

OXYGEN ISOTOPES IN GEOLOGY

by

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B.Sc., University of Toronto, 1961

A THESIS SUBMITTED IN PARTIAL FULFILMENT
OF THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF SCIENCE

in the Department
of
PHYSICS

We accept this thesis as conforming to the
required standard

THE UNIVERSITY OF BRITISH COLUMBIA

February, 1963

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ABSTRACT

A critical survey has been conducted on the research done in oxygen isotopes. Only those aspects are considered which are of interest to the earth scientists.

Oxygen isotopes have been used for geothermometric purposes and for rock genesis problems. The physical principles underlying these two lines of research are stressed. Assumptions which are usually implied are explicitly stated. It is shown that the influence of pressure on the equilibrium constant of oxygen isotope exchange reactions is only a minor one in comparison with the temperature influence.

The significance of determined temperatures is discussed in the light of possible oxygen diffusion in silicates and carbonates. It is concluded that diffusion is usually neglected without justification. As far as data are available it is shown that diffusion can be responsible for many discrepancies between oxygen isotope temperatures and temperatures derived by other means.

Studies on the origin of rocks by means of oxygen isotopes are discussed. Attention is focussed on the Southern Californian batholith. The results of Taylor and Epstein's preliminary study of this batholith are interpreted here as evidence in favour of a metamorphic origin of this huge rock body.

ACKNOWLEDGEMENT

The author would like to acknowledge the suggestions he received from Professors W. F. Slawson and G. P. Erickson, who both read the draft of this thesis; especially he is grateful to Professor W. F. Slawson, who assisted him in general practical matters. To Professor R. D. Russell, the writer is in particular indebted for the way in which he made it possible for the author to switch from geology to the study of physics, and for the suggestion of this research. Thanks are due to the staff of the Science Division of the Library, who have aided the author frequently in obtaining valuable references and foreign periodicals, and to Miss N. Beman who typed this thesis. The author would like to express his appreciation for a bursary and a studentship from the National Research Council of Canada.

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INTRODUCTION

This thesis is a review and critical discussion of research done on oxygen isotopes from 1950 to 1962. Only those areas are surveyed which are of interest to earth scientists. Meteorological aspects, snow and ice, are not considered.

A knowledge of oxygen isotope distributions in minerals and rocks may provide information about the temperature of formation of the minerals and about the genesis of rocks. This is a reason why earth scientists are interested in oxygen isotopes. In this thesis attention is mainly directed toward these two aspects. Other naturally occurring stable isotopes are in principle also suitable for investigation along this line, but the great natural abundance of oxygen, the relatively large mass difference between O^{18} and O^{16} , and the well developed analytical procedures favour the usage of oxygen.

The theory of isotopic equilibrium has been discussed by Urey (158) and by Bigeleisen and Mayer (15). It will be assumed that the reader has a knowledge of these two important papers. Oxygen isotopes were reviewed by Dole (55) in 1952, by Ingerson (97) in 1953 and Rankama (129) in 1954. From 1951 to 1956 annual reviews (2) were published on isotopes in general. In 1959 Epstein (72) wrote a general paper about O^{18}/O^{16} ratio variations in nature. The last review published in the English language was by Mayne (114) in 1960. An exhaustive bibliography

on oxygen isotopes was compiled by Samuel and Steckel (135); it covers papers published before 1959. In 1961 a supplement (136) to this bibliography appeared for the period 1958-1960.

CHAPTER 1

DETERMINATION AND REPORTING OF THE O^{18}/O^{16} RATIO

1.1 Introduction

Over the years, gas source mass spectrometry has proven to be the most precise method for the determination of O^{18}/O^{16} ratios. It is for this reason that only data obtained by this method will be considered here. Almost all of the abundance ratios have been determined using a Nier type spectrometer, although some investigators (55, 119) have made modifications in the basic instrument. Two features normally employed for oxygen ratio determination are dual collection of the desired isotopes and provisions for rapid intercomparison with a standard sample.

1.2 Mass spectrometer gases

Oxygen is usually introduced into the mass spectrometer as carbon dioxide, but carbon monoxide and molecular oxygen have also been used. Sulphur dioxide is not suitable because of "memory" effects (95). Water has the same disadvantage. Carbon monoxide has the problem of a quite large background in the mass range 28 and 30 due to the almost universal

presence of molecular nitrogen and hydrocarbons. Fortunately these adverse features can be obviated (26). On the other hand carbon monoxide has a number of distinct advantages.

- In many processes in which oxygen is extracted from rock samples, the oxygen is released as carbon monoxide and not as carbon dioxide.
- The pump out time of carbon monoxide is shorter than for carbon dioxide (105).
- "Memory" effects for carbon monoxide are almost completely absent (105).

Molecular oxygen has been used by Baertschi and Silverman (7). They mention the possibility of oxidation of the tungsten mass spectrometer filament. This has been further investigated and confirmed (40). The oxidation process will cause a fractionation and shorten the life time of the filament.

Carbon dioxide has been used most frequently as a mass spectrometer gas for $^{18}\text{O}/^{16}\text{O}$ determinations. Widely accepted standards of this gas are readily available (122). Craig (41) has given absolute abundance ratios for several carbon dioxide standards. He also has published correction factors for the mass spectrometrical analysis of this gas.

1.3 Methods of extracting oxygen

To obtain accurate results, either the $^{18}\text{O}/^{16}\text{O}$ ratio of the mass spectrometer gas sample must be identical to the $^{18}\text{O}/^{16}\text{O}$ ratio of the rock sample, or the precise calculation of this latter ratio should be possible. Therefore, when the oxygen from a rock sample is extracted, the following requirements should be fulfilled:

- All the oxygen of the rock sample is converted to gas sample. Thus,

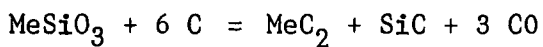
100% conversion is usually needed to be sure that no fractionation of an unknown extent occurs during the conversion in process.

- All possible precautions against oxygen contamination are taken.
- The gas sample does not interact with the apparatus resulting in a fractionation of its $^{18}\text{O}/^{16}\text{O}$ ratio.

1.3.1 Silicates and iron oxides

Carbon reduction method.

In 1952 Baertschi and Schwander (6) described a method in which the rock sample was reacted with carbon at 2000°C in a high vacuum resistance furnace. According to the reaction:

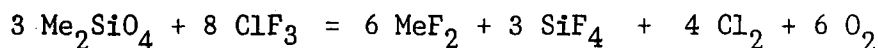


carbon monoxide was produced. By this method 60-80% of the oxygen in the silicate was liberated. The carbon monoxide was used as the mass spectrometer gas. A detailed account and results are published by Schwander (137). Comparison with more recent results have shown that Schwander's method is not free of fractionation. Possible causes for this are discussed by Clayton and Epstein (28, 32). In 1959 Dontsova (59) has described a very similar technique. She claimed an oxygen yield of 95-100%. Clayton and Epstein (28, 32) applied a modified form of this method in which the resistance furnace was replaced by an induction heater, and the carbon monoxide was converted to carbon dioxide over a nickel catalyst. They obtained yields of 90-100% for quartz, iron oxide and zircon. For all other minerals the oxygen

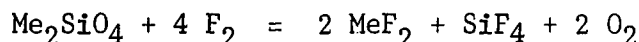
recovery was significantly less. However Russian workers (59, 166, 167) judged the carbon reduction method as successful for all minerals.

Halogen method.

This method was devised by Baertschi and Silverman (7). They used either chlorine trifluoride or pure fluorine.



and



The reaction was carried on at about 430⁰ C, and oxygen yields were 80-100% for most minerals and rocks. A drawback of the method is that everything which comes in contact with fluorine or chlorine trifluoride has to be made of nickel, inconel or other inert materials. Taylor and Epstein (144, 147) used fluorine and found it satisfactory for all but a few minerals, such as magnetite, epidote and garnet. Taylor converted the molecular oxygen which is produced to carbon dioxide. He has described extensively his experimental technique and how to purify the fluorine, which is often contaminated with oxygen. Fluorine and chlorine trifluoride have in common that they react with the nickel reaction chambers at 500⁰ C, so this becomes a temperature limit. The effect of this limit may have been the reason why Taylor did not have any success with epidote, magnetite and garnet.

Finally in 1962, Clayton and Mayeda (34) have refined the method

so that it is suitable for all minerals. They use bromine pentafluoride, which is less reactive towards nickel, thus removing the limitation encountered by Taylor. They have described their apparatus and technique in full detail (34). Oxygen yields of $100 \pm 2\%$ of the theoretical amount are obtained. Their isotopic reproducibility is 0.1-0.2%. This method seems to be the best one available at present. Hoekstra and Katz (93) report on the usage of bromine trifluoride for the quantitative determination of oxygen in various metal oxides. They claim an accuracy of 0.4%. A list of metal oxides which may be treated in this way is given in their publication. However, Clayton and Mayeda judged bromine pentafluoride to be more suitable because of its higher vapour pressure.

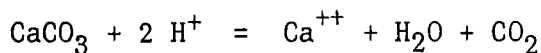
1.3.2. Carbonates

The carbon reduction method is in general not applicable to carbonates. However it has been used to determine the $^{18}\text{O}/^{16}\text{O}$ ratio in manganese carbonate (32).

Thermal decomposition of carbonates has been attempted unsuccessfully. McCrea (115) states: "The kinetics of the decomposition of calcium carbonate thermally are such that carbon dioxide can not be obtained with the desired reproducibility of isotopic composition". Vedder (163) noticed that thermal decomposition readily takes place in an environment of 0.1 mm.Hg water vapour. The water vapour has a catalytic influence. However carbon dioxide obtained in this way can only be used for carbon isotope analysis, because of oxygen exchange between the water vapour and the carbon dioxide.

The most frequently used way to decompose carbonates is by means

of acid (115). The carbonate powder is treated with 100% phosphoric acid.



It is important that the conditions under which the conversion takes place are known, because there will be a temperature dependent oxygen fractionation between the reaction products. Oxygen exchange between the orthophosphate ion and carbon dioxide or the carbonate ion is negligible. This is shown by McCrea (115) and Ault (3). The reproducible fractionation (α') between the reaction products has been determined recently by Clayton (30).

$$\alpha' = \frac{(\text{O}^{18}/\text{O}^{16}) \text{ in CO}_2 \text{ from acid decomposition of carbonate}}{(\text{O}^{18}/\text{O}^{16}) \text{ carbonate}}$$

1.1

$$= 1.00999$$

This is for 100% phosphoric acid decomposition of calcium carbonate at 25° C. The $\text{O}^{18}/\text{O}^{16}$ ratio in the denominator of eqn. 1.1 was determined by means of the fluoride method (30). For 100% phosphoric acid decomposition of rhodocrosite (MnCO_3) at 25° C, Clayton and Epstein (32) measured $\alpha' = 1.010$ by means of the carbon reduction method. McCrea's work (115) had already indicated that the α' 's for calcium-, strontium-, and barium carbonate are virtually the same.

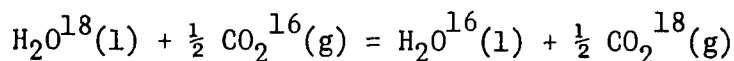
1.3.3 Phosphates

Phosphates can be treated by bromine trifluoride (155). All the oxygen is released without fractionation and the precision is claimed to be 0.15%.

There are several other methods, but usually not all of the oxygen is released. Orthophosphate can be pyrolysed to metaphosphate and water (36) and the water may then be analysed by one of the methods mentioned below. One may heat Ag_3PO_4 to 1000°C to give molecular oxygen (1). Another method is to heat KH_2PO_4 with $\text{Hg}(\text{CN})_2$ to produce carbon dioxide (87). Cohn and Drysdale (37) heated $\text{Ba}_3(\text{PO}_4)_2$ with carbon to 1350°C to produce carbon monoxide, while Boyer et al. (20) thermally reacted with KH_2PO_4 with guanidine hydrochloride and achieved in this way that two oxygens per KH_2PO_4 molecule were liberated as carbon dioxide.

1.3.4 Water

The older method of measuring the density of water (104) is not considered here. Equilibration with carbon dioxide is most often used at present. A measured volume of water is put in a flask together with a certain amount of carbon dioxide whose $^{18}\text{O}/^{16}\text{O}$ ratio is known. The temperature of the flask is kept constant at say 25°C . When isotopic equilibrium is attained between the water and the carbon dioxide a small sample of gas is withdrawn and analysed mass spectrometrically. Because the fractionation factor for the exchange reaction

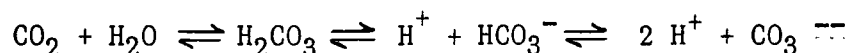


at 25° C is known, the O^{18}/O^{16} ratio of the water can be deduced. This fractionation factor was measured by Compston and Epstein (39)

$$\alpha = \frac{(O^{18}/O^{16}) \text{ in } CO_2}{(O^{18}/O^{16}) \text{ in } H_2O} = 1.04070 \quad 1.2$$

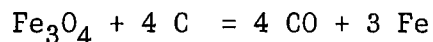
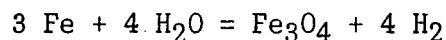
at 25° C.

The rate of this reaction is pH dependent (121). To obtain equilibrium in a reasonable time interval it is necessary that the water is acidic (pH = 5-6) because the oxygen exchange between water and carbon dioxide is due to reversible hydration of the carbon dioxide



and no direct exchange occurs between the bicarbonate ion and the water. The experimental procedure has been described by Epstein and Mayeda (77). Craig (41) gives correction formulae for this procedure and Dansgaard (46) also provides particulars. To assure that isotopic equilibrium is established Hoering (95) added the enzyme carbonic anhydrase to the water. Disadvantages of the equilibration method are that it takes at least two hours (Epstein and Mayeda waited 3 days) before equilibrium is reached, that small quantities of water are difficult to handle, and that the water has to be in the liquid phase. Dostrovsky and Klein (60) reduced the equilibration from hours to minutes by speeding up the reaction. This is done by the catalysing action of a hot platinum wire. Unfortunately this procedure does not yield reproducible results with different equilibration chambers (81).

Cameron et al. (25) used a similar technique but equilibrated the water with molecular oxygen. The exchange, catalysed by a red hot platinum filament, was completed in about one half hour. The final composition of the oxygen equilibrated with water of known O^{18} content agreed exactly with the value calculated from the mole ratio water/oxygen. Falcone (80) catalysed the reaction through a high voltage discharge. Boyer et al. (20) heated the water with HCl guanidine and thus converted the oxygen in the water to carbon dioxide. A way to treat small amounts of water or water vapour is described by Compston and Epstein (39). The procedure is based on the reactions



The water vapour is reduced at 500°C by a mixture of iron and carbon; at this temperature no carbon monoxide is formed and hydrogen is released. Then the temperature is increased to 1000°C , the iron oxide is reduced by carbon and carbon monoxide is produced which may be converted to carbon dioxide over a nickel catalyst.

1.3.5 Inorganic compounds

According to Finikov (81), many oxygen containing solids can be treated with $\text{K}_4\text{Fe}(\text{CN})_6$ at temperatures lower than 600°C . Oxygen is released without fractionation as carbon dioxide. Finikov analysed successfully Al_2O_3 , Li_2SO_4 , BaSO_4 , $\text{Ba}_3(\text{PO}_4)_2$, and NaWO_4 .

1.3.6 Organic compounds

Organic compounds can be analysed in different ways, depending on the type of compound. The Untersaucher (157) method is often used. In this method the compound is pyrolysed on a carbon surface, carbon monoxide is formed, and subsequently converted to carbon dioxide. For full particulars see (24,54). A variety of organic compounds can be treated with O-phenylendiamine monohydrochloride; the oxygen is converted quantitatively to water in this reaction. The process takes place at 300° C and the duration is about three hours (46).

1.4 Contamination

Contamination of the gas sample produced by exchange with oxide layers or with oxygen containing parts of the apparatus used is discussed briefly. This effect is in practice evaluated by the usage of blanks.

Experimentally it is determined that there is no measurable exchange between a clean and baked out silica vessel and dry carbon dioxide or dry molecular oxygen at 900° C (8). Maass (113) did a series of experiments to measure the exchange between water and glass. A measurable exchange was found only above 100° C. A similar observation is published by Mills and Hindin (121). They sealed water enriched in O^{18} in pyrex vessels and maintained the temperature at 105° C for periods up to four days. The same is done with 0.1 N. alkaline solutions at 100° C for periods of eight hours. In neither case has exchange been observed.

Dole (55) summarised data about the oxygen exchange between metal oxides and water, carbon dioxide or molecular oxygen. In the majority

of cases no exchange takes place at temperatures lower than 100° C. Winter's (177) experiments are in agreement with this. Hence the major source of contamination will be leaks and exchange between gases absorbed to the walls of the apparatus and the gas sample to be analysed.

1.5 Reporting of O^{18}/O^{16} ratios

When carbon dioxide or molecular oxygen is used and O^{18}/O^{16} ratios are mentioned, one means more often than not the $O^{18}O^{16}/O^{16}O^{16}$ ratio. The latter is the ratio which is actually measured. The oxygen isotopic ratio is usually given as a δ value

$$\delta = \left\{ \frac{(O^{18}O^{16}/O^{16}O^{16})_{\text{sample}}}{(O^{18}O^{16}/O^{16}O^{16})_{\text{standard}}} - 1 \right\} 1000 \quad 1.3$$

During the last decade a great variety of standards has been used. Presently the most used standards are SMOW (Standard Mean Ocean Water) and PDB (see Sect. 4.2). Relationships between the standards and the absolute oxygen isotope ratios of various standards are given by Craig (41).

When carbon monoxide or water are employed as a mass spectrometer gas, true O^{18}/O^{16} ratios are reported. It is only in rare cases when authors state whether they record their results as the $O^{18}O^{16}/O^{16}O^{16}$ ratio or as the O^{18}/O^{16} ratio. It is also rare when mention is made of the nature of the corrections which were applied to the raw mass spectrometer data. Generally, American investigators seem to apply Craig's corrections (41). Russian data appear not to be corrected for O^{17} while Baertschi and Dansgaard apply this correction.

The Russian analogue for the δ value is

$$\delta'' = \left\{ \frac{(\text{O}^{18}/\text{O}^{16})_{\text{sample}}}{(\text{O}^{18}/\text{O}^{16})_{\text{standard}}} - 1 \right\} 100$$

Among the Russian standards are

- River water (58)

$$\delta''_{\text{atmospheric oxygen/river water}} = 3.2 \quad 1.4$$

Atmospheric oxygen is fairly uniform in its isotopic composition.

Nier* (125) gives

$$\frac{\text{O}^{18}\text{O}^{16}}{\text{O}^{16}\text{O}^{16}} = 408.8 \times 10^{-5} \quad 1.5$$

for atmospheric oxygen.

Hence Russian river water has the ratio

$$\frac{\text{O}^{18}\text{O}^{16}}{\text{O}^{16}\text{O}^{16}} = 396 \times 10^{-5} \quad 1.6$$

and thus

$$\delta_{\text{river water/PDB}} = -47 \quad 1.7$$

$$\delta_{\text{river water/SMOW}} = -9 \quad 1.8$$

- Quartz from the Neroika deposit from the Artic Urals (165).

* Nier made a small numerical error in the percentage calculation of O^{18} for atmospheric oxygen; this should be 0.2035% instead of 0.2039%.

Absolute ratio of the quartz standard

$$\frac{O^{18}}{O^{16}} = \frac{1}{487 \pm 1}$$

Chupakhin (26) has described how this ratio was determined.

Thus

$$\frac{O^{18}O^{16}}{O^{16}O^{16}}_{\text{quartz standard}} = 412 \times 10^{-5} \quad 1.9$$

and

$$\delta_{\text{Neroika quartz/SMOW}} = 30 \quad 2.0$$

In the calculation of eqns. 1.8 and 2.0 the $[O^{18}O^{16}/O^{16}O^{16}]_{\text{SMOW}}$ ratio as given by Craig (42) was used.

The δ value for the Neroika quartz is far beyond the range of quartz δ values measured by investigators in the U.S.A. (see also graph 9.6). Moreover no published exchange of samples between Russian and Western laboratories has taken place, to establish a direct correlation. Therefore, it is not possible to compare quantitatively the Russian results (165, 167) measured relative to Neroika quartz, with results obtained elsewhere. The Russian river water standard agrees better with similar measurements done outside the USSR.

Not all investigators use the δ notation. Some notable exceptions are Rankama (129) and Dansgaard (46). Rankama records the data as the absolute or relative value of the O^{18}/O^{16} ratio. Dansgaard follows

the usage of tracer technique workers who report concentrations of the rare isotope in parts per million. Dansgaard records the O^{18} content as parts per million of the total oxygen content of the sample with respect to the Danish standard. He has correlated his Danish standard with American standards.

In this survey the American practice is followed; wherever O^{18}/O^{16} ratios are mentioned, the molecular $O^{18}O^{16}/O^{16}O^{16}$ ratio is meant.

CHAPTER 2

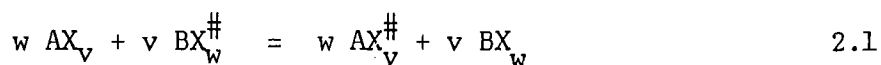
ISOTOPIC EQUILIBRIUM THEORY

2.1 Introduction

This chapter deals with the calculation of the equilibrium constant for isotopic exchange reactions, from spectroscopic data. It is assumed that the reader is familiar with the publications by Urey (158) and by Bigeleisen and Mayer (15).

2.2 Ideal gases

Consider the exchange reaction



The superscript # denotes the presence of the heavy (usually the rarer) isotope. The compounds AX_v and BX_w are ideal gases. By definition

$$K_{\text{eq}} = \frac{\left[\frac{(\text{AX}_v^{\#})}{(\text{AX}_v)} \right]^w}{\left[\frac{(\text{BX}_w^{\#})}{(\text{BX}_w)} \right]^v} \quad 2.2$$

Theoretically successful calculations of K_{eq} have been performed only

for ideal gases. These calculations have been the subject of many papers, among which references (15, 56, 133, 156, 158, 168 and 174) are only a few. Thermodynamically the equilibrium constant is related to the free energy by

$$- RT \ln K_{eq} = \Delta F^0 \quad 2.3$$

where

F^0 = standard free energy,

R = gas constant,

T = absolute temperature.

The free energy is related to the partition function Q according to

$$F = - RT \ln \frac{Q_e}{N} \quad 2.4$$

where

e = base of natural logarithme,

N = Avogadro's number.

To a very good approximation the potential energy functions are the same for isotopically different molecules. Therefore it is justified to take as the reference datum for the energies appearing in the partition function, the hypothetical vibrationless state of the molecule. For normal chemical reactions this procedure is not followed, the ground state of the molecule is taken as reference level, and the zero point energy is neglected. However, since it is mainly the difference in zero

point energies which make isotopically substituted molecules behave differently, it is essential not to neglect the zero point energy. Thus zero point energy is included in the energy appearing in the partition function.

For reaction 2.1

$$\begin{aligned} \Delta F^0 &= (wF_{AX_v^\#}^0 - vF_{BX_w}^0) - (wF_{AX_v}^0 - vF_{BX_w^\#}^0) \\ &= -RT \ln \left[\frac{Q_{AX_v^\#}}{Q_{AX_v}} \right]^w / \left[\frac{Q_{BX_w^\#}}{Q_{BX_w}} \right]^v + \\ &\quad + \left[w(V_{AX_v^\#} - V_{AX_v}) - v(V_{BX_w^\#} - V_{BX_w}) \right] P \end{aligned} \quad 2.5$$

where

V_{AX_v} = volume of molecule AX_v in the ground state,

P = pressure.

Usually the change in volume due to isotopic substitution is neglected, because its influence on K_{eq} is only a minor one. Therefore

$$K_{eq} = \frac{\left[Q_{AX_v^\#} / Q_{AX_v} \right]^w}{\left[Q_{BX_w^\#} / Q_{BX_w} \right]^v} \quad 2.6$$

Under nonextreme conditions the partition function may be approximated by

$$Q = Q_{tr} Q_{vib} Q_{rot} \quad 2.7$$

where

Q_{tr} = translational partition function,

Q_{vib} = vibrational partition function,

Q_{rot} = rotational partition function.

Using this approximation the partition function ratio becomes

$$\frac{Q^\#}{Q} = \frac{s^\#}{s} \left[\frac{I_x^\# I_y^\# I_z^\#}{I_x I_y I_z} \right]^{\frac{1}{2}} \left[\frac{M^\#}{M} \right]^{3/2} \prod_i \frac{e^{-u_i^\#/2}}{1 - e^{-u_i^\#}} \frac{1 - e^{-u_i}}{e^{-u_i/2}} \quad 2.8$$

where

s = symmetry number,

I_x, I_y, I_z = the three principal moments of inertia,

$u_i = h \nu_i / kT$,

i = vibration frequency of the i^{th} mode,

h = Planck's constant,

k = Boltzmann's constant,

T = absolute temperature,

M = molecular weight.

Degenerate modes of vibration are counted as many times as they are degenerate. After making use of the Teller-Redlich product rule (131) which states

$$\left[\frac{I_x^\# I_y^\# I_z^\#}{I_x I_y I_z} \right]^{\frac{1}{2}} = \left[\frac{M^\#}{M} \right]^{3/2} \left[\frac{m}{m^\#} \right]^{3n/2} \prod_i \frac{u_i}{u_i^\#} = 1 \quad 2.9$$

one obtains

$$\frac{Q^\#}{Q} \left[\frac{m}{m^\#} \right]^{3n/2} = \frac{s}{s^\#} \prod_i \frac{u_i^\#}{u_i} \frac{e^{-u_i^\#/2}}{1 - e^{-u_i^\#}} \frac{1 - e^{-u_i}}{e^{-u_i/2}} \quad 2.10$$

where

n = number of isotopic atoms being exchanged,
 $m, m^\#$ = atomic weights of the two isotopes.

Following Bigeleisen and Mayer (15) one defines

$$f = \frac{Q^\#}{Q} \left[\frac{m}{m^\#} \right]^{3n/2} \quad 2.11$$

as the reduced partition function ratio.

Thus

$$K_{eq} = \frac{[f_{AX}]^w}{[f_{BX}]^v} \quad 2.12$$

and

$$\frac{s^\#}{s} f = \prod_i \frac{u_i^\#}{u_i} \frac{e^{-u_i^\#/2}}{e^{-u_i/2}} \frac{1 - e^{-u_i}}{1 - e^{-u_i^\#}} \quad 2.13$$

Substituting $u_i = u_i^\# + \Delta u_i$ into eqn. 2.13 and expanding the result, one obtains

$$\begin{aligned} \ln \frac{s^\#}{s} f = & \sum_i \left[\frac{1}{2} - \frac{1}{u_i^\#} - \frac{1}{e^{u_i^\#}} \right] \Delta u_i + \left[\frac{1}{2u_i^\#{}^2} - \frac{1}{2!(1 - e^{-u_i^\#})^2} \right] \Delta u_i^2 \\ & - \left[\frac{1}{3u_i^\#{}^3} - \frac{1}{3!} \frac{e^{-u_i^\#} - e^{-2u_i^\#}}{(1 - e^{-u_i^\#})^3} \right] \Delta u_i^3 + \dots \end{aligned} \quad 2.14$$

Vojta (169) gives a detailed account of this expansion. When Δu_i is small, the higher powers of eqn. 2.14 may be neglected.

Put

$$G(u_i) = \frac{1}{2} - \frac{1}{u_i^\#} + \frac{1}{e^{u_i^\#} - 1} \quad 2.15$$

Eqn. 2.13 becomes now

$$\ln f = \ln \frac{s}{s^\#} + \sum_i G(u_i) \Delta u_i \quad 2.16$$

Except for the case of very light atoms (Hydrogen), Δu_i will be small enough to make this approximation a good one. Values for the function $G(u_i)$ are calculated and tabulated conveniently by Bigeleisen and Mayer (15). These tables are reproduced in (56). The equilibrium constant is given by

$$\ln K_{eq} = w \left[\ln \frac{s}{s^\#} + \sum_i G(u_i) \Delta u_i \right]_{AX_v} - v \left[\ln \frac{s}{s^\#} + \sum_i G(u_i) \Delta u_i \right]_{BX_w} \quad 2.17$$

Higher accuracy may be obtained by including the second term of eqn. 2.14 in the calculations for K_{eq} .

When one defines

$$S(u_i) = \frac{1}{u_i} - \frac{u_i e^{u_i}}{(e^{u_i} - 1)^2} \quad 2.18$$

an alternative equation for $\ln f$ is obtained

$$\ln f = \ln \frac{s}{s^\#} + \sum_i G(u_i) \Delta u_i + \sum_i S(u_i) (\Delta u_i)^2 / 2u_i \quad 2.19$$

This development is due to Bigeleisen (13, 14) who has also published tabulated values for the function $S(u_i)$ (13).

2.3 Limitations of the theoretical treatment

2.3.1 Idea gas assumption

Eqns. 2.17 and 2.19 are only valid for ideal gases. In applying them to condensed phases one neglects the influence of the presence of other molecules on the internal vibrations of the molecule under consideration.

2.3.2 Anharmonicity

In the derivation of eqn. 2.17 the vibrational partition function for the harmonic oscillator was used. At moderate temperatures this will be adequate, but anharmonicity becomes more pronounced when the temperature increases. The usual procedure is to correct only the zero point vibrational energy for anharmonicity. Thus

$$E_0 = \frac{1}{2} hc \sum_i \omega_i - \frac{1}{4} hc \sum_i \sum_j (x_{ij}^\# - x_{ij}) \quad 2.20$$

where

$$\omega_i = \frac{\nu_i}{c}$$

Then the correction for $\frac{s^\#}{s}$ f will be

$$e^{-\sum_i \sum_j \frac{1}{4} \frac{hc}{kT} (x_{ij}^\# - x_{ij})} \quad 2.21$$

because the anharmonicity contribution to the partition function is

$$Q_{anh} = e^{-\frac{1}{4} \frac{hc}{kT} \sum_i \sum_j x_{ij}} \quad 2.22$$

Therefore

$$\ln f = \ln \frac{s^\#}{s} + \sum_i G(u_i) \Delta u_i - \frac{hc}{4kT} \sum_i \sum_j (x_{ij}^\# - x_{ij}) \quad 2.23$$

Normally the anharmonicity constants x_{ij} for the isotopically substituted molecule are not known. But these constants can be calculated, provided they are known for the nonsubstituted molecule

$$\frac{x_{ij}^\#}{x_{ij}} = \frac{\omega_i^\# \omega_j^\#}{\omega_i \omega_j} \quad 2.24$$

With respect to eqn. 2.24, Herzberg (91) remarks that it has not been rigorously proven, but that results justify it, i.e. it agrees with the experimentally determined values. At low temperature the influence of anharmonicity is unimportant. One may also consider the influence of anharmonicity on the total vibrational energy. According to Vojta (170) this correction would amount to 0.1% to 1% of the anharmonicity correction for the zero point energy at about 273° K. It would increase to

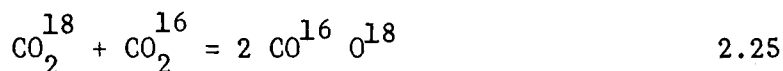
0.5% to 5% at about 500 K.

The correction for the anharmonicity can be evaluated theoretically when one uses a semi-empirical potential energy function like the Morse potential, instead of the Hooke's law potential, in the wave functions for the oscillator.

The Teller-Redlich product rule which is used to derive eqn. 2.10 can not be applied when the vibrations are anharmonic.

2.3.3 Intramolecular fractionation and the fractionation factor

Generally it is assumed that the distribution of the isotope $X^{\#}$ in the molecular species AX_v is governed only by the symmetry numbers of the various isotopic configurations of the species AX_v . In other words the heavy isotope will be distributed at random through the assemblage of molecules of a certain species. For example



$$K_{eq} = \frac{[CO^{16}O^{18}]^2}{[CO_2^{18}][CO_2^{16}]} = 4 \quad 2.26$$

Because when eqn. 2.17 is applied one finds that

$$K_{eq} = \frac{1}{s_{CO^{16}O^{18}}} \bigg/ \frac{1}{s_{CO_2^{18}}} \times \frac{1}{s_{CO_2^{16}}} \quad 2.27$$

$$= \frac{1}{\frac{1}{2} \times \frac{1}{2}} = 4$$

However eqn. 2.27 represents an idealization and observations (116) have shown that for reaction 2.25

$$K_{eq} = 3.983$$

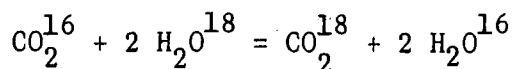
The discrepancy of 0.017 is due to intramolecular fractionation caused by the presence of the heavy isotope. The presence of the heavy isotope has changed the vibrational frequencies of the molecule. In this case the concentration of O^{18} is very small with respect to the O^{16} concentration and the effect is not of practical importance as long as all oxygen atoms occupy structurally equivalent positions in the molecule. Intramolecular fractionation can be evaluated only if one knows all zero order vibrational frequencies of the differently substituted molecules.

In the course of numerical evaluation of the equilibrium constant (see sect. 2.6) it is implicitly assumed that there will be no intramolecular fractionation. One takes for granted that all atoms which can be exchanged have equal probabilities of doing so, provided they are in structurally equivalent positions.

The fractionation factor α is defined as

$$\alpha = \left[\frac{O^{18}}{O^{16}} \right]_{\text{in } CO_2} / \left[\frac{O^{18}}{O^{16}} \right]_{\text{in } H_2O} \quad (*)$$

for the reaction



(*) With regard to the usage of O^{18}/O^{16} ratios see sect. 1.5.

while

$$K_{eq} = \frac{[CO_2^{18}]}{[CO_2^{16}]} \bigg/ \frac{[H_2O^{18}]^2}{[H_2O^{16}]^2}$$

now

$$\alpha = \frac{2[CO_2^{18}] + [CO^{16}O^{18}]}{[CO^{16}O^{18}] + 2[CO_2^{16}]} \bigg/ \frac{[H_2O^{18}]}{[H_2O^{16}]}$$

$$\alpha = K_{eq}^{\frac{1}{2}}$$

provided eqn. 2.26 is valid.

Hence the relation

$$K_{eq} = \alpha^{vw} \quad 2.28$$

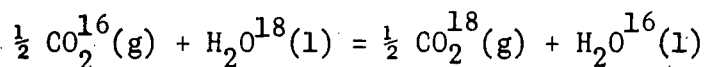
for the reaction 2.1 is also an idealization.

2.3.4 Zero point energy

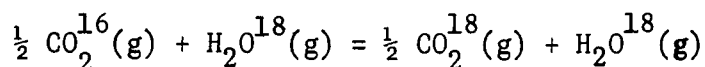
For the calculations of K_{eq} one must use zero order frequencies. From empirical formulae for the molecular energy levels one can estimate the zero point energy and thus one may convert the observed frequencies to zero order frequencies.

2.4 Liquids

The equilibrium constant for an isotopic exchange reaction between a gas and liquid phase is easily evaluated provided information is available about the vapour pressure of the normal and of the isotopic liquid. Let α_1 be the fractionation factor for the reaction



and α is the fractionation factor for the corresponding reaction



then

$$\alpha_1 = \alpha \frac{P_{\text{H}_2\text{O}^{18}}}{P_{\text{H}_2\text{O}^{16}}} \quad 2.29$$

where $P_{\text{H}_2\text{O}^{18}}$ = vapour pressure of H_2O^{18} .

Theoretical calculations of vapour pressures of isotopic liquids are not trivial and have been successfully undertaken only for argon, neon, etc. But there are experimental equations available to calculate the vapour pressure ratio. Riesenfeld and Chang (132) found experimentally

$$\log \frac{P_{\text{H}_2\text{O}^{16}}}{P_{\text{H}_2\text{O}^{18}}} = \frac{2.74}{T} - 0.0056 \quad 2.30$$

Zhavoronkov et al. (179) derived from an independent set of experimental data

$$\log \frac{P_{H_2O^{16}}}{P_{H_2O^{18}}} = \frac{3.449}{T} - 0.00781 \quad 2.31$$

Eqns. 2.30 and 2.31 give the same result at room temperatures, but differ slightly for high and low temperatures. Devyatekh et al. (53) derived the equation

$$\ln \frac{P_{CO^{16}}}{P_{CO^{18}}} = \frac{5.41}{T} - 0.0610 \quad 2.32$$

But usually such equations are not available.

Waldmann (174) gives the following rule of thumb: the phase in which the molecule or atom group has the most vibrational degrees of freedom, will be enriched in the heavy isotope.

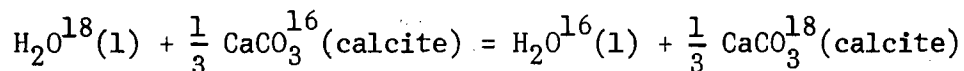
2.5 Solids

As will be shown in the numerical example of isotopic exchange between gaseous carbon dioxide and water (sect. 2.6), the calculated values are slightly different from the experimental ones. The difference in the example is only 2.2% but it is still far greater than the present day experimental accuracy. This discrepancy between theoretical and experimental values will increase when one applies the calculations of sect. 2.2 to solids. The reason being that the assumptions become worse and the spectroscopic data less dependable. Only two cases of isotopic exchange calculations involving solids are reported in the

recent literature.

Grant (85) assumed that the isotopic exchange of silicon isotopes in silicates is exclusively governed by the internal vibrations of the orthosilicate ion. By means of this approximation the problem was reduced to an ideal gas case.

McCrea (115) tried to determine the temperature dependence of the fractionation factor for



He assumed that the internal vibrations remained unchanged and he tried to evaluate the contribution of the lattice motions to the fractionation. The acoustical mode of the calcite lattice was approximated by a Debye function, while the optical modes and the rotation of the CO_3^{--} ion were expressed as Einstein functions. Because of several ad hoc assumptions, necessitated by lack of data and the complexities of the problem, McCrea's treatment could not be expected to give quantitatively correct results. However qualitatively the agreement between McCrea's calculations and the experiment is fairly good. The greatest drawback seems to be the lack of good spectroscopic data, which results from the inherent difficulties in the interpretation of Raman and Infrared spectra.

2.6 Numerical example

The theoretical calculation of the equilibrium constant for the exchange reaction

$$\frac{1}{2} \text{CO}_2^{16} + \text{H}_2\text{O}^{18} = \frac{1}{2} \text{CO}_2^{18} + \text{H}_2\text{O}^{16}$$

is performed to various degrees of accuracy (table 2.3). Table 2.1 gives the vibrational wave numbers which were used.

TABLE 2.1

Normal vibrations of the carbond dioxide and the water molecule

Normal vibrations	CO_2^{16} cm ⁻¹	CO_2^{18} cm ⁻¹	H_2O^{16} cm ⁻¹	H_2O^{18} cm ⁻¹
ω_1	1351.20	1273.9	3825.32	3815.5
ω_2	672.20 ^(x)	661.94 ^(x)	1633.91	1647.8
ω_3	2396.4	2359.81	3935.59	3919.4

(x) The ω_2 vibration is twice degenerate for carbon dioxide. All data are from Urey (158).

For H₂O the symmetry numbers s and s[#] are always unity. For CO₂ the ratio s/s[#] equals one because all oxygen atoms are considered to be exchanged (see eqn. 2.17). To calculate the anharmonicity correction (eqn. 2.23) the coefficients of table 2.2 were used.

TABLE 2.2

Anharmonicity coefficients for CO₂ and H₂O. Ref. (158)

Anharmonicity coefficient	CO ₂ ¹⁶ cm ⁻¹	CO ₂ ¹⁸ cm ⁻¹	H ₂ O ¹⁶ cm ⁻¹	H ₂ O ¹⁸ cm ⁻¹
x ₁₁	- 0.3	- 0.27	- 43.89	- 43.66
x ₂₂	- 1.3	- 1.26	- 19.5	- 19.36
x ₃₃	-12.5	-12.12	- 46.37	- 45.99
x ₁₂	+ 5.7	+ 5.29	- 20.02	- 19.89
x ₁₃	-21.9	-20.33	-155.06	-154.03
x ₂₃	-11.0	-10.67	- 19.81	- 19.66

From data given in tables 2.1 and 2.2 the following fractionation factors are calculated (table 2.3).

TABLE 2.3

Fractionation factors calculated for the systems
water vapour - carbon dioxide and water - carbon dioxide
at 25.1° C and 1 atmosphere pressure

System water vapour - carbon dioxide	α
(a) from eqn. 2.17	1.0450
(b) from eqn. 2.19	1.0458
(c) from eqns. 2.19, 2.21	1.0468
System water - carbon dioxide	
(d) from eqns. 2.19, 2.21, 2.29	1.0385
(e) experimentally determined (39)	1.0407

The data of table 2.3 show how by refining the calculations the accuracy may be increased, provided the basic information (vibrational frequencies and anharmonicity coefficients) allows this. If eqn. 2.17 is used to calculate α , all but the first term of eqn. 2.14 are neglected; if eqn. 2.19 is used, only the first two terms of eqn. 2.14 are employed. Since eqn. 2.14 converges fairly rapidly, these first two terms should give a good approximation. Usually one neglects even

the second term of eqn. 2.14. By means of eqn. 2.21 the anharmonicity correction can be evaluated. Line (c) in table 2.3 gives thus the best value of α for the system water vapour - carbon dioxide. Applying eqn. 2.29 one obtains the fractionation factor for the system water - carbon dioxide. It is generally felt that the experimental value is more accurate than the theoretically derived one. However it should be noted that the actual difference between the two α 's (lines (d) and (e)) is fairly small, when one considers all the approximations used to arrive at the theoretically derived α .

In conclusion one may say that theoretically derived α 's are only of value for semi-quantitative purposes. However a theoretical calculation of α will provide insight about the phenomena one may anticipate, because it illustrates the basic features of isotope behaviour.

CHAPTER 3

FACTORS INFLUENCING THE EQUILIBRIUM CONSTANT

3.1 Introduction

This chapter is a continuation of chapter 2. The equilibrium constant is dependent on the temperature, pressure and thermodynamical activity. These three factors are considered in some detail. Formulae for the temperature and pressure dependence are derived.

3.2 Temperature dependence

When $s = s^\ddagger$, eqn. 2.17 becomes

$$\ln K_{eq} = \left[w \sum_i G(u_i) \Delta u_i \right]_{AX_v} - \left[v \sum_i G(u_i) \Delta u_i \right]_{BX_w}$$

Bigeleisen and Mayer (15) have pointed out that the function $G(u_i)$ may be approximated by $u_i/12$ when $u_i \leq 2$. As u_i becomes large the approximation becomes bad (see table 3.1).

TABLE 3.1

Comparison between $G(u_i)$ and $u_i/12$

u_i	$u_i/12$	$G(u_i)$	$u_i/12 - G(u_i)$	% difference
1	0.083	0.082	0.001	1
2	0.167	0.157	0.010	6
3	0.250	0.219	0.031	14
4	0.333	0.267	0.066	25
5	0.416	0.307	0.109	35
6	0.500	0.336	0.164	49

At high temperatures u_i becomes small enough to justify the approximation

$$\ln K_{eq} = x/T^2 + y \quad 3.1$$

From tables 3.1 and 3.2 and eqns. 2.15 and 2.17 one may conclude that if u_i is large, at low temperatures, K_{eq} is better approximated by

$$\ln K_{eq} = \frac{r}{T} + s \quad 3.2$$

where x , y , r and s are constants. T is the absolute temperature.

Most polyatomic oxygen containing compounds have vibrational frequencies of the order of 1000 cm^{-1} . But O-H bonds have vibrational frequencies of about 4000 cm^{-1} .

TABLE 3.2

Values of u for different temperatures and frequencies

Temperature $^{\circ}\text{K}$	$\omega = 1000\text{ cm}^{-1}$ u	$\omega = 4000\text{ cm}^{-1}$ u
273	5.28	21.1
400	3.60	14.4
500	2.88	11.5
600	2.40	9.60
700	2.06	8.25
800	1.80	7.20
1200	1.20	4.80

Therefore when no O-H bonds are involved one may anticipate a temperature dependence like eqn. 3.1 (c.f. tables 3.1 and 3.2).

When the temperature increases various assumptions employed in eqn. 3.1 become less good. The anharmonicity becomes more pronounced. The rigid rotator assumption does not hold any longer, because of stretching of the molecule by its own centrifugal force, and therefore one finds

an increase in the difference between the average moment of inertia of the molecule in an excited vibrational state and that of the molecule in the ground state. The usage of the Teller-Redlich product rule becomes less justifiable. At very high temperatures all partition functions have their classical value and no isotopic fractionation will take place.

Cross over temperature

It is fairly common that a phase which concentrates the light isotope at low temperatures, will concentrate the heavy isotope at high temperatures. This phenomenon is called "cross-over". It may happen phase A is enriched in the heavy isotope at low temperature and has lower vibrational frequencies than phase B, which is enriched in the light isotope at that low temperature. Phase A will have more vibrational degrees of freedom than phase B in this case. The occurrence of "cross over" under these circumstances follows directly from eqn. 2.17 and from the fact that $G(u_i)$ is a monotonically increasing function of u_i (see table 3.1) for which $\frac{dG(u_i)}{du_i}$ tends to zero when u_i increases.

3.3 Pressure dependence

Returning to eqn. 2.5 one obtains for the equilibrium constant

$$K_{eq} = \frac{\left[\frac{Q_{AX_v^\#}}{Q_{AX_v}} \right]^w}{\left[\frac{Q_{BX_w^\#}}{Q_{BX_w}} \right]^v} e^{-P(w \Delta V_A - v \Delta V_B)/RT} \quad 3.3$$

where

$$\Delta V_A = V_{AX_v^\#} - V_{AX_v}$$

and

$$\frac{\partial \ln K_{eq}}{\partial P} = -(w\Delta V_A - v\Delta V_B)/RT \quad 3.4$$

since

$$\frac{\partial \ln K_{eq}}{\partial P} \ll 1$$

$$\frac{\partial K_{eq}}{\partial P} \approx -(w\Delta V_A - v\Delta V_B)/RT \quad 3.5$$

Following the method of Joy and Libby (100) the term $(w\Delta V_A - v\Delta V_B)$ will now be estimated. They assume that the fractional volume change on isotopic substitution is about equal to the cube of the fractional change in the distance from the centre of the molecule to the furthest position of any constituent atom in the course of normal vibrations of the molecule in the ground state. Also it is assumed that the bonds are harmonic oscillators. The bond length itself will not be affected by isotopic substitution, however, the root mean square distance between the atom's position and its equilibrium site will change as a result of the substitution. The wave function for the groundstate of the harmonic oscillator is

$$\psi_0 = \left[\frac{4\pi\nu m}{h} \right]^{\frac{1}{4}} e^{-2\pi^2\nu m x^2/h} \quad 3.6$$

The root mean square expectation value of x

$$\sqrt{x^2} = \left[\frac{h}{8\pi^2\nu m} \right]^{\frac{1}{2}} \quad 3.7$$

and

$$\nu = \frac{1}{2\pi} \sqrt{\frac{f}{m}} \quad 3.8$$

where

ν = vibration frequency of the harmonic oscillator,

f = force constant,

m = reduced mass.

Only the stretching mode (ν_1) is considered in the calculation of the change in distance on isotopic substitution.

$$\begin{aligned} \Delta r &= \sqrt{x^2} - \sqrt{x^{\#2}} \\ &= \left[\sqrt{\omega_1} - \sqrt{\omega_1^{\#}} \right] \sqrt{\frac{hc}{2f}}_{\text{stretching}} \quad 3.9(*) \end{aligned}$$

and

$$\frac{\Delta V}{V} = \frac{3 \Delta r}{r} \quad 3.10$$

The distance r may be calculated from the molecular volume or may be

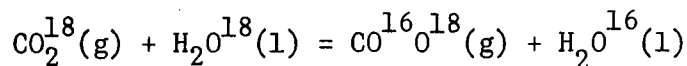
(*) The corresponding formula as given in (100) is in error, see also (106).

put equal to half of the distance between the centres of neighbouring molecules in the solid state. The vibration frequency of the stretching mode of the isotopically substituted molecule can be calculated by means of the product rule.

Hoering (94) has asserted that the maximum effect of pressure on the equilibrium constant can be derived from the anharmonicity correction to the ratio of the vibrational partition functions. This is based on the following line of reasoning: If chemical bonds are harmonic oscillators, then the effect of isotopic substitution will be only a change in frequency, the amplitude and hence the volume of the molecule will be constant. But actually, chemical bonds are anharmonic oscillators, thus the amplitude will change as a result of isotopic substitution. Therefore, the anharmonicity correction is a measure of the maximum influence of pressure on the equilibrium constant. It is true that classically the amplitude of any harmonic oscillator depends only on the initial conditions, and is thus mass independent. However the same is true for the anharmonic oscillator. Quantum mechanically the concept of amplitude is empty, but the root mean square expectation value for x (eqn. 3.7) is mass dependent for a harmonic oscillator. In section 4.7 it will be shown that the pressure dependence in carbonate palaeothermometry is relatively insignificant.

3.4 Thermodynamic activity

Besides the temperature and the pressure, the thermodynamic activity of the components of the system will influence the equilibrium constant. Thus for the reaction



$$\begin{aligned}\alpha' &= \left[\frac{a^\#}{a} \right]_{\text{CO}_2} / \left[\frac{a^\#}{a} \right]_{\text{H}_2\text{O}} \\ &= \left[\frac{\gamma^\#}{\gamma} \right]_{\text{CO}_2} \left[\frac{\text{CO}^{16}\text{O}^{18}}{\text{CO}_2^{16}} \right] / \left[\frac{\gamma^\#}{\gamma} \right]_{\text{H}_2\text{O}} \left[\frac{\text{H}_2\text{O}^{18}}{\text{H}_2\text{O}^{16}} \right] \\ &= \alpha f(\gamma)\end{aligned}\tag{3.11}$$

where

a = thermodynamic activity,

γ = activity coefficient,

α = fractionation factor for the system with activity coefficient ratios equal to unity,

$f(\gamma)$ = function of the activity coefficients,

α' = actual measured fractionation factor.

Hoering (94) has measured the change in α' when one replaces the pure water by a 10 molar aqueous lithium chloride solution. It is believed that the lithium chloride interacts solely with the water, therefore only the ratio $(\gamma^\#/\gamma)_{\text{H}_2\text{O}}$ is affected. Taking $f(\gamma) = 1.000$ for the system with pure water Hoering has observed $f(\gamma) = 1.0008$ for the lithium chloride solution. He attributes this to selective solvation of the lithium ions by water, so that the solvent becomes enriched in O^{16} .

Unfortunately little is known about activity coefficients of hydrothermal solutions. It should be noted that Hoering's solution is quite concentrated. Thus for natural occurring aqueous solutions one may anticipate that the activity dependence of K_{eq} is only of secondary importance.

CHAPTER 4

PALAEOTHERMOMETRY

4.1 Introduction

Palaeothermometry utilizes the temperature dependence of the equilibrium constant for the oxygen isotope exchange reaction between calcite and water. Urey (158) suggested that palaeotemperatures could be determined in this way. In 1948 he published some preliminary results (159).

Experimentally one does not determine the constant K_{eq} but the fractionation factor α . McCrea has grown calcium-carbonate very slowly from an aqueous solution at different temperatures. In this way he determined the temperature dependence of α . The fractionation factor could not be evaluated because of the constant fractionation occurring when calcite is treated with acid to produce CO_2 (see sect. 1.3.2). The CO_2 is used to measure the O^{18}/O^{16} ratio of the calcite mass spectrometrically.

By comparing McCrea's inorganic results with organically precipitated calcite one can conclude whether the biogenic calcite was precipitated in thermodynamical equilibrium with the water or not. This has been done by Epstein et al. (73). Marine calcareous shelled invertebrates were

grown at known temperatures and their shells were analysed. Because of difficulties in the purification of biogenic calcite, Epstein et al. (74) had to publish a revision of their 1951 paper (73). A temperature relationship was established between the O^{18}/O^{16} ratios of the water and of the calcite. This relationship is in virtual agreement with McCrea's work.

Urey et al. (161) have calculated Upper Cretaceous temperatures. They used belemnite guards, and assumed that the guards were in isotopic equilibrium with the Upper Cretaceous ocean. This assumption has withstood the test of internal consistency of results. They also assumed the habitat of belemnites was characterised by a salinity of 34.8%, that of the present ocean, and a δ sea water/PDB = -0.47. The absolute temperature measured in this way may not be too significant because of the uncertainty in the O^{18}/O^{16} ratio of the sea water. But their tentative conclusions about temperature trends during the Upper Cretaceous have been later confirmed by Lowenstam and Epstein (111). Emiliani and Epstein (68) have shown that certain recent foraminifera form their tests in isotopic equilibrium with their surroundings. This has been the start of the Pleistocene temperature work.

Once the pioneering papers (73, 74, 161) were published a great many publications appeared dealing with Pleistocene, Tertiary, Cretaceous, Jurassic and Permian temperatures. The majority of them are listed by Samuel and Steckel (135, 136). Among the papers published in 1961 and 1962 are:

- (134, 162) on Pleistocene temperatures;
- (166, 67, 69) on Tertiary temperatures;
- (19) on Jurassic temperatures.

This subject is reviewed by Durham (61) and Thorley (153).

In the following sections various aspects of carbonate thermometry will be considered.

4.2 Temperature formulae

Epstein et al. (74) have derived experimentally the equation

$$t = 16.5 - 4.3 \delta + 0.14 \delta^2 \quad 4.1$$

where

t = temperature in $^{\circ}\text{C}$ at which the carbonate is formed,

δ = the per mil difference between the $\text{O}^{18}/\text{O}^{16}$ ratio of CO_2 obtained from the sample and a standard CO_2 .

The standard carbon dioxide is produced by reacting the calcitic guard of *Belemnitella americana* with 100% phosphoric acid at 25.2°C . This is the PDB standard. The belemnite was collected from the Upper Cretaceous Peedee formation in South Carolina.* Equation 4.1 is only applicable when

$\delta_{\text{sea water/PDB}} = -0.1$ (see Craig (41)). To avoid confusion, this value -0.1 is the δ value of the carbon dioxide, equilibrated with mean ocean water at 25°C . It was realized that locally the ocean water $\text{O}^{18}/\text{O}^{16}$ ratio may vary appreciably from the ratio for mean ocean water (76) and thus eqn. 4.1 was changed to

$$t = 16.5 - 4.3 (\delta - A) + 0.14 (\delta - A)^2 \quad 4.2$$

* Parenthetically, there are also authors who claim that the belemnite was collected in North Carolina.

Again δ refers to the O^{18}/O^{16} ratio of the carbonate and A equals the δ value for the water in which the sample carbonate precipitated.

Equations 4.1 and 4.2 are based on data in the temperature range $0 - 30^{\circ} \text{C}$.

Employing high pressure techniques Clayton (29) has been able to obtain experimentally the following equation which fits the data over the range $0 - 750^{\circ} \text{C}$.

$$\ln K = 2730 T^{-2} - 0.00256 \quad 4.3$$

K = fractionation factor for the water - calcite system. Clayton's nomenclature is followed here.

T = absolute temperature in degrees Kelvin.

Since Clayton used Epstein's low temperature results eqns. 4.2 and 4.3 give practically the same result in the interval $0 - 30^{\circ} \text{C}$.

4.3 O^{18}/O^{16} ratio of ocean water

Epstein and Mayeda (76) have analysed 93 marine water samples and found that the O^{18}/O^{16} ratio of normal marine water (i.e. not surficial or shoal water, or water contaminated with fresh water) varies only 0.3%. Due to evaporation surficial marine water is more salty and enriched in O^{18} , while fresh water is enriched in O^{16} . The reason for this is the higher vapour pressure of H_2O^{16} , as compared to H_2O^{18} , under meteorological conditions. In palaeotemperature work it is often assumed that the ocean in the past had the same O^{18}/O^{16} ratio as the ocean has presently, i.e. A = 0 in eqn. 4.2. Emiliani (64) approximates the

O^{18}/O^{16} ratio of the ocean in the past by taking the weighted average of this ratio for the present day hydrosphere. This is, of course, for nonglacial times. For glacial times he assumes that the glacier ice in the past had the same average O^{18}/O^{16} ratio as at present. By estimating the extent of past glaciations one can deduce the O^{18}/O^{16} ratio of the ocean during these glaciations. In this way he arrives at the following values for A:

- at maximum glaciation: $A = + 0.4$, corresponding to a temperature correction of $+ 1.7^{\circ} \text{ C}$.
- at nonglacial times: $A = - 0.3$, corresponding to a temperature correction of $- 1.3^{\circ} \text{ C}$.

Emiliani (64) has taken for the present day volume of ice $18.8 \times 10^6 \text{ km}^3$ with an average $\delta = - 25$. Both values seem to be underestimated in the light of recent measurements. Information given by Epstein and Benson (77) for ice from Antarctica and Greenland indicates that the average δ value for glacier ice at present is approximately $- 35$. Donn et al. (57) report two estimates on the present world ice volume which are given in table 4.1. These estimates have been used to calculate weighted average δ 's for the hydrosphere (these are possible values of A) and corresponding temperature corrections for nonglacial times (see table 4.1).

The suggestion that the isotopic composition of the ocean has been constant for a significant part of the geological history is attractive and positive evidence for this hypothesis is available (see also sect. 9.2.5).

TABLE 4.1

Distribution of O^{18} in the hydrosphere at present

	I(*) volume(**) 10^{-6} km^3	II volume 10^{-6} km^3	δ_{SMOW}
ocean	1360.0	1360.0	- 0.1
ice	30.6	25.0	-35
fresh water	0.5	0.5	- 7
total hydrosphere	1391.1	1385.5	
$\delta_{\text{hydrosphere/SMOW}}$ ("A" for nonglacial times)	-0.87	-0.73	
temperature correction for nonglacial times	-3.6°C	-3.1°C	

(*) columns I and II are different because of the different present day glacier ice volume estimations by respectively Novikov (126) and Crary (43).

(**) all volumes are given as water at STP, taking the average density of ice as 0.88 gram/cm^3 .

4.4 Phosphate geothermometry

The difficulties caused by the uncertainty about the values of the O^{18}/O^{16} ratio of the ocean in the past can perhaps be circumvented. Urey (159) suggested in 1948 that probably use could be made of the temperature dependence of the fractionation factor for the hypothetical exchange reaction between cogenetic phosphate and carbonate in shells. Although this attractive possibility existed, it was not until 1960 that Tudge (155) published a method, accurate enough, for extracting oxygen from orthophosphates.

Oxygen isotope exchange does not take place directly between the solid phosphate and the solid carbonate. But it may be possible that equilibrium is established between these two substances, via the water in which the animal lives. Unfortunately there is apparently no oxygen exchange between water and orthophosphate under inorganic conditions. The extent to which this is also true for organic conditions is not yet known. Hence it is not certain whether this line of approach will be successful.

4.5 Vital effects

The subject of biological fractionation has been reviewed by Bowen (18).

It will be obvious that the biogenic carbonate used for palaeo-temperature measurements must have been formed under equilibrium conditions. Urey et al. (161) have concluded that nonair breathing invertebrates have a body temperature equal (within $0.5^{\circ}C$) to the surrounding water and that their body fluids are in isotopic equilibrium

with the water. Lowenstam and Epstein (111) have reported in their study of recent marine invertebrate skeletal material, that only exoskeletons seem to be formed in isotopic equilibrium. Recent echinoderms secrete their skeleton not in equilibrium with the water. Nonequilibrium precipitation is also indicated for shoal water corals and some algae (112). According to Emiliani (64), isotopic exchange between the oxygen liberated by Zooxanthella and the algal- and coral carbonate is the cause of this phenomenon. Zooxanthella is a symbiotic organism living in the tissue of the corals and algae under consideration.

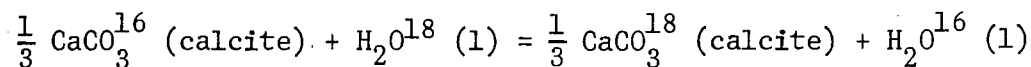
4.6 Insensitivity of the fractionation factor

The fractionation factor for the system carbonate - water is not influenced by the kind of water used, oceanic or fresh (72) (c.f. sect. 3.4). Small changes in pH and/or ionic strength appear to be of no importance. Epstein (72) reports that also small amounts of magnesium and/or strontium ions in the carbonate lattice do not affect in a measurable way the fractionation factor. Moreover, the crystal symmetry (rhombohedral calcite or orthorhombic aragonite) does not have a significant influence. The physical reason for the last two points is that the fractionation is mainly dependent on the internal vibrations of the carbonate ion; these vibrations appear to be influenced only in a minor way by crystal symmetry and small amounts of impurities.

4.7 Influence of pressure

The pressure dependence of the fractionation factor seems to be unimportant in carbonate thermometry. This will be illustrated by an

example



To estimate the influence of pressure the following simplifying assumptions are made:

- All molecules involved in the exchange are in the groundstate.
- The molar volume of the water molecule does not change upon oxygen isotopic substitution. Because of the central position of the oxygen atom in the water molecule, this assumption should be reasonably good.
- The effective volume of the carbonate ion is spherically shaped.

Applying eqn. 3.10, one obtains

$$\Delta V = \sqrt[3]{36\pi V^2 \Delta r} \quad 4.4$$

Insert this into eqn. 3.6 and put $V_B = 0$

$$\frac{\partial K}{\partial P} = -\frac{1}{3} \sqrt[3]{36\pi V^2} \cdot \frac{\Delta r}{RT} \quad 4.5$$

$$\omega_1 = 1087 \text{ cm}^{-1}$$

$$\omega_1^\# = 1025 \text{ cm}^{-1} \quad (\text{Ref. 158})$$

$$f_{\text{stretching}} = 10.65 \times 10^5 \text{ dynes cm}^{-1} \quad (\text{Ref. 91}).$$

$$\text{Molecular volume of calcite} = 6.179 \times 10^{-23} \text{ cm}^3.$$

Thus

$$\Delta V = - 0.043 \text{ cm}^3 \text{ mole}^{-1}$$

and

$$\frac{\partial K}{\partial P} = 6 \times 10^{-7} \text{ atm}^{-1}$$

Therefore, at depth of 1 km in the ocean K will be increased by 6×10^{-5} . This would cause an error of less than 1° C , which is not significant when compared with other uncertainties.

4.8 Purification

Biogenic carbonate is always contaminated with organic oxygen containing compounds. A successful way to get rid of these compounds is described by Epstein et al. (74). They roast the sample in a platinum boat for 30 minutes. During this process a continuous flow of purified helium gas sweeps away the volatile decomposition products of the heated organic compounds and provides an inert atmosphere over the sample. Before the helium sweeps the sample it passes a copper filled furnace at 500° C and a liquid nitrogen trap filled with activated charcoal, to purify the helium. Craig (41) has checked this procedure by treating in the same manner a sample of Ticino marble and measuring its $\text{O}^{18}/\text{O}^{16}$ ratio before and after the treatment. He did not detect a difference between the two measurements.

Russian workers (123, 151) use a simplified version of this process.

4.9 Significance of measured temperatures

The interpretation of the measured data requires that the stratigraphic range, the habitat and the growth characteristics of the fossil material used are known. The stratigraphic range of many fossils is well established, but the habitat of most fossils is only crudely known. For instance, it is known that a certain animal is pelagic, but it is usually not known in what depth range the animal lived. This is important because marine water temperatures change considerably with depth. The surface temperature in the Eastern equatorial Pacific is about 26° C but the water temperature at 200 meters is about 11° C. This aspect is considered by Emiliani and Epstein (62, 68) for pelagic foraminifera. Further the habitat may be characterized by a certain O^{18}/O^{16} ratio different from SMOW. Only limited information is available about the growth characteristics of most fossils. It appears that the growth of many invertebrates is chiefly confined to a particular season (see for example (84)). Thus, generally one determines the temperature of the growth season of the animal. Epstein and Lowenstam (75, 111) have investigated this.

One may conclude that the carbonate thermometer is a powerful tool in palaeothermometry. Its weakest spots are the uncertainties about the O^{18}/O^{16} ratio of the ocean in the past, and the required detailed palaeontological knowledge of the fossil material used.

CHAPTER 5

HIGH TEMPERATURE GEOTHERMOMETRY

Soon after the low temperature carbonate geothermometer (chapt. 4) was established, work started on the isotope determination of higher temperatures. This work was mainly done by Clayton and Epstein. They considered oxygen isotope exchange reactions among cogenetic mineral pairs, because the melt or hydrothermal solutions from which minerals were precipitated are not available anymore. Obviously, the cogenetic pairs should be in thermodynamic equilibrium. Whether this is the case or not can be shown to various degrees of conclusiveness.

Take for example the mineral pair quartz - calcite. δ_Q stands for δ_{quartz} and δ_C stands for δ_{calcite} .

- When $\delta_C > \delta_Q$ then it is certain that the calcite and the quartz are not in equilibrium, because if equilibrium were established quartz would be enriched in O^{18} with regard to the calcite, according to the experimentally obtained eqn. 5.2
- The δ_Q and δ_C of equilibrium pairs precipitated from hydrothermal solutions with approximately the same O^{18}/O^{16} ratio are related in a simple linear fashion (28, 33).

- If there are three cogenetic minerals, the three possible pairs should give consistent results.
- If the quartz and the calcite are in equilibrium with the same solution, then the δ values calculated for this solution from δ_Q and δ_C should be identical.

Clayton (29, 30) has measured the fractionation factor for the system calcite - water over the temperature range $190^\circ - 750^\circ \text{ C}$ under pressure of 1000 atmospheres.

$$\ln K_{CW} = 2730 T^{-2} - 0.00256 \quad 5.1$$

where

$$K_{CW} = \frac{[O^{18}/O^{16}]_{\text{CaCO}_3}}{[O^{18}/O^{16}]_{\text{H}_2\text{O}}}$$

The low temperature data of Epstein et al. (74) are incorporated in eqn. 5.1. The water was replaced by a dilute aqueous ammonium chloride solution in Clayton's experiments. In 1961 O'Neil and Clayton (127) have reported a similar relationship for the system quartz - water.

$$\ln K_{QW} = 3629 T^{-2} - 0.00256 \quad 5.2$$

Equation 5.2 was derived from experiments done in the range $380^\circ - 700^\circ \text{ C}$ under 1000 bars pressure. This time the water was replaced by a dilute aqueous sodium fluoride solution. From eqns. 5.1 and 5.2 one can deduce the relationship

$$\ln K_{QC} = 899 T^{-2} \quad 5.3$$

for the oxygen isotope exchange between quartz and calcite.

Equations 5.2 and 5.3 had been deduced by Clayton and Epstein when only the K_{CW} temperature relationship was known (33). This was done by assuming that the equations would have the general form

$$\ln K = x T^{-2} - y \quad 5.4$$

as was indicated by the theory (see sect. 3.2). Further it was assumed that the fractionation factor for systems not involving water would become unity at high temperatures. This is because in systems involving water the "cross over" phenomenon is bound to occur (see sect. 3.2). Finally they took for granted that the minerals quartz, calcite and hematite which appeared to be cogenetic in some of their samples, were also in thermodynamic equilibrium. This provided enough information to deduce eqns. 5.2 and 5.3.

In addition to this they could plot also $\ln K_{QH}$ vs $\ln K_{CH}$ for their samples and obtain the relationship

$$\ln K_{QH} = 1.388 \ln K_{CH} \quad 5.5$$

where K_{QH} stands for the fractionation factor of the system quartz-hematite.

The convenient equation

$$1000 \ln K_{AB} = \Delta_{AB}$$

where

$$\Delta_{AB} = \delta_A - \delta_B$$

is generally employed to give a relationship between δ values and the fractionation factor. This eqn. is easily derived (33).

$$K_{AB} = \frac{[O^{18}/O^{16}]_A}{[O^{18}/O^{16}]_B} = \frac{1 + A/1000}{1 + B/1000}$$

$$\approx 1 + (\delta_A - \delta_B)/1000$$

For oxygen exchange reactions $K_{AB} \leq 1.04$

thus

$$K_{AB} = 1 + \ln K_{AB}$$

By means of eqn. 5.5 the following relations could be deduced

$$\ln K_{QH} = 3216 T^{-2} \quad 5.6$$

$$\ln K_{CH} = 2317 T^{-2} \quad 5.7$$

$$\ln K_{HW} = 413 T^{-2} - 0.00256 \quad 5.8$$

In the empirical derivation of eqn. 5.5 Clayton and Epstein (32, 33) used the data shown in table 5.1.

TABLE 5.1

Cogenetic quartz - calcite - haematite values(**)

Sample	δ_Q	δ_C	δ_H
32	24.4	17.3	0.3
33	18.0	12.8	-2.8
34	12.3	8.2	2.2
35	10.4	7.4	1.6
I.S. (*)	6.8	6.5	3.3

(*) I.S. is a cogenetic quartz - calcite - magnetite sample from Iron Springs. The fractionation factor for the system magnetite - haematite was believed to be very small.

(**) All δ values are with respect to SMOW as reported in (32, 33).

From data in table 5.1 the temperatures shown in table 5.2 may be deduced for each of the cogenetic mineral pairs.

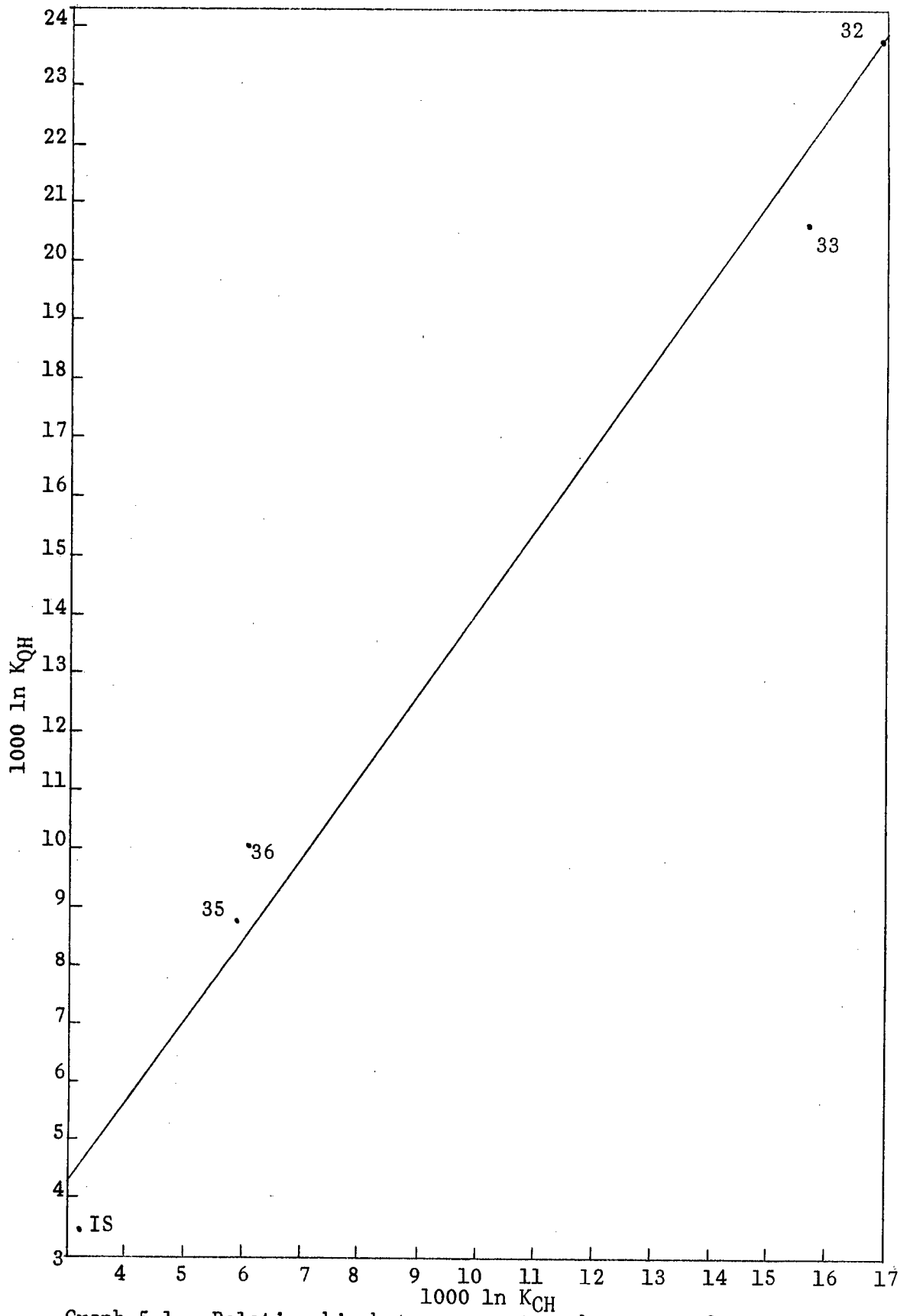
TABLE 5.2

Temperatures of freezing in of the O^{18}/O^{16} ratio of
three cogenetic mineral pairs

Sample	t_{QC}^* °C	t_{QH} °C	t_{CH} °C
32	87	94	97
33	147	119	113
34	195	293	350
35	277	331	359
I.S.	1244	684	593

(*) t_{QC} stands for the temperature derived from the
 Σ values of the cogenetic mineral pair quartz-
calcite.

Equation 5.5 was determined by means of a least square fit for the graph of $\ln K_{QH}$ vs $\ln K_{CH}$ (graph 5.1). The least square method presupposes that errors are distributed at random. This is not the case here. In general high temperature data will be more questionable than low temperature ones. Therefore, it seems preferable to assume that sample 32 is all right and that the graph $\ln K_{QH}$ vs $\ln K_{CH}$ will pass through the origin (see graph 5.1). One obtains then



Graph 5.1 - Relationship between quartz - haematite fractionation and calcite - haematite fractionation in quartz - calcite haematite rocks.

$$\ln K_{QH} = 1.404 \ln K_{CH} \quad 5.9$$

and subsequently

$$\ln K_{QH} = 3124 T^{-2} \quad 5.10$$

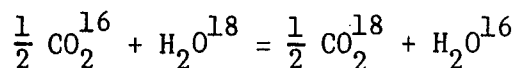
$$\ln K_{CH} = 2225 T^{-2} \quad 5.11$$

$$\ln K_{HW} = 505 T^{-2} - 0.00256 \quad 5.12$$

In the derivation of eqn. 5.9 the δ values of table 5.1 were recalculated. This was necessary because Clayton and Epstein (32) used the formula

$$\delta_{x/SMOW} = 1.0399 \delta_{x/PDB} + 39.9 \quad 5.13$$

to convert their measurements with respect to PDB, to values with respect to SMOW. Equation 5.13 is based on the indirect determined δ value for Hawaiian sea water (taken to be the same as SMOW in (32)) namely $\delta_{\text{Hawaiian sea water}/PDB} = -38.4$. But later in 1958 Compston and Epstein (39) reported for the reaction



$$\alpha = 1.0407 \text{ at } t = 25^\circ \text{ C}$$

Therefore eqn. 5.13 should be modified to

$$\delta_{x/SMOW} = 1.0407 \delta_{x/PDB} + 40.7 \quad 5.14$$

because $\delta_{SMOW/PDB} = 0$, when the 0.1‰ is neglected (see Craig (41)).

Equation 5.14 is in agreement with the absolute atomic O^{18}/O^{16} ratio for SMOW as published by Craig (42). Applying eqns. 5.9, 5.10, 5.11 and 5.12 one obtains the result tabulated in table 5.3.

TABLE 5.3

Modification of table 5.2

Temperatures of freezing in of the O^{18}/O^{16} ratios for
three cogenetic mineral pairs

Sample	t_{QC} °C	t_{QH} °C	t_{CH} °C
32	89	89	89
33	150	116	104
34	205	285	331
35	287	325	342
I.S.	1487	673	562

Although the data of table 5.3 are not overwhelmingly impressive, they are somewhat more consistent than those presented in table 5.2. The question is now, what causes these temperatures to be so different and what may one deduce from this.

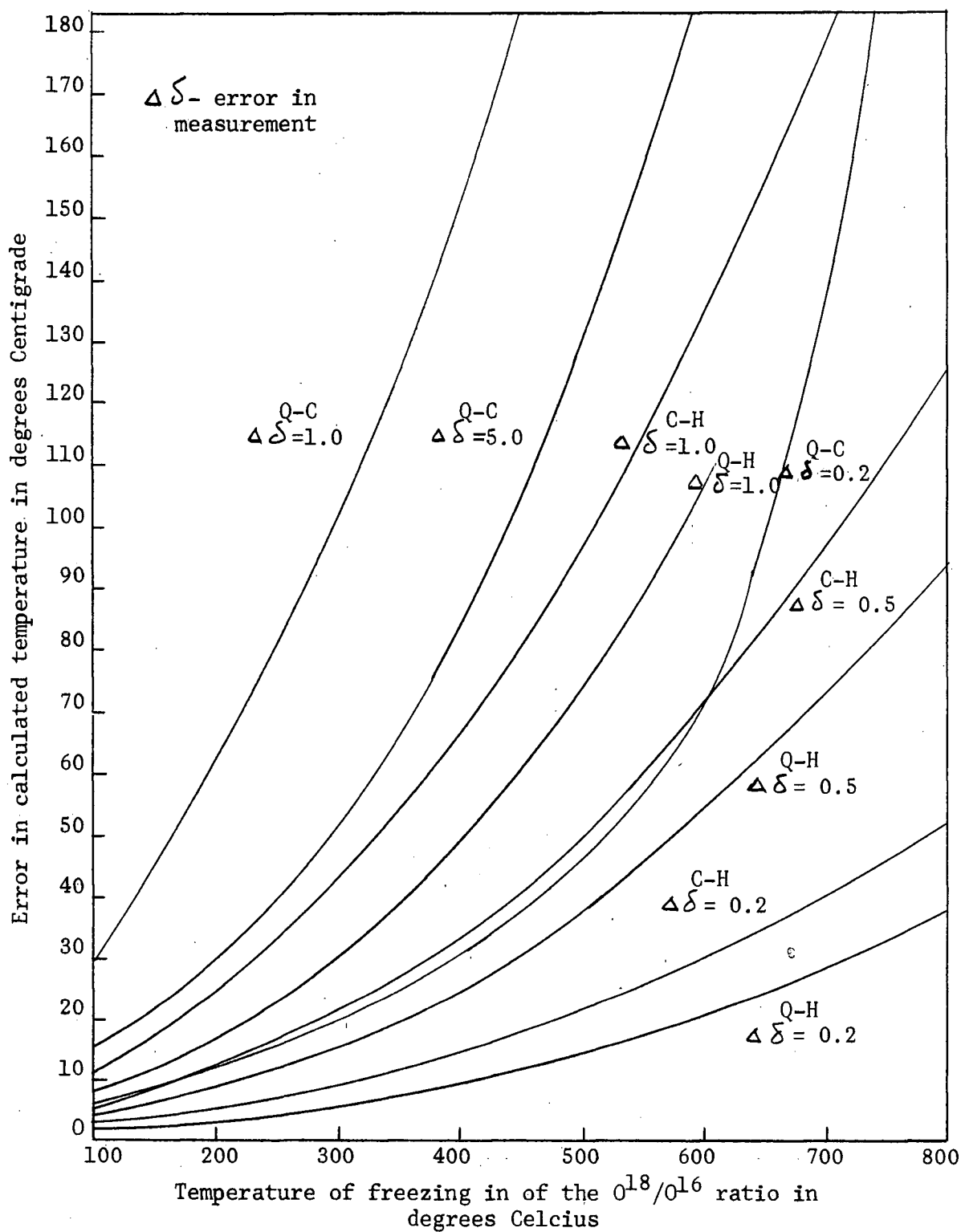
Experimentally δ can be measured with an accuracy of ± 0.2 (presently even better accuracy is obtained). The errors due to accuracy limitations become appreciable at high temperature; this will be evident from an inspection of graphs 5.2 and 5.3. In these graphs it is shown how a certain error in δ measurement ($\Delta\delta$) for a particular mineral pair corresponds to a certain temperature difference (Δt) for a given temperature of freezing in of the O^{18}/O^{16} ratio. If one assumes that the samples 32, 33, 34, and 35 were precipitated from aqueous solutions, which can be treated as pure water, then the various δ values for these solutions can be evaluated (table 5.4). Of course this is only possible if the isotopic composition of the solution remained constant as long as appreciable exchange took place. These are not unreasonable assumptions when one takes in consideration the low solubility of quartz, calcite and haematite.

To explain the results presented in table 5.4 one may invoke the following mechanisms:

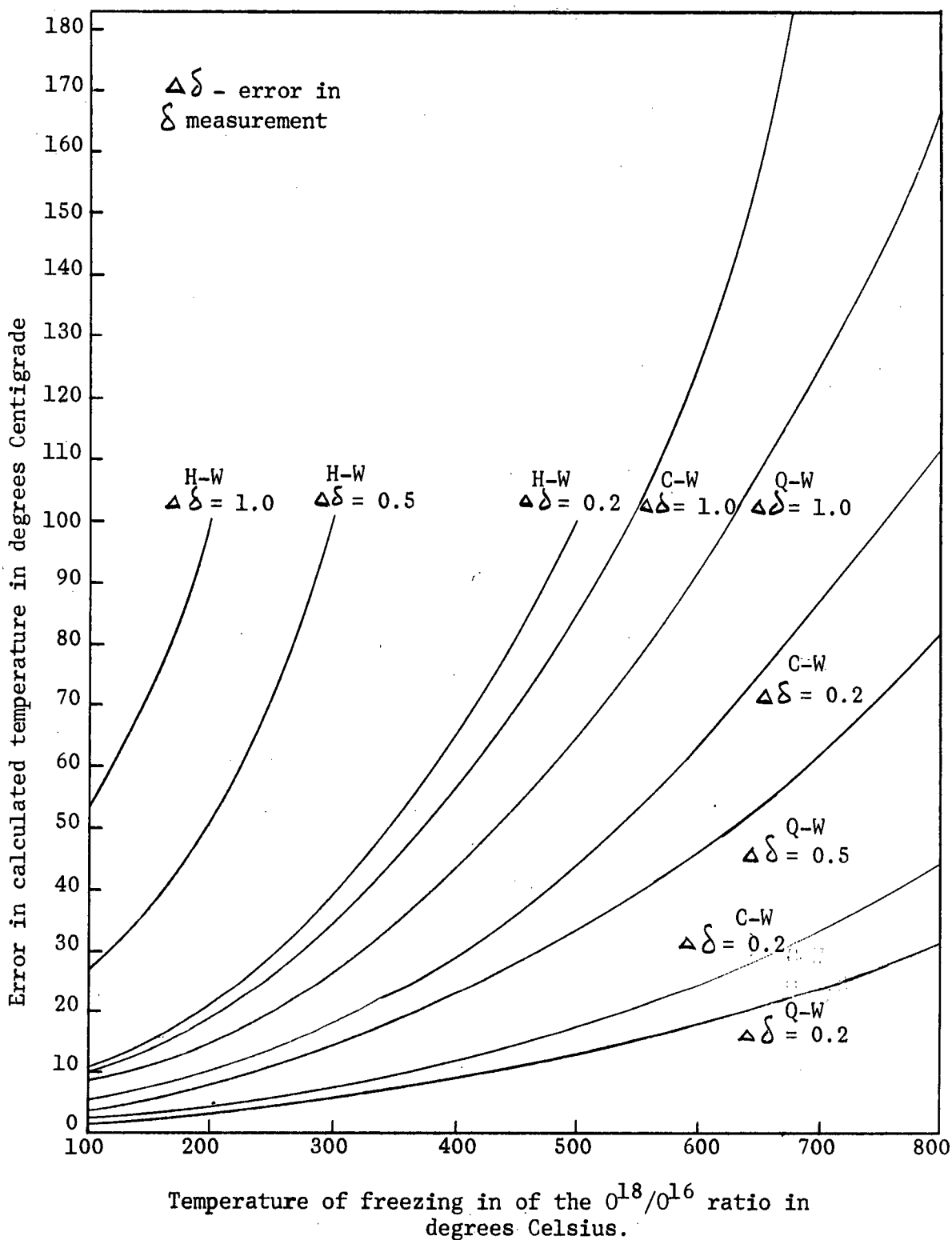
- solid state diffusion;
- nonequilibrium precipitation;
- mineral pairs were not truly cogenetic;
- changes in isotopic composition of the hydrothermal solutions.

Assuming that:

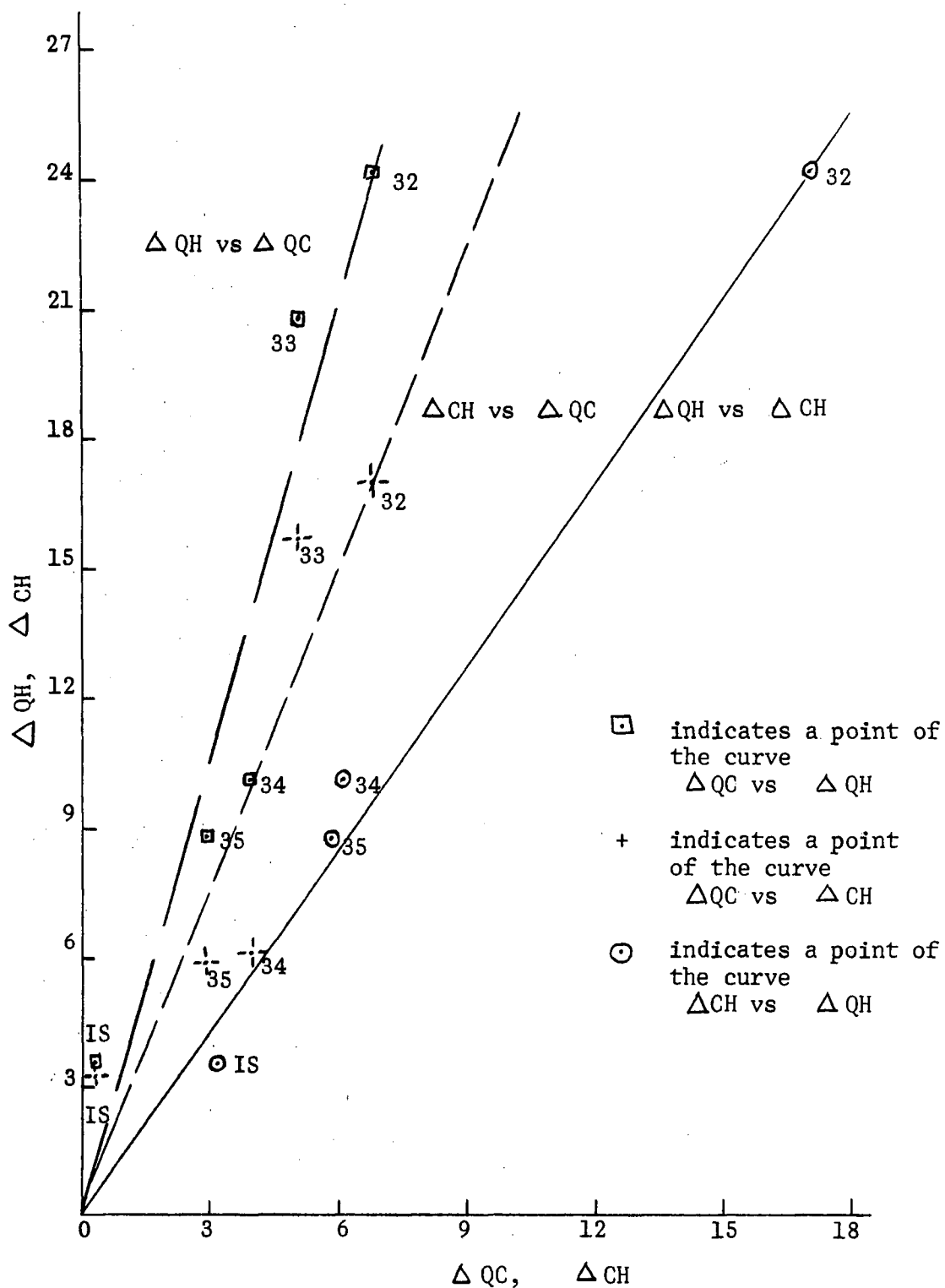
- The O^{18}/O^{16} ratio of the hydrothermal solutions remained constant as



Graph 5.2 - Errors in calculated temperatures, due to errors in δ measurements, for the mineral pairs quartz - calcite (Q-C), quartz - haematite (Q-H) and calcite - haematite (C-H).



Graph 5.3 - Errors in calculated temperatures, due to errors in measurements, for equilibria quartz - water (Q-W), calcite - water (C-W) and haematite - water (H-W).



Graph 5.4 - Fractionation relationships between the mineral pairs quartz - calcite (QC), calcite - haematite (C-H) and quartz - haematite (Q-H).

TABLE 5.4

δ values for hydrothermal solutions with respect to PDB

Sample	Temp. °C	Mineral pair	δ_W from Q(*)	δ_W from C	δ_W from H
32	89		-39.3	-39.3	-39.3
33	150	Q-C	-38.3	-38.3	-41.3
33	116	Q-H	-41.8	-41.3	-41.8
33	104	C-H	-43.3	-42.0	-42.0
34	205	Q-C	-39.4	-39.5	-36.0
34	285	Q-H	-35.3	-36.4	-35.4
34	331	C-H	-33.6	-35.2	-35.2
35	287	Q-C	-37.1	-37.0	-35.9
35	325	Q-H	-35.8	-36.1	-35.7
35	342	C-H	-35.2	-35.7	-35.7

(*) δ_W from Q stands for the δ value of the hydrothermal solution calculated by means of eqn. 5.2.

long as appreciable exchange of oxygen took place. This assumption is necessitated by lack of additional information.

- The simplest mechanism which can provide a physically and geologically acceptable explanation is most likely the main cause of the observed pattern of δ values.

The data of table 5.4 are explained here in the following way:

Sample No. 32

The consistency of results is forced by the initial assumption that this sample represented cogenetic quartz - calcite - haematite pairs which are in thermodynamical equilibrium. Graph 5.1 was based on this and it had as a consequence the modification of eqn. 5.5 to eqn. 5.9. But even when one applies eqns. 5.6, 5.7, and 5.8 instead of eqns. 5.10, 5.11, and 5.12 the consistency for this sample is far better than for any of the other samples. A thin section study revealed a sequence of crystallization, the large equigranular quartz was formed first followed successively by haematite, calcite, dendritic haematite and fine grained quartz.*

Sample No. 33

The three different temperatures for this sample may be explained by diffusion of oxygen in the calcite, by isotopic disequilibrium precipitation of the quartz, or by the possibility that the quartz was formed at a somewhat higher temperature than the calcite and haematite. In the last

* The author feels it may be concluded the quartz calcite and haematite used by Clayton and Epstein (32) were cogenetic. Professor H. James of the University of Minnesota was so kind as to provide samples 32, 34 and 35. Professors K. McTaggart and J. V. Ross of the Geology Department of the University of British Columbia determined the order of crystallization of the minerals under consideration by examining thin sections of these samples.

two cases δ_Q will be too low, while in the first case δ_C will be too high. If oxygen diffusion in the calcite occurred then t_{QH} (i.e. the temperature as derived from eqn. 5.10) should be right. However it is reasonable to suppose that no significant oxygen diffusion took place when one considers the quantitative information available about oxygen diffusion in calcite (see sect. 7.2). Moreover samples 34 and 35 do not show a pattern which could be caused by calcite solid state diffusion. If the inconsistencies are caused by a too low value for δ_Q then t_{CH} should be right. From graphs 5.1 and 5.4 it may be concluded that δ_Q is 1.3 too low. This can be checked by calculating t_{QC} and t_{QH} and using a δ value for quartz of $\delta_Q + 1.3$. This gives $t_{QC} = t_{QH} = 104^\circ \text{C}$ and a δ value for the water as calculated from the quartz of -42.0 with respect to PDB. Geological evidence should decide whether this is a case of disequilibrium formation of quartz, or that the quartz was formed at a slightly higher temperature. If the quartz was formed first, its temperature of crystallization will have been 114°C . Pure coincidence is responsible for the equivalence of δ_W as calculated from quartz, and δ_W as calculated from calcite at a temperature of 150°C . The coincidence is caused by the fact that

$$\frac{d K_{CW}}{d T} \bigg/ \frac{d K_{QC}}{d T} = \frac{150 - 114}{150 - 104}$$

in the temperature interval $100 - 200^\circ \text{C}$.

Sample No. 34

The different temperatures of table 5.4 may be explained by oxygen

diffusion in quartz and haematite or by a later crystallization of these minerals. Russian results (56) give a qualitative indication that if oxygen diffusion in quartz was significant, it should have been significant in haematite too. The pattern can not be explained by oxygen diffusion in calcite. If diffusion occurs, the crystalline state can reequilibrate with the hydrothermal solution at a lower temperature than the crystallization temperature. Haematite diffusion will not cause any great changes since the fractionation between water and haematite is very small. All data will be in harmony if

- the quartz was formed at a slightly lower temperature,
- the quartz, because of solid state diffusion, reequilibrated with the hydrothermal solution at a temperature lower than its formation temperature,
- the quartz exchanged just a part of its oxygen with the hydrothermal solution at a lower temperature.

In all cases $t_{CH} = 331^{\circ} \text{C}$ should be about right and δ_w should be -35.2 with regard to PDB. The temperature at which the quartz may have crystallized or reequilibrated is 290°C . The order of crystallization as established from thin section study is as follows: carbonate, and quartz and haematite simultaneously.

Sample No. 35.

Qualitatively the explanation is the same as for sample No. 34. $t_{CH} = 342^{\circ} \text{C}$ is supposed to be the right temperature of calcite crystallization. The quartz O^{18}/O^{16} ratio may have been frozen in at 327°C under equilibrium conditions. Thin section evidence gives as order of crystallization carbonate, quartz, haematite.

A recent application of eqn. 5.3 is reported by Schwarcz et al. (138). They have investigated Palaeozoic metamorphic rocks from Vermont and determined the following temperatures:

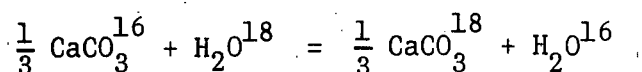
chlorite zone : 200 - 250° C

biotite zone : 250 - 350° C

garnet zone : 275 - 450° C

staurolite zone: 320 - 550° C

Following the procedures of sect. 4.7, the influence of pressure will be again illustrated for the reaction:



At $t = 200^\circ \text{C}$ and a pressure of 1000 bars one finds a change in fractionation factor of 3.7×10^{-4} if pressure is neglected which amounts to an error in temperature of approximately -7°C . One should be aware that the assumptions underlying this method become worse at high temperatures. On the other hand, Clayton derived the equations 5.1 and 5.2 under pressurized conditions.

Finally it should be remarked that although the figures mentioned in table 5.4 look very accurate, they are not necessarily accurate, because of uncertainties of pressure conditions and of activity coefficients. Moreover, the statistical basis for eqn. 5.5 is physically not acceptable in the author's opinion and this basis is absent for the alternative eqn. 5.9.

From the above discussion it should be clear that oxygen isotopes are very useful for geothermometric purposes. However the interpretation

of the results is not as straightforward as one could wish. Specifically high temperature geothermometry is in comparison with carbonate low temperature palaeothermometry fairly intricate, because of the possible occurrence of diffusion and the uncertainties about the pressure and activity dependence of α . These three factors are relatively unimportant in low temperature palaeothermometry, but may play significant roles in high temperature geothermometry. Under geological conditions high temperatures are usually concomitant with high pressures. At high temperatures it is to be anticipated that the molecules are in excited states (quantum mechanically) and thus the square root expectation value of x (eqn. 3.7) will increase and thus the pressure dependence (see sect. 3.3) will become more significant. On the other hand in eqn. 3.5 there appears a temperature term in the denominator which makes the pressure dependence at high temperatures insignificant. The thermodynamic activity of the hydrothermal solutions is not known, hence this factor cannot be evaluated. Diffusion becomes more pronounced at higher temperatures, hence one measures freezing in temperatures of the $0^{18}/0^{16}$ ratio rather than temperatures of crystallization of a particular mineral. It should be possible to evaluate this effect, once the necessary diffusion constants are known.

CHAPTER 6

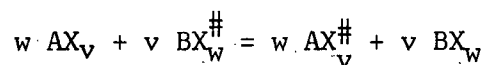
ISOTOPIC EXCHANGE REACTION KINETICS

6.1 Introduction

In this chapter isotopic exchange reactions are discussed from a kinetic viewpoint. The usual assumptions which are made in the derivation of rate equations are pointed out. First the homogeneous exchange reaction is considered in some detail, followed by the heterogeneous ones. In the case of a heterogeneous exchange reaction three possible rate determining steps are discussed, i.e. diffusion in phase I, diffusion in phase II, and the surface reaction.

6.2 Homogeneous exchange reactions

Returning to the reaction



the fractionation factor may be defined as

$$K = \frac{c_A^{\#}}{c_A - c_A^{\#}} \bigg/ \frac{c_B^{\#}}{c_B - c_B^{\#}}$$

where

C_A = total concentration of element X occurring in compound

AX_V and $AX_V^\#$ in gram atoms per unit volume.

$C_A^\#$ = concentration of $X^\#$.

In calculations on how the reaction proceeds, the following assumptions are usually made implicitly or explicitly:

(a) $C_A^\# \ll C_A$ and $C_B^\# \ll C_B$

Assumption (a) is always justified in oxygen studies because of the relative rarity of O^{18} .

(b) The distribution of $X^\#$ in each of the molecular species is random under equilibrium conditions. There are no $X-X$ bonds in either of the compounds. This means that the partition function of the variously labelled molecules obey "the rule of the geometric mean" (see also (158)).

(c) The rates of the forward and the reverse reaction are not a function of the isotopic nature of the molecule involved. This assumption is justified by a theorem due to Slater (142): The rate of bond rupture is only dependent on the two atoms involved, and independent of the rest of the molecule. Bigeleisen (12) concluded, consequently, that if this were true for bond rupture, it should also be true for bond formation.

(d) Assumption (b) is valid throughout the exchange process. This is justified by assumption (c).

(e) The rates of the forward and the reverse reaction are similar.

Bunton et al. (23) have shown that only a minor error is introduced in this way.

- (f) All isotope effects are neglected. This follows in part from the previous assumptions. Due to the small mass difference between O^{18} and O^{16} and the small concentration of O^{18} , the errors introduced in this way will be only minor ones.

Thus

$$\begin{aligned} \frac{d C_A^\#}{dt} &= - \frac{d C_B^\#}{dt} \\ &= R \left[\frac{C_B^\#}{C_B} \frac{C_A - C_A^\#}{C_A} - \frac{C_A^\#}{C_A} \frac{C_B - C_B^\#}{C_B} \right] \end{aligned} \quad 6.1$$

where R is the gross rate of exchange.

According to the material balance

$$C_A^\# - C_A^\infty = C_B^\# - C_B^\infty \quad 6.2$$

The subscript ∞ indicates the value of $C_A^\#$ when equilibrium is reached.

Further

$$\frac{C_A^\#}{C_A - C_A^\#} = \frac{C_B^\#}{C_B - C_B^\#} \quad 6.3$$

because there is no isotope effect.

Consequently

$$\frac{C_A^\#}{C_B^\#} \approx \frac{C_A}{C_B} \quad 6.4$$

Using eqns. 6.1, 6.2, 6.3, and 6.4

$$\frac{d C_A^\#}{dt} = \frac{R}{C_A C_B} [C_A + C_B] [C_{A_\infty}^\# - C_A^\#] \quad 6.5$$

This integrates to

$$1 - F = \frac{C_{A_\infty}^\# - C_A^\#}{C_{A_\infty}^\# - C_{A_0}^\#} = \exp \left[-\frac{R}{C_A C_B} (C_A + C_B) t \right] \quad 6.6$$

where

$C_{A_0}^\#$ = the initial value of $C_A^\#$ at $t = 0$,

F = fraction of exchange which has occurred.

For practical purposes

$$1 - F = \frac{r_{A_\infty} - r_A}{r_{A_\infty} - r_{A_0}} \quad 6.7$$

where

$$r_A = \left[\frac{O^{18}}{O^{16}} \right]_A \quad 6.8$$

These or similar equations have been derived by several investigators (23, 89, 117, 118).

Bigeleisen (10) has derived formulae for the ratio of the rate constants for the competitive reactions of isotopic molecules. The

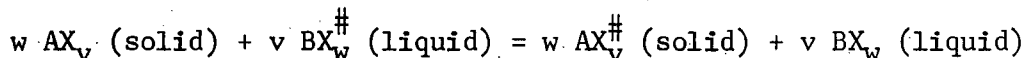
problem was treated from the point of view of the "theory of absolute rates" (11, 83).

6.3 Heterogeneous exchange reactions

Zimens (180, 181) has treated heterogeneous exchange reactions kinetically. In this kind of exchange one of the following three processes may be rate determining:

- oxygen diffusion in phase I,
- oxygen diffusion in phase II,
- surface reaction by which the exchange of oxygen isotopes between phase I and II takes place.

Consider the reaction



and define

n = total mass of exchangeable atoms, in gram atoms

$n^{\#}$ = total mass of atoms $X^{\#}$, in gram atoms

C = concentration of exchangeable atoms (gram atoms/unit volume)

$C^{\#}$ = concentration of $X^{\#}$

$$r = \frac{n^{\#}}{n} = \frac{C^{\#}}{C}$$

A = abbreviation for compound AX_v (solid state)

B = abbreviation for compound BX_w (liquid state)

$$q = \frac{n_A}{n_A + n_B}$$

V = volume

S = surface area

D_B = diffusion constant of $X^{\#}$ or X in BX_w

Assume that initially ($t = 0$): $n_A^\# = C_A^\# = 0$

then,

$$n_B^\# + n_A^\# = n_{B_0}^\#$$

further when equilibrium is attained ($t = \infty$)

$$\frac{n_{B_\infty}^\#}{n_{A_\infty}^\#} = \frac{n_A}{n_B}$$

or

$$r_{A_\infty} = r_{B_\infty} = r_\infty$$

Hence

$$r_\infty = r_{B_0}(1 - q) \quad 6.9$$

Although the situation will not be very common in geology, it is possible that the diffusion of $X^\#$ in the adhesive layer of B surrounding A is rate determining for the exchange. The steady state concentration gradient in the adhesive layer will be linear. This layer also plays an important role in the Nernst-Brunner (22) theory of dissolution. It is much thicker than an absorbed film. It may be identified with the boundary layer in hydrodynamic theory. This theory gives for its approximate thickness

$$L = \sqrt{\frac{\eta \epsilon}{\rho v}} \quad 6.10$$

where η = viscosity of the fluid,

ρ = density of the fluid,

ξ = linear dimension of the surface of the solid,

V = velocity of the fluid,

L = thickness of adhesive layer.

For the diffusion of X and $X^\#$ in this layer one can apply Ficks law

$$-\frac{d n_B^\#}{dt} = S_A D_B C_B \frac{r_B - r_{B(A)}}{L} \quad 6.11$$

where

$r_{B(A)} = r_B$ at the solid - liquid interface.

Assuming that diffusion in the adhesive layer is rate determining

$$r_{B(A)} = r_A$$

Hence

$$\begin{aligned} r_B - r_{B(A)} &= \frac{1}{q} (r_B - r_\infty) \\ &= \frac{r_\infty - r_A}{1 - q} \end{aligned} \quad 6.12$$

is obtained by combining eqns. 6.9 and 6.11.

Therefore

$$\begin{aligned} 1 - F &= \frac{r_\infty - r_A}{r_\infty} = \frac{r_B - r_\infty}{r_{B_0} - r_\infty} \\ &= \exp \left[- \frac{S_A D_B t}{q V_B} \right] \end{aligned} \quad 6.13$$

for the case that diffusion in the adhesive layer is rate determining.

It is also possible that the surface reaction is the rate determining step. When one considers the exchange between the fluid and the solid phase only, then the number of atoms X and $X^\#$ which pass the interface in one direction is equal to the number that pass in the opposite direction. \dot{n} - number of exchangeable atoms which pass one cm^2 of the interface in one direction per second.

$$-\frac{d n_B^\#}{dt} = S_A \dot{n} (r_B - r_A) \quad 6.14$$

Applying eqn. 6.12 one obtains after integration

$$1 - F = \exp \left[- \frac{\dot{n} S_A}{n_B q} t \right] \quad 6.15$$

when the surface reaction is rate determining.

Most likely it is the solid state diffusion of X and $X^\#$ which is rate determining. Solid state diffusion has been treated by several authors; among the more recent of these are Crank (44) and Jost (99). The solution of this problem is the solution of the diffusion equation

$$\frac{\partial C_A^\#}{\partial t} = D_A \frac{\partial^2 C_A^\#}{\partial x^2} \quad 6.16$$

fitted to the proper boundary conditions.

If the solid has the shape of a slab and the liquid phase is present at both sides of the slab then

$$1 - F = \frac{C_{A\infty}^{\#} - C_A^{\#}}{C_{A\infty}^{\#} - C_{A_0}^{\#}}$$

$$= \frac{8}{\pi^2} \sum_{p=0}^{\infty} \frac{1}{2p+1} \exp \left[- (2p+1)^2 \frac{\pi^2 D_A t}{h^2} \right] \quad 6.17$$

where h is the thickness of the slab.

When the solid has the shape of a cube

$$1 - F = \frac{512}{\pi^6} \left[\sum_{p=0}^{\infty} \frac{1}{(2p+1)^2} \exp \left\{ - (2p+1)^2 \frac{\pi^2 D_A t}{h^2} \right\} \right]^3 \quad 6.18$$

where h is the length of a side of the cube. Anisotropy in solids can be dealt with by varying h for the different crystallographic directions.

When the solid has the shape of a sphere

$$1 - F = \frac{6}{\pi^2} \sum_{p=1}^{\infty} \frac{1}{p^2} \exp \left\{ - \frac{p^2 \pi^2 D_A t}{h^2} \right\}$$

where h is the radius of the sphere.

In the derivation of eqns. 6.17, 6.18, and 6.19 it was assumed that at $t = 0$ the solid phase had the uniform concentration $C_{A_0}^{\#}$. Instantaneously, after $t = 0$ the surface of the solid phase reequilibrated and acquired the concentration $C_A^{\#}$. Compared with the slowness of solid state diffusion the reequilibration of the surface layer of the solid is instantaneous. Urey et al. (161) give some numerical results for eqn. 6.18. These simplify considerably the process of calculating the diffusion constant from a set of experimental data.

TABLE 6.1

Solutions of eqns. 6.17 and 6.18 Ref. (161)

$\frac{D_A \pi^2 t}{h^2}$	1 - F for the slab	1 - F for the cube
0.1	0.773	0.461
0.05	0.839	0.590
0.01	0.926	0.795
0.005	0.949	0.854
0.001	0.971	0.915
0.0001	0.988	0.964
0.00001	0.991	0.972

The theory developed in this chapter, especially the diffusion equation, is the background for the material presented in chapter 7.

CHAPTER 7

DIFFUSION

7.1 Introduction

As far as homogeneous exchange reactions are concerned, Brodsky (21) has given general rules for the relative exchange velocities for reactions between water and other compounds. Many homogeneous exchange reactions for oxygen have been described (see Dole (55)). Publications about heterogeneous oxygen isotope exchange reactions are relatively rare and only a few of direct interest to earth scientists are known to the author.

Cameron et al. (25) have investigated the systems vanadium pentoxide (solid) - water - oxygen (gaseous) and vanadium pentoxide - oxygen. This is one of the few papers in which surface reactions as well as solid state diffusion are considered. They found that the oxygen exchange in the system vanadium pentoxide - water - oxygen between 400° and 550° C was about 25 times faster than exchange in the system vanadium pentoxide - oxygen, under similar conditions. They also found that whether the exchange rate was surface or diffusion controlled depended on the surface/volume ratio and on the crystallinity of the

vanadium pentoxide. High specific surface values and an amorphous phase favoured a surface reaction controlled exchange rate; while for crystalline solids and for low specific surface values a diffusion controlled rate is most likely. In the case of a diffusion controlled rate one finds that initially the rate of exchange is relatively high, but drops as exchange proceeds. When the surface becomes saturated the exchange rate drops under the controlling influence of solid state diffusion.

Johnston et al. (98) have reported essentially the same thing for the oxygen exchange between uranium oxides and water. Diffusion mechanisms are known for the most simple compounds only. Hence, it is not astonishing that the catalytic action of water is not yet explained. Haul and Stein (90) noticed that water also speeded up the carbon exchange between gaseous carbon dioxide and calcite. The size of their crystalline grains was smaller than 50μ . They found that even at 20°C measurable exchange occurred when water was present, while no measurable exchange occurred under dry conditions.

That amorphous material exchanges its oxygen more rapidly than crystalline is shown too by Dontsova (58). She performed a series of exchange experiments in which quartz, sphene, albite, mica, and diatomite exchanged their oxygen with the gaseous carbon dioxide. Unfortunately, these essentially very interesting experiments have qualitative significance only, since the grain sizes used were very small (12μ) and the effect of water on the exchange rates was neglected.

Experiments by Hutchinson (96) on oxygen isotope exchange between silica, water and oxygen have shown that no exchange takes place at 1000°C when the system is dry. However, the exchange between silica

and water is relatively rapid. At 960°C the half time of this exchange reaction is 47 minutes. At 750°C the half time is 100 minutes.

Hutchinson believes that the reaction at 960°C is a homogeneous phase reaction between dissolved silica and water, while at 750°C the exchange rate is controlled by a surface reaction. That no exchange takes place in the dry system silica glass - oxygen is confirmed by Bank (8). However, this should not be generalized. Kingery and Lecron (102) have shown that isotopic exchange between carbon dioxide and glass occurs, and that the chemical composition of the glass plays an important part.

The evidence these last two investigators have presented to show that the exchange rate is solid state diffusion controlled is unsatisfactory in the author's opinion. As is done very often, they based their conclusion concerning the rate determining step solely upon the exponential variation with time of O^{18} concentration in the gas phase. However this exponential variation does not uniquely indicate a diffusion process as the rate determining step. The surface reaction controlled rate of exchange shows a similar exponential decay for the O^{18} concentration of the gas phase (c.f. eqns. 6.19 and 6.15). To distinguish the two processes one should vary the surface area across which the exchange takes place.

Solid state diffusion as a cause of isotopic fractionation has been treated by Senftle and Bracken (140). They concluded that generally the effect was only of minor importance.

7.2 Oxygen diffusion in carbonates

Diffusion constants for the carbonate ion in carbonates have been

estimated by Urey et al. (161) for several temperatures ($15^{\circ} - 160^{\circ} \text{ C}$) showing a variation from $4.4 \times 10^{-23} \text{ cm}^2 \text{ sec}^{-1}$ to $1.9 \times 10^{-19} \text{ cm}^2 \text{ sec}^{-1}$. Haul and Stein (90) have measured a diffusion constant for carbon in calcite under dry conditions. They obtained $D_C = 4.5 \times 10^{-4} \exp - 58000/RT \text{ cm}^2 \text{ sec}^{-1}$. The activation energy is expressed in calories.

Haul and Stein did not reach a conclusion about the mechanism by which the diffusion took place. They considered three diffusing units:

- carbonate ions, the oxygen diffusion should be about three times as large as D_C ,
- carbon dioxide, D_O should be about twice D_C ,
- carbon atoms.

Urey et al.'s (161) estimations of D_O appear to be too high when compared to the Haul and Stein measurements under dry conditions. But from two preliminary experiments also reported by Haul and Stein one may obtain an estimate of D_C under wet conditions at temperatures of 300° C and 20° C . It is realized that it may not be proper to call these constants, diffusion constants. Assuming that $D_O = 2 D_C$, the following estimates were made.

TABLE 7.1

"Diffusion" of oxygen in calcite under wet conditions	
Temperature $^{\circ} \text{C}$	Diffusion constant D_O $\text{cm}^2 \text{ sec}^{-1}$
20	3×10^{-24}
300	5×10^{-22}

These values resemble those of Urey et al. quite closely. However the speculative nature of these values can not be overstressed.

Urey et al. (161) have calculated, on the basis of their estimation of D_0 , that a calcite crystal of 1 mm. dimensions will retain 96.4% of its original O^{18} concentration, relative to the equilibrium concentration of a changed environment for $7 \times 10^{+8}$ years, provided the temperature remained at 20° C. during this period. If the temperature was raised to 100° C this period would be only 64000 years. These figures do certainly not contradict the available empirical evidence.

It is found that coarse crystalline material retains its original O^{18}/O^{16} ratio very well. Beartschi (5) has measured a change in δ value of 5 over a distance of 1 cm in a large calcite crystal of unknown age. Urey et al. (161) have observed that a Jurassic belemnite guard maintained its different O^{18} concentrations due to seasonal temperature variations, while the O^{18}/O^{16} ratio of the chalk in which the belemnite was embedded was not preserved. Compston (38) has measured variations of 0.5% in the O^{18}/O^{16} ratio for different portions of a Permian brachiopod shell. As far as the author knows no occurrences have been published of preservation of O^{18}/O^{16} ratios by fossils older than the Carboniferous. Compston (38) reported on one questionable Devonian sample.

Engel et al. (71) have published data on the metamorphism and O^{18}/O^{16} ratios of the Leadville limestone. They noticed the coarse crystalline dolomite showed a linear variation of its δ value with distance. Near the Gilman ore δ coarse dolomite = + 16.5 and at 10,000 feet away from the ore δ coarse dolomite = + 23. But the dense fine grained dolomite which occurred together with the coarse material does not show

this linear variation; it has essentially the same δ value at the ore and at 10,000 feet away from it: δ dense fine grained dolomite = + 23. This suggests solutions came up via the Gilman ore conduit and moved radially away from it. A temperature gradient was established which was negative away from the ore. This gradient was maintained long enough so that all dolomite could equilibrate with the solution. Subsequently the temperature dropped, the drop was rapid enough that only the fine grained dolomite could exchange its oxygen with the cooler solutions. It happened at the temperature characterized by $\delta = 23$ (it is assumed the δ of the solution was constant) the exchange became negligible, because of the exponential decrease of the diffusion constant with temperature. The original gradient is best reflected by the most coarse material. This explanation is not a unique one, but its essential features are in agreement with the general interpretation of the Gillman ore and its surrounding as given by Lovering and Tweto (107).

7.3 Oxygen diffusion in quartz

The amount of solid state diffusion data available on quartz is very small. D_0 along the c axis of quartz was estimated to be $3 \times 10^{-11} \text{ cm}^2 \text{ sec}^{-1}$ at 500° C by Verhoogen (164). This value is based on electrical conductivity studies. Verhoogen assumed that the conductivity was caused by migrating oxygen ions. This is not self-evident. From exchange experiments done by Wyart et al. (178) a few D_0 values for quartz were calculated by the author (table 7.2). These calculations indicate Verhoogen's value for D_0 could be too high by about two orders of magnitude. Wyart et al.'s experiments are the only set of exchange

data published which allow some quantitative conclusions and which have a definite bearing on geological circumstances.

TABLE 7.2

Oxygen exchange between water and silicates during a period of 24 hours. Ref. (178)

Sample	Grain size μ	Temp. $^{\circ}\text{C}$	Press. bars	F(*)	$D_0^{(**)}$ $\text{cm}^2\text{sec}^{-1}$
Quartz	60	360	170	0.10	7.6×10^{-14}
Quartz	60	445	250	0.14	1.7×10^{-13}
Quartz	60	610	350	0.16	2.4×10^{-13}
Microcline	25	690	400	0.37	2.8×10^{-13}
Granite	-	800	500	0.26	-
Granite (fused)	-	800	1800	0.72	-

(*)F - fraction of exchange which has occurred.

(**) because of the small values of F, the reliability of the calculated D_0 is small.

The importance of these data will be evident from the following hypothetical example. Assume an amount of quartz is precipitated at 600°C from an aqueous solution under equilibrium conditions. The $\text{O}^{18}/\text{O}^{16}$ ratio of the solution remains constant, while the temperature drops to 500°C . How long will it take before a given amount of

isotopic exchange has occurred between the aqueous solution at 500°C and the quartz precipitated at 600°C ? For sake of simplicity the quartz is supposed to have a cubic shape and to be isotropic. Using eqn. 6.18 and data of table 6.1, the calculations are readily performed. The results are tabulated in table 7.3.

TABLE 7.3

Oxygen exchange between water and quartz at $t = 500^{\circ}\text{C}$

$h^{(*)}\text{cm}$	$\Delta\delta^{(**)} = 0.1$	$\Delta\delta = 0.2$	$\Delta\delta = 0.5$
10^{-2}	5 hours	1.3 days	11.6 days
5×10^{-2}	5.5 days	33 days	289 days
10^{-1}	21 days	130 days	3.2 years
5×10^{-1}	1.5 years	9 years	79 years

(*) h = side of the cube.

(**) $\Delta\delta$ = the average change of δ value for the crystal.

$\Delta\delta = 0.1$ is about the present-day accuracy for measuring values.

$\Delta\delta = 0.2$ means an error in temperature determination of 10°C at $t = 500^{\circ}\text{C}$.

$\Delta\delta = 0.5$ means an error in temperature determination of 30°C at $t = 500^{\circ}\text{C}$.

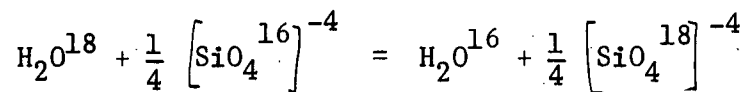
These results indicate that diffusion is a real problem in high temperature geothermometry. The temperatures measured in this way represent only freezing in temperatures of the O^{18}/O^{16} ratio. Of course, if the quartz is precipitated from a dry melt, the measured temperatures will be nearer to the true crystallization temperatures because water catalyses the exchange considerably.

7.4 Oxygen diffusion in silicates

The chilled gabbroic margins of the Skaergaard intrusion have exceptionally low δ values. The δ value for the total rock equals 3.7 which is nearly 2.5% lighter than normal olivine basalt. Taylor and Epstein (144, 149) have tried to explain this by postulating that the minerals in the chilled margin have equilibrated with meteoric water supposedly present in the country rock. Here a somewhat different explanation is advanced. According to Kennedy (101) the cooled edges of the intrusion will have been enriched in water. This is also indicated by Wager (172). From the example given in sect. 7.3 it is plausible that at $900^{\circ}C$ the exchange of oxygen between silicates and water is rapid. It is supposed that at about this temperature the chilled margins solidified.

To evaluate the fractionation factors for the oxygen exchange reaction between the orthosilicate group and water one has to know the normal modes of the internal vibrations of the orthosilicate group. These are known but not too accurately because of the difficulties in assigning force constants for the orthosilicate group. The Teller-Redlich product rule (91) makes it possible to calculate the frequencies

of two of the four normal modes of the O^{18} substituted orthosilicate group. The frequencies of the remaining two normal modes of the substituted orthosilicate group were estimated in such a way that the Teller-Redlich product rule was satisfied. Following the procedures outlined in section 2.2, the fractionation factor for the reaction



was approximated for various temperatures. The results are tabulated in table 7.4.

TABLE 7.4

Fractionation factors for the system orthosilicate ions - water

$t^{\circ} C$	α
0	0.9897
100	0.9859
150	0.9856
200	0.9857
250	0.9862
300	0.9869
500	0.9894
700	0.9919
900	0.9935
1100	0.9948

According to table 7.4 water is enriched in O^{18} with regard to the orthosilicate ion. These fractionation factors should not be taken too seriously, since all solid state effects were neglected. But, since the internal vibrations of the orthosilicate ion are mainly responsible for the fractionation, it seems likely that the calculations are qualitatively significant.

The extremely low δ values found for the chilled margin of the Skaergaard rocks may be the result of equilibration of the silicates with water from the intrusion itself and from water released by the country rock. Assuming the calculated fractionation factors to be satisfactory, then at $900^{\circ}C$ water with a $\delta/_{SMOW} = +7$ will be in isotopic equilibrium with olivine with $\delta/_{SMOW} = +2$. This refers to equilibrium conditions though it is noticed by Taylor and Epstein (144, 149) that the chilled marginal olivine gabbro is not in isotopic equilibrium; $\delta_{\text{plagioclase}} - \delta_{\text{clinopyroxene}} = -1.3$ while this value is positive under equilibrium conditions. Due to the rapid rate of cooling diffusion became negligible before equilibrium was reached. Besides it is to be anticipated that the oxygen diffusion constants are different for plagioclase and pyroxene. Further one should take into account that above $220^{\circ}C$, H_2O^{18} is more volatile than H_2O^{16} , under 1 atmosphere pressure. This may cause a somewhat anomalous δ value of the water in the chilled margins. To recapitulate, the low δ value of the chilled border rock is due to equilibration between water (from the wall rock and the intrusive) and the chilled border rock. But a low initial δ value for the water is not postulated, as was done by Taylor and Epstein, because it is believed here the fractionation factors for oxygen exchange

between silicates and water are close to unity or smaller than unity at 900° C. This is physically likely and may explain the exceptionally low δ values of the chilled borders.

The catalytic action of water on exchange reactions is also evident from the gneissic inclusions which are found in the Northern border group of the Skaergaard intrusion. Notwithstanding these inclusions are fused by the intrusion, they have essentially the same δ value as the country rock, while $\delta_{\text{country rock}}$ is very unlike the δ value of intrusion. The Skaergaard melt was apparently very dry (101) and consequently no significant exchange occurred. Likewise clinopyroxene from the fayalite - ferro gabbro contains more or less the original $^{18}\text{O}/^{16}\text{O}$ ratio of wollastonite from which the clinopyroxene is an inversion product (149).

In conclusion, it is suggested here that under wet high temperature conditions solid state oxygen diffusion can be important.

CHAPTER 8

OTHER PROCESSES BY WHICH OXYGEN ISOTOPES MAY BE SEPARATED

8.1 The Rayleigh distillation process (130)

The derivation of the Rayleigh equation comes from consideration of an isolated quantity of liquid crystallizing at constant temperature. An assumption is made that no isotopic exchange takes place between the crystalline phase and the melt. Using the symbols defined as follows:

n = total mass of exchangeable atoms in gramatoms,

$n^{\#}$ = total mass of isotopic atoms,

f = indicates the liquid phase,

s = indicates the solid phase,

$$r = \frac{n^{\#}}{n}$$

And the initial conditions of $t = 0$ sec, $n_s = 0$ an arbitrary stage of the solidification process can be described as;

$$n_f^{\#} = n_f r_f$$

Hence,

$$dn_f^{\#} = n_f dr_f + r_f dn_f$$

8.1

and

$$dn_s^{\#} = - dn_f^{\#} = - r_s' dn_f \quad 8.2$$

where r_s' is the value of r_s for the quantity dn_f . The fractionation factor α is given by

$$\alpha = \frac{r_s'}{r_f} \quad 8.3$$

Therefore,

$$\frac{dr_f}{r_f} = (\alpha - 1) \frac{dn_f}{n_f} \quad 8.4$$

which integrates to

$$r_f = r_{f_0} F_f^{(\alpha - 1)} \quad 8.5$$

which is the Rayleigh equation.

Where,

$$F_f = \frac{n_f}{n_{f_0}}$$

and n_{f_0} is the initial value of n_f .

To obtain a value for r_s (this is the average value for the total amount of precipitate at any moment),

$$n_{f_0} r_{f_0} = n_s r_s + n_f r_f \quad 8.6$$

$$n_s = n_{f_0} - n_f \quad 8.7$$

and r_f is given by eqn. 8.5, thus

$$r_s = r_{f_0} \frac{1 - F_f}{1 - F_f} \propto \quad 8.8$$

It is crucial that the fractionation factor remains constant during the process. Therefore the following requirements should be met:

- The temperature remains constant during the total process.
- The pressure remains constant (less important than the temperature).
- The structure of the liquid does not change.
- The chemical composition of the liquid does not change.
- The solid phase does not exchange oxygen with the remaining liquid.
- The system is closed.

It is clear that these stringent requirements are never met under the usual capricious geological conditions. Semiquantitative useful results may be obtained as is demonstrated by Dansgaard (46) for water evaporation, and by Taylor and Epstein (151) for the solidification of the Skaergaard intrusion.

8.2 Gravitational settling

One may envision that gravitational forces may cause a measurable separation of light and heavy isotopes in a melt. Using Stokes' formula,

$$6 \pi \eta a v = (M^\# - M) g \quad 8.9$$

one may estimate the velocity v , at which the two isotopically different flow units will be separated.

η = viscosity of the melt,

a = characteristic dimension of the flow unit,

M = weight in grams of the flow unit,

g = gravitational acceleration.

It is unlikely that the melt is a continuous medium with respect to the flow units. Hence strictly Stokes' formula can not be applied. Further it is by no means established what the flow unit is in silicate melts. But following the time honoured practice of neglecting those aspects of the problem which can not be evaluated, one can proceed with the calculations.

Estimating that the characteristic radius " a " of a flow unit equals 1.5×10^{-8} cm, one finds $v = 9 \times 10^{-17}$ cm \cdot sec $^{-1}$ if only one oxygen atom in the flow unit is replaced by O^{18} . Hence in 3×10^{12} years a separation of 1 cm would be obtained. A value of 21 poise was selected as the viscosity for the melt at 1450° C. The Handbook of physical constants (16) gives viscosities for melts of natural occurring rocks which are much greater than the value used. Hence it seems that this mechanism is not significant.

8.3 Other possible separation processes

When a thermal gradient exists in a melt the Soret effect will be operative, i.e. heavy molecules will in effect migrate towards cool regions and light molecules towards warm regions. In the Clusius-Dickel mechanism use is made of the Soret effect. By means of a system of

convection currents the heavy isotopes migrate effectively towards the cool wall and are concentrated at the bottom of the system while the light isotopes are concentrated at the top. These mechanisms could certainly be important in nature. But unfortunately not enough molecular data are available to make even rough calculations at present. The difficulty is the estimation of the thermal diffusion constants for oxygen in silicate melts.

The mechanism of solid diffusion can not produce significant isotopic separation as was shown by Senftle and Bracken (140) and by Grant (85). The reason for this is the extraordinary smallness of solid state diffusion constants.

CHAPTER 9

O^{18}/O^{16} RATIOS OF ROCKS

9.1 Igneous rocks

Unfortunately the extensive work done by Vinogradov et al. (166, 167) and by Schwander (137) could not be considered in this review. As remarked earlier Vinogradov's work can not be correlated with results obtained by other investigators (see sect. 1.5). Schwander's conclusions are at variance with present-day observations; this is attributed to a systematic error in his measurements (28, 32, 144).

9.1.1 Southern Californian batholith - Acidic rocks

The batholith has been described by Larsen (104) and the oxygen isotopic work on it has been done by Taylor and Epstein (144, 147, 148). Their data are reproduced in table 9.1 and form the basis of graphs 9.1, 9.2, and 9.3. It was shown in chapter 5 that $1000 \ln K_{AB} = \delta_A - \delta_B = \Delta_{AB}$. Hence Δ_{AB} is essentially only temperature dependent. In graphs 9.1, 9.2 and 9.3 the Δ values of various mineral pairs are plotted respectively against $\Delta Q - C$, $\Delta Q - K$ feldsp., and ΔK feldsp. - biotite. These relationships are essentially only temperature dependent.

if the pairs under consideration are in equilibrium. The inclined lines give the straight line relationships between 2 pairs of minerals; these lines have not been calculated, but are drawn by eye. The vertical lines marked with capital letters, connect the various mineral pairs belonging to the same rock sample. From these graphs it can be seen that the Rubidoux Mountain leucogranite shows the highest temperature of freezing in of O^{18}/O^{16} ratios followed in order by Shakeflat quartz monzonite, Rock Creek pegmatite and Bonsal tonalite. The last two formations show approximately the same temperature (see graph 9.1). Further it is clear that the minerals of the Woodson Mountain granodiorite are not in isotopic equilibrium.

It is also evident from the graphs that the minerals are not in complete equilibrium but are approaching it. This feature could be expected on grounds of solid state diffusion. But this is also explainable when one considers the crystallization process somewhat more closely. This is done by Taylor and Epstein (148) who focussed their attention on the following two possible sequences:

- During crystallization only the outer portions of the crystals are in continuous equilibrium with the melt. The inner parts of the crystal do not reequilibrate. Zoning in plagioclases is explained in this way. This is considered a Rayleigh process by Taylor and Epstein.
- The crystal is at all times in isotopic equilibrium with the melt, because continuous exchange between melt and crystal takes place.

The possible relationship resulting from these two processes is shown graphically by Taylor and Epstein (148) for a simple binary system from which minerals A and B crystallize. A is deficient in O^{18} with regard

TABLE 9.1

δ Values with respect to Hawaiian sea water(*) for various rocks and their constituent minerals. Ref. (147)

	Peridot dunite bomb	Olivine pyroxenite	Steens basalt	San Marco gabbro	Duke island gabbro
quartz				10.2	
plagioclase			6.6	7.5	7.4
K.feldspar					
biotite					
muscovite					
hornblende				6.5	
clinopyroxene		6.3		5.9	5.9
orthopyroxene	6.4			6.6	
olivine	5.1	5.1			
apatite				9.1	
magnetite				1.6	
ilmenite					2.1
total rock	5.2	6.0	6.6	7.0	6.3

* δ Hawaiian sea water / SMOW \approx 0

TABLE 9.1

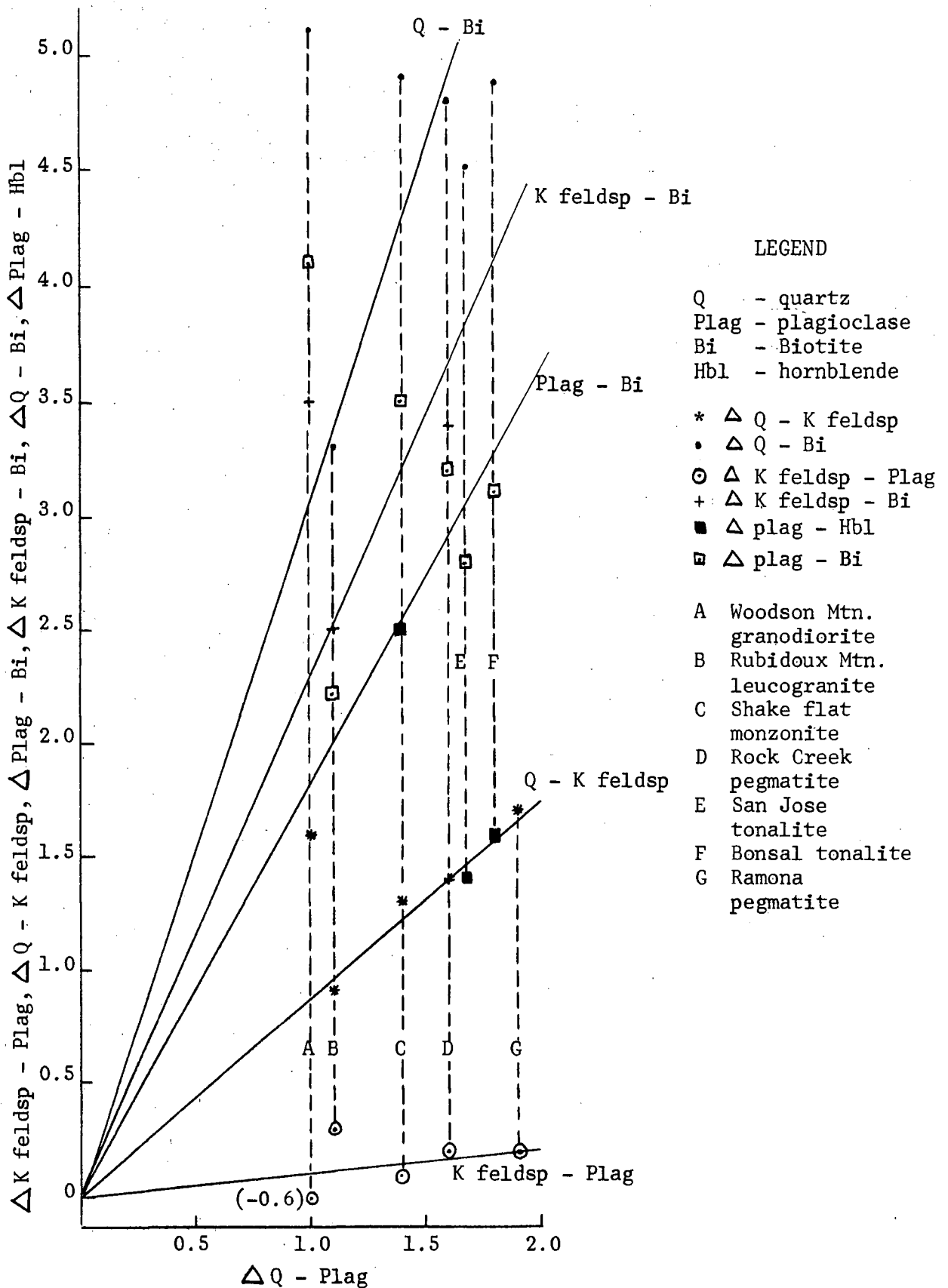
(continuation)

	Gabbro EG 5112	Gabbro EG 5181	Bonsal tonalite	San Jose tonalite	Woodson Mtn. granodiorite
quartz			10.3	9.7	9.5
plagioclase	6.8	6.7	8.5	8.0	8.5
K.feldspar					
biotite			5.4	5.2	4.4
muscovite					
hornblende			6.9	6.6	7.9
clinopyroxene	5.6	5.7			
orthopyroxene	5.6				
olivine	4.5				
apatite			6.7		
magnetite					
ilmenite					
total rock	6.0	5.8	8.3	7.8	8.6

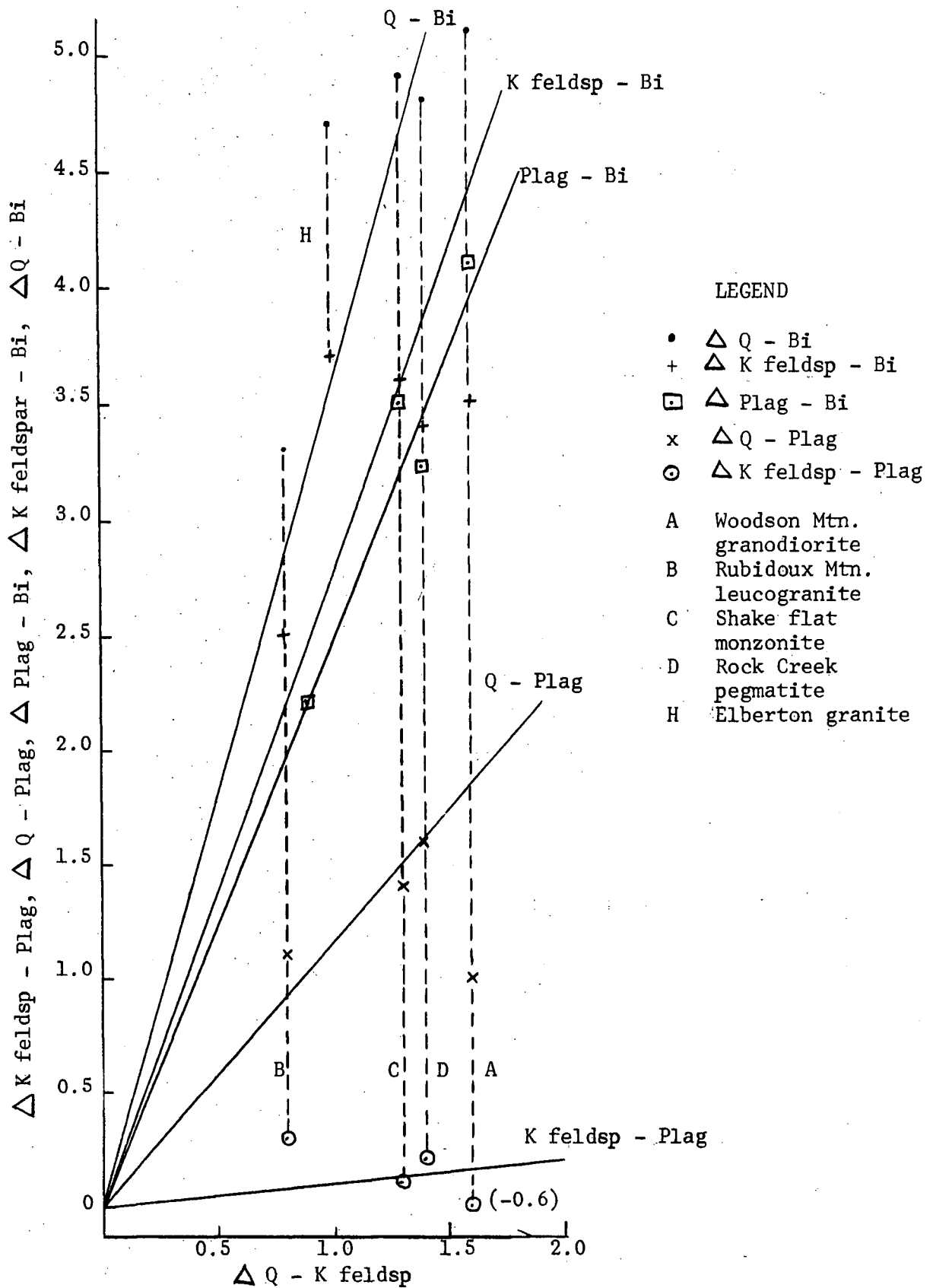
TABLE 9.1

(continuation)

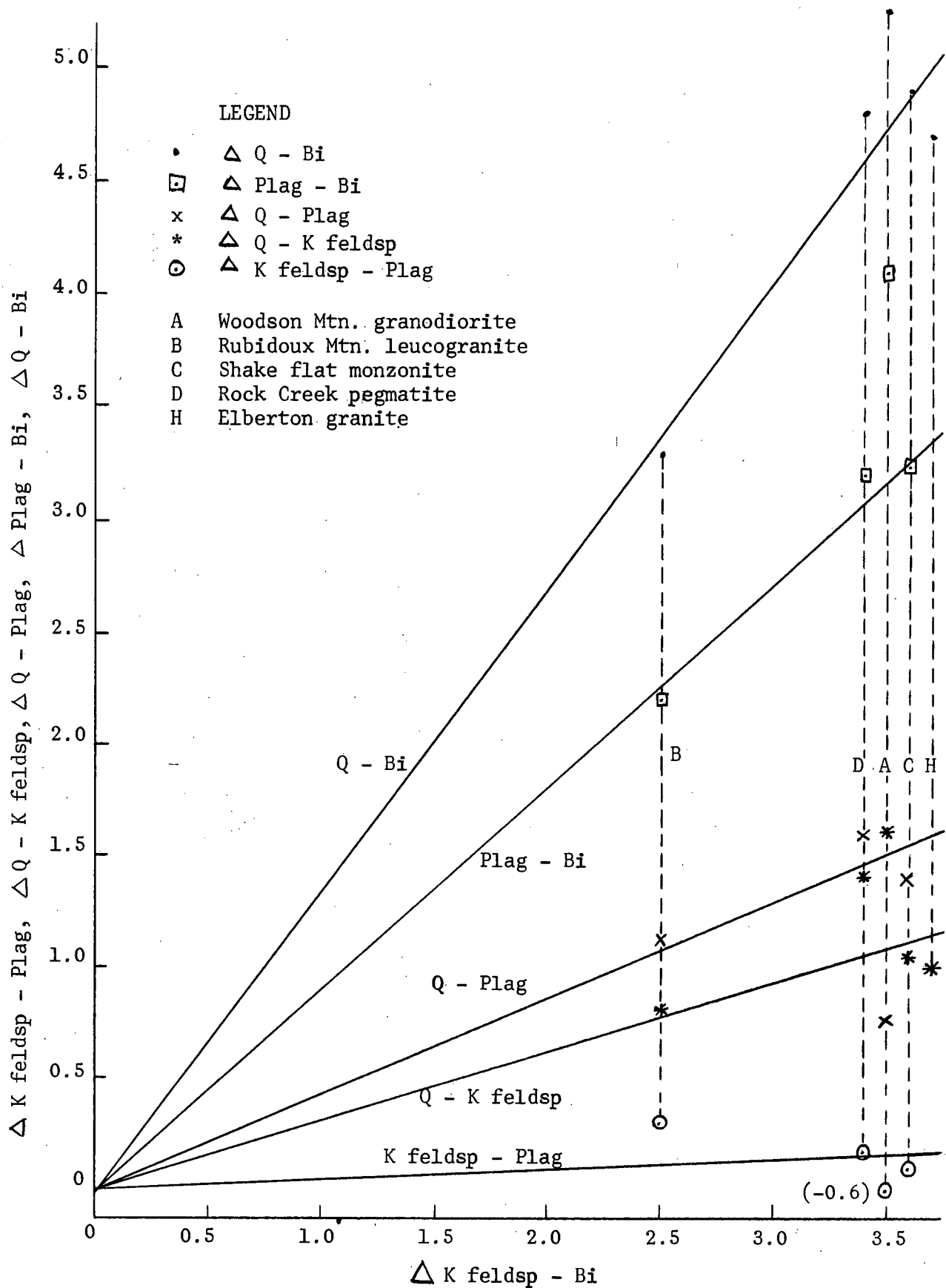
	Rubidoux Mtn. granodiorite	Shake flat monzonite	Elberton granite	Rock creek pegmatite	Ramona pegmatite
quartz	9.9	10.3		11.9	10.5
plagioclase	8.8	8.9	9.4	10.3	8.6
K.feldspar	9.1	9.0	8.4	10.5	8.8
biotite	6.6	5.4	4.7	7.1	
muscovite			7.3		
hornblende		6.4			
clinopyroxene					
orthopyroxene					
olivine					
apatite					
magnetite					
ilmenite			2.8		
total rock	9.2	9.1	8.5	10.9	9.4



Graph 9.1 - Fractionation relationships between mineral pairs in acidic rocks (see text) I.



Graph 9.2 - Fractionation relationships between mineral pairs in acidic rocks II.

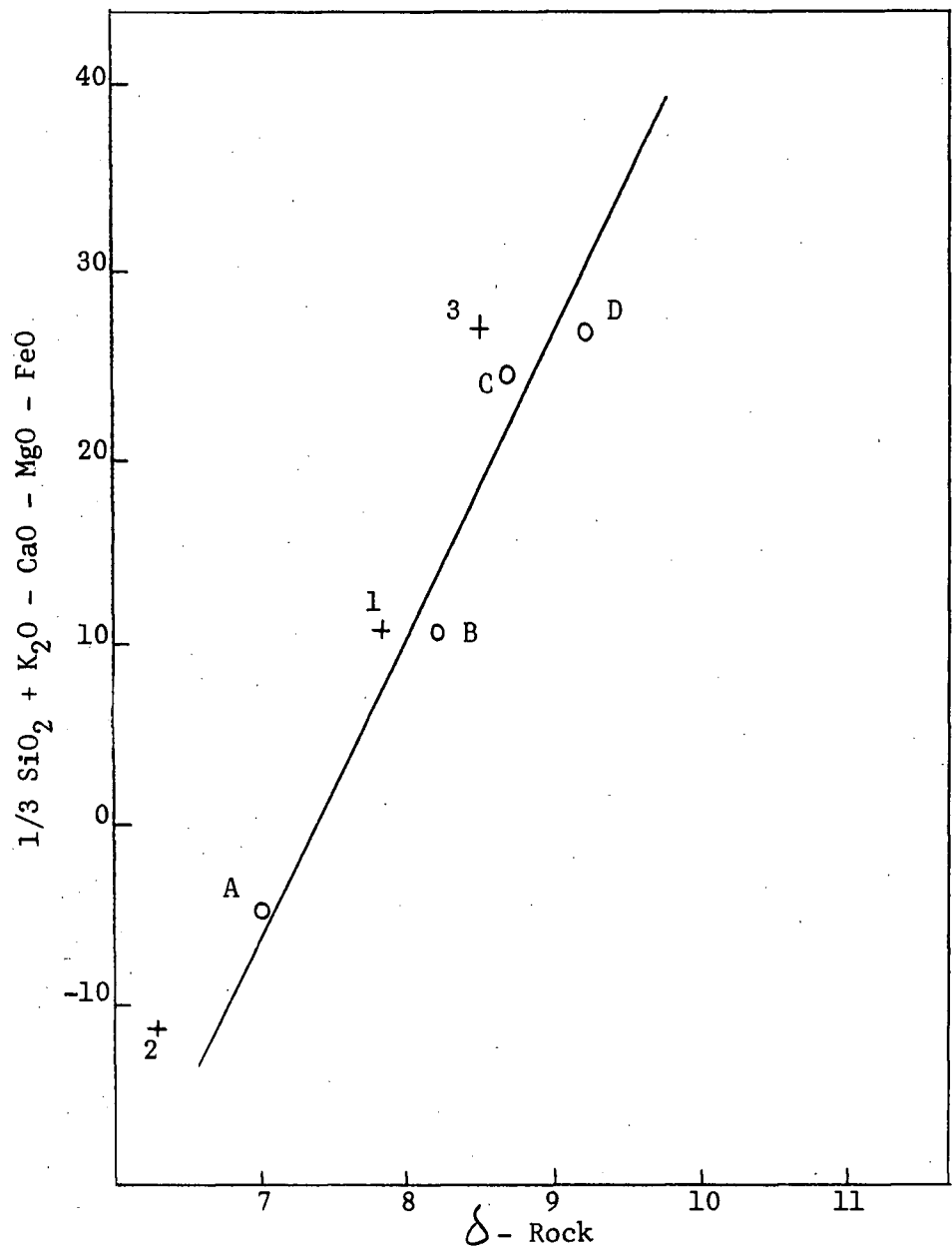


Graph 9.3 - Fractionation relationships between mineral pairs in acidic rocks III.

to the melt and B is enriched in O^{18} . Crystallization starts with the formation of A, and B does not begin to crystallize until later. It is then shown that the final δ value of A will be somewhat smaller than its equilibrium value and the final average δ value of B will be somewhat larger than its equilibrium value if the Rayleigh process takes place. By means of eqn. 8.5 Taylor and Epstein calculated the O^{18} relationships between the melt and the formed crystals.

According to Larsen (104) the Southern Californian Batholith was emplaced by magmatic stoping in the following sequence: San Marcos gabbro, Bonsal tonalite, Woodson Mountain granodiorite, Rubidoux leucogranite, and other minor granite bodies. Aptly Taylor and Epstein (144, 147, 148), remark that four samples are most certainly not sufficient to explain the origin of the batholith. Notwithstanding this they have observed: "... "this (oxygen isotope) evidence adds to the growing accumulation of data which suggests that the various rock types of the batholith are of magmatic origin, are intimately related and come from a well mixed source". As evidence for this conclusion they present a variation diagram, which is reproduced here as graph 9.4. San Marcos gabbro, Bonsal tonalite, Woodson Mountain granodiorite and Rubidoux Mountain leucogranite are plotted by Taylor and Epstein. The other three rocks are added by the author. The information for these three rocks is obtained from Taylor and Epstein (144, 147). From graph 9.4 it can be seen that a straight line on a variation diagram does not uniquely indicate a monomagmatic genetic relationship.

Taylor and Epstein (144, 147, 148) consider it compatible with the isotopic data that the leucogranite and the granodiorite are differentiation products of the Bonsal tonalite magma. But the same isotopic data



Graph 9.4 - Variation diagram showing the relationship between chemical composition and oxygen isotope composition for various rocks.

- A - San Marcos gabbro
- B - Bonsal tonalite
- C - Woodson Mtn. granodiorite
- D - Rubidoux Mtn. leucogranite
- 1 - San Jose tonalite
- 2 - Gabbro N 36-8
- 3 - Elberton granite

indicate that the freezing in temperature of the O^{18}/O^{16} ratio for the mineral pair quartz plagioclase is far lower for the Bonsal tonalite than for the Woodson Mountain and the Rubidoux Mountain formation. Whether this implies that the Woodson Mountain granodiorite has also a higher temperature of solidification than the Bonsal tonalite is difficult to ascertain, since the granodiorite is non-equilibrium assemblage. However the Rubidoux Mountain leucogranite most likely has a higher solidification temperature than the Bonsal tonalite because Δ quartz - biotite and Δ plagioclase - biotite are smaller for the leucogranite than for the tonalite. This appears to contradict Taylor and Epstein's deduction.

If, as Larsen proposed, the parent magma is gabbroic then it should have a δ value of about 7 (see graph 9.6). But all rocks which are formed from this gabbroic parent magma have δ values greater than 7. What happened to the excess O^{16} resulting from this fractionation? The postulated existence of a huge unexposed mafic body with a δ value between 5 and 6 would be a suitable deus ex machina. It is impossible to hold the 3 or 4% original water content of the magma responsible for carrying away the excess O^{16} . A simple but tedious calculation will show that if the original magma contained 3% water and the δ value of the original magma was 7, then the δ value of the escaping water should have been -15. The impossibility of this will be evident (see also sect. 7.4).

Again it is emphasized that four samples picked at random can not invalidate Larsen's conclusions, which were made after an intensive and careful analysis of the geological evidence. It is only demonstrated

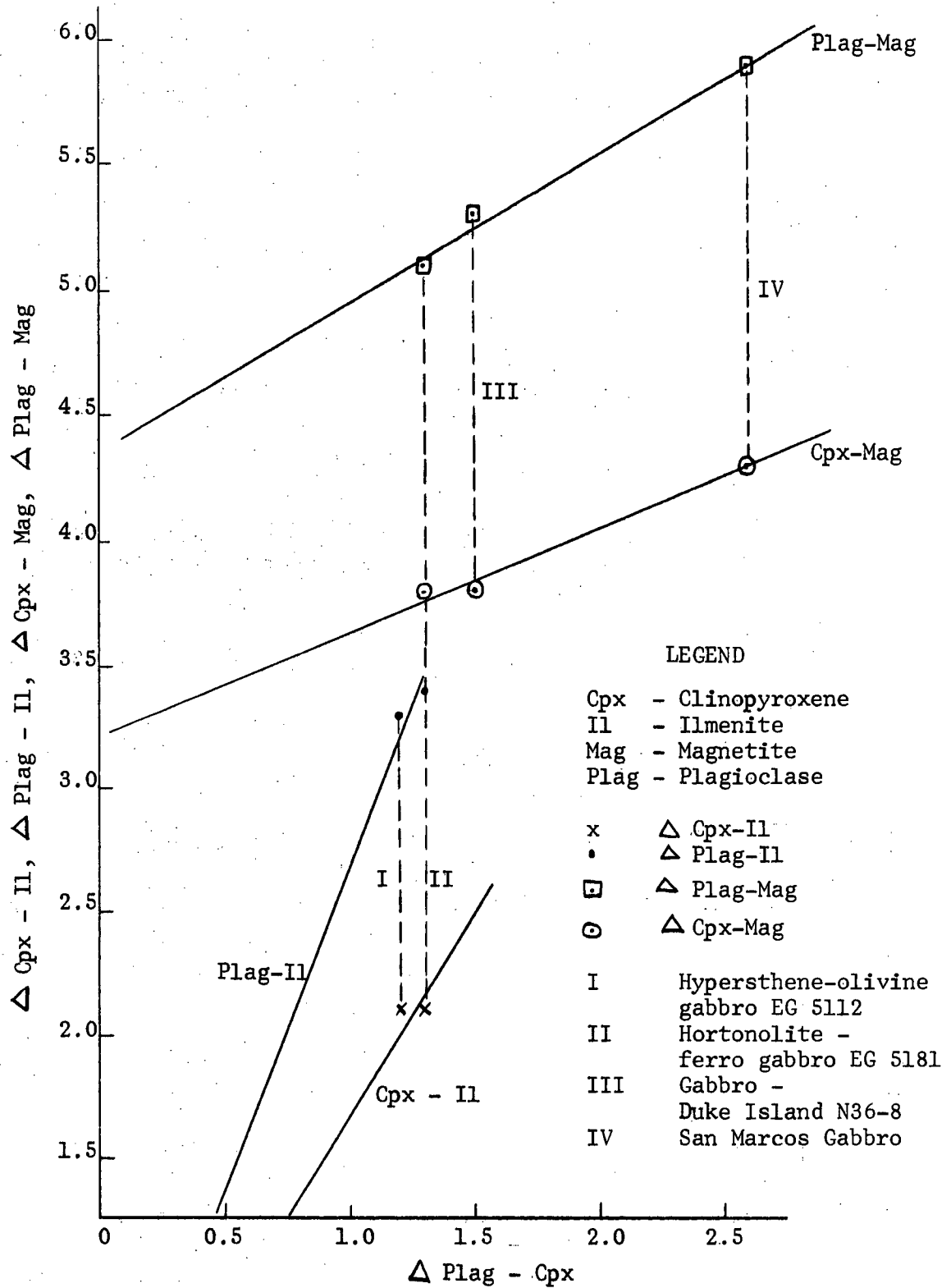
what could be done with oxygen isotopes if sufficient data were available.

When crystal fractionation is responsible for the differentiation of a magma, which was a closed system as far as oxygen is concerned, then the last minerals to be formed should be enriched in O^{16} . The reason for this is feldspars and quartz are always enriched in O^{18} with respect to the melt from which they precipitate and these two minerals contain more oxygen than all other minerals precipitated from this melt. That the last minerals formed in a system where crystal fractionation has been operating are enriched in O^{16} is observed in the Skaergaard intrusion (144, 149). The upper parts of this laccolith which solidified last show progressive enrichment in O^{16} .

9.1.2 Basic rocks

Oxygen isotope data for basic rocks are even more scanty than for acidic rocks. Graph 9.5 is similar to 9.1, 9.2, and 9.3. All the O^{18}/O^{16} measurements used have been published by Taylor and Epstein (144, 147, 148, 149). A few points are suggested by this graph:

- The minerals of the four gabbros form isotopic equilibrium assemblages.
- The fractionation factor for the mineral pairs clinopyroxene - magnetite and plagioclase - magnetite do not approach unity in a simple way at high temperatures as is the case for the mineral pairs considered in graphs 9.1, 9.2, and 9.3. This is not astonishing since the fractionation between water and magnetite is very small and it is known that "cross-over" occurs in systems where water is present (30).
- The temperature at which isotopic exchange becomes negligible is highest for the hypersthene - olivine gabbro followed by the



Graph 9.5 - Fractionation relationships between mineral pairs in basic rocks.

hortonolite - ferro gabbro, the Duke Island gabbro and the San Marcos gabbro.

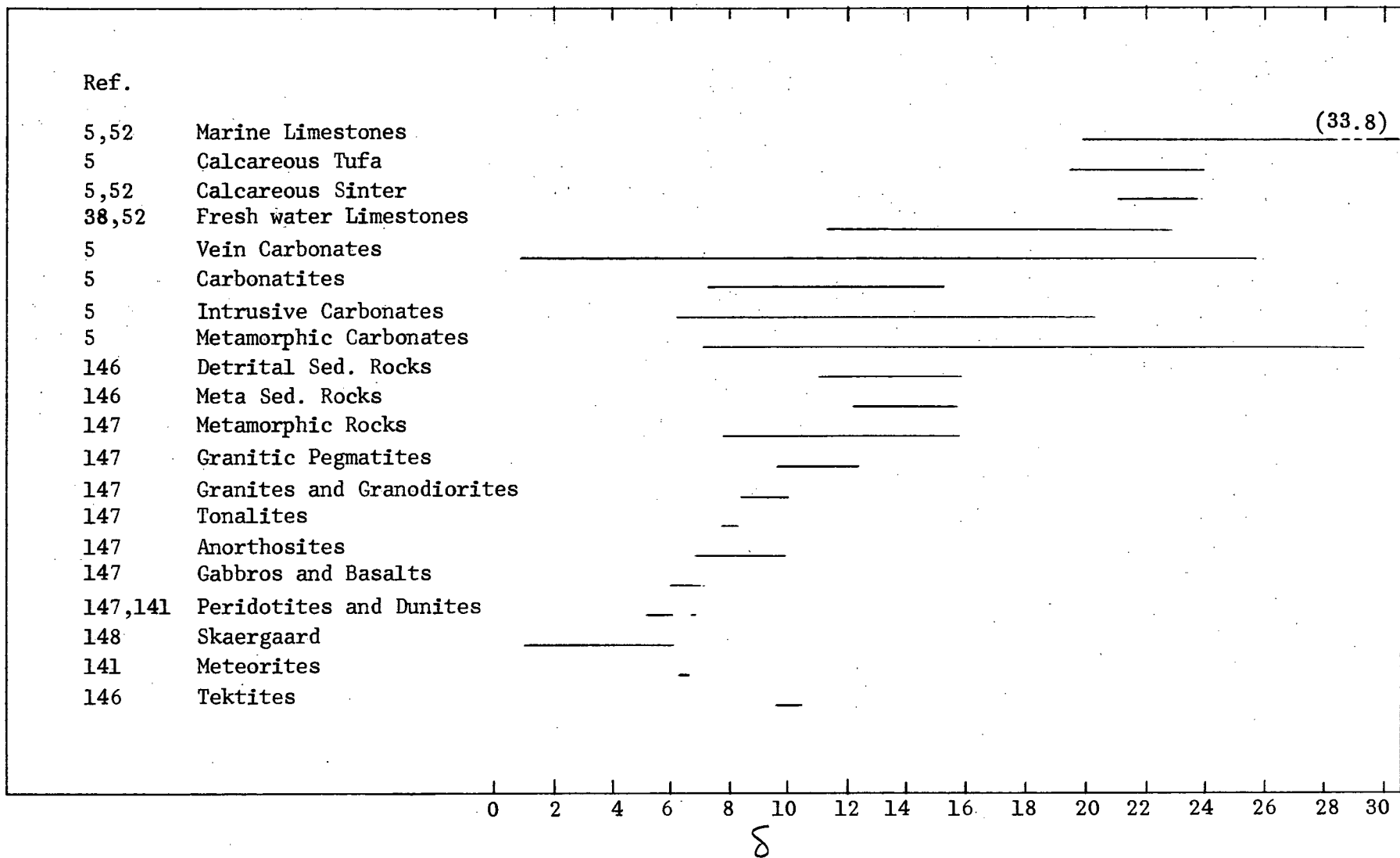
The composition of the upper mantle (taking the Mohorovicic discontinuity as the upper boundary of the mantle) is suggested to be peridotite (92, 171). The measured δ values for dunite and peridotite range from 5.2 to 6 (144, 147, 148). Basalts which are supposed to be products of partial melting of the peridotite have δ values from 6 to 7. Assuming that this difference is real, one faces the question of what happened to the excess O^{16} created in the process of partial melting of peridotite. For the time being the question will remain unanswered, again due to lack of sufficient information about oxygen isotope distribution in rocks.

Graph 9.6 summarizes the information available about O^{18}/O^{16} ratios in different rock types.

9.2 Sedimentary rocks

9.2.1 General

In the weathering process and during the erosion of igneous rocks the minerals will in general exchange their oxygen with the hydrosphere when they undergo chemical alteration. Isotopic exchange with the atmosphere is of no importance (see also Dontsova (58)). If the igneous rocks are reduced to detrital fragments without chemical alteration, exchange is less likely to happen (see table 9.2). This can be seen from Silverman's data (141).



Graph 9.6 - Oxygen isotope composition of various rock types, all δ values with respect to SMOW.

TABLE 9.2

O^{18}/O^{16} ratios for various quartzose rocks

Sample	$\delta^{(*)}$	% secondary silica
St. Peter sandstone 46	11.0	0
Basal breccia 45	15.7	10-15
Wishart orthoquartzite F-75	15.9	20

(*) δ values are with respect to SMOW from Clayton and Mayeda (34).

Hydrothermal solutions usually have a higher O^{18}/O^{16} ratio than the hydrosphere, besides fractionation factors at lower temperatures are greater (differ more from unity) than those at igneous temperatures. Thus the net result is that minerals which are precipitated from the hydrosphere usually have a higher δ value than their igneous counterparts. This is shown for quartz and can also be seen when carbonatite δ values are compared with those of sedimentary limestones.

Because fresh water has lower δ values than marine water, sediments equilibrated with fresh water should have a lower δ value than sediments equilibrated with marine water, at comparable temperatures. This is the basis for distinguishing marine and nonmarine carbonates and cherts by means of the O^{18}/O^{16} ratios (see 31, 52). This method is

quite powerful when one is dealing with post Palaeozoic sediments. Older marine sediments become less distinct because of exchange with ground water which has lower O^{18}/O^{16} values than marine water (50). Often the exchange takes place by means of a reversible hydration mechanism, as is the case for carbonates, thus the exchange reaction will be faster if the circulating ground water has a $pH \leq 6$ (120). The grainsize of the sediment is of prime importance (see chapt.7) as far as exchange is concerned. This was shown by Urey et al. (161) and also by Gross (86). Other factors are pressure and temperature, which may promote dissolution and reprecipitation, during which exchange most likely occurs. Graf (84) published recently a compilation of O^{18}/O^{16} ratios for sedimentary carbonates.

9.2.2 Origin of chert

Degens and Epstein (52) have tried to establish the origin of chert. To this end they have measured the O^{18}/O^{16} ratios of coexisting carbonates and cherts of marine and fresh water origin. From their data (table 9.3) some interesting conclusions may be drawn.

If one assumes the δ value for ocean water has been more or less constant and approximately equal to zero since the Cambrian, then the δ value for ground water will have been approximately -10. Supposing the carbonate was formed in equilibrium with sea water and that oceanic temperatures have always been less than $50^{\circ} C$, then judging from Degens' and Epstein's work all Precretaceous marine carbonates have exchanged their oxygen to some degree with percolating ground water. A Permian and a Jurassic sample are the only exceptions among the 18 Precretaceous samples under consideration. Clayton and Degens (31) report on

TABLE 9.3

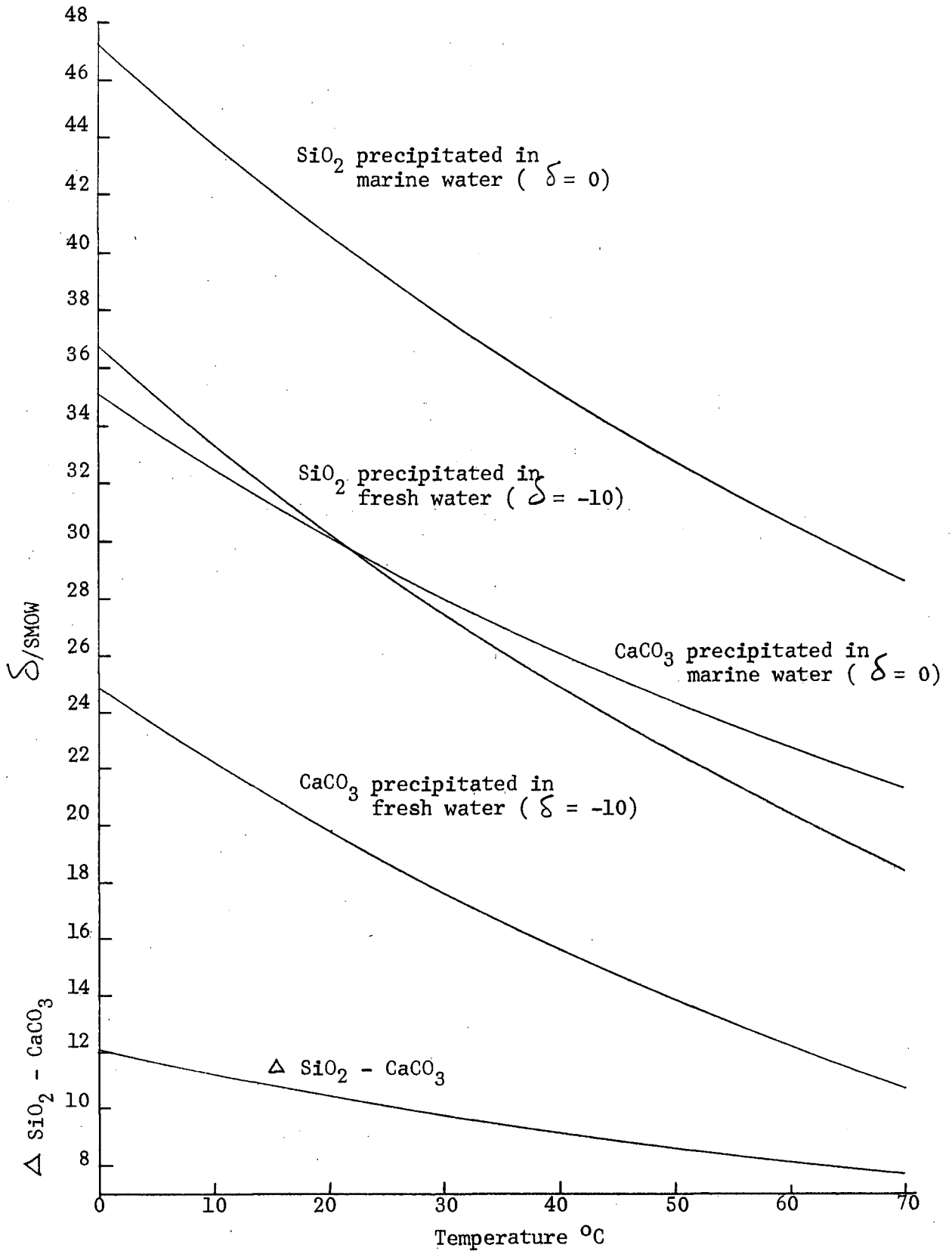
O^{18}/O^{16} ratios of coexisting marine cherts and limestones

No.	Sample Age	$\delta_{SiO_2/SMOW}$	$\delta_{CaCO_3/SMOW}$	Locality
1	Danian	32.6	28.4	Denmark
4	Danian	30.1	27.2	Denmark
6	Maastrichtian	32.9	28.6	Germany
9	Santonian	32.5	26.7	England
11	Campanian	32.5	27.3	Germany
12	Turonian	33.8	27.8	France
13	Jurassic	32.7	27.3	Greece
14	Jurassic	28.7	23.7	Germany
15	Jurassic	28.6	25.2	Germany
16	Permian	28.8	27.7	Texas
17	Permian	25.7	23.3	Arizona
18	Permian	24.2	23.2	Arizona
19	Pennsylvanian	27.7	27.7	Utah
20	Pennsylvanian	26.6	22.1	Arizona
21	Mississippian	25.9	24.3	Arizona
22	Devonian	26.3	23.0	Pennsylvania
23	Devonian	26.0	21.3	Pennsylvania
24	Silurian	25.6	22.9	Nevada
25	Silurian	24.7	21.5	Nevada

(continuation of table 9.3)

No.	Sample Age	δ SiO ₂ /SMOW	δ CaCO ₃ /SMOW	Locality
26	Ordovician	25.8	20.4	Pennsylvania
27	Ordovician	25.0	20.7	Pennsylvania
28	Ordovician	24.2	21.2	Pennsylvania
29	Cambrian	24.2	20.4	Pennsylvania
30	Cambrian	22.7	21.4	Pennsylvania

eleven Precretaceous marine carbonate samples, which all confirm the above mentioned conclusion. The Postjurassic marine carbonates seem to have retained their original O^{18}/O^{16} ratios fairly well. All Post-permian marine chert samples (52) have O^{18}/O^{16} ratios which indicate that they may have equilibrated with ground water. The equilibration temperature will have been between $15^{\circ} - 20^{\circ} C$, if the ground water had a δ value of -10. This can be deduced from graph 9.7. But all Prejurassic marine cherts (only one Permian exception) either have exchanged their oxygen with ground water with a δ approximately equal to -15, or they have experienced a temperature of $45^{\circ} C$. The likelihood of a temperature rise to $45^{\circ} C$ is difficult to judge without more evidence. The samples under consideration here are from Nevada, Arizona and Pennsylvania; a lowering of the δ value for ground water to -15 over so large an area may mean an isotopic change in composition of the ocean. Unfortunately the Prejurassic carbonates do not seem to



Graph 9.7 - Relationships between $\delta_{\text{SiO}_2/\text{SMOW}}$ and $\delta_{\text{CaCO}_3/\text{SMOW}}$ for quartz and calcite, precipitated under equilibrium conditions from marine ($\delta = 0$) and fresh water ($\delta = -10$) and the temperature at which equilibrium is attained.

be in isotopic equilibrium with percolating ground water and hence they do not provide much information. This nonequilibrium feature is obvious when Δ chert - carbonate values are inspected. They indicate temperatures of over 100° C. The Degens-Epstein paper does not mention any evidence for such high temperatures.

As far as the origin of the chert is concerned, the O^{18}/O^{16} ratios indicate that the supposed change from marine precipitated silica to chert takes place in a fresh water environment. It is implied that the system is open for water and during the formation of chert the SiO_2 equilibrates with the water. Alternatively, it has been proposed that the silica of chert is derived from diatomites. This line of reasoning was investigated by Degens and Epstein (52). Generally, the modern marine diatomites have δ values which are very similar to the Postpermian marine cherts. If the chert is just reorganized diatomite then during this reorganization process the system chert - diatomite has been closed for water, or no oxygen isotopic exchange has occurred, which suggests the reorganization does not proceed via dissolution and reprecipitation.

- From the δ values for marine diatomites one may conclude that:
- The diatomite skeleton is not in equilibrium with sea water. This may be due to biological fractionation. However one would expect a diatomite skeleton, initially not in equilibrium with sea water, would reequilibrate fairly rapidly (c.f. sect. 7.1).
- or that:
- The fractionation factor for amorphous silica is smaller than for crystalline silica. This is physically acceptable.

Finally if one suggests that the Prejurassic chert is not in equilibrium with the ground water then one is forced to postulate an even greater change in δ value for the ground water or a greater change in temperature.

9.2.3 Origin of dolomite

The origin of dolomite is still controversial. Recently two important observations were made. Wells (175) observed that dolomite was formed on the upper parts of tidal flats near Quatar, Persian Gulf. He did not establish whether the dolomite was primary or a penecontemporaneous replacement of pre-existing carbonate. Epstein and his associates (32, 71) noticed that Δ quartz - dolomite values were always near to zero, for hydrothermal cogenetic pairs. Under those circumstances Δ quartz - calcite is about 10. Degens and Epstein (51) investigated isotopically about 100 samples of coexisting dolomite and calcite. In some of the samples the calcite and the dolomite were of synsedimentary origin. They noticed that there was very little difference (max. 30/00 in O^{18}/O^{16} ratios between cogenetic calcites and "primary" dolomites. If there was a difference the dolomite was slightly enriched in both O^{18} and C^{12} . They concluded that as the calcite changed to dolomite, almost no isotopic exchange occurred and roughly the dolomite inherited the O^{18}/O^{16} ratio from its calcitic progenitor. This implies sedimentary "primary" dolomite does not exist but all sedimentary dolomite is derived from calcite. A year later Epstein et al. (78) reported they had shown experimentally that hydrothermal dolomite had approximately the same O^{18}/O^{16} ratio as quartz and this reflected the equilibrium δ value for dolomite.

9.2.4 Origin of aragonite needles

The origin of aragonite needles has been traced isotopically. These needles occur in recent marine carbonate oozes of shallow water origin. It was held they have an inorganic origin. Lowenstam (108) found the needles could be derived from the disintegration of aragonitic calcifications of a great many algae. The algae produce needles which are very similar to those found in recent sediments. Lowenstam and Epstein (112) have measured the range of δ values for oxygen and carbon, of aragonitic carbonates such as needle secreting algae, oolites, grape-stones and sedimentary aragonite needles, from the Bahama Bank area. Their conclusions are that the oolites are most likely of inorganic origin, while the aragonite needles have an algal origin. However not everyone (35) seems to be convinced by their logical account.

9.2.5 The oxygen isotope ratio of the ocean

The O^{18}/O^{16} ratio of the ocean at present is fairly well known (76). But the same can not be said for the ocean in the past. This causes uncertainty in carbonate geothermometry. Moreover, a knowledge of the O^{18}/O^{16} ratio of the oceans in the past could reveal something about their history. The variation in the oceanic O^{18}/O^{16} ratio due to the Pleistocene glaciation has already been treated (see sect. 4.3). Sedimentary carbonate deposits and O^{18}/O^{16} ratios of belemnites make it fairly certain that the oceanic O^{18}/O^{16} ratio has not changed significantly from the Jurassic to the present.

It is claimed by Degens that the oceans have had a constant isotopic composition since the Cambrian (47, 48). In another paper Degens (49)

attempts to show the δ value of the ocean was +2 with respect to SMOW, 2500 x 10⁶ years ago. Notwithstanding Degens' positive assertions, the question is still far from settled, for Degens' evidence (47, 48, 49) is not firmly established. The ground for Degens' choice of δ value +2 for the ocean 2.5 eons ago, is a suggestion that $\delta_{\text{juvenile water}} = +2$ (32). However this suggestion was made before it was realized how common the "cross-over" phenomenon is in exchange reactions involving water (30). Since then it has been clear that the high temperature extrapolation, used to estimate $\delta_{\text{juvenile water}} = +2$, can not be applied. Degens' claim of constant oxygen isotopic ratio for the ocean since the Cambrian is based on fossil evidence as presented by Compston. (see next paragraph). But this fossil evidence goes only as far back as the Permian. From there to the Cambrian is a considerable extrapolation.

Compston (38) has measured O^{18}/O^{16} ratios in Permian and Devonian brachiopods. He checked the shell microstructure of all his specimens. Bøggild (17) suggested that recrystallization of aragonitic shells to calcitic ones would destroy the microstructure. This suggestion has been used successfully (88, 143). In this process O^{18}/O^{16} ratios would most likely not be preserved. Compston also checked carefully the amount of secondary calcite in his samples, because secondary calcite usually has a considerably different oxygen isotope ratio, compared with the ratio of the original shell carbonate. His results have produced Permian temperatures which are consistent and similar to present day oceanic temperatures. This is certainly positive evidence for a constant O^{18}/O^{16} ratio for the oceans since the Permian. Unfortunately his Devonian samples did not fulfil the requirements of preserved microstructure and absence

of secondary calcite for being useful. This is generally the case for Palaeozoic fossils.

Lowenstam (109) has compared O^{18}/O^{16} ratios, strontium and magnesium contents in recent and fossil brachiopods. The uptake of strontium and magnesium is determined by temperature, crystal chemistry and physiology of the organism. Lowenstam has shown that the O^{18}/O^{16} ratios, the $SrCO_3$ and $MgCO_3$ contents in certain fossils are compatible with those in recent counterparts of these fossils. He has concluded this can be best explained by accepting the Sr/Ca and O^{18}/O^{16} ratios of the ocean have remained essentially unchanged since the late Palaeozoic.

This problem can in principle also be solved by the method of "material balance". This line of approach has been followed by Degens (48) and by Silverman (141). However the calculations of these two investigators should perhaps be judged as premature since there is simply not enough information available about O^{18}/O^{16} ratios in various rock types, to warrant the use of any method based on statistical averages.

9.3 Metamorphic rocks

The few measurements available for metamorphic rocks are summarized in graph 9.6. Because metamorphism is often a wet process it can be anticipated that the minerals will exchange their oxygen relatively fast. Diffusion constants and exchange rates will be different for different minerals, hence different temperatures for the freezing in of the O^{18}/O^{16} ratio should be expected.

The coarsest fraction of the minerals will indicate a temperature which is nearest to the maximum temperature of metamorphism. From the

pattern of δ values one may conclude whether the system was open to water or not. Equilibration with limited amounts of water may produce δ values which lie outside the normal range. If the system is open to water then the δ values for cogenetic mineral pairs should be related in a simple linear way. In the case of dry metamorphism nearly no exchange occurs, as is shown by the Skaergaard inclusions (see sect. 7.4).

All the work done on metamorphic rocks since 1950 is published in papers (5, 32, 70, 71, 138, 141, 147, 148, 150). Not enough is known about equilibrium constants, their pressure and temperature dependences and diffusion constants, to give any rules of thumb for the O^{18}/O^{16} ratio in different types of metamorphic rocks.

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