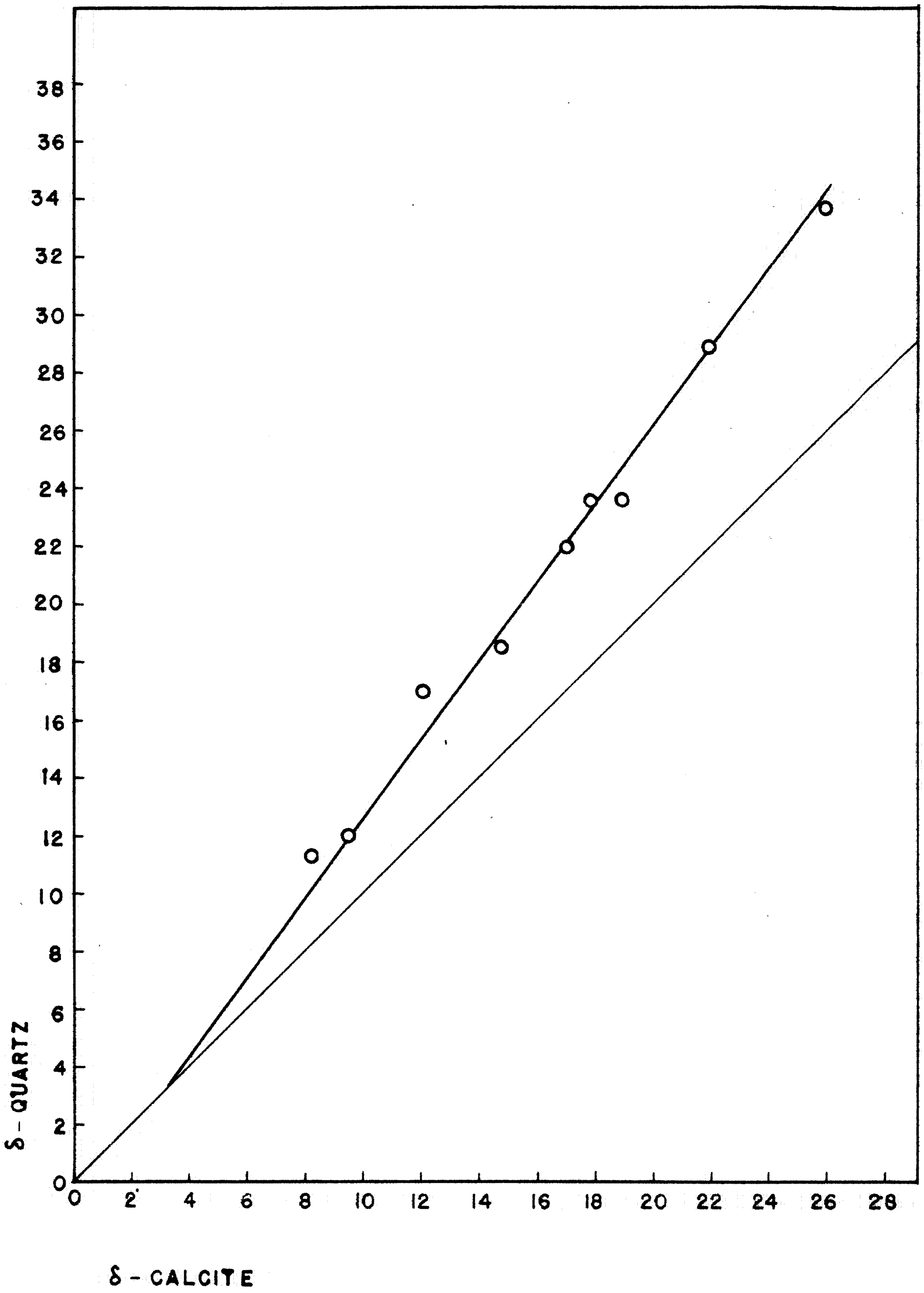


Fig. 5. Isotopic Analysis of Equilibrium Quartz-calcite Pairs.

From the graph several conclusions can be drawn:

(a) There exists a measurable isotopic fractionation between quartz and calcite, with O^{18} concentrated in the quartz phase.

(b) A line through the experimental points converges with the line of zero fractionation (δquartz = δcalcite) at the high temperature end, in accord with our expectations.

Several samples have been analyzed which do not fall near the curve of Fig. 5. The first group consists of minerals formed as coatings in open cavities. The isotopic analyses for these samples are:

Sample #	δ-Quartz	δ-Calcite
10	9.8	15.9
11	16.0	18.8
12	11.6	14.6
13	12.9	21.0

It is clear that in all these cases the quartz was crystallized at considerably higher temperature than the calcite. This sequence of crystallization is that deduced from studies of ore deposits.

Another pair of samples fall off the curve significantly:

(14) This sample is a calcite-dolomite-quartz marble formed by recrystallization of the chert limestone (2) under the influence of the intrusion of an igneous rock. (Leadville, Colorado).

(15) This is similar geologically to (13) but is from the Adirondack Mountains, New York.

The isotopic analyses are:

Sample #	δ-Quartz	δ-Calcite
14	22.7	20.5
15	25.7	22.5

The points for these two rocks fall off the curve in the direction of the line of zero fractionation. A plausible interpretation is that this represents a fairly high temperature equilibration in an environment without a large excess of water. Without the possibility of isotopic exchange with a large amount of water, the overall isotopic composition of the rock would not be as greatly changed as it would be if water were present at this temperature.

The last group of samples which do not fall on the curve of Fig. 5, contains samples in which the carbonate was dolomite ($CaMg(CO_3)_2$) rather than calcite.

The isotopic analyses are:

Sample #	δ-Quartz	δ-Dolomite
16	23.1	22.3 (Palos Verdes, Calif.)
17	22.7	22.2 (Leadville, Colo.)
18	17.0	16.0 (Leadville, Colo.)
19	23.9	21.5 (Leadville, Colo.)

These points also fall between the curve and the line of zero fractionation. It is apparent that the phases dolomite and calcite behave differently, either by having different fractionation relative to quartz, or by giving a fractionation different from calcite in the analytical procedure. The latter possibility can be checked in the laboratory.

Fig. 6 is a graph similar to Fig. 5, but containing the results of the analyses on all the samples 1 - 18.

B. An Isotopic Temperature Scale

In order to discuss the behaviour of an isotopic fractionation factor as a function of temperature, it is profitable to consider the

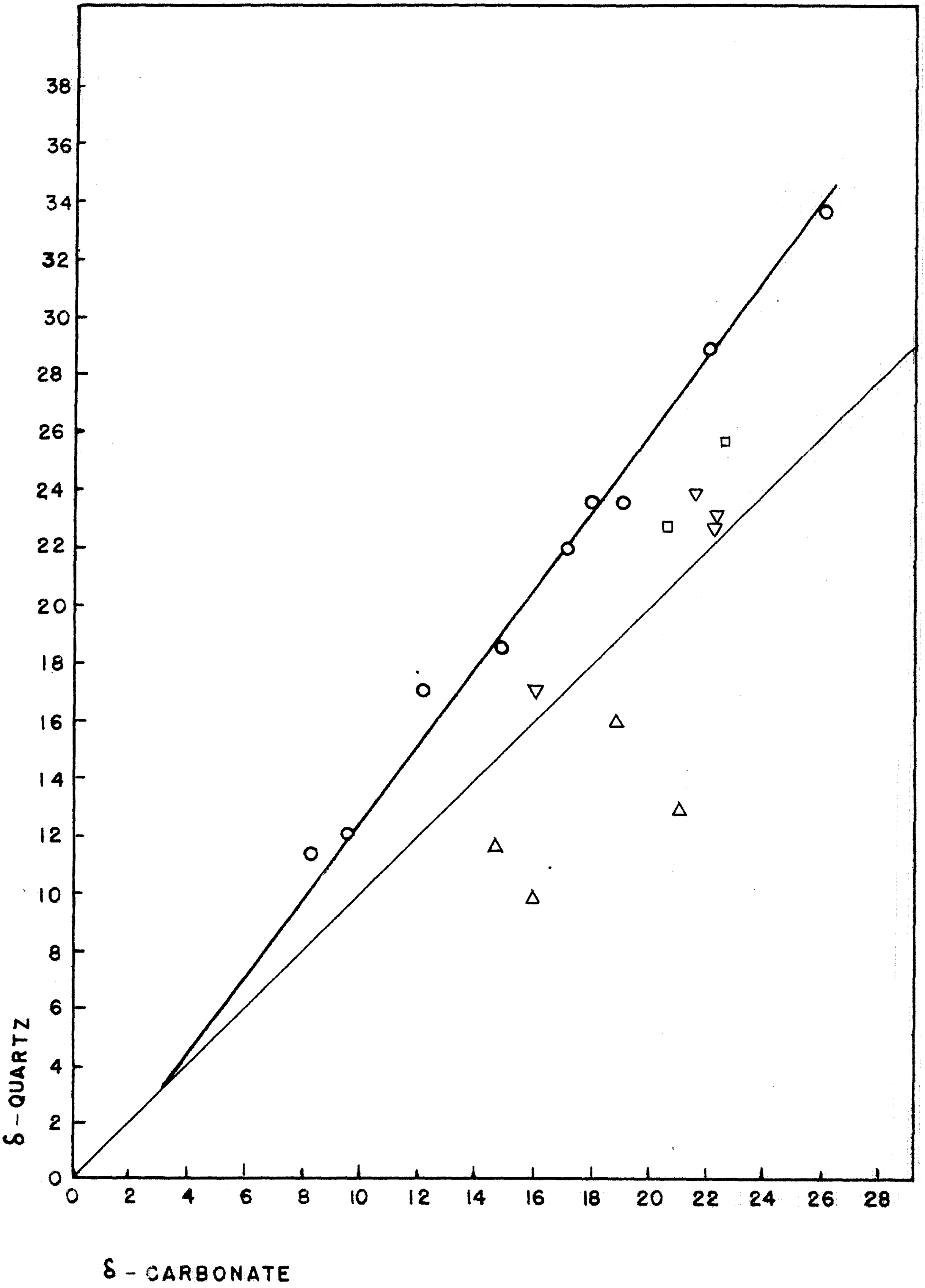


Fig. 6. Isotopic Analysis of All Quartz-carbonate Pairs.

theoretical calculations made by Urey(1), and by Bigeleisen, Mayer.(2) For exchange reactions involving gas molecules only, it is possible to calculate the equilibrium constants by use of the observed vibrational frequencies. In Urey's paper the results of such calculations for many reactions are tabulated.

According to the well known thermodynamic formula:

$$\frac{d\ln K}{d(\frac{1}{T})} = \frac{\Delta H}{R}$$

that is, lnK is directly proportional to $\frac{1}{T}$ only if ΔH is constant with temperature. For isotopic exchange reactions, H is not constant, but in general decreases at high temperatures. Graphs of lnK vs $\frac{1}{T}$ are shown in Fig. 7 for the following isotopic exchange reactions, using Urey's data.

$$(1)\ \tfrac{1}{2}SO_2{}^{16} + \tfrac{1}{2}ClO_2{}^{18} \rightleftharpoons \tfrac{1}{2}SO_2{}^{18} + \tfrac{1}{2}ClO_2{}^{16}$$

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

$$(3)\ \tfrac{1}{2}O_2{}^{18} + \tfrac{1}{2}CO_2{}^{16} \rightleftharpoons \tfrac{1}{2}O_2{}^{16} + \tfrac{1}{2}CO_2{}^{18}$$

$$(4)\ \tfrac{1}{2}O_2{}^{18} + CO^{16} \rightleftharpoons \tfrac{1}{2}O_2{}^{16} + CO^{18}$$

If these reactions are taken in pairs, and lnK for one reaction plotted against lnK for another, for points corresponding to equal values of T, curves such as those in Fig. 8 are obtained. Actually in Fig. 8, the values of (K-1) are plotted instead of lnK. These two quantities are proportional within a few percent for $1 < K < 1.04$, as it is for most reactions.

In the treatment of the experimental data, the assumption will be made that the curves analogous to those of Fig. 8 can be approximated adequately by straight lines through the origin. It will be of interest to extrapolate low temperature data to infinite temperature. From the curves of Fig. 8, it can be seen that a linear extrapolation can result

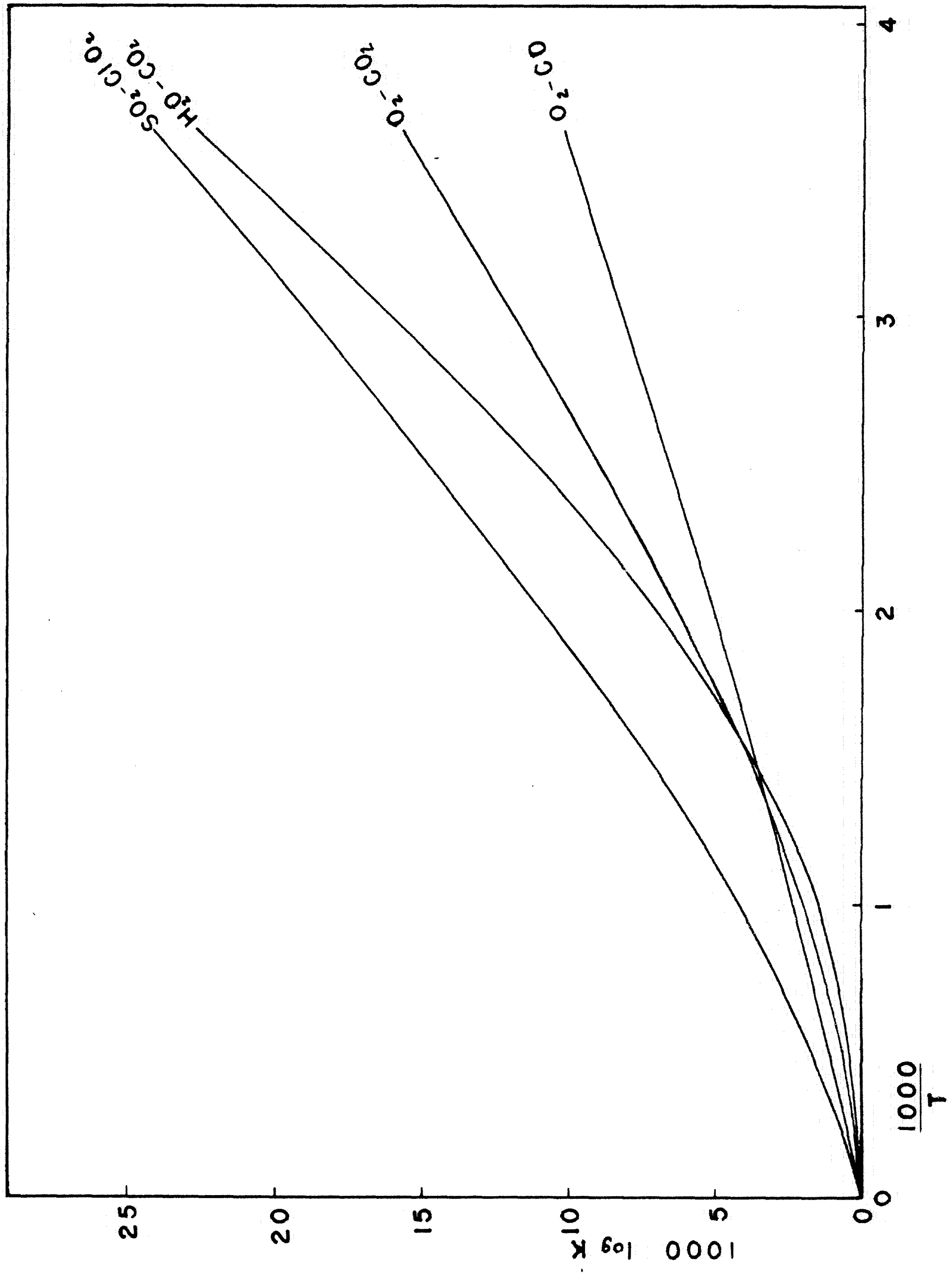


Fig. 7. Theoretical Isotope Fractionation as a Function of Temperature.

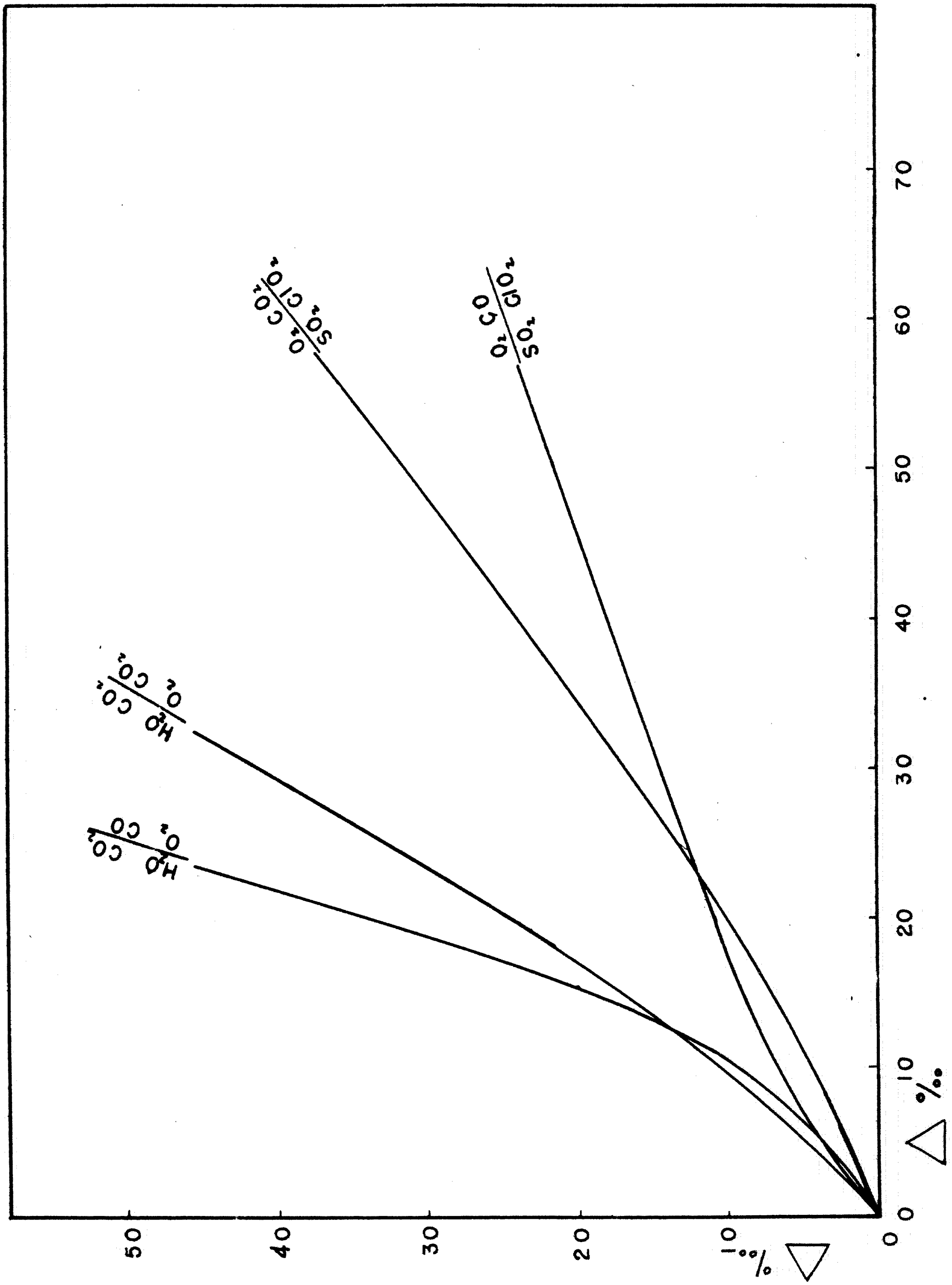


Fig. 8. Comparison of Theoretical Isotope Fractionations in Pairs.

in errors of as much as 8‰. Only the fact that independent sets of data lead to the same conclusion lends strength to the assumption which has been made.

(1) Quartz-Calcite

Observation of the data on quartz-calcite samples as given in Fig. 6, shows that the results of individual specimens may deviate from a simple relationship for three reasons: (1) lack of isotopic equilibrium between the mineral phases; (2) formation with a small amount of water; (3) influence of chemical differences as in case of dolomite. Samples for which the geological evidence indicates that one of these factors is important have been avoided. Samples #1-9 inclusive have been selected, since these are believed to consist of quartz and calcite crystallized together in equilibrium with a large quantity of water. It is assumed that the isotopic composition of the water for the various samples will not differ much from its average value δ_W. Let the isotopic composition of a quartz sample be δ_Q and the isotopic fractionation between quartz and water be $\Delta_{QW} = (\delta_Q - \delta_W)$. The experimentally determined numbers are δ_Q and δ_C; we can then plot $\delta_Q = (\Delta QW + \delta W)$ vs $\Delta QC = (\delta_Q - \delta_C)$. This is shown in Fig. 9. According to the previous discussion this curve is assumed to be linear, such that the intercept on the δ_Q axis is equal to δ_W. The equation for this line fitted by least squares is: $\delta_Q = 3.1 + 3.95\,\Delta_{QC}$ (1)

From this we may conclude that the average isotopic composition of the water with which the minerals were in equilibrium is +3.1‰ relative to mean ocean water. Deviation of individual points from the line are interpreted as due to variation in the isotopic composition of the water. The isotopic composition of the water associated with each individual specimen is 3.1‰ + the distance of the point above the line.

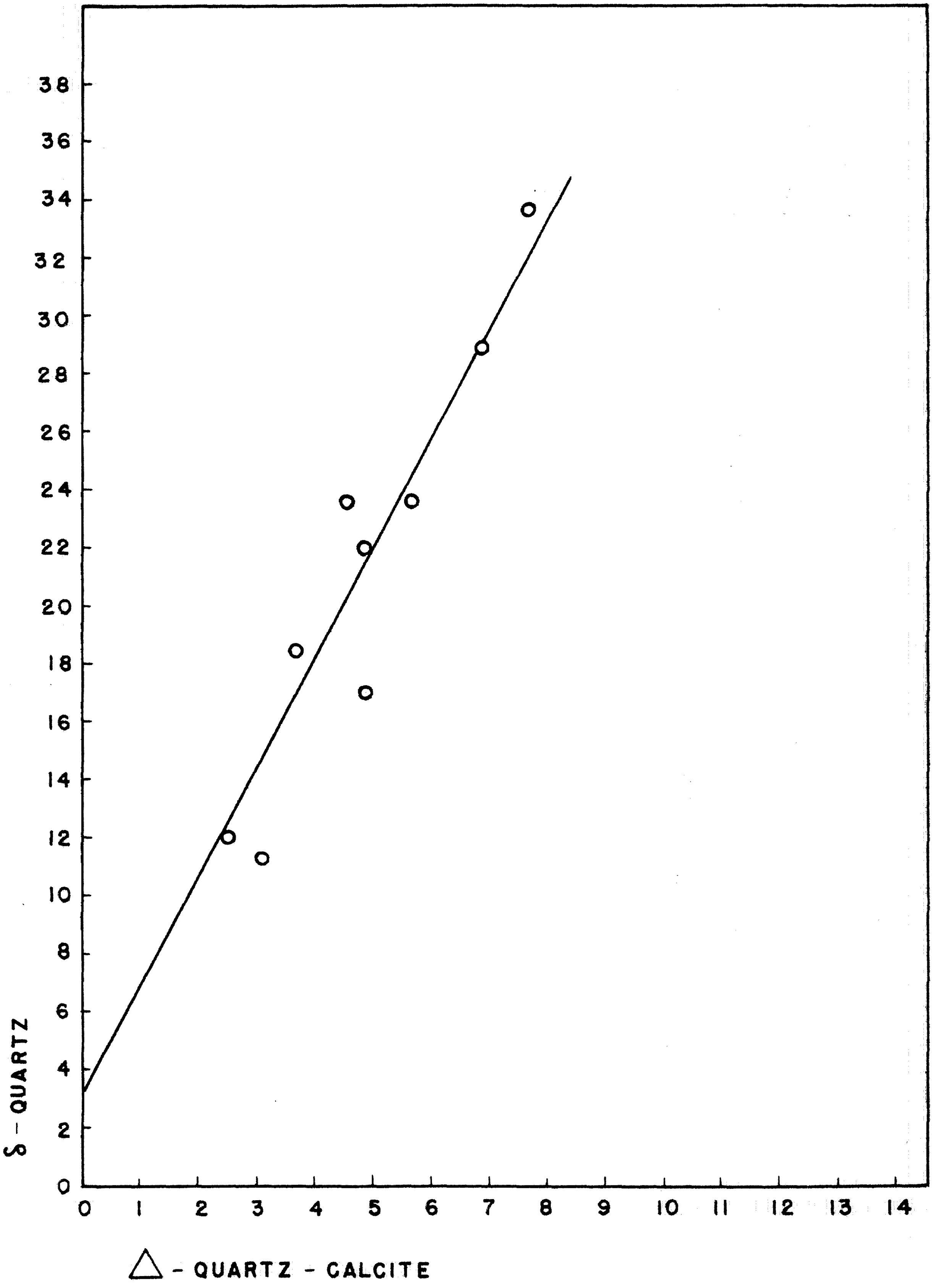


Fig. 9. Isotopic Composition of Quartz vs. Quartz-calcite Fractionation.

The range of isotopic composition for water associated with the samples analyzed is from -2‰ to +5‰. (Ocean water is 0‰ and most fresh water is about -7‰.)(16)

(2) Quartz-Magnetite

Magnetite (Fe_3O_4) is a mineral which can be analyzed using the carbon reduction technique. It also is found in nature in rocks of widely different types. It occurs commonly as an accessory mineral in igneous rocks and as a major or minor mineral in metamorphic and hydrothermal rocks. Both quartz and magnetite have been analyzed from rocks including granites, high- and low-temperature metamorphic rocks, and the results are given in Table XII.

Table XII

Results of Quartz-Magnetite Analyses

Sample	δ-Quartz	δ-Magnetite	Δ QM
20	16.5	2.0	14.5
21	16.2	2.0	14.2
22	10.4	-0.1	10.5
23	16.1	3.3	12.8
24	14.8	3.7	11.1
25	12.3	4.2	8.1
26	13.6	-0.1	13.7
27	12.6	0.8	11.8
28	12.0	2.9	9.1
29	11.9	3.3	8.6
30	10.5	1.7	8.8
31	10.4	2.2	8.2
32	9.6	1.7	7.9
33	8.0	0.6	7.4

In a manner similar to that used for quartz-calcite, δ_Q can be plotted against $\Delta_{QM} = \delta_Q - \delta_M$, and a straight line fitted by least squares. Its equation is:

$$\delta_Q = 3.1 + 0.89\,\Delta_{QM} \qquad (2)$$

This equation again gives $\delta_W = +3.1‰$, suggesting that the assumptions which have been made are valid.

From equation (1) we have: $\Delta_{QW} = 3.75\,\Delta QC$ (1A)

From equation (2) we have: $\Delta QW = 0.89\,\Delta QM$ (2A)

$$\Delta QM = 4.22\,\Delta QC. \qquad (3)$$

Using this scale factor, the data from both sets of samples can be plotted on the same graph, as shown in Fig. 10.

This relationship has the following consequences:

(a) Both the quartz-calcite and quartz-magnetite systems will make suitable geological thermometers. Before isotopic fractionation can be used for quantitative temperature determination, it is necessary to calibrate the scales by laboratory experiments (see Conclusions).

(b) All the samples analyzed appear to have been in equilibrium with water of average isotopic composition = +3.1‰, with the maximum deviation of about 5‰. The fact that the points for several magmatic rocks fall on the same curve as the metamorphic and hydrothermal rocks is interesting. It can be concluded that the water which was in isotopic equilibrium with the silicate melt as it crystallized had this same isotopic composition of +3‰.

(c) The isotopic fractionation between water and magnetite is small. Δ WM at room temperature $\backsim$3.5‰ (by extrapolation), and at several hundred degrees Δ WM $\backsim$0.8‰. The isotopic composition of the

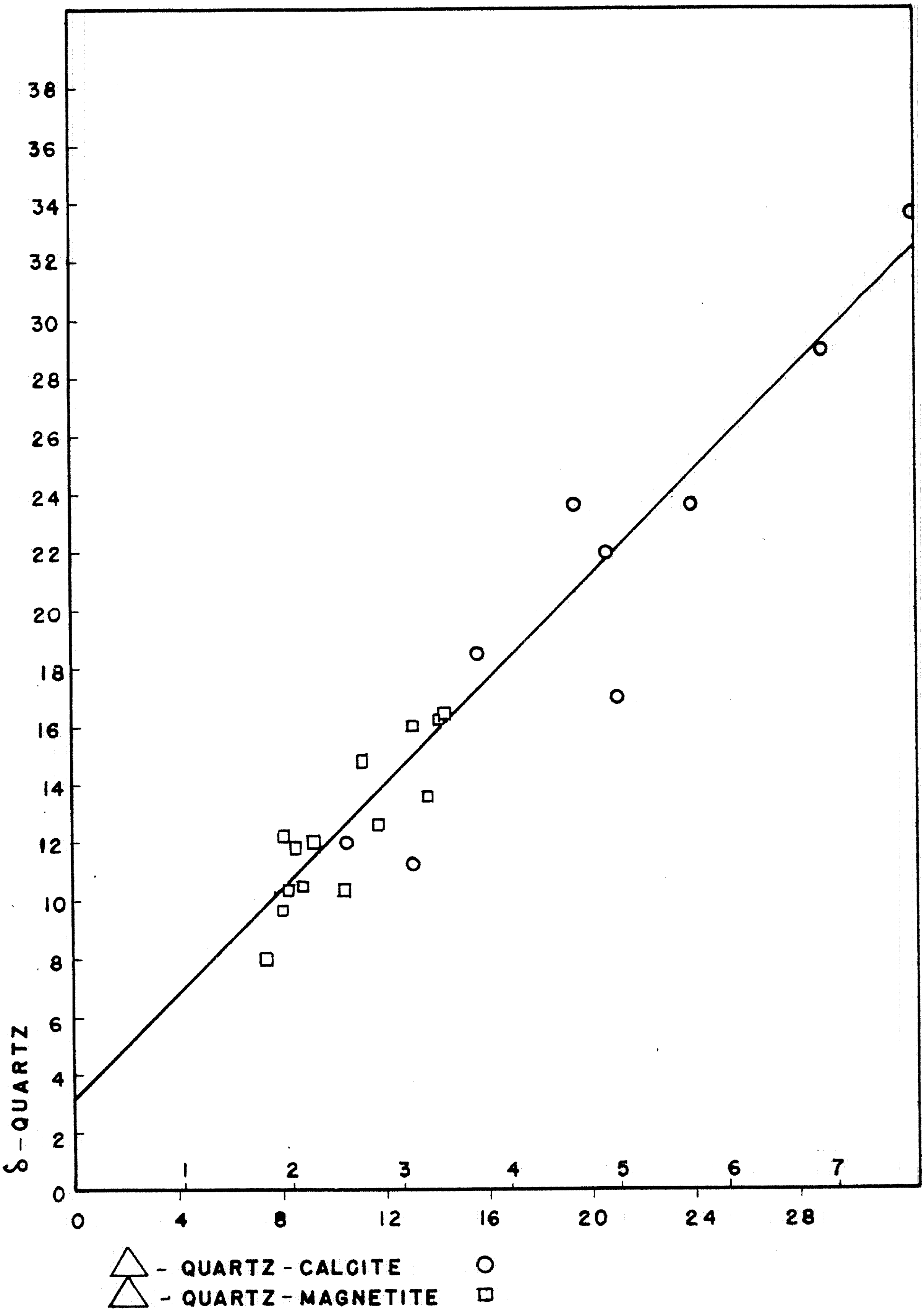


Fig. 10. Combination of Quartz-calcite and Quartz-magnetite Results.

magnetite in any sample then ought to be very nearly that of the water from which the sample was formed. This simple means of estimating the isotopic composition of hydrothermal water is of great geological importance.

Discussion of Geologically Related Samples

A. Leadville, Colorado

The Leadville limestone is an undeformed formation of Mississippian age (250 million years), which is 99% $CaCO_3$, with remarkably uniform concentrations of minor elements. Chert nodules (microcrystalline quartz) are present in some beds of the limestone. These nodules probably formed at the same time as, or shortly after, the formation of the limestone, and had opportunity to equilibrate with the same water from which the limestone was formed. There is also one bed, only a fraction of an inch thick, which contains detrital sand grains, that is, fragments of older quartz which were mechanically introduced into the limestone during its precipitation.

The limestone can be followed laterally into an area of extensive hydrothermal activity, where the calcite has been completely changed to dolomite, the chert has recrystallized, and veins containing lead, zinc, and silver ores have been formed.

Samples have been obtained of chert and carbonate from the unaltered limestone, and from a zone transitional into the mineralized area, as well as recrystallized quartz in the area of most extreme hydrothermal activity. The analytical results are shown in Table XIII.

Table XIII

	Unaltered - #2	Transition - #4	Mineralized - #34
SiO_2	28.9%	22.0	16.1
$CaCO_3$	22.0	17.1	13.5

The detrital sand bed was sampled in the unaltered limestone and in the mineralized region.

	Unaltered - #35	Mineralized - #18
Detrital SiO_2	+13.9	+17.0

The isotopic compositions of the unaltered chert and limestone are those expected for silica and calcium carbonate in equilibrium with water at low temperatures, and probably had isotopic compositions close to those of sample #1 when originally formed. No calcium carbonate in fossils as old as this has been found in which it can be shown that the isotopic composition has not changed since the shell was formed in the ocean. It is likely that the present O^{18}/O^{16} ratio results from exchange with ground water after burial of the sediments.

The value of $\delta = +13.9$ for the detrital quartz is typical of that for material of igneous or high temperature vein origin. In passing to the area of hydrothermal activity, both the detrital sand grains and the chert nodules have been recrystallized, and have undergone isotopic exchange, approaching the same isotopic composition from both sides, a satisfactory criterion that equilibrium has been reached.

The same Leadville limestone can be followed in another direction to a place where it has been completely recrystallized to form a coarse white marble by the high temperatures caused by the intrusion of a body of igneous rock. The isotopic analyses here are:

quartz	+22.7	
calcite	+20.5	
dolomite	+22.2	(samples #14 and 17).

The quartz-calcite fractionation is small, indicating a high temperature of formation, and the small change of the isotopic composition from the original suggests either that these samples were in equilibrium with a large amount of water of unusual isotopic composition ($\delta = +14.4$‰), or with a small amount of water of unknown isotopic composition. The second alternative appears more likely and an estimate of the relative amounts of water and rock can be made. On the graph of Fig. 10, sample #14 would fall above the line by 11.3‰; this, added to the average δ to which the line corresponds, 3.1‰, gives the isotopic composition of water in equilibrium with the rock at the end of the recrystallization. If the original water oxygen is assumed to have been +3.1‰, then it has changed its O^{18}/O^{16} ratio by 11.3‰ by exchanging with the oxygen of the carbonate and silica. The corresponding change of δ in the rocks is about 1.5‰ (from 22.0 to 20.5 for the calcite which constitutes most of the rock). Then the ratio of oxygen in the water to oxygen in the exchanged rocks is $1.5/11.3 = 0.13$, from which one can calculate that the weigh ratio of water to carbonate rock is about 0.07.

This calculation is intended only to illustrate the type of conclusion which can be drawn from the data, based on geologically reasonable assumptions. In the actual application of this approach to a problem much more extensive sampling and analysis would be necessary.

B. Iron Ores

In spite of their very great commercial importance, and the resulting interest of many geologists, relatively little is known about the method of formation of most iron ores. Probably the main reason for this is that the ores are usually very simple mineralogically and texturally, so that little information can be derived from petrographic or ordinary chemical methods. The minerals magnetite, hematite (Fe_2O_3), and quartz appear to form a stable assemblage over a vast range of temperature and composition. In this area, then, where quantitative data of any kind are so scarce, the study of oxygen isotope abundances may prove fruitful.

With the cooperation of Dr. H. L. James of the United States Geological Survey, a beginning has been made on the iron ore problem. In a preliminary survey, several samples typical of various kinds of ore have been analyzed. Some contained silica with the iron oxide, others did not. Results of the analyses are shown in Table XIV, with James' geological classification of the samples.

Table XIV

Isotopic Analyses of Iron Ores

Geological classification Sample No.	Magnetite	Hematite	Quartz	Calcite
Vug minerals (low temperature, probably meteoric waters)				
36	-	-2.6		
37	-7.8	-5.4		+20.2
Oxidized iron formation (oxidation of carbonate, presumably low temperature				
40		-4.0		
41		-2.2	+17.8	
Primary iron formation (in order of increasing metamorphic grade)				
20	+2.0		+16.5	
21	+2.0		+16.2	
38		+5.4		
39		+2.7	+12.4	
22	-0.1		+10.4	
Pyrometasomatic ores				
42	+3.4			
43	+3.5		+6.8	
Hydrothermal (high temperature)				
44	-2.4	-2.8		

If these data are considered to represent the result of equilibrium isotopic fractionation following these general rules: (1) Δ_{QM} is about 35‰ at room temperature, and decreases to 8‰ at several hundred degrees; (2) Δ_{WM} is of the order of one or two permil, and therefore δ_M is an approximation to the isotopic composition of water in equilibrium with the crystallizing minerals; (3) the isotopic fractionation between magnetite and hematite is probably very small, due to their chemical similarity -- then the agreement between the inferences from the isotope data and the conclusions based on geological evidence is remarkably good. In all cases but one (#43) the quartz-magnetite fractionation puts the samples in proper relative positions with respect to the geological ideas of the temperature of formation. It seems unreasonable that $\Delta_{QM} = 3.3$ for sample #43 could represent an equilibrium fractionation, and even here there is geological agreement: J. Hoover Mackin, U. S. Geological Survey, who collected the specimen, wrote as follows, "...the quartz may have formed somewhat later than the iron, and is not necessarily blood brother to the ore." The O^{18}/O^{16} ratio of the quartz of sample #43 is unusually low; no explanation is offered for this. The value of δ_W derived from the δM's, is about +3‰ for the metamorphic and metasomatic rocks, but is much lower for the samples formed from surface waters, which have an isotopic composition around -7‰.(16)

The quartz-hematite specimens were not used in construction of the graph of Fig. 10, but the data from samples 38, 39, 41 all fall close to the curve, indicating again that the magnetite-hematite fractionation is quite small.

C. Granitic Rocks

The controversy over the origin of granite has not been settled to anyone's satisfaction. In a large number of cases, it is not possible to prove, using existing techniques, whether a granitic rock formed by crystallization of a silicate melt, or by replacement of pre-existing rocks at a lower temperature, without the existence of a silicate melt. Perhaps isotope studies can add one more piece of experimental evidence which must be accounted for by any theory of the formation of granites. Quartz and magnetite have been analyzed from several granitic rocks, some of which are probably truly igneous, others of which are believed to be of metamorphic origin. The results are shown in Table XV.

Table XV

Quartz-Magnetite Analyses from Granitic Rocks

1. Igneous rocks.

Sample #	Rock type	% SiO_2 in rock	δQ	δM	ΔQM
33	Rhyolite	72	8.0	0.6	7.4
32	Granodiorite	73	9.6	1.7	7.9
31	Granite	74	10.4	2.2	8.2
29	Granite	--	11.9	3.3	8.6
26	Alaskite	76	13.6	-0.1	13.7

2. Metamorphic rocks

Sample #	Rock type	% SiO_2 in rock	δQ	δM	ΔQM
30			10.5	1.7	8.8
28			12.0	2.9	9.1
27			12.6	0.8	11.8

Among the magmatic rocks, both δ_Q and δ_M increase as the temperature of formation (given by Δ_{QM}) decreases. There is good correlation between the rock type and the temperature sequence. According to the principles of petrogenesis proposed by Bowen(39), the chemical composition of a silicate melt changes on partial crystallization, so that the proportion of silica in the remaining melt increases. Therefore, the more silicic rocks are believed to have crystallized at lower temperatures.

Something can be said about the change in the overall oxygen isotope ratio in the magma as material crystallizes. According to Silverman's data(29), the isotopic composition of granitic rocks is about +8‰. It is seen from Table XV, that magnetite crystallizing from a magma where $\delta \backsim 8$‰, has an isotopic composition of $\delta \backsim +2$‰, that is, the fractionation between granitic magma and magnetite is about 6‰, and should increase as the temperature of crystallization decreases. The value of δ_M itself increases as the temperature of formation decreases, so that the O^{18}/O^{16} ratio in the magmas must increase as they evolve by fractional crystallization. That is, the early-forming minerals must have a lower value of O^{18}/O^{16} than the magma from which they form. This is entirely compatible with Silverman's observation that basalts and other basic rocks (formed early in magmatic differentiation) have less O^{18} than granites, although Silverman was not willing to attribute this to the effects of fractional crystallization. He writes, "It is difficult to explain the higher O^{18} abundances in granitic rocks as compared with the basic rocks. If the granitic rocks have originated by differentiation from a magma, then on the basis of energy considerations, the earlier crystallizing fraction, i.e. the basic rocks, should be richer in the heavy isotope than the later fractions (granitic rocks)".

However the experimental work on silicon isotopes, supported by theoretical calculations(8), indicate that the Si^{30}/Si^{28} ratio increases in a magma as it crystallizes. It is not unreasonable that oxygen should behave similarly.

Our data and conclusions are exactly opposite to those of Schwander(31), who not only believes that isotopically heavy minerals crystallize first, but reports experimental numbers to back him up. He says,

> Es konnte festgestellt werden, dass bei der sukzessiven Festwerdung eine Sauerstoffisotopenfraktionierung stattfindet und zwar offenbar in dem Sinne, dass die Produkte, welche in einem zeitlich früheren Stadium der magmatischen Kristallization augeschieden wurden, einen höhern O^{18} Gehalt aufwiesenals solche, die später gebildet wurden.

This discrepancy cannot be discussed further, in view of the doubts raised earlier concerning the validity of the data.

The data on igneous and metamorphic "granitic" rocks do not show any marked distinction between the two groups. Many minerals from a large number of the most clear-cut geological examples will have to be analyzed before the usefulness of isotopic information in this problem can be evaluated.

D. Pegmatites

Pegmatites are small bodies of rock, generally igneous and granitic, characterized by the large size of the mineral crystals. They are sometimes interpreted as representing the last stages of crystallization of a silicate melt, and might therefore be expected to show extremes in isotopic composition. Since magnetite and calcite are not commonly found in pegmatites, other minerals were chosen to form a pair with quartz, which is very common. The results on several rocks, all supplied by Dr. R. H. Jahns, are shown in Table XVI.

Table XVI

Isotopic Composition of Some Pegmatite Minerals

Sample #	Mineral	δ	Δ
45	Quartz	10.8	
	Columbite	2.4	8.4

Sample #	Mineral	δ	Δ
46	Quartz	9.3	
	Columbite	1.6	7.7
47	Quartz	10.0	
	Ilmenite	-0.5	10.5
48	Quartz	6.5	
	Ilmenite	-2.0	8.5

The values of δ for columbite ($(Fe,Mn)(Nb,Ta)_2O_6$) and ilmenite ($FeTiO_3$) are probably a little higher than would be the corresponding value for magnetite (see samples #26 and #27). These results then fall within the range of the other igneous rocks which have been studied, and show no striking irregularities. The possible exception to this is sample #48, which contains quartz with the smallest value of δ as yet observed in a natural sample.

Some pegmatite bodies are zoned, containing different regions distinguished by their crystal size and mineralogy. There is good evidence that some of these bodies have formed by crystallization from a melt from the outside toward the center. Samples from successive zones might show the trend of the isotopic composition during crystallization. Specimens from three zones of the New York Pegmatite, Custer Co., South Dakota were supplied by Dr. M. L. Keith of the Pennsylvania State University, and are described in a paper by Keith and Tuttle(37) in which the temperature of inversion to high quartz was measured for a large number of samples. The isotopic composition of quartz from the three successive zones is given in Table XVII.

Table XVII

Isotopic Composition of Quartz from a Zoned Pegmatite

Sample #	Keith and Tuttle's Sample #	δ ‰	
49	48-1	13.9	outer zone
50	48-4	13.1	
51	48-3	13.3	inner zone

The variation among the three samples is not great. A sample of the pure quartz core of the pegmatite was not available.

E. Rhyolites and Porphyries

Rhyolite is a fine-grained rock chemically similar to granite. It may contain some large crystals, phenocrysts, of some of the minerals in the rock. This texture is developed by rapid cooling of a granitic magma, frequently as a result of volcanic action. Granite porphyry is a rock of granitic composition in which the grain size of one mineral is much larger than that of the others in the rock. Both these rock types represent a different cooling history from that of a normal igneous granite. Keith and Tuttle(37) have found that the average inversion temperature of quartz from a large number of rhyolites and porphyries is less than the average of quartz from a large number of granites by about 1°C. Their conclusion is that the granites had undergone recrystallization at some temperature below their temperature of formation, while the more rapidly cooled rocks had not. The results of isotopic analysis of three of these quartz samples, donated by Dr. Keith, are shown in Table XVIII.

Table XVIII

Isotopic Composition of Quartz from Rhyolites and Porphyries

Sample #	Keith and Tuttle's Sample #		δ ‰
52	49-19	granite porphyry	11.6
53	49-25	rhyolite	10.3
54	49-106	intrusive porphyry	9.7

These values are in the range of quartz from granites. Apparently the different cooling histories of these rocks compared to deep-seated granites, have not caused any observable differences in the oxygen isotopic composition of the quartz.

F. Vein Quartz

Also from the collection of Keith and Tuttle came four samples taken at different elevations in a quartz vein of the Wright-Hargreaves Gold Mine, Kirkland Lake, Ontario. The isotopic analyses and depths below the surface are given in Table XIX.

Table XIX

Isotopic Composition of Quartz from a Gold-bearing Vein

Sample #	Keith and Tuttle's Sample #	Depth (ft.)	δ ‰
55	49-171	1000	12.7
56	49-173	3000	11.9
57	49-175	5100	12.5
59	49-179	6150	11.1

This series indicates the type of variation which may be expected in a large hydrothermal process. The variations may reflect temperature changes or local changes in the isotopic composition of oxygen in the hydrothermal fluids. The average value of $\delta = 12‰$ is low for vein quartz, suggesting a fairly high temperature of formation, of the order of 500°C.

CONCLUSIONS

The relative merits of the carbon reduction method and the fluorine oxidation method (or its modifications using chlorine trifluoride or bromine trifluoride) can be evaluated. For compounds for which it is useable, the carbon reduction method works very well, giving good yields of oxygen with isotopic reproducibility of 0.2% or better. This technique, however, cannot be used for samples containing appreciable amounts of alkalies, alkaline earths, aluminum, zinc, lead or other metals which do not have stable carbides, and which are volatile in vacuum at 1500°C. This restriction eliminates a large number of interesting materials. The fluorine procedure on the other hand, is much less limited in the compounds which can be attacked, the only troublesome element known being iron. The disadvantage with the fluorine procedure is its inherent susceptibility to contamination by foreign oxygen, which will probably make the reproducibility of this method poorer than that of the reduction method.

Wherever possible it is of great importance to test the various analytical procedures by running identical samples by very different techniques and in different laboratories.

The results of isotope analyses of two mineral pairs, quartz-calcite and quartz-magnetite, show consistency among the samples of each group, consistency between the two groups, and consistency with the geological evidence concerning the specimens analyzed. Either of the two fractionations studied should serve as a satisfactory thermometer for geologic events of the past, and certainly many other mineral pairs may be found to be as good. At present, only semi-quantitative estimates can be made of the actual temperature to which a measured isotopic fractionation corresponds. The next step in this field, therefore, will be the establishment of the relationship between temperature and the equilibrium isotopic fractionation in the systems quartz-water, calcite-water, quartz-calcite, quartz-magnetite, etc. This problem can be attacked by means of the high temperature, high pressure apparatus commonly used for mineral synthesis and phase studies. Preliminary, and so far unsuccessful, experiments toward this end have been carried out. In cooperation with the writer, Dr. H. S. Yoder of the Geophysical Laboratory, Carnegie Institution of Washington has attempted to prepare quartz and magnetite at isotopic equilbrium in a bomb at 750°C, and 1000 bars of water pressure. In his first experiment, Yoder synthesized quartz and magnetite by reaction of water with elemental silicon and iron; the isotopic analyses indicated that equilibrium had not been reached. In the second experiment, previously analyzed quartz and magnetite were held at 750°C with water to see whether there was isotopic exchange. Both quartz and magnetite were exchanged somewhat after a week, but were still far from equilibrium. It is planned to carry on these exchange experiments both at the Geophysical Laboratory and at the California Institute, to determine the equilibrium fractionations for as many systems as are geologically interesting.

At the present time, other "geological thermometers" are being developed, all based on the changes with temperature in solubility of one component in a solid solution. Kullerud(41) has a thermometer using the concentration of iron in sphalerite (ZnS). Buddington's(42) scale is determined by the concentration of titanium in magnetite; Goldsmith(43) uses the concentration of magnesium in calcite. For a temperature determination by one of these methods to be valid, one must be able to demonstrate that the system was saturated with respect to the trace element, by showing that this element was forming its own mineral in equilibrium with the solid solution being studied. It is better to measure the distribution of a trace element between two phases as a function of temperature. This method then approaches the stable isotope method, if the rare isotope is considered as the trace element.

The results of the various methods have not been cross-checked; this will give a good indication of the validity and relative merits of the various techniques. But in general the oxygen isotope method will have a broader application since almost all important rock-forming minerals have oxygen as a major constituent. Stable isotopes also often serve as natural tracers to point to the origin of material. For instance, if it can be established with certainty that the oxygen isotope ratio in hydrothermal solutions has a certain value or narrow range, then postulates for the origin of these solutions must be able to explain this isotopic composition. The use of isotopes as natural tracers in geological problems can be applied as a test of many existing theories of the formation of rocks and ore deposits.

The frozen-in distribution of oxygen isotopes among the mineral phases in a rock can reveal the physical-chemical conditions under which the rock was formed, and in favorable cases can tell the source of the material or type of process involved.

REFERENCES

1. Urey, H. C., J. Chem. Soc., 1947, 562.
2. Bigeleisen, J., and Mayer, M. G., J. Chem. Phys., 15, 261 (1947).
3. Redlich, Z. Physikal. Chem. 28B, 371 (1935).
4. Green, M., and Martin, G. R., Trans. Far. Soc., 48, 416 (1952).
5. McCrea, J. M., J. Chem. Phys., 18, 849 (1950).
6. Grant, F. S., Geochim. et Cosmochim. Acta, 5, 225 (1954).
7. Reynolds, J. and Verhoogen, J., Geochim. et Cosmochim. Acta, 4, 224 (1953).
8. Allenby, R. J., Geochim. et Cosmochim. Acta 5, 40 (1954).
9. Nier, A. O., Rev. Sci. Instrum. 18, 398 (1947).
10. McKinney, C.R., McCrea, J. M., Epstein, S., Allen H. A., and Urey, H. C., Rev. Sci. Instrum. 21, 724 (1950).
11. Dole, M., J. Am. Chem. Soc., 57, 2731 (1935).
12. Dole, M., J. Chem. Phys. 4, 268 (1936).
13. Swartout, J. A., and Dole, M., J. Am. Chem. Soc. 61, 2025 (1939).
14. Dole, M., Lane, G. A., Rudd, D. P., and Zaukelies, D. A., Geochim. et Cosmochim. Acta, 6, 65 (1954).
15. Kirshenbaum, I., Physical Properties and Analysis of Heavy Water, edited by G. M. Murphy and H. C. Urey. McGraw-Hill Book Co., Inc., New York (1951).
16. Epstein, S., and Mayeda, T., Geochim. et Cosmochim. Acta. 4, 213 (1953).
17. Dansgaard, W., Tellus, 5, 461 (1953).
18. Dansgaard, W., Nature, 174, 234 (1954).
19. Dansgaard, W., Geochim. et Cosmochim. Acta 6, 241 (1954).
20. Dole, M., and Slobod, R. L., J. Am. Chem. Soc. 62, 471 (1940).
21. Urey, H. C., Lowenstam, H. A., Epstein, S., and McKinney, C. R., Bull. Geol. Soc. Am. 62, 399 (1951).
22. Epstein, S., Buchsbaum, R., Lowenstam, H. A., and Urey, H. C., Bull. Geol. Soc. Am., 62, 417 (1951).

23. Epstein, S., Buchsbaum, R., Lowenstam, H. A., and Urey, H. C., Bull. Geol. Soc. Am., 64, 1315 (1953).

24. Epstein, S., and Lowenstam, H. A., J. Geol., 61, 424 (1953).

25. Baertschi, P., Nature, 168, 288 (1951).

26. Manian, S. H., Urey, H. C., and Bleakney, W., J. Am. Chem. Soc., 56, 2601 (1934).

27. Tokuda, T. and Kashida, T., Collected Papers from the Faculty of Science, Osaka University series (1949 2 (no. 6) 1-2. (Quoted by Silverman(29)).

28. Baertschi, P. and Silverman, S. R., Geochim. et Cosmochim. Acta. 1, 317 (1950).

29. Silverman, S. R., Geochim. et Cosmochim. Acta, 2, 26 (1951).

30. Baertschi, P., and Schwander, H., Helv. Chim. Acta, 35, 1748 (1952).

31. Schwander, H., Geochim. et Cosmochim. Acta, 4 261 (1953).

32. Adams, L. H., Carnegie Institution of Washington Year Book 49, 36 (1949-50).

33. Donstova, E. I., Doklady Akad. Nauk S.S.S.R. 71, 905 (1950).

34. Titani, T., Nakata, S., and Kanome, A., Bull. Chem. Soc. Japan 17, 288 (1942).

35. Sidgwick, N. V., The Chemical Elements and Their Compounds, p. 1354, Oxford Press, London (1950).

36. Kelley, K. K., U. S. Bureau of Mines Bull. 476 (1949).

37. Rossini, F. D., Wagman, D. D., Evans, W. H., Levine, S., Jaffe, I., Selected Values of Chemical Thermodynamic Properties, Circular of the National Bureau of Standards 500 U. S. Government Printing Office, Washington (1952).

38. Lewis, G. N., and Randall, M., Thermodynamics and the Free Energy of Chemical Substances, McGraw-Hill Book Co., Inc., New York (1923).

39. Bowen, N. L., The Evolution of Igneous Rocks, Princeton University Press, Princeton (1928).

40. Keith, M. L., and Tuttle, O. F., Am. J. Science 1952, 203.

41. Kullerud, G., Norsk geol. Tids. 32, 61 (1953).

42. Buddington, A. F., Am. J. Science (in press).

43. Goldsmith, J., personal communication.

APPENDIX

Table of Analytical Results

Sample #	Description	Collector	Locality	Mineral	δ ‰	Av. ‰
1	Hard black chert (microcrystalline quartz) in a soft white chalk (calcium carbonate shells); Cretaceous age.	A.E.J. Engel	France	Quartz	33.7	
					33.7	33.7
				Calcite	26.0	26.0
2	Black chert in fine-grained limestone; Mississippian age.	A.E.J. Engel	Leadville, Colorado	Quartz	28.9	
					28.8	28.9
				Calcite	21.0	
					23.0	22.0
3	"Herkimer diamonds" - very clear quartz crystals growing loosely in cavities in sandstone. Partially embedded in the quartz are small crystals of calcite.	A.E.J. Engel	Herkimer Co., New York	Quartz	23.6	
					23.5	23.6
				Calcite	17.9	17.9
4	Chert from same bed as sample #2, but here the limestone has recrystallized to coarse calcite.	A.E.J. Engel	Leadville, Colorado	Quartz	21.9	
					22.0	22.0
				Calcite	17.1	17.1
5	Hydrothermal vein containing coarsely crystalline intergrown quartz and calcite.	A.E.J. Engel	Hot Springs, Arkansas	Quartz	18.2	
					18.8	18.5
				Calcite	14.8	14.8
6	Recrystallized chert nodule in calcite marble. A rim of wollastonite ($CaSiO_3$) surrounds the chert.	C.W. Burnham	Crestmore, California	Quartz	23.6	
					23.7	
					23.9	

Sample #	Description	Collector	Locality	Mineral	δ ‰	Av. ‰
6 (con't)				(Quartz)	23.2	23.6
				Calcite	19.0	19.0
7	Hydrothermal zinc ore, containing sphalerite (ZnS), chalcopyrite ($CuFeS_2$), calcite and quartz.	C.W. Burnham	Santa Eulalia, Chihuahua, Mexico	Quartz	17.2	
					16.7	17.0
				Calcite	12.0	
					12.1	12.1
8	Quartz and calcite from the core of a pegmatite.	C.W. Burnham	Crestmore, California	Quartz	11.2	11.3
					11.3	
				Calcite	8.2	8.2
9	Scheelite ($CaWO_4$) ore containing quartz and calcite.	J.A. Noble	Hermosillo, Sonora, Mexico	Quartz	11.8	
					12.2	12.0
				Calcite	9.5	
					9.7	9.6
10	Quartz and calcite crystals in an open cavity.	C.I.T. collections	St. Gothard, Switzerland	Quartz	9.9	
					9.7	9.8
				Calcite	16.0	
					15.9	
					15.7	15.9
11	Quartz and calcite crystals with native copper.	C.I.T. collections	Northern Michigan	Quartz	15.0	
					16.9	16.0
				Calcite	18.8	18.8

Sample #	Description	Collector	Locality	Mineral	δ ‰	Av. ‰
12	Amethyst (quartz) crystals overgrown with small white calcite crystals - open cavity.	C.I.T. collections	Guanajuato, Mexico	Quartz	11.6	
					11.5	11.6
				Calcite	14.6	14.6
13	Zinc ore with coarsely crystalline sphalerite, open cavity coatings of quartz and calcite crystals.	C.W. Burnham	Hanover, New Mexico	Quartz	12.9	
					12.9	12.9
				Calcite	31.0	
					30.9	31.0
14	Quartz and calcite metamorphosed from material like sample #2.	A.E.J. Engel	Leadville, Colorado	Quartz	22.5	
					22.8	22.7
				Calcite	20.5	20.5
15	Quartz and calcite from metamorphic marble.	A.E.J. Engel	Adirondack Mts., New York	Quartz	25.8	
					25.6	25.7
				Calcite	22.5	22.5
16	Quartz and dolomite ($CaMg(CO_3)_2$) in a marble.	C.I.T. collections	Palos Verdes, California	Quartz	22.7	
					23.4	23.1
				Dolomite	22.3	22.3
17	Quartz and dolomite from same place as sample #14.	A.E.J. Engel	Leadville, Colorado	Quartz	22.5	
					22.8	22.7
				Dolomite	22.2	22.2
18	Quartz recrystallized from material similar to sample #35, in crystalline dolomite.	A.E.J. Engel	Leadville, Colorado	Quartz	17.1	
					16.9	17.0
				Dolomite	16.0	16.0

Sample #	Description	Collector	Locality	Mineral	δ ‰	Av. ‰
19	Chert and dolomite formed from material like sample #2.	A.E.J. Engel	Leadville, Colorado	Quartz	23.8	
					23.9	23.9
				Dolomite	21.7	
					21.2	21.5
20	Fine-grained intergrown quartz and magnetite.	H. L. James	Vicar Mine, Michigan	Quartz	16.8	
					16.4	
					16.4	16.5
				Magnetite	2.0	2.0
21	Fine-grained intergrown quartz and magnetite	H. L. James	Ishpeming, Michigan	Quartz	16.0	
					16.3	16.2
				Magnetite	2.0	2.0
22	Magnetite interlayered with grunerite (Fe, Mg silicate) and quartz.	H. L. James	Republic, Michigan	Quartz	10.0	
					10.8	10.4
				Magnetite	-0.2	
					-0.0	-0.1
23	Metamorphic quartz and magnetite.	C.I.T. collections	Olympic Peninsula, Washington	Quartz	16.5	
					15.6	16.1
				Magnetite	3.3	
					3.3	3.3
24	Quartz and magnetite from biotite gneiss.	A.E.J. Engel	Adirondack Mts., New York	Quartz	15.0	
					14.5	14.8
				Magnetite	3.7	3.7

Sample #	Description	Collector	Locality	Mineral	δ ‰	Av. ‰
25	Quartz and magnetite from contact metamorphic rock.	A.E.J. Engel	Adirondack Mts., New York	Quartz	12.3	
					12.2	12.3
				Magnetite	4.4	
					3.9	
					4.2	4.2
26	Microperthite alaskite with accessory ilmenomagnetite and ferricilmenite.	A.F. Buddington	Adirondack Mts., Mew York	Quartz	13.5	
					13.6	13.6
				Magnetite	-0.1	-0.1
				Ilmenite	+3.8	
					3.5	3.7
27	Hornblende microcline-oligoclase granite gneiss.	A.F. Buddington	Adirondack Mts., New York	Quartz	12.8	
					12.4	12.6
				Magnetite	0.8	
					0.7	0.8
				Ilmenite	3.0	
					3.1	3.1
28	Hornblende microcline granite gneiss.	A.F. Buddington	Adirondack Mts., New York	Quartz	12.0	12.0
				Magnetite	2.9	
					2.9	2.9
29	Hornblende granite gneiss	A.F. Buddington	Adirondack Mts., New York	Quartz	11.9	11.9
				Magnetite	3.2	
					3.4	3.3
30	Biotite pegmatite veined microcline quartz gneiss.	A.F. Buddington	Adirondack Mts., New York	Quartz	10.5	10.5
				Magnetite	1.1	
					2.2	1.7

Sample #	Description	Collector	Locality	Mineral	δ ‰	Av. ‰
31	Rubidoux Mt. leucogranite.	L.T. Silver	Riverside Co., California	Quartz	10.3	
					10.4	10.4
				Magnetite	1.7	
					2.6	2.2
32	Woodson Mt. Granodiorite.	L.T. Silver	Riverside Co., California	Quartz	9.5	
					9.7	9.6
				Magnetite	1.7	
					1.6	1.7
33	Quartz and magnetite phenocrysts from a rhyolite ash.	J. Boyd	Mt. Everts, near Mammoth Hot Springs, Yellowstone Park, Wyoming	Quartz	7.9	
					8.1	8.0
				Magnetite	0.5	
					0.7	
					1.1	
					0.2	0.6
34	Milky quartz crystals recrystallized by ore forming solutions from material like sample #2.	A.E.J. Engel	Leadville, Colorado	Quartz	16.2	
					16.0	
				Calcite	13.5	13.5
35	Detrital sand grains forming a thin bed in limestone.	A.E.J. Engel	Leadville, Colorado	Quartz	13.8	
					14.0	13.9
36	Specular hematite (Fe_2O_3) crystals in an open cavity.	H.L. James	Iron River, Michigan	Hematite	-2.9	
					-1.8	
					-3.1	-2.6

Sample #	Description	Collector	Locality	Mineral	δ‰	Av. ‰
37	Hematite, magnetite and calcite crystals in an open cavity in iron ore.	H.L. James	Iron River, Michigan	Hematite	-5.5	
					-5.4	-5.4
				Magnetite	-7.8	
					-7.7	-7.7
				Calcite	+20.2	+20.2
38	Interlayered blue hematite and jaspery quartz.	H.L. James	Iron Mountain, Michigan	Hematite	+5.4	
					5.3	5.4
				Quartz	16.0	
					16.3	16.2
39	Interlayered specular hematite and quartz.	H.L. James	Republic, Michigan	Hematite	+2.6	
					2.8	
					2.6	2.7
				Quartz	12.3	
					12.4	12.4
40	Hematite ore.	H.L. James	Iron River, Michigan	Hematite	-3.9	
					-4.2	-4.0
41	Interlayered hard red hematite and chert.	H.L. James		Hematite	-2.4	
					-2.0	-2.2
				Quartz	+17.5	
					17.7	
					18.2	17.8
42	Coarsely crystalline magnetite.	H.L. James	Iron Springs, Utah	Magnetite	4.1	
					3.0	
					2.7	
					3.7	3.4

Sample #	Description	Collector	Locality	Mineral	δ ‰	Av. ‰
43	Quartz crystals on coarsely crystallized magnetite.	H.L. James	Iron Springs, Utah	Quartz	6.9	
					6.6	6.8
				Magnetite	3.4	
					3.6	3.5
44	Specular hematite.	H.L. James	Inyo Co., California	Magnetite	-2.4	-2.4
				Hematite	-2.4	
					-3.1	-2.8
45	Pegmatite	R.H. Jahns	Ramona, California	Quartz	10.8	
					10.8	10.8
				Columbite	2.0	
					2.8	2.4
46	Pegmatite	R.H. Jahns	Pala, California	Quartz	9.4	
					9.1	9.3
				Columbite	1.9	
					1.3	1.6
47	Pegmatite	R.H. Jahns	Petaca, New Mexico	Quartz	9.9	
					10.1	10.1
				Ilmenite	-0.4	
					-0.6	-0.5
48	Pegmatite	R.H. Jahns	Petaca, New Mexico	Quartz	6.5	
					6.5	6.5
				Ilmenite	-1.6	
					-2.3	-2.0

Sample #	Description	Collector	Locality	Mineral	δ ‰	Av. ‰
49	Outer zone of pegmatite (albite, quartz, muscovite).	M.L. Keith	Custer Co., South Dakota	Quartz	13.9 13.8	13.9
50	Middle zone of pegmatite (quartz, albite).	M.L. Keith	Custer Co., South Dakota	Quartz	12.9 13.2	13.1
51	Inner zone of pegmatite (quartz, cleavelandite).	M.L. Keith	Custer Co., South Dakota	Quartz	13.4 13.1	13.3
52	Phenocrysts from "Elk" porphyry.	M.L. Keith	Eagle Co., Colorado	Quartz	11.3 11.8	11.6
53	Phenocrysts from rhyolite.	M.L. Keith	Lake Co., Colorado	Quartz	10.3 10.2	10.3
54	Phenocrysts from intrusive porphyry.	M.L. Keith	Northern New Mexico	Quartz	9.6 9.8	9.7
55	Quartz vein, 1000 ft. level	M.L. Keith	Kirkland Lake, Ontario	Quartz	12.7 12.7	12.7
56	Quartz vein, 3000 ft. level	M.L. Keith	Kirkland Lake, Ontario	Quartz	11.9 11.9 11.9 11.8	11.9

Sample #	Description	Collector	Locality	Mineral	δ‰	Av. ‰
57	Quartz vein, 5100 ft. level	M.L. Keith	Kirkland Lake, Ontario	Quartz	12.7 12.2	12.5
58	Quartz vein, 6150 ft. level	M.L. Keith	Kirkland Lake, Ontario	Quartz	11.3 10.8	11.1

PROPOSITIONS

(1) If there was ever chemical equilibrium in the matter which forms the earth, there must have been no ferric iron. The major processes causing formation of +3 iron in the crust of the earth appear to be (1) oxidation by oxygen of the atmosphere in the weathering of rocks, and (2) oxidation by water(1) according to the equation:

$$Fe^{++} + H_2O \longrightarrow Fe^{+++} + 1/2H_2 + OH^-$$

The following reactions can be considered:

1. $3FeSiO_3 + H_2O \longrightarrow Fe_3O_4 + H_2 + 3SiO_2 \qquad \Delta F_{298} = +12,040$

$\Delta F_{1000} \backsim +44,000.$

2. $3Fe_2SiO_4 + 2H_2O \longrightarrow 2\ Fe_3O_4 + 2H_2 + 3SiO_2 \qquad \Delta F_{298} = +6,680$

$\Delta F_{1000} = +30,000.$

3. $3Fe_2SiO_4 + Mg_2SiO_4 + 2H_2O \longrightarrow 2Fe_3O_4 + 2H_2 + 6MgSiO_3$

$\Delta F_{298} = -59,920$

$\Delta F_{1000} \backsim -95,000.$

These data show that water is capable of oxidizing ferrous iron in a material containing olivine ($(Fe,Mg)_2SiO_4$) but not in a more acid rock, which contains only pyroxene ($(Fe,Mg)SiO_3$).

In silicate melts, we know, from observations of lavas at the surface, from the compositions of observed deep-seated rocks and from laboratory experiments, that the first iron bearing minerals to crystallize are olivine and minerals of the spinel type (magnetite, chromite). These minerals have a lower ratio of Si/O than the melt, and the melt therefore becomes more acid, i.e. the Si/O ratio increases. This goes on until the crystallization of olivine ceases, and the olivine then reacts with the more acid magma to form pyroxenes:

$$Fe_2SiO_4 + SiO_2 \longrightarrow 2FeSiO_3$$

If we start with a basic magma, from which olivine can crystallize, it should react with any water present until (a) the water is all gone, or (b) until the crystallization has proceeded to the stage where the magma is too acid to permit the reaction to continue.

This type of process should have the following consequences: (1) There probably is no "primary magmatic water"; the water found in igneous rocks has been derived from the surroundings after the magma had become sufficiently acid to tolerate water. Chemical analyses of olivine bombs and dunites (rocks largely olivine) show water to be very low ($< .01\%$).

(2) The amount of ferric iron in an igneous rock is determined by the history of the magma while it was still basic, and becomes fixed at a certain point in the evolution of the silicate melt. From this some light may be shed on the origin of magmas.

(1) Goldschmidt, V. M., Geochemistry, p. 657. Oxford University Press. London, 1954.

(2) Quantitative analysis of oxygen in most organic compounds can be done by an isotope dilution technique, involving combustion of the sample in oxygen enriched in O^{18}, followed by isotopic analysis. With existing techniques, the amount of oxygen in a specimen could be determined within better than 0.5 micrograms.

(3) Commercial fluorine contains as impurities: hydrogen fluoride, about one percent, and oxygen, .5-20%. If the gas is to be used for liberation of oxygen for isotopic analysis, its oxygen contamination

must be reduced to as low a level as possible. It is proposed that the reaction:

$$2FeF_3 + 3/2O_2 \longrightarrow Fe_2O_3 + 3F_2$$

be used to remove oxygen from fluorine.

(4) In the preparation of synthetic minerals, and the study of the phase relationships among compounds, it is not always easy to determine whether chemical equilibrium has been established. Since chemical equilibrium is a prerequisite for isotopic equilibrium, the measurement of isotopic fractionation between phases might be used as a criterion for chemical equilibrium.

(5) In Urey's paper in 1947(1) theoretical equilibrium constants for a large number of isotope exchange reactions were given, based on observed molecular vibration frequencies. A large number of the reactions have been investigated experimentally, and good agreement has been found in all cases but one:

$$B^{10}Cl_{3(l)} + B^{11}Cl_{3(g)} \rightleftharpoons B^{10}Cl_{3(g)} + B^{11}Cl_{3(l)}$$

For this reaction Urey calculates an equilibrium constant of 1.014, whereas Green and Martin(2) measured the constant as 0.9962. Urey's calculation was based on the Raman spectrum data of Anderson, Lassettre, and Yost(3), who determined the fundamental vibration frequencies of boron trichloride in both the liquid and vapor, and for both boron isotopes. It is very difficult to see how the calculation can be wrong for this case.

It is proposed that the relative vapor pressures of $B^{10}Cl_3$ and $B^{11}Cl_3$ be further investigated, with particular attention to (1) the method of isotope analysis (using mass spectrometer rather than neutron absorption) and (2) the effect of the chlorine isotopes on the fractionation of boron isotopes in the fractional process.

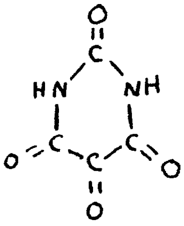
(1)Urey, H. C., J. Chem. Soc., 1947, 562.

(2)Green, M. and Martin, G. R., Trans. Far. Soc. 48, 416 (1952).

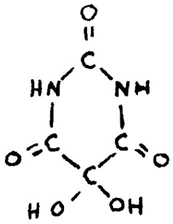
(3)Anderson, Lassettre, and Yost, D. M., J. Chem. Phys. 4, 703 (1936).

(6) In the geochemical cycle of carbon, carbon is removed from the ocean-atmosphere system by burial in sediments, and is added to this system by weathering of rocks. One important piece of information necessary for quantitative treatment of the cycle is the isotopic composition of "juvenile" carbon, the carbon brought to the surface of the earth by igneous rocks. Former estimates of its composition were based on carbon dioxide from volcanoes and hot springs, or on graphite or small amounts of carbonate in igneous rocks. These sources of carbon are very likely to contain large and probably overwhelming amounts of non-juvenile carbon gathered as the rock was emplaced and later weathered. It is proposed that a more reliable source would be carbon substituting in silicon positions in the structure of a silicate mineral. This could be extracted only by drastic treatment on the mineral: dissolution or melting, in a system in which very small amounts of carbon dioxide could be collected.

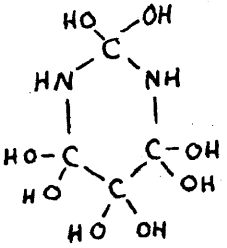
(7) Alloxan (I) forms two hydrates (II) and (III)



I



II



III

It is proposed that the structure of (I) involves a planar ring; that hydrate (II) is formed because of the effect of the two adjacent carbonyl groups, as in mesoxalic acid; and that the resulting tendency to achieve tetrahedral configuration permits hydration of the other three carbonyl groups to give the tetrahydrate (III), which should have a puckered ring.

(8) It was found that carbon dioxide and fluorine do not react at 500°C in a period of two hours (see page 17 of the thesis). The available thermodynamic data given in the National Bureau of Standards Circular No. 500 gives ΔF_{298} for $CF_4 = -151.8$ Kcal, and ΔF_{298} for $CO_2 = -94.3$ Kcal. Hence ΔF_{298} for the reaction is -57.5 Kcal. Using the heat capacity data tabulated by Kelley(1), ΔF_{700} is calculated to be -43.1 Kcal. It is highly unlikely that the reaction would be too slow to observe, especially since the carbon dioxide is formed from solid calcium carbonate in the presence of excess fluorine. It is proposed that the reported heat of formation of carbon tetrafluoride(2) is too great by perhaps 50 Kcal/mol.

The value of the heat of formation of carbon tetrafluoride can be determined by the measurement of equilibrium concentrations in the system CO_2-CF_4-O_2-F_2 at temperatures around 300-400°C.

Estimating ΔH for carbon tetrafluoride as -112, taking the heat of dissociation of fluorine as 38 Kcal, and the heat of sublimation of graphite as 124 Kcal, the energy of the C-F bond in carbon tetrafluoride is calculated as 78 Kcal (compared to C-Cl = 66.5, C-Br = 54.0, C-I = 45.5 and C-F = 107.0 as given by Pauling).

(1) Kelley, K. K., U. S. Bureau of Mines, Circular No. 476, (1949).

(2) von Wartenberg, H., and Schutte, R., Z. anorg. Chem. <u>211</u>, 222 (1933).

(3) Pauling, L., Nature of the Chemical Bond, p. <u>53</u>, Cornell University Press, Ithaca. (1948).

(9) It is proposed that the formulas of hydroxide complex ions (amphoteric anions) in solution, such as stannite, stannate, plumbite, arsenite, arsenate, chromite, zincate, etc. be determined by an O^{18} tracer method.

(10) The Chemistry Division library is inferior to other department libraries on the campus in several respects. It is proposed that it could be made a more comfortable place to work if (1) the temperature were better controlled and (2) more comfortable chairs were provided. One could also work more efficiently if some periodicals now found only in the Physics library were duplicated in the Chemistry library (e.g. Proceedings of the Royal Society, Naturwissenschaften). The non-periodical book section is too small. The libraries of the Divisions of Biology and Geology would serve as good examples to be copied.