

THE UNIVERSITY OF CALGARY

OXYGEN AND SULFUR ISOTOPE  
STUDIES OF NATURAL SULFATES

by

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## ABSTRACT

Although sulfur isotope abundances in sulfates have been analyzed since 1971 at The University of Calgary, this thesis represents the first time that oxygen isotope analyses of sulfate have been carried out in this laboratory.

In addition to the experimental techniques, data, and interpretation, two chapters have been devoted to reviewing the natural variations of oxygen and sulfur isotopes.

A number of water samples and a few barite specimens were chosen for study. Many of the water samples were obtained from a four-year project on the regional hydrology south of Great Slave Lake, originated jointly in 1977 by the National Hydrology Research Institute (N.H.R.I.) of the Federal Department of Environment and Cominco Ltd., operator of Pine Point Mines, Ltd.

It was found that  $\text{SO}_4^{2-}$  extracted by ion exchange columns or  $\text{BaSO}_4$  precipitates which had undergone chemical cleanup gave better reproducibilities in isotope determinations than those simply precipitated by addition of  $\text{BaCl}_2$ .

Upper Hot Springs at Banff and springs near Buffalo River south of Great Slave Lake had  $\delta$ -values for sulfur and oxygen consistent with those for Devonian evaporites.

Whereas plots of  $\delta^{34}\text{S}$  versus  $\delta^{18}\text{O}$  for sulfates usually yield positive slopes, such a plot for samples taken a few hundred km along Buffalo River gave a negative slope. This is interpreted

to mean that  $\text{SO}_4^{2-}$  is derived from a number of different sources and is further subjected to varying extents of bacterial  $\text{SO}_4^{2-}$  reduction which is isotopically selective.

In a mining pit over a relatively smaller area, a plot of  $\delta^{18}\text{O}$  versus  $[\text{SO}_4^{2-}]^{-1}$  yielded a straight line with a negative slope and a correlation coefficient of 0.95. The y-axis intercept of this line gave a  $\delta^{18}\text{O}$  value consistent with Devonian evaporites. Thus a mathematical two source mixing model in which one source with variable concentration is the Devonian evaporites seems to account well for the data. Complications arise when bacterial  $\text{SO}_4^{2-}$  reduction is considered, particularly if it occurred before mixing of  $\text{SO}_4^{2-}$  from the two sources.

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## CHAPTER 1

## INTRODUCTION

1.1 Historical Overview

The principles of isotope abundance variations are being utilized to unravel mysteries of nature and are becoming increasingly helpful in multifarious disciplines such as Physics, Chemistry, Paleontology, Meteorology, Geothermometry, Biology, Geology, Environmental Studies, Oceanography, Paleoclimatology and Paleoecology.

Isotopes of heavier elements were discovered in the beginning of this century when studies of radioactivity were undertaken. SODDY (1909) coined the word ISOTOPES [ISOS (SAME), TOPOS (PLACE)] to signify that these species occupy the same place in the periodic table of elements. Sir J.J. THOMSON (1912) demonstrated that isotopes also existed for low atomic weight elements by using electric and magnetic fields to separate beams of different ionized atoms. This was followed by the mass spectrographic determinations of ASTON (1919) which provided an extensive knowledge of the isotopes of elements and their masses.

Isotopes of some of the lighter elements (hydrogen, carbon, nitrogen and oxygen) were first discovered by optical spectroscopy rather than by the mass spectrograph (NAUDE, 1930; UREY et.al., 1932). Additional wavelengths in the molecular spectra of compounds containing these elements could only be explained by the existence of isotopes.

Whereas it was obvious that isotopes differed in their nuclear properties, the fact that they might differ in other physical and

chemical properties was not immediately accepted. Events changed when UREY et al (1932) employed statistical mechanics to show that a large difference in the vapour pressures of the isotopic molecules of hydrogen,  $H_2$ , HD, and  $D_2$ , was to be expected. Using this concept, they concentrated the heavy isotope of hydrogen sufficiently to make its detection possible. LEWIS and CORNISH (1933) showed that the isotopically different molecules of water  $H_2^{16}O$ ,  $D_2^{16}O$  and  $H_2^{18}O$  have different vapour pressures. UREY and RITTENBERG (1933) theoretically predicted that marked differences in the equilibrium constants of exchange reactions between  $H_2$  and  $D_2$  on the one hand, and the hydrogen and deuterium compounds of the halogens (chlorine, iodine etc.) on the other should exist. The isotope exchange reaction between  $H_2$ ,  $D_2$  (diplogen) and HD was studied experimentally by FARKAS and FARKAS (1934).

Differences in the chemical properties of the hydrogen isotopes, protium and deuterium, were expected because of the large percentage mass difference. UREY and GREIFF (1935) extended the methods of thermodynamics and statistical mechanics to exchange reactions involving other light elements like boron, carbon, nitrogen and oxygen and predicted smaller but measureable differences in the chemical properties of other isotopic compounds of low atomic weight.

Today, differences in the chemical properties of isotopic compounds of heavier elements such as selenium ( $Z=34$ ) and tellurium ( $Z=52$ ) (RASHID, 1978; SMITHERS and KROUSE, 1968) have also been measured

despite the fact that at larger atomic weights, the percentage mass difference between isotopes decreases, and the differences in physical and chemical properties correspondingly diminish.

## 1.2 Structure of Isotopes

With the discovery of the neutron (CHADWICK, 1932) scientists began to comprehend the internal structure of atoms. This discovery had a profound effect on the clear understanding of the differences and similarities that exist in the atomic structure of the different isotopes of the same element. The number of protons in the nucleus is the criterion which distinguishes one element from another. For example hydrogen has one proton, carbon six, oxygen eight and sulfur has sixteen protons in its nucleus. Isotopes of an element are distinguished by their neutron number. Thus the oxygen isotopes  $^{16}_8\text{O}$  and  $^{18}_8\text{O}$  have eight and ten neutrons respectively. Similarly  $^{32}_{16}\text{S}$ ,  $^{33}_{16}\text{S}$ ,  $^{34}_{16}\text{S}$  and  $^{36}_{16}\text{S}$ , all have 16 protons but 16, 17, 18 and 20 neutrons respectively.

Some isotopes of an element may not be stable and undergo radioactive decays. For instance,  $^{40}_{19}\text{K}$  decays to  $^{40}_{20}\text{Ca}$  by  $\beta^-$ -decay and to  $^{40}_{18}\text{Ar}$  by K-electron capture.

The extra nuclear structure of an atom is responsible for most, if not all, of the chemical properties of an element. Thus  $^{16}_8\text{O}$  and  $^{18}_8\text{O}$  have the same peripheral electronic configuration viz  $s^2 p^4$ . They are expected to have very similar chemical properties. However, the different nuclear structures exhibit small but definite differences in chemical and physical behavior.

TABLE 1 depicts very clearly the differences in the physical and chemical properties of  $H_2O$  and  $D_2O$ .

TABLE 1. (PROPERTIES OF  $H_2O$  and  $D_2O$ ; DATA FROM HOEFS, 1973)

Constants	$H_2O$	$D_2O$
Density ( $20^\circ C$ , $gm/cm^3$ )	0.9982	1.1050
Temperature of greatest density ( $^\circ C$ )	4	11.6
Mole Volume ( $20^\circ C$ , $cm^3$ mole $^{-1}$ )	18.049	18.124
Melting point (760 torr)	0.00	3.82
Boiling point (760 torr)	100	101.42
Vapour Pressure (at $100^\circ C$ in torr)	760	721.60
Viscosity (at $20.2^\circ C$ in centipoise)	1.00	1.26
Ionic Product (at room temperature)	$1 \times 10^{-14}$	$0.16 \times 10^{-14}$

### 1.3 Variations in Isotope Abundances

NIER (1950) employed two mass spectrometers of the  $60^\circ$  magnetic sector type and carefully measured the relative abundances of the isotopes of carbon, nitrogen, oxygen, argon and potassium. Abundances for atmospheric oxygen isotopes were reported by him as follows:

$$^{16}_O - 99.759$$

$$^{17}_O - 0.0374$$

$$^{18}_O - 0.2039$$

The mean mass number, considering the following,

$$\frac{{}^{16}_0\text{O} \quad {}^{18}_0\text{O}}{{}^{16}_0\text{O} \quad {}^{16}_0\text{O}} = 0.004088$$

$$\frac{{}^{16}_0\text{O} \quad {}^{17}_0\text{O}}{{}^{16}_0\text{O} \quad {}^{16}_0\text{O}} = 0.000749$$

was reported as  $16.004452 \pm 7$ .

It was realized that these abundances are variable in nature. To quote Nier: "Recent results of other investigations on oxygen isotope abundances include, for  ${}^{16}_0\text{O}/{}^{18}_0\text{O}$ : Mücke and Childs, 630; Smythe for oxygen prepared from  $\text{PbO}_2$ ,  $503 \pm 10$  ----- the accuracy of measurement has now reached the stage where it is meaningless to speak of precise atomic weights unless the source of the material is clearly defined".

In stable isotope research, usually the variations in the ratio of the two most abundant isotopes are studied. Thus  ${}^{18}_0\text{O}/{}^{16}_0\text{O}$ ,  ${}^{34}_\text{S}/{}^{32}_\text{S}$ ,  ${}^{13}_\text{C}/{}^{12}_\text{C}$  and D/H are considered. The  ${}^{18}_0\text{O}/{}^{16}_0\text{O}$  ratio in nature has been found to vary by as much as 10% (10 per cent) or  $100^0/\text{oo}$  (100 p.p.t or per mil). The highest value is for the  ${}^{18}_0\text{O}/{}^{16}_0\text{O}$  ratio in atmospheric  $\text{CO}_2$  and the lowest in the water of glaciers found at the poles. The  ${}^{34}_\text{S}/{}^{32}_\text{S}$  ratio varies in nature by approximately 15% or  $150^0/\text{oo}$  but the processes which affect these variations differ from those for oxygen.

The alteration of the relative abundances of the stable isotopes is called stable isotope fractionation. The basis of fractionation is

the slight differences in the physical and chemical properties of the isotopes. Fractionations, their mechanisms and theories will be explored extensively in Chapter 3.

## CHAPTER 2

## NOTATIONS, TERMINOLOGY, AND STANDARDS

2.1 The  $\delta$ -value

In stable isotope research, the variations in the abundances of the isotopes of an element are reported as  $\delta$ -values defined below:

$$\begin{aligned}\delta_x &= \left[ \frac{R_x - R_{std}}{R_{std}} \right] \times 10^3 \\ &= \left[ \frac{R_x}{R_{std}} - 1 \right] \times 10^3\end{aligned}$$

where  $R_x = (D/H)_x$ ,  $(^{13}C/^{12}C)_x$ ,  $(^{18}O/^{16}O)_x$ ,  $(^{34}S/^{32}S)_x$  etc.

$R_x$  is the ratio of the abundance of the heavier isotope to that of the lighter (and in the above cases most abundant) isotope in the sample under investigation.  $R_{std}$  is the ratio defined above for the standard. The reason for using a  $\delta$ -scale is that  $\frac{R_x}{R_{std}}$  can be compared with precisions of better than  $\pm 0.01\%$  whereas determinations of  $R_x$  or  $R_{std}$  alone would have much larger errors.

Consider, as an example, the  $^{34}S/^{32}S$  ratios of sulfur found in nature. The standard chosen is troilite from the Canon Diablo meteorite and suppose that its  $^{34}S/^{32}S$  value for a sulfide mineral

was found to be 0.0470, then its  $\delta^{34}\text{S}$  value would be

$$\left[ \frac{R_x}{R_{\text{std}}} - 1 \right] \times 10^3 = \left[ \frac{0.0470}{0.0450} - 1 \right] \times 10^3$$

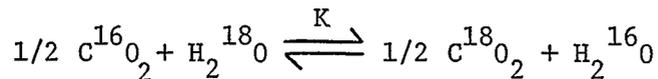
$$\delta^{34}\text{S} = 44.4^\circ/\text{oo}. \quad = \left[ 1.0444 - 1 \right] \times 10^3$$

This means that this sample is enriched in  $^{34}\text{S}$  (or is greater in the  $^{34}\text{S}/^{32}\text{S}$  ratio) by 4.44% or 44.4 parts per 1000 or per mil ( $^\circ/\text{oo}$ ). In the case above, it is very unlikely that two laboratories would obtain the same absolute values  $R_i$  for the troilite and the sulfide mineral. They would, however, agree closely on the value of the ratio  $R_x/R_{\text{Troilite}}$  since many errors which enter an absolute determination, cancel when the ratio of two samples is measured. A sample with a  $\delta^{18}\text{O}$  of -10.0 is impoverished in  $^{18}\text{O}$  (or is smaller in the  $^{18}\text{O}/^{16}\text{O}$  ratio) by 10 per mil or 1 per cent. Negative  $\delta$ -values indicate that the sample is depleted by that amount relative to the standard.

## 2.2 The Fractionation factor, $\alpha$

This term has been used in many ways and it is important to ascertain the meaning intended in a given report. One usage pertains to isotope

exchange reactions. Consider the exchange of oxygen isotopes between  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .



In this reaction, the heavy isotope,  $^{18}\text{O}$  is favoured in the carbon dioxide and the equilibrium constant

$$K = \frac{[\text{C}^{18}\text{O}_2]^{1/2} [\text{H}_2^{16}\text{O}]}{[\text{C}^{16}\text{O}_2]^{1/2} [\text{H}_2^{18}\text{O}]} = \frac{[\text{C}^{18}\text{O}_2]^{1/2} / [\text{C}^{16}\text{O}_2]^{1/2}}{[\text{H}_2^{18}\text{O}] / [\text{H}_2^{16}\text{O}]}$$

$K = 1.044$  at  $0^\circ\text{C}$ . This means that there is 4.4 per cent more  $^{18}\text{O}$  in the  $\text{CO}_2$  than in the water.

The fractionation factor,  $\alpha$  is defined as:

$$\alpha = \frac{\left( \frac{^{18}\text{O}}{^{16}\text{O}} \right)_{\text{CO}_2}}{\left( \frac{^{18}\text{O}}{^{16}\text{O}} \right)_{\text{H}_2\text{O}}}$$

In the above,  $\text{C}^{18}\text{O}_2$  is equivalent to  $\text{C}^{18}\text{O}^{18}\text{O}$ . In general, the isotope fractionation factor between two substances, A and B, is defined as:

$$\alpha_{\text{A-B}} = R_{\text{A}}/R_{\text{B}}$$

This can be related to  $\delta_{\text{A}}$  and  $\delta_{\text{B}}$  as follows:

$$\alpha_{\text{A-B}} = \frac{R_{\text{A}}/R_{\text{std}}}{R_{\text{B}}/R_{\text{std}}}$$

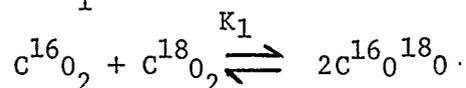
$$\therefore \alpha_{\text{A-B}} = \frac{1 + \delta_{\text{A}}/1000}{1 + \delta_{\text{B}}/1000}$$

$$\therefore \alpha_{\text{A-B}} = \frac{1000 + \delta_{\text{A}}}{1000 + \delta_{\text{B}}}$$

Consider now the relation between  $\alpha$  and  $K$ . From the above definitions of  $\alpha$  and  $K$ ,

$$\alpha = \frac{2 [C^{18}O_2] + [C^{16}O^{18}O]}{[H_2^{18}O] / [H_2^{16}O]} \Big/ \frac{2 [C^{16}O_2] + [C^{16}O^{18}O]}{[H_2^{18}O] / [H_2^{16}O]}$$

On the assumption that the two isotopes  $^{16}O$  and  $^{18}O$  will be distributed randomly between the molecules  $C^{16}O_2$ ,  $C^{18}O_2$  and  $C^{16}O^{18}O$  the equilibrium constant  $K_1$  for the reaction



is given as:

$$K_1 = \frac{[C^{16}O^{18}O]^2}{[C^{16}O_2][C^{18}O_2]} = 4$$

$$\text{Hence } [C^{16}O^{18}O] = 2 [C^{16}O_2]^{1/2} [C^{18}O_2]^{1/2}$$

and the expression for  $\alpha$  reduces to

$$\alpha = \frac{[C^{18}O_2]^{1/2} / [C^{16}O_2]^{1/2}}{[H_2^{18}O] / [H_2^{16}O]}$$

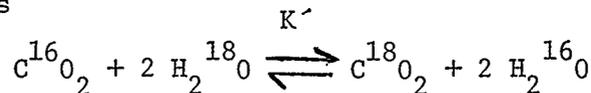
Thus

$$\alpha = K$$

In general, if there are  $n$  exchangeable atoms, then

$$\alpha = \frac{1}{K^{1/n}}$$

It may be noted, however, that if the water-carbon dioxide exchange reaction had been written as



$$\text{then } K' = \frac{[C^{18}O_2] / [C^{16}O_2]}{[H_2^{18}O]^2 / [H_2^{16}O]^2}$$

$$\text{and } \alpha = \sqrt{K'}$$

For simplicity, isotope exchange reactions are usually written such that only one atom is exchanged and that  $\alpha = K$  holds. Values of  $\alpha$  are normally very close to unity. For example, the equilibrium constant for sulfur isotope exchange between ZnS and PbS at 200°C is 1.0036. Although it is not strictly correct, (see below) it is common parlance to state that at 200°C the sphalerite-galena "fractionation" is 3.6 (or 3.6 per mil) or sphalerite is enriched in  $^{34}\text{S}$  by 3.6 per mil relative to galena.

### 2.3 The $\Delta$ -value

$\Delta_{A-B}$  is by definition equal to the difference of  $\delta_A$  and  $\delta_B$ .

It is also designated  $\Delta\delta$ . i.e.

$$\Delta_{A-B} = \delta_A - \delta_B = \Delta\delta$$

The reason for defining  $\Delta_{A-B}$  will become evident in the following.

Mathematically,  $\ln 1.00x \sim .00x$  e.g.  $\ln 1.0036 = 3.594 \times 10^{-3}$ .

More generally,  $\ln 1 + 10^{-3}x \sim 10^{-3}x$ . Since  $\alpha$  can be put in the form  $1 + 10^{-3}x$ ,

$$\ln \alpha = \ln (1 + 10^{-3}x) \\ \sim 10^{-3}x$$

$$\therefore 10^3 \ln \alpha \sim x$$

$$\therefore \boxed{10^3 \ln \alpha \sim \text{"per mil fractionation"}}$$

From a previous result,  $\alpha = \frac{1 + 10^{-3} \delta_A}{1 + 10^{-3} \delta_B}$

Hence  $\ln \alpha = \ln (1 + 10^{-3} \delta_A) - \ln (1 + 10^{-3} \delta_B)$

$$\sim 10^{-3} \delta_A - 10^{-3} \delta_B$$

$$\therefore 10^3 \ln \alpha \sim \delta_A - \delta_B$$

TABLE 2. COMPARISON BETWEEN VALUES OF  $\Delta$ ,  $\alpha$ , and  
 $10^3 \ln \alpha$  (From FRIEDMAN and O'NEIL (1978)).

$\delta_A$	$\delta_B$	$\Delta_{A-B}$	$10^3 \ln \alpha_{A-B}$	$\alpha$
1.00	0	1.00	1.00	1.00000
5.00	0	5.00	4.99	1.00500
10.00	0	10.00	9.95	1.01000
12.00	0	12.00	11.93	1.01200
15.00	0	15.00	14.89	1.01500
20.00	0	20.00	19.80	1.02000
10.00	5.00	5.00	4.96	1.00498
20.00	15.00	5.00	4.91	1.00493
30.00	25.00	5.00	4.87	1.00488
30.00	20.00	10.00	9.76	1.00980
30.00	15.00	15.00	14.67	1.01478
30.00	10.00	20.00	19.61	1.01980

Table 2 is a comparison between  $\Delta$  and  $10^3 \ln \alpha$  to illustrate the magnitudes of the approximations. Some recent papers define  $\Delta = 10^3 \ln \alpha$  but as the figures in Table 2 indicate, it is imperative to calculate the precise value of  $10^3 \ln \alpha$  when the per mil fractionations or the  $\delta$ -values exceed 10.

The function  $10^3 \ln \alpha$  has theoretical and experimental significance in stable isotope research. For perfect gases,  $\ln \alpha$  varies as  $\frac{1}{T^2}$  and  $\frac{1}{T}$  in the high and low temperature limits, respectively. In addition, smooth and often linear curves have also been obtained when  $10^3 \ln \alpha$  is plotted against  $\frac{1}{T^2}$  for experiments involving mineral pairs or mineral-water pairs. Departures from smooth curves can often be related to phase changes in the system.

#### 2.4 Isotopic standards

For oxygen there are two internationally accepted reference scales used to report variations in its isotope ratios; PDB and SMOW. The PDB standard is normally used in ocean paleotemperature studies wherein  $\text{CaCO}_3$  from fossil shells is analyzed. The PDB standard is a sample of a Cretaceous Belemnite, Belemnitella Americana, from the Peedee formation of South Carolina. This was the laboratory working standard used at the University of Chicago during the time that the oxygen isotope paleotemperature scale was developed. It may be noted that the PDB standard is the untreated ground carbonate and not the acid liberated  $\text{CO}_2$ . The original supply of this standard has long been exhausted but numerous other standards have been developed and exchanged among workers in this field. The oxygen isotopic composition of carbonates is

determined by the analyses of  $\text{CO}_2$  generated from the carbonates by reaction with 100 per cent phosphoric acid. Only two thirds of the oxygen is liberated from the carbonate during acid decomposition.

The SMOW (Standard Mean Ocean Water) standard was originally a hypothetical water sample with isotope ratios of oxygen and hydrogen similar to those of an average sample of ocean water. It was defined by H. CRAIG (1961) in terms of a NBS (National Bureau of Standards) reference water, NBS-1 as follows:

$$\left( \frac{^{18}\text{O}}{^{16}\text{O}} \right)_{\text{SMOW}} = 1.008 \left( \frac{^{18}\text{O}}{^{16}\text{O}} \right)_{\text{NBS-1}}$$

Subsequent to this definition two additional SMOW standards have appeared causing some confusion. Taylor and Epstein have used a standard called SMOW against which the Caltech internal standard (a sample of Potsdam sandstone) is  $15.5^\circ\text{oo}$ . Finally, H. Craig prepared a large quantity of water called SMOW for the International Atomic Energy Commission in Vienna as one of four standard reference waters available to stable isotope researchers. This latter SMOW has been analyzed in many laboratories and the oxygen isotope composition has been found by most investigators to be identical to the originally defined SMOW within the limits of analytical uncertainty, that is,  $\pm 0.05^\circ\text{oo}$ . SMOW is a water standard and in order to relate oxygen isotope composition of non-aqueous substances to it, it is necessary to analyze it directly by fluorination or carbon reduction techniques or by equilibration of  $\text{CO}_2$  with the water and subsequent analysis of the carbon dioxide. In the latter method one needs to know the  $\alpha_{\text{CO}_2-\text{H}_2\text{O}}$  at the fractionation

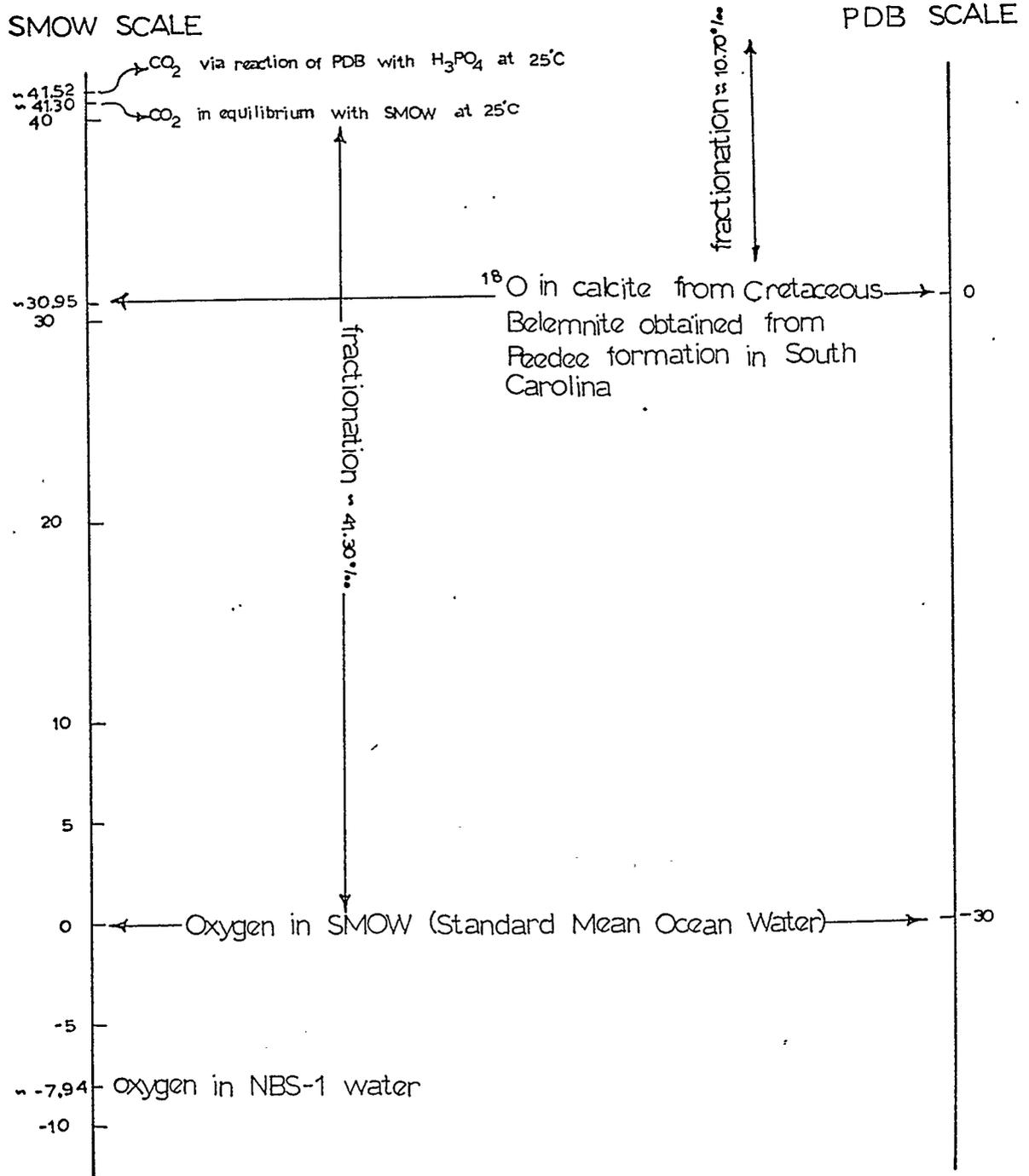


FIG. 1 Relationship between PDB, SMOW, and other oxygen standards.

temperature. This may be taken as 1.0413 at 25°C (FRIEDMAN and O'NEIL, 1978)..

The  $\delta^{18}\text{O}$  value of the  $\text{CO}_2$  produced by the reaction of 100%  $\text{H}_3\text{PO}_4$  with PDB calcite at 25°C is 0.22‰ relative to  $\text{CO}_2$  equilibrated at 25°C with SMOW water. To relate the  $\delta^{18}\text{O}$  values of calcite on the PDB and SMOW scale, the following expressions are used:

$$\delta_{\text{SMOW}}^{18\text{O}} = 1.03095 \delta_{\text{PDB}}^{18\text{O}} + 30.95$$

$$\delta_{\text{PDB}}^{18\text{O}} = 0.96998 \delta_{\text{SMOW}}^{18\text{O}} - 30.02$$

To relate the  $\delta^{18}\text{O}$  values of barites on the PDB and SMOW scale use the following:

$$\delta_{\text{SMOW}}^{18\text{O}} \text{ of sample w.r.t. SMOW} = 1.0413 \delta_{\text{PDB}}^{18\text{O}} \text{ of sample w.r.t. PDB} + 41.3\text{‰}$$

Troilite from the  $\hat{\text{C}}\text{a}\hat{\text{n}}\hat{\text{o}}\hat{\text{n}}$  Diablo meteorite is the internationally accepted standard for reporting  $\delta^{34}\text{S}$  variations. The mass spectrometric corrections for  $\text{SO}_2$  are large (see Chapter 7). More recently, there has been a trend to use sulfur hexafluoride ( $\text{SF}_6$ ) for analyses. Since  $^{19}\text{F}$  is the only stable isotope of fluorine, corrections are minimal and  $\delta^{33}\text{S}$  and  $\delta^{36}\text{S}$  values may be also determined.

To convert  $\delta$ -values from one standard to another, CRAIG (1957) has given the following equation.

$$\delta_{\text{x-A}} = \delta_{\text{x-B}} + \delta_{\text{B-A}} + 10^{-3} \delta_{\text{x-B}} \delta_{\text{B-A}}$$

where  $\delta_{\text{x-A}}$  means the  $\delta$ -value of sample x with respect to standard A and  $\delta_{\text{B-A}}$  is the  $\delta$ -value of B with relation to A.

A standard should fulfil the following requirements.

1. Used worldwide.
2. Homogeneous in composition.
3. Available in large amounts.
4. Easy to handle for chemical preparation, and isotopic measurements.
5. Has an isotopic composition close to that of the naturally occurring specimens.

## CHAPTER 3

## ISOTOPE FRACTIONATIONS AND MECHANISMS

3.1 Isotope Fractionation

Stable isotope fractionation means the alteration of the abundances of isotopes by various processes and mechanisms in nature or in laboratory experiments. Since many processes in nature are mass dependent, isotope fractionation is commonly observed. Phenomena producing isotope fraction may be categorized under Isotope Exchange Reactions and Kinetic Isotope Effects. The latter depend on the differences in the reaction rates of isotopic molecules and may occur in physical, chemical or biological conversions.

Statistical thermodynamics can be used to theoretically evaluate the differences in the physical and chemical properties of isotopic molecules. The molecule containing the heavy isotope has a lower zero-point energy than the molecule containing the light isotope. In the simplest case of a diatomic molecule approximated by a harmonic oscillator, the vibrational frequency of the heavy molecule,  $\nu_H$  is related to  $\nu_L$ , the frequency for the lighter molecule, by

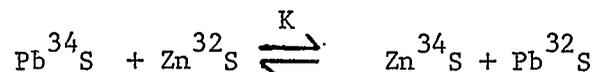
$$\nu_H/\nu_L = \sqrt{\mu_L/\mu_H}$$

where  $\mu$  is the reduced mass.

Therefore, the energy spacings  $\left\{ E_n = (n+1/2) h\nu \right\}$  for the light isotopic molecules are further apart and the molecule is more readily ruptured. In reality the computations are quite involved for a given situation, since the reaction mechanism must be considered.

### 3.2 Theory of Equilibrium Isotope Exchange Reactions

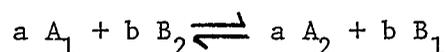
An example of an equilibrium exchange reaction is that of sulfur isotopes between sphalerite and galena.



$K = 1.0036$  at  $200^\circ\text{C}$ . If isotopic equilibrium is achieved, then at  $200^\circ\text{C}$ , the sphalerite is enriched in  $^{34}\text{S}$  by 3.6 per mil with respect to the galena.

UREY (1947) and BIGELEISEN and MAYER (1947) have applied the principles of statistical thermodynamics to evaluate the equilibrium exchange constant,  $K$  from the data of molecular spectra.

A typical isotope exchange reaction is written



where  $A_1$  is molecule A containing the light isotope and  $B_2$  is the molecule B bearing the heavy isotope. Light and heavy isotopes are exchanging between molecules A and B. The equilibrium constant for this reaction may be written as:

$$K = \left[ \frac{Q_{A_2}}{Q_{A_1}} \right]^a / \left[ \frac{Q_{B_2}}{Q_{B_1}} \right]^b$$

where the  $Q$ 's are the total partition functions of the molecules. The partition function of a molecule is a "sum over states" function of energy

$$Q = \sum_i g_i \exp \left( -\epsilon_i/kT \right)$$

The calculation of an equilibrium constant therefore involves the calculation of partition function ratios for two isotopic species of a molecule. It turns out that the partition function ratio for isotopic species, at room temperature, with the exception of some molecules of hydrogen, is essentially the ratio of the vibrational partition functions. For non-linear molecules, the ratio of the vibrational partition functions is

$$Q_2/Q_1 = \prod_i^{3n-6} \frac{U_{2i}}{U_{1i}} \cdot \frac{e^{-U_{2i}/2}}{e^{-U_{1i}/2}} \cdot \frac{1 - e^{-U_{1i}}}{1 - e^{-U_{2i}}}$$

where  $U_i \equiv h\nu_i c/kT$  and  $\nu_i$  is the  $i$ th vibrational frequency.

$h$  = Planck's constant

$k$  = Boltzmann's constant

$T$  = absolute temperature

$c$  = speed of light in cm/sec

$\prod_i^{3n-6}$  is the product over the  $3n-6$  fundamental frequencies for non-linear molecules. For linear molecules, the product extends over  $3n-5$  fundamental frequencies.

BIGELEISEN and MAYER (1947) have given this ratio in a convenient form as follows:

$$Q_2/Q_1 = \frac{\sigma_1}{\sigma_2} \left[ 1 + \sum_i G(U_i) \Delta U_i \right]$$

where the ratio of the symmetry numbers,  $\sigma_1/\sigma_2$  reduces to unity if only one atom is exchanged. The function  $G(U)$ , called the free energy function is

$$G(U) = 1/2 - \frac{1}{U} + \frac{1}{e^U - 1}$$

and  $\Delta U_i = U_{1i} - U_{2i}$  is always positive.

Thus it turns out that although the calculation of a single partition function is difficult, the calculation of the partition function ratio for two isotopic molecules or species can be done from a knowledge of the vibrational frequencies of the molecule.

The equilibrium constant,  $K$ , depends on the absolute temperature  $T$  as follows:

$$\ln K \propto \frac{1}{T^2} \text{ in most cases.}$$

At sufficiently high temperatures the thermal contribution to the vibrational energy of the molecule would become great enough to eclipse the mass contribution due to the isotope effect. Under these conditions the exchange constant becomes equal to unity and no fractionation should occur.

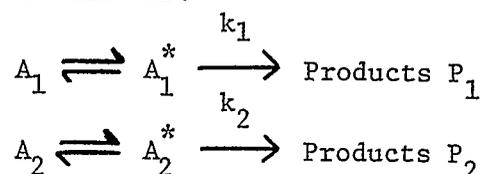
### 3.3. Kinetic Isotope Effects in Chemical Reactions

Isotope fractionations during irreversible chemical reactions usually preferentially enrich the lighter isotope in the products of the reaction. The greater zero point energy of the lighter isotopic species effectively aids it in passing over the energy barrier presented by the activated complex (see below) along the reaction coordinate.

The theory of kinetic isotope effects in chemical conversions is based on the absolute reaction rate theory or the transition state theory of reaction kinetics (EYRING, 1935). According to this theory, a chemical reaction proceeds from some initial to a final configuration by a continuous change in the co-ordinates and there is some critical intermediate configuration called the "Activated Complex" or "transition state" through which the reaction proceeds to the final configuration

or products. The theory then assumes that there are a small number of activated molecules in equilibrium with the reacting species and that this rate is controlled by the decomposition of the activated species.

If a lighter isotopic molecule  $A_1$  with a rate constant  $k_1$  competes with a heavier molecule  $A_2$  with a different rate constant  $k_2$  then we may depict this as:



Bigeleisen's expression for such unidirectional conversions is as follows:

$$\frac{k_1}{k_2} = \frac{Q_2/Q_1}{Q_2^*/Q_1^*} \cdot \frac{v_{1L}^*}{v_{2L}^*}$$

$Q_2/Q_1$  is the partition function ratio for the reactants and

$Q_2^*/Q_1^*$  is that for the activated complex

$v_{1L}^*/v_{2L}^*$  is the ratio of the frequencies which become imaginary in the activated complex. This ratio may be evaluated in terms of the reduced masses of the activated complexes as they traverse the critical region of the reaction coordinate.

$$v_{1L}^*/v_{2L}^* = (\mu_2^*/\mu_1^*)^{1/2}$$

where  $\mu = mM/m+M$

Depending on the bond being ruptured,  $m$  and  $M$  may be the atomic or fragment masses. Making use of the  $G(U) \Delta U$  function described previously,  $k_1/k_2$  can be rewritten.

$$k_1/k_2 = (\mu_2^*/\mu_1^*)^{1/2} \left[ 1 + \sum_i^{3n-6} G(U_i) \Delta U_i - \sum_i^{3n-7} G(U_i^*) \Delta U_i^* \right]$$

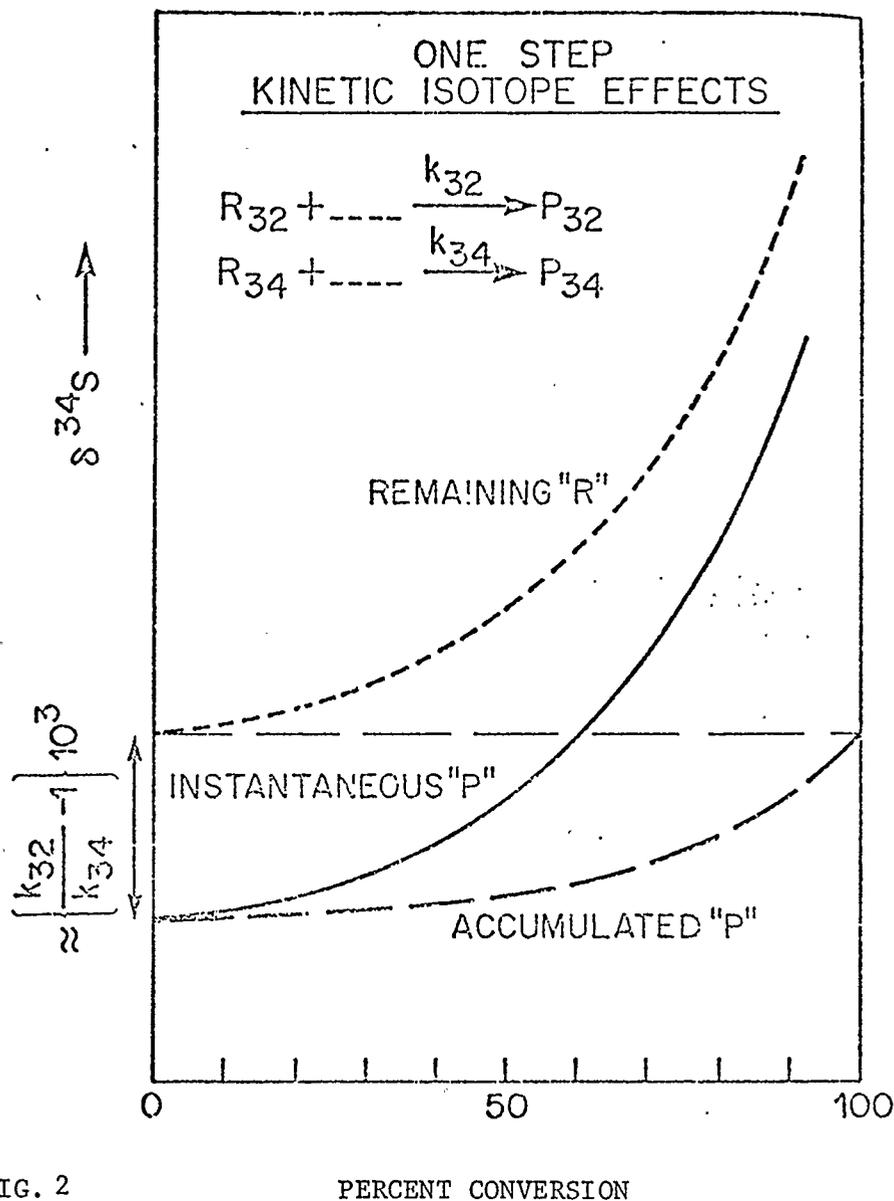


FIG. 2

Isotopic behaviour of components during a simple one-step first-order process where the ratio of the rate constants  $k_{32}/k_{34}$  is larger than unity. The "instantaneous" product curve refers to the product formed at a given instant. It parallels the remaining reactant curve. The "accumulated" product curve refers to all product formed up to a given point in the conversion.

In the high temperature limit the ratio of the partition functions tends to unity and on the assumption that the activated complex is identical to the reactant, we have

$$k_1/k_2 = (\mu_2/\mu_1)^{1/2}$$

when 
$$\sum_i^{3n-6} G(U_i)\Delta U_i = \sum_i^{3n-7} G(U_i^*)\Delta U_i^*$$

The other limit which yields maximum value of  $k_1/k_2$  results when the vibration isotopic partition function ratio of the activated complex becomes insensitive to isotopic substitution e.g. complexing of the reactant molecule by other molecules in the medium. In that event

$$Q_2^*/Q_1^* \longrightarrow 1$$

Hence  $k_1/k_2 = (Q_2/Q_1) (\mu_2^*/\mu_1^*)^{1/2}$

An appreciable kinetic isotope effect can only be expected if a bond involving the isotope in question is ruptured in the rate determining step. In other words, kinetic isotope effects are indicative of bonds breaking in the rate determining step. Since the isotopes participate at different rates, their relative numbers will be altered as the reaction proceeds. This behaviour is shown in Fig. 2.

### 3.4 Physico-Chemical Effects

Phenomena like diffusion, evaporation and condensation, crystallization and melting, absorption and desorption belong to this category. For example, the kinetic theory of gases concludes that at a given temperature, molecules containing the light isotope move more rapidly than those with the heavy isotope since  $T \propto 1/2 mv^2$ . A related concept is Graham's law of diffusion where the rate of diffusion of two

gases through an orifice is inversely proportional to the square roots of the masses.

$$\frac{v_1}{v_2} = \sqrt{\frac{m_2}{m_1}}$$

For interstitial diffusion in a lattice, the isotopic diffusion coefficients  $D_1$  and  $D_2$  are usually given by

$$\frac{D_1}{D_2} = \sqrt{\frac{M_2}{M_1}} .$$

However for other diffusion mechanisms, the isotopic dependence is more complex and may involve the host atoms.

Differences in the vapor pressures of isotopic compounds leads to fractionations. For example, the vapor pressure of  $H_2^{16}O$  is greater than that for  $H_2^{18}O$ . Hence the lighter molecular species are preferentially enriched in the vapor phase, the extent depending upon the temperature and whether there is effective isotopic exchange between the liquid and vapor phases. When the system is undergoing net evaporation, it may be described theoretically by the Rayleigh fractionation formula.

$$\frac{R}{R_0} = f^{(1-\alpha)}$$

where  $f$  = fraction of the initial liquid remaining.  $f$  is 1 at the start and approaches zero as distillation progresses.

$\alpha$  = fractionation factor. In the case of  $H_2^{18}O$  and  $H_2^{16}O$ ,

$$\alpha = \left( \frac{H_2^{18}O}{H_2^{16}O} \right)_{\text{liquid}} / \left( \frac{H_2^{18}O}{H_2^{16}O} \right)_{\text{vapor}}$$

$R = \frac{H_2^{18}O}{H_2^{16}O}$  ratio of the residual liquid water.

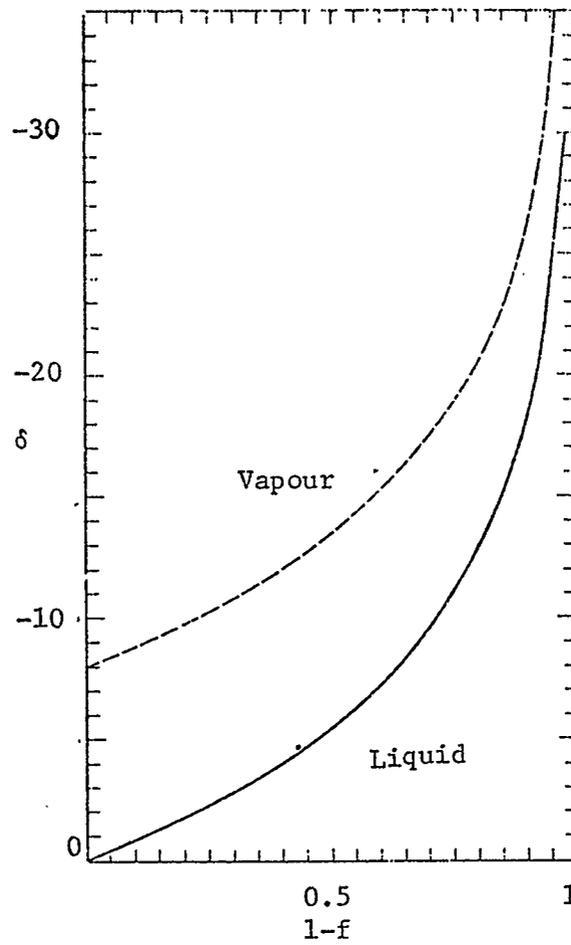


FIG. 3 Variation of the  $\delta^{18}\text{O}$  value of water and vapor, with degree of condensation of a water vapor system with  $\alpha = 1.008$ . The condensed phase is continuously removed from the system.

$R_0$  = initial value of R.

If net condensation from vapor in a closed system is occurring, then

$$\frac{R}{R_0} = f^{\alpha-1}$$

where  $R_0$  and R are the  $H_2^{18}O/H_2^{16}O$  ratios of the initial water vapor and of the water vapor after partial condensation, respectively.  $f$  is the fraction of vapor remaining in the system. This behaviour is plotted in Fig. 3 for  $\alpha = 1.008$  where the  $\delta^{18}O$  values for water and vapor are given as a function of the extent of condensation. The condensed phase is continuously removed from the system.

### 3.5 Biological Isotope Fractionation

In a manner similar to chemical conversions, the lighter isotopic molecules tend to be ruptured preferentially in biological conversions. For example, during photosynthesis, the assimilated carbon in the vegetation is isotopically enriched in the lighter  $^{12}C$  as compared to the  $^{13}C/^{12}C$  abundance ratio for atmospheric carbon dioxide. Another example to be discussed later is the tendency of sulfate-reducing bacteria to reduce  $^{32}SO_4^{2-}$  faster than  $^{34}SO_4^{2-}$  with the result that for partial conversions, product  $H_2S$  is usually enriched in  $H_2^{32}S$  compared to the unreacted  $SO_4^{2-}$ .

## CHAPTER 4

 $^{18}\text{O}/^{16}\text{O}$  VARIATIONS IN NATURE4.1 General

Oxygen is the most important element from a geochemical standpoint since it comprises about 46% of the lithosphere, 86% of the hydrosphere and 23% of the atmosphere by weight. The percent abundances of the three stable isotopes of oxygen in ocean water are:

GARLICK (1969)

$^{16}\text{O}$	99.7633%
$^{17}\text{O}$	0.0372%
$^{18}\text{O}$	0.1995%

The percentage abundances for atmospheric oxygen isotopes is (NIER, 1950)

$^{16}\text{O}$	99.759%
$^{17}\text{O}$	0.0374%
$^{18}\text{O}$	0.2039%

Thus the  $^{18}\text{O}/^{16}\text{O}$  abundance ratios for sea water and air are:

$$1.9997 \times 10^{-3}$$

and

$$2.0439 \times 10^{-3} \text{ respectively.}$$

Hence oxygen in the atmosphere is 23‰ enriched in  $^{18}\text{O}$  relative to sea water. The natural  $^{18}\text{O}/^{16}\text{O}$  ratio has a variation of about 10 percent. In terms of  $\delta^{18}\text{O}$  on the SMOW scale, the range is from +41 per mil for atmospheric carbon dioxide to -60 per mil for

Antarctic snow. The largest isotopic fractionation results from evaporation and condensation in the hydrologic cycle. This and other isotopic fractionation mechanisms are discussed below.

#### 4.2 Meteorites and Tektites

Meteorites may be categorized under iron meteorites, stony-iron meteorites and stone meteorites.<sup>1</sup>

Tektites are silica rich glasses with high potash and lime but low magnesia and soda. They are often regarded as the product of the impact of comets and huge meteorites on the earth.

SILVERMAN (1951) determined the  $\delta^{18}\text{O}$  values of a few meteorites and tektites and concluded that meteorites and terrestrial igneous rocks do not differ in isotopic composition by more than a few per mil.  $\delta^{18}\text{O}$  values for two stony meteorites,  $6.3^\circ/\text{oo}$  and  $6.5^\circ/\text{oo}$  fall within the range assigned to the primordial composition of our planet (see below) and may be taken as evidence that meteorites and our earth contain elements from a common nucleosynthesis. Higher  $\delta^{18}\text{O}$  values ( $+10.4^\circ/\text{oo}$ ) for two tektites bring them within the range of sedimentary rocks (see below) but do not necessarily rule out an extra terrestrial origin.

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<sup>1</sup>Iron meteorites consist predominantly of metallic iron with 5.5 to 20% alloyed nickel. Other minor constituents are troilite, cohenite and graphite. Approximately 5% of the observed meteoritic falls are of this type. Stony-iron meteorites are mainly classified into pallasites and mesosiderites and have appreciable nickel-iron contents albeit lower than that in iron meteorites. Stony meteorites consist chiefly of silicate materials like pyroxene [ $\text{CaMg}(\text{SiO}_3)_2$ ] and olivine,  $\text{Mg}_2\text{SiO}_4$ . Chondrites and achondrites are the two major kinds of stony meteorites. Among other differences, they are distinguished by the presence or absence of chondrules, small ( $\approx 1$  mm) spheres of olivine or pyroxene. A minor but significant group of meteorites is the carbonaceous chondrites which have greater water and carbon contents than ordinary chondrites. Interesting constituents of carbonaceous chondrites for stable isotope research are carbonates, sulfates, sulfides and "organic" carbon compounds.

More recent work shows that groups of meteorites as determined by differences in elemental composition and structural features are also differentiated in terms of their  $\delta^{18}\text{O}$  values. TAYLOR et al (1965) separated the stony meteorites into three groups, viz:

1. Basaltic achondrites and mesosiderites, with pyroxene  $\delta$ -values of +3.7 to +4.4 per mil.
2. H-type and L-type chondrites with pyroxene  $\delta$ -values of +5.3 to +6.3 per mil.
3. Types I, II and III carbonaceous chondrites with highly variable olivine and pyroxene  $\delta$ -values from  $-1^{\circ}/\text{oo}$  to  $+12^{\circ}/\text{oo}$ .

These authors suggested that the meteorites within each group are genetically related to one another, but that the three groups may themselves be only distantly related. The isotopic compositions of pyroxenes in terrestrial igneous rocks are similar to those of group 2 meteorites.

The  $\delta^{18}\text{O}$  values of most stony meteorites and of lunar rocks (see below) are compatible with those of terrestrial rocks and are explicable in terms of isotope exchange among the constituent minerals at different temperatures. However, CLAYTON et al (1973) reported that certain high-temperature phases in several carbonaceous chondrites, including Allende, are anomalously enriched in  $^{16}\text{O}$ . On a whole rock basis, the C3 meteorites (Allende is also class C3) were reported to have  $\delta^{18}\text{O} \sim 0$  per mil relative to SMOW. Since all

samples with the same nucleosynthetic history should plot  $\delta^{17}\text{O}$  versus  $\delta^{18}\text{O}$  linearly with a slope of 1/2 and this was not found to be true, the best explanation of this anomaly is that the high-temperature phases include grains containing pure  $^{16}\text{O}$  that did not mix with the oxygen of the solar nebula. This exotic oxygen may have been formed by nuclear reactions in a star which exploded and injected matter into the solar nebula. This discovery by CLAYTON and his colleagues is very significant because it is the first indication that the solar nebula contained matter ejected by more than one star and that it was not homogeneous isotopically. More recently, isotope anomalies have also been reported for magnesium (GRAY and COMPSTON, 1974) mercury (JOVANOVIĆ and REED, 1976), and sulphur (REES and THODE, 1977) in carbonaceous chondrites.

#### 4.3 Lunar Rocks

The  $\delta^{18}\text{O}$  values of minerals from Apollo 11 lunar gabbros and basalts were found by EPSTEIN and TAYLOR (1970) to have the following ranges:

Plagioclases	+6.06 to +6.33
Pyroxenes	+5.70 to +5.95
Ilmenites	+3.85 to +4.12

The uniformity of these data indicates isotopic equilibrium in the mineral assemblages. The constructed curves are

$$1000 \ln \alpha_{\text{Q-I}} = 1.35 + 4.56 (10^6 T^{-2})$$

$$1000 \ln \alpha_{\text{P-I}} = 0.72 + 3.22 (10^6 T^{-2})$$

where Q-I is quartz-ilmenite and P-I is plagioclase-ilmenite. The P-I temperatures for lunar samples are around 1200°C which may be compared to 920°C for Skaergaard gabbro, Greenland. The inference can be drawn that the lunar gabbros crystallized and cooled very rapidly under relatively "drier" conditions than many terrestrial gabbros.

#### 4.4 The Lithosphere

In dealing with the lithosphere the challenge is to obtain the "primordial"  $\delta^{18}\text{O}$  value which refers to the molten stage in the earth's history. Since fractionation of isotopes should be small at high temperatures, the oxygen isotopes were probably distributed uniformly during the molten stage of the earth. Samples of the lithosphere believed to have not been altered by erosional processes or uncontaminated by remelted or assimilated sediments are olivine basalt from Tahiti, Disco basalt from Oviqak, Greenland and the Columbia River basalt from Oregon, with  $\delta^{18}\text{O}$  values ranging from 6.4 to 7.0‰ (SILVERMAN, 1951). This range of isotopic composition may be regarded as the primordial composition.

It is an empirical observation that  $^{18}\text{O}/^{16}\text{O}$  ratios of co-existing silicate materials, in igneous and metamorphic rocks, are approximately related to their chemical compositions according to the following equations:

$$\delta^{18}\text{O} = KI + C$$

where  $I = \frac{\text{Si} + 0.58 \text{ Al equivalents}}{\text{Total Equivalents}}$

TABLE 3.

An attempt to arrange coexisting minerals according to their relative tendencies to concentrate  $^{18}O$ . The  $^{18}O$  content decreases in going down the table. (From GARLICK (1969).

quartz, dolomite (anhydrite)  
alkali feldspar, calcite, aragonite  
leucite  
muscovite, nepheline  
anorthite (kyanite)  
glaucophane (staurolite)  
lawsonite  
garnet, common pyroxenes, and amphiboles  
biotite  
olivine (sphene)  
chlorite  
ilmenite (rutile)  
magnetite (hematite)  
pyrochlore

K is a constant determined by the temperature of equilibration.

C reflects the bulk isotopic composition of the rock.

Table 3 is an attempt to arrange coexisting minerals according to their relative tendencies to concentrate  $^{18}\text{O}$ . This order of decreasing affinity for  $^{18}\text{O}$  is attributed to a crystal-chemical relationship. Minerals containing Si-O-Si bonds preferentially concentrate  $^{18}\text{O}$  over other minerals. At igneous temperatures, the Si-O-Al types contain approximately 4‰ less  $^{18}\text{O}$  and the Si-O-Mg and Si-O-Fe types contain 2‰ less  $^{18}\text{O}$ . The OH bearing minerals have anomalously low  $^{18}\text{O}/^{16}\text{O}$  ratios suggesting that the OH-group may be lower in  $^{18}\text{O}$  than the rest of the oxygen in the silicate structure.

Basalts, gabbros and anorthosites are isotopically almost indistinguishable from one another. Usually, granitic rocks show a wider spread of  $\delta$ -values (7 to 13‰) than most other igneous rocks. The granites intruded into a non-metamorphic zone show normal  $\delta^{18}\text{O}$  values between 8 and 9‰ whilst those intruded into a regional metamorphic zone are enriched in  $^{18}\text{O}$  ( $\delta^{18}\text{O}$  10 to 13‰). This enrichment is attributed to isotopic exchange between the granitic magma and the surrounding metamorphic rocks during regional metamorphism. Metamorphism is therefore associated with a depletion of  $^{18}\text{O}$ . Ultra mafic rocks ( $\text{SiO}_2 < 45\%$ ) exhibit a very narrow range in  $\delta^{18}\text{O}$  from 5.4 to 6.6‰ i.e. they are practically identical to those of chondritic meteorites.

Siliceous volcanic rocks, presumably derived by fractional crystallization from basaltic magmas, have isotopic compositions in the range +6 to +9 per mil (GARLICK, 1969). This is the range expected for siliceous rocks in high temperature isotopic equilibrium with basalts of composition 5.5 to 7.5 per mil. Exceptions to this mode of behaviour are the rocks in the Skaergaard intrusion, (see sec. 4.3) which are anomalously depleted in  $^{18}\text{O}$ . This has been attributed to exchange with meteoric waters during crystallization and post-crystallization cooling.

Carbonatites are magmatic carbonates, mostly calcite and dolomite associated with alkaline rocks. The  $\delta^{18}\text{O}$ -values expected of carbonatites in equilibrium with igneous rocks at high temperature range from +6 to +10 per mil. Magnetite is less amenable to isotopic alteration than is calcite.

Hydrothermal deposits have  $\delta$ -values varying from 0 to +13 per mil. This has been attributed to the isotopic mixing of  $^{18}\text{O}$  - poor meteoric water with magmatically derived hydrothermal fluid. Significant quantities of meteoric water were involved in the genesis of hydrothermal deposits.

Sedimentary rocks may be categorized as clastic (or detrital), and chemical. The detrital grains are those derived from pre-existing rocks whereas those of chemical origin are a consequence of reactions, and precipitation following evaporation or precipitation via the shells and skeletons of animals. Most of the soils found on earth have  $\delta^{18}\text{O}$  values from +15 to +25 $^{\circ}$ /oo (HOEFS, 1973).  $^{18}\text{O}/^{16}\text{O}$  ratios of modern ocean sediment core samples indicate that generally the authigenic

components may be distinguished from detrital components.

Detrital minerals of high temperature origin are generally 10 to 30<sup>o</sup>/oo impoverished in  $\delta^{18}\text{O}$  compared to authigenic minerals.

$^{18}\text{O}/^{16}\text{O}$  ratios of detrital minerals appear to reflect the provenance and mode of origin. Detrital quartz, for instance, seems to be resistant to weathering, and it will retain its original  $^{18}\text{O}$  content as established in the parent rocks.

The  $\delta^{18}\text{O}$  values of marine limestones of Recent age vary from +28 to +30<sup>o</sup>/oo SMOW and decrease with increasing geologic age to about +20<sup>o</sup>/oo for rocks of Cambrian age (KEITH and WEBER, 1964).

This trend is generally attributed to post depositional recrystallization and oxygen isotope exchange with water depleted in  $^{18}\text{O}$  compared to sea water. The  $\delta^{18}\text{O}$  values of fresh water limestones of Mesozoic to Recent age are generally lower than those of marine limestones of comparable age because fresh water is variably depleted in  $^{18}\text{O}$  relative to sea water. Similarly, the shells of fresh water mollusk have lower  $\delta^{18}\text{O}$  values than the shells of marine mollusks.

Metamorphic rocks are mineralogically transformed sedimentary or igneous rocks. The temperature range of metamorphism is generally between that of the sedimentary environment and that at which magma is generated by rock fusion. Regional metamorphism occurs on a scale up to thousands of square kilometers. Contact metamorphism takes place in heated rocks bordering magmatic intrusions. The most striking feature of regional metamorphic rocks is that the  $^{18}\text{O}/^{16}\text{O}$  ratios of

pelitic rocks, which are the metamorphic equivalents of argillaceous rocks, tend to decrease with increasing metamorphic grade. (Variation  $\approx 8^{\circ}/\text{oo}$ ).  $^{18}\text{O}/^{16}\text{O}$  ratios in contact metamorphic rocks remain exceedingly constant throughout the entire contact aureole.

#### 4.5 Paleothermometry

An oxygen isotope paleotemperature scale is based on the isotope exchange reaction between  $\text{CaCO}_3$  (calcite, aragonite) and  $\text{H}_2\text{O}$  and may be written



with the equilibrium constant, K given as:

$$K = \frac{([\text{CaC}^{18}\text{O}_3]/[\text{CaC}^{16}\text{O}_3])^{1/3}}{[\text{H}_2^{18}\text{O}]/[\text{H}_2^{16}\text{O}]}$$

$$K = 1.0286 \text{ at } 25^{\circ}\text{C} \text{ (O'NEIL and CLAYTON, 1964).}$$

Consequently, calcite is enriched in  $^{18}\text{O}$  relative to water when isotopic equilibrium has been established and will have a  $\delta^{18}\text{O}$  value of  $+28.6^{\circ}/\text{oo}$  if the  $\delta$ -value of sea water is taken as zero.

CRAIG (1965) has given the following equation expressing the relationship between the temperature of the water and the  $\delta$ -values of calcite and water:

$$t^{\circ}\text{C} = 16.9 - 4.2 (\delta\text{c}-\delta\text{w}) + 0.13 (\delta\text{c}-\delta\text{w})^2$$

$\delta\text{c}$  is the true  $\delta$ -value of  $\text{CO}_2$  gas prepared from the carbonate (in the calcareous shells) with 100 percent phosphoric acid at  $25^{\circ}\text{C}$  and

$\delta_w$  is the true  $\delta$ -value of  $\text{CO}_2$  gas equilibrated with the water at  $25^\circ\text{C}$ , and both are measured with reference to the same oxygen isotope standard. It may be noted that the above empirical relationship is based on the PDB rather than on the SMOW scale. Measurements of  $\delta^{18}\text{O}$  accurate to 0.1 per mil permit determinations of the temperature of precipitation of calcite shells in ocean water with an accuracy of  $\pm 0.5^\circ\text{C}$ .

Because of the wide variations of  $\delta^{18}\text{O}$  of fresh water, it is generally not possible to measure paleotemperatures by analysis of calcite deposited in fresh water. Such measurements are possible for marine calcite or aragonite (biogenic or inorganically precipitated) because it is assumed that the  $\delta^{18}\text{O}$  value of sea water remained constant to a first approximation. Nevertheless, the accuracy of paleotemperature determinations of skeletal  $\text{CaCO}_3$  of marine organisms is limited by several important pre-requisite conditions.

First, we must know the  $\delta^{18}\text{O}$  value of the sea water with which a given specimen of  $\text{CaCO}_3$  equilibrated. The  $\delta^{18}\text{O}$  values are related to salinities and in general a difference in salinity of 1‰ implies a difference of  $1^\circ\text{C}$  in the paleotemperature scale. The importance of continental glaciations on the isotopic composition of oxygen in sea water is widely recognized.

A second important limitation arises owing to "vital effects". Some organisms like corals and echinoderms do not precipitate their

carbonates in equilibrium with their environments. This apparent disequilibrium may be due to the influence of respiratory  $\text{CO}_2$  which may exchange oxygen with bicarbonate ions in solution.

Finally, we must be concerned with the preservation of the isotopic composition of fossil shells. It is well known that significant mineralogical and chemical changes occur in  $\text{CaCO}_3$  shells after the death of the organism.

#### 4.6 The Hydrosphere

Isotopic species of water are fractionated significantly in the water cycle. The term "meteoric" applies to water that has gone through the meteorological processes of evaporation, condensation and precipitation and includes rivers, lakes and glaciers. Because of seepage, meteoric water is also found in the lithosphere. The ocean, although it continuously receives continental run-off of meteoric waters as well as rain, is by general agreement not regarded as being meteoric.

Fresh Water: Variations in the isotopic composition of surface waters are due almost entirely to evaporation and condensation processes. Water condensed from atmospheric vapor is enriched in  $^{18}\text{O}$  and deuterium relative to the vapor. The residual vapor is consequently depleted in the heavy isotopes and subsequent precipitation is lighter than the initial precipitation. For many locations throughout the world there is a correlation between  $\delta\text{D}$  and  $\delta^{18}\text{O}$  contents of meteoric

waters approximated by

$$\delta_D \approx 8.1 \delta^{18}_O + 11 \text{ per mil. (DANSGAARD, 1964).}$$

The dependence of  $\delta^{18}_O$  for precipitation on latitude and temperature are quite easily explained. Water becomes isotopically lighter with increasing latitude. In Figure 4 it is noticed that Mt. Logan is almost as depleted in  $^{18}_O$  as the South Pole because of its altitude. As one goes higher, the temperature becomes colder and there is also the effect of depleting residual vapour in the heavier isotopes as the air mass rises.

Because of the temperature effect and factors such as changing storm paths, there is a seasonal dependence as exemplified by precipitation on an Austrian glacier where the mean oscillation between winter and summer snow is 14 per mil from -24 in winter to -10 in summer.

Departures from the  $\delta_D \approx 8.1 \delta^{18}_O + 11^{\circ}/\text{oo}$  relation are observed in rivers and lakes in arid regions and in rain falling through dry air. Continued evaporation, without recharge, leads to a steady state isotopic composition determined by the prevailing humidity, vapor composition and salinity. LLOYD (1966) has shown that brines originating by evaporation of sea water in a humid coastal environment will attain  $\delta^{18}_O$  values no higher than  $6^{\circ}/\text{oo}$ . It has been postulated that removal of vapor is characterized by a kinetic isotope effect rather than by the loss of equilibrium vapor from the system. Hence instead of a continuous increase in  $\delta^{18}_O$ , a stationary isotopic

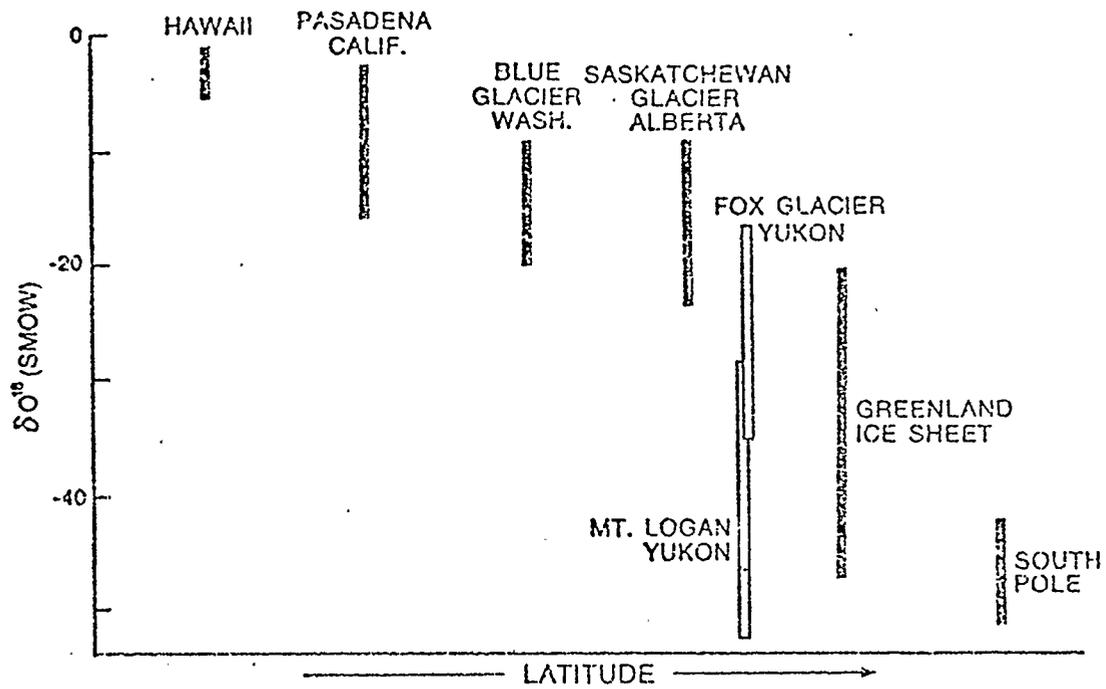


FIG. 4  $\delta^{18}\text{O}$  Variation with Latitude  
(From KROUSE, 1973).

composition is reached when evaporation has reduced the liquid phase to some 15 to 25 percent of its original mass. The enrichment of the liquid phase in the equilibrium model is governed by the Rayleigh distillation equation given as:

$$\delta^{18}_w - \delta^{18}_o = -\alpha \ln f$$

where  $\delta^{18}_o$  is the original isotopic composition of the water  
 $\delta^{18}_w$  is the value when fraction  $f$  of the water is left  
 $\alpha$  is the fractionation factor which is 1.009 at room temperature.

Since salinity is an inverse linear function of  $f$ , a plot of  $\delta^{18}_w - \delta^{18}_o$  versus  $\ln$  (salinity) plots as a straight line. However, if the Sverdrup model employing the kinetic effect is invoked then, the fact that at higher salinities ( $\sim 50^\circ/\text{oo}$ ) the data depart from the equilibrium curve and show a systematic decrease in the rate of isotopic enrichment, can easily be explained (Fig. 5).

Ocean Water: The  $\delta^{18}_o$  of present ocean water is fairly constant and nearly  $0^\circ/\text{oo}$  on the SMOW scale by definition. Whether this value has changed in past geological eras and if so to what extent are debatable questions. Based on analyses of marine chert deposits (PERRY, 1967) and carbonates (WEBER, 1965) it has been suggested that the  $\delta^{18}_o$  of sea water has increased monotonically at a rate of  $5^\circ/\text{oo}$  per billion years. However, a study of 2.9 billion year old hydrothermally altered granites (TAYLOR and MAGARITZ, 1975) suggests that the isotopic composition of sea water has not changed markedly during

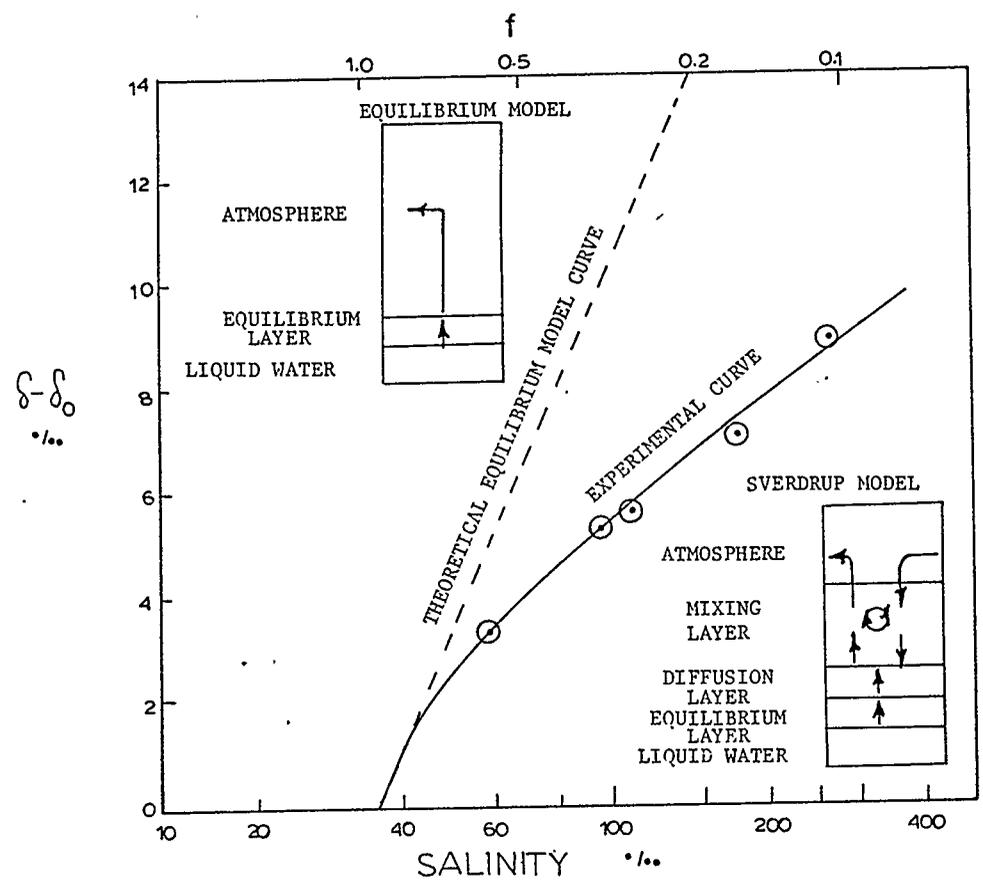


FIG. 5  $\delta^{18}O$  versus salinity for Equilibrium Model and for Experimental Evaporation.

the past 3 billion years. CHASE and PERRY (1972) argue that there is no a priori reason to assume that the oceans have maintained a constant oxygen isotope composition. The observed increase in  $\delta^{18}\text{O}$  of chert in the last  $3 \times 10^9$  years is about  $15^\circ/\text{oo}$ . If we assume that this change has been owing to a temperature change in the ocean, resulting in a change in the partitioning of  $^{18}\text{O}$  between  $\text{SiO}_2$  and water then that would require early Precambrian Ocean to have a temperature of  $100^\circ\text{C}$ ! The only plausible alternative is to postulate a parallel change in  $\delta^{18}\text{O}$  of ocean water, in which case the  $\delta^{18}\text{O}$  of the ocean at any time would have been 34 per mil lower than the  $\delta^{18}\text{O}$  of marine chert. If it is assumed that the  $3.9 \times 10^{22}$  mole of oxygen in ocean water are derived from mantle water with  $\delta^{18}\text{O} = 7^\circ/\text{oo}$ , the oceans must have become depleted in  $^{18}\text{O}$  by  $(3.9 \times 10^{22}) \times 7 = 27 \times 10^{22}$  per mil moles. The mantle provides an effectively infinite reservoir of oxygen and in contrast to isotope exchange reactions at the earth's surface, water silicate exchanges occurring at mantle temperatures are characterized by small fractionation.

CHASE and PERRY have delved into mathematical treatments which is essentially reductio ad absurdum. Assuming that  $\delta^{18}\text{O}$  of sea water has been constant in the past at its present value requires the unlikely coincidence that a sum of products of mass transport rates and isotopic shifts has remained equal to zero throughout geologic time. However, this concept can have a profound effect on Paleothermometry wherein

it is assumed that  $\delta^{18}\text{O}$  of water has been the same as it is today. Geothermal Waters from various regions throughout the world have deuterium contents similar to those of local rain or snow, though they are generally enriched in  $^{18}\text{O}$  relative to meteoric waters. This is interpreted to mean that geothermal waters are principally composed of recycled meteoric waters that have experienced oxygen exchange with the rocks through which they flowed.

#### 4.7 Atmosphere

Atmospheric oxygen has an isotopic composition of +23 per mil and shows no deviations exceeding 0.5 per mil up to an altitude of 30 km. Since UREY (1947) calculated the equilibrium constant for the exchange reaction between oxygen and water to be very close to unity, it appears that atmospheric oxygen is not in equilibrium with any part of the hydrosphere. The high  $^{18}\text{O}$  content of atmospheric oxygen, termed the "Dole" effect is due to preferential consumption of  $^{16}\text{O}$  during respiration of plants and animals which, at steady state, must remove oxygen equal in composition to photosynthetic oxygen added to the atmosphere. The composition of photosynthetic oxygen is roughly +6<sup>o</sup>/oo from surface ocean water and -1<sup>o</sup>/oo from fresh water having  $\delta^{18}\text{O}$  equal to -6<sup>o</sup>/oo. This yields a weighted average of +5<sup>o</sup>/oo for the total oxygen delivered to the atmosphere. Fractionation accompanying respiration is organism dependent. Oxygen removed by respiration is enriched in  $^{16}\text{O}$  with  $k_{16}/k_{18}$  measured as 1.018 for man, 1.015 for bacteria; 1.020 fungi; 1.017 land plants; 1.015 forest litter; 1.011 crab; 1.007 frog. The  $^{18}\text{O}/^{16}\text{O}$  ratio of dissolved oxygen at various

TABLE 4.

General range of  $\delta^{18}\text{O}$  values for a variety of oxygen containing substances found in nature. (From BROWNLOW (1979)).

Material	Permil $\delta$ value range
<i>Meteorites</i>	
Achondrites	4-5
Chondrites	5-6
Carbonaceous chondrites	-1 to +12
<i>Igneous rocks</i>	
Granite pegmatites	7-14
Granites and quartz monzonites	7-9
Basalts and gabbros	6-7
Ultramafic rocks	5-6
<i>Igneous minerals</i>	
Quartz	8.9-10.3
K-feldspar	7.0-9.1
Plagioclase	6.5-9.1
Hornblende	5.9-6.9
Pyroxene	5.5-6.3
Biotite	4.4-6.6
Magnetite	1.0-3.0
<i>Metamorphic rocks</i>	
Marbles	15-27
Pelitic schists	12-18
Quartzites	10-15
Amphibolites	7-13
<i>Metamorphic minerals</i>	
Quartz	8-19
Plagioclase	7-14
Muscovite	6-20
Biotite	4-11
Garnet	4-12
Ilmenite	3-7
Magnetite	6-7
Chlorite	3-9
<i>Sedimentary rocks</i>	
Marine limestones	22-30
Freshwater limestones	18-25
Arkosic sandstones	12-16
Shales	14-19
Cherts and diatomites	28-36
<i>Waters</i>	
Ocean water	-0.5 to +0.5
Temperate fresh waters	-10 to -4
Snow and ice	-60 to -20
Meteoric and geothermal waters	-24 to -7

depths in the Pacific Ocean water increases with depth as oxygen content decreases.  $^{16}\text{O}$  is preferentially consumed by a factor of 1.009 (RABINOWITCH, 1945; DOLE et.al. 1954).

Atmospheric  $\text{CO}_2$  has been found to have a  $\delta^{18}\text{O}$  of +41 per mil. Since the fractionation factor for  $\text{CO}_2\text{-H}_2\text{O}$  exchange is 1.0413 at  $25^\circ\text{C}$  we conclude that atmospheric  $\text{CO}_2$  is in approximate isotopic equilibrium with ocean water at  $25^\circ\text{C}$ .

## CHAPTER 5

 $^{34}\text{S}/^{32}\text{S}$  VARIATIONS IN NATURE5.1 Introduction

Sulfur (Z=16) has four stable isotopes in nature,  $^{32}\text{S}$ ,  $^{33}\text{S}$ ,  $^{34}\text{S}$  and  $^{36}\text{S}$ . The following percentage abundances were measured for the sulfur isotopes in sulfur vapor from native sulfur from a dome in Wharton County, Texas (BRADT et al 1956).

$^{32}\text{S}$	95.0%
$^{33}\text{S}$	0.76%
$^{34}\text{S}$	4.22%
$^{36}\text{S}$	0.014%

The  $^{32}\text{S}/^{34}\text{S}$  ratio calculated from these percentages is 22.51. Figure 6 is a simplified version of the global sulfur cycle. It is seen that sulfur occurs in various oxidation states from -2 (sulfide) through 0 (elemental sulfur) to +6 sulfates) in nature and this leads to natural variations in  $\delta^{34}\text{S}$  of about 150<sup>o</sup>/oo. The heaviest sulfates have  $\delta^{34}\text{S}$  greater than 90<sup>o</sup>/oo and the lightest sulfides have  $\delta^{34}\text{S}$  values around -50<sup>o</sup>/oo (Fig. 7). It is also seen in Figure 7 that meteoritic sulfur has remarkably constant  $\delta$ -values, which fall more or less in the middle of the terrestrial range. These factors make meteoritic sulfur an ideal standard for the  $\delta^{34}\text{S}$  scale. (HULSTON and THODE, 1965; RANKAMA, 1963).

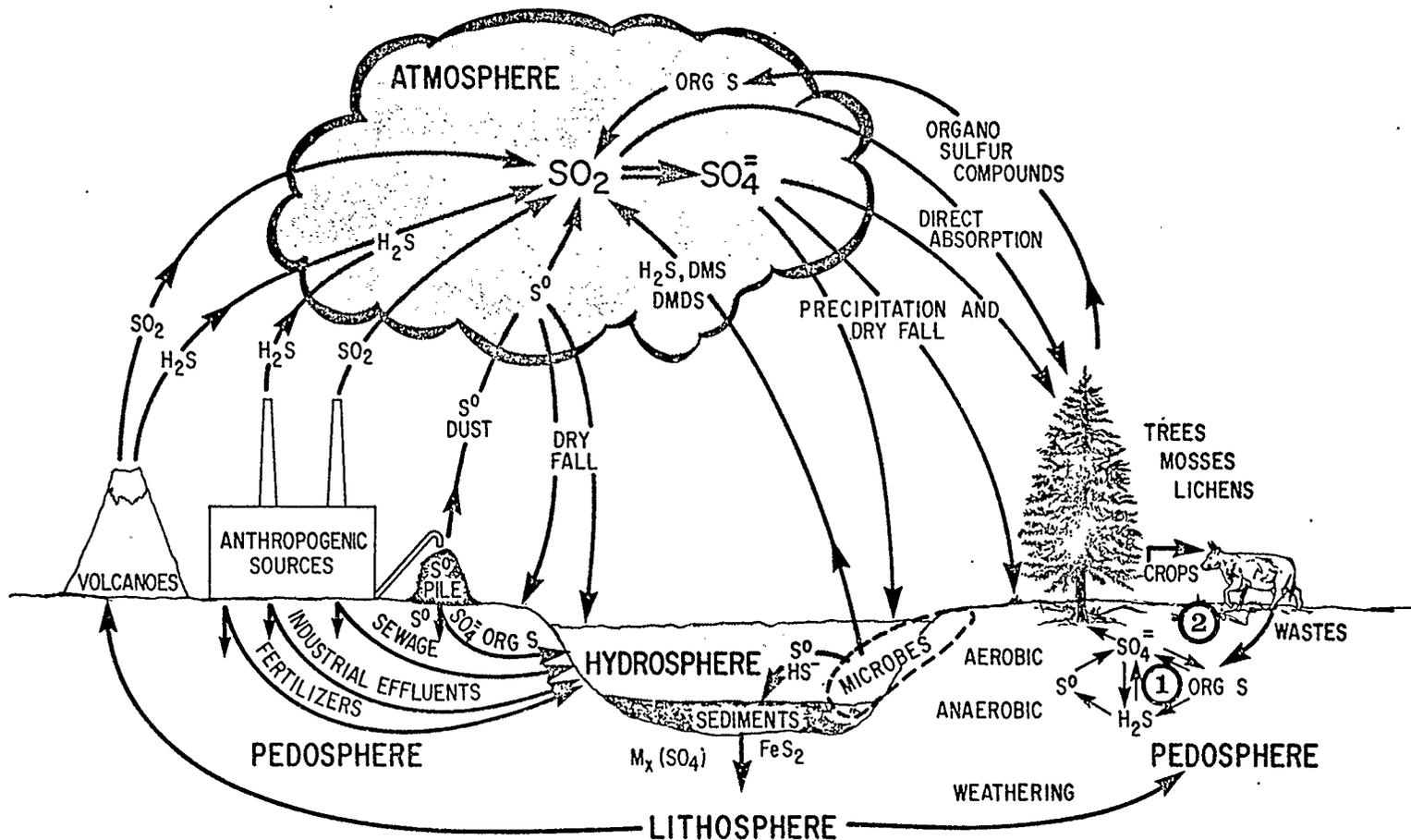
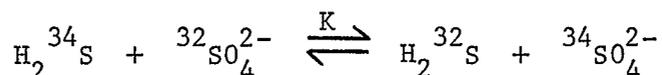


FIG. 6 Global cycling of sulfur. The encircled "1" is the microbial cycle while the encircled "2" represents a food cycle with higher animals. Abbreviations: DMS (dimethyl sulphide), DMDS (dimethyl disulphide). (From KROUSE, 1978).

## 5.2 Mechanism for Fractionation of Sulfur Isotopes

The isotopic fractionation of sulfur isotopes can be considered in terms of isotope exchange reactions and kinetic isotope effects.

Equilibrium exchange: Among sulfur compounds of different valence states, isotope exchange factors have been calculated theoretically (TUDGE and THODE, 1950; SAKAI, 1957, 1968). Of these, the equilibrium constant for the exchange reaction



is interesting for a number of reasons. It involves the highest and lowest valence states (+6 and -2) of sulfur in nature and the predicted K has a large value (1.074 at 25°C). Hence if equilibrium is established, the  $\delta^{34}\text{S}$  of  $\text{H}_2\text{S}$  with respect to sulfate would be -74‰ at 25°C. This equilibrium is difficult to effect in chemical systems. TRUDINGER and CHAMBERS (1973) have recognized the possibility that the equilibrium might be established by enzymes of the sulfate reduction pathway in bacteria provided this pathway is reversible and they report experiments supporting this idea. More recent work has shown a favourable exchange rate at low pH values in chemical exchange reactions (IGUMNOV, 1976; ROBINSON, 1978).

Small differences occur in the  $\delta^{34}\text{S}$  values of sulfide minerals co-precipitating from aqueous solutions or crystallizing from sulfide melts. The existence of these differences was first pointed out by SAKAI (1957). Subsequent work by other investigators indicate

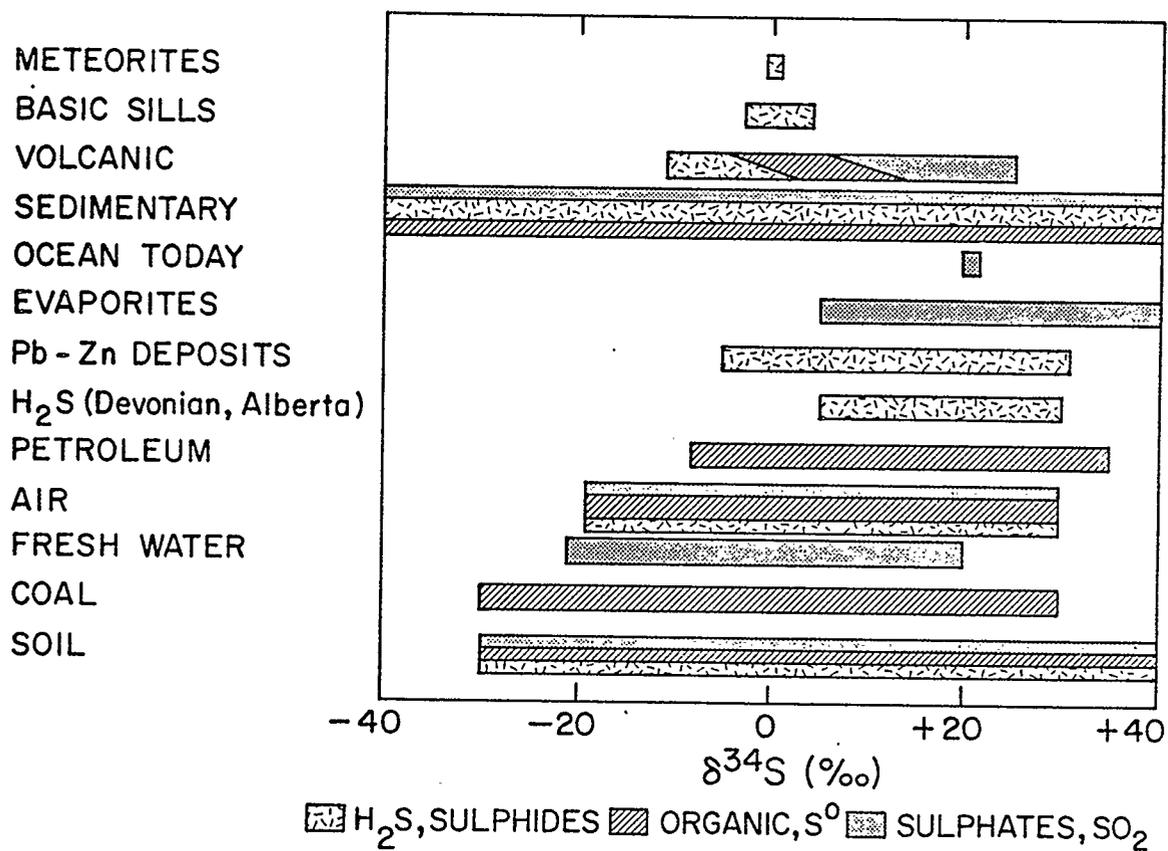


FIG. 7  $\delta^{34}\text{S}$  variations in some naturally occurring sulfur compounds ( $\delta$ -variations in ‰ relative to Canyon Diablo troilite).

that in many types of mineral deposits, a regular trend of isotopic fractionation is observed among co-existent sulfide minerals. The enrichment of the heavy isotope ( $^{34}\text{S}$ ) is usually pyrite > sphalerite  $\sim$  pyrrhotite > chalcopyrite > galena (GROOTENBOER and SCHWARCZ, 1969; KAJIWARA et al, 1969; KAJIWARA and KROUSE, 1971). Analytical data from the workers for co-existing suites of these minerals generally indicate that isotopic equilibrium may be closely approached by these minerals in nature. Consequently, the  $\delta^{34}\text{S}$  values of cogenetic sulfide minerals may be used to determine the temperature of equilibration.  $\Delta\delta^{34}\text{S} = \delta^{34}\text{S}_A - \delta^{34}\text{S}_B$  for minerals A and B is usually related to the equilibration temperature as  $\Delta\delta^{34}\text{S} = A \times 10^6/T^2$  where A is a constant.

Because the vibrational energy of the sulfur atom in  $\text{SO}_4^{2-}$  is modified only slightly upon crystallization, the isotopic composition of sulfate minerals differ only slightly from the associated aqueous sulfate ions. At room temperatures, a small enrichment of  $^{34}\text{S}$  is expected in the mineral phase in the following order: anglesite < barite < celestite < gypsum < anhydrite. Even in the case of anhydrite the separation factor would not exceed 3<sup>o</sup>/oo at room temperatures (SAKAI, 1968).

Kinetic isotope effects: HARRISON and THODE (1957) found that the isotope fractionation during inorganic chemical sulfate reduction at temperatures below 100<sup>o</sup>C could be approximated by a one-step first order process with  $k_{32}/k_{34} = 1.022$ . They associated this value with

the initial S-O bond cleavage. KAPLAN and RITTENBERG (1964) obtained  $^{32}\text{S}$  enrichments in  $\text{H}_2\text{S}$  of up to 46 $^{\circ}$ /oo relative to sulfate during bacterial reduction. Moreover sulfide minerals in recently deposited sediment may be enriched in  $^{32}\text{S}$  by about 50 $^{\circ}$ /oo. Hence from the environmental viewpoint, the reduction of sulfate at low temperatures appears to be exclusively effected by micro-organisms. The isotopic fractionation in these conversions is more complex than in the chemical reduction.

There are certain species of bacteria, of which the best known is Desulfovibrio desulfuricans, living under anaerobic conditions, which preferentially reduce  $^{32}\text{SO}_4^{2-}$  to  $\text{H}_2^{32}\text{S}$  yielding very large isotope fractionations with  $\Delta\delta^{34}\text{S} = (\delta^{34}\text{S})_{\text{SO}_4^{2-}} - (\delta^{34}\text{S})_{\text{H}_2\text{S}}$  often greater than 50 $^{\circ}$ /oo in nature. The process is more complex than the chemical reduction and in simplified terms has been described as involving:

1. intake of  $\text{SO}_4^{2-}$
2. organic complexing of sulfate
3. reduction of sulfate to sulfite ( $\text{SO}_3^{2-}$ )
4. reduction of organically bound sulfite
5. production of hydrogen sulfide

However, in recent years, the reduction has been found to be more complex and involves  $\text{S}_2\text{O}_3^{2-}$  and  $\text{S}_3\text{O}_6^{2-}$  formation (KOBAYASHI et.al. 1975). REES (1973) has explained fractionation factors  $\sim 1.05$  produced by D. desulfuricans on the basis of multiple steps in which the first process of sulfate activation follows zero order kinetics and

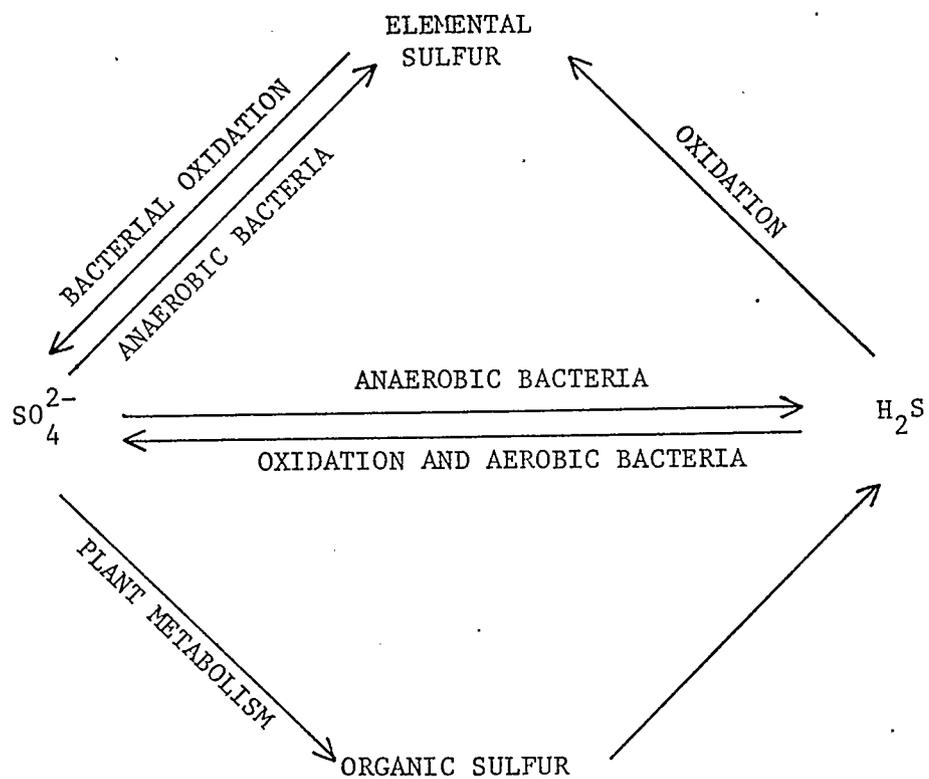


FIG. 8 Microbial sulfur cycle in nature.

subsequent steps follow first order kinetics. Hence two S-O rupturing steps may each result in enrichment of  $\sim 25^{\circ}/\text{oo}$  in  $^{32}\text{S}$  in the product.

Other organisms which have been found capable of isotope fractionation during  $\text{SO}_4^{2-}$  and/or  $\text{SO}_3^{2-}$  reduction include Clostridium pasteurianum, Desulfotomaculum, Salmonella sp., and Saccharomyces cerevisiae (TRUDINGER, 1969; LAISHLEY and KROUSE, 1978; McCREADY et al 1974; KROUSE et al 1967). It is now generally recognized that during  $\text{SO}_4^{2-}$  metabolism by micro-organisms, two pathways are followed. An assimilatory pathway for nutritional needs in which ATP-activated sulfate is converted to APS and then to PAPS followed by reduction to sulfite and finally to sulfide involving  $\text{NADPH}_2$  (reduced nicotinamide adenine dinucleotide phosphate). In the dissimilatory pathway for respiratory needs, activation to APS is followed by reduction to sulfite and then to sulfide by cytochrome  $\text{C}_3$  and possibly ferredoxin.

There are obvious difficulties associated with extending the results of laboratory experiments to the explanation of isotope fractionation effects in the microbial sulfur cycle (Figs. 6 and 8). Reduction of sulfate may occur in open systems where incoming sulfate replaces that reduced and the sulfide produced has a constant  $\delta^{34}\text{S}$ -value relative to the sulfate. In a closed system a high extent of reaction can occur because the amount of sulfate is limited. Hence

the  $\delta^{34}\text{S}$ -values of the sulfide produced and of the residual sulfate will depend on the extent of reaction (Fig. 2).

Generally, during biological oxidation, the  $\text{SO}_4^{2-}$  product is depleted in  $^{34}\text{S}$  relative to starting  $\text{HS}^-$  indicating that the  $\text{H}^{32}\text{S}^-$  is oxidized preferentially. This is opposite to the equilibrium exchange conditions noted previously where the heavier  $^{34}\text{S}$  is favoured in the sulfate.

### 5.3 Variations in Nature

Meteorites and the lithosphere: Troilite is the most abundant sulfur compound of iron meteorites and shows  $\delta^{34}\text{S}$ -values from 0 to 0.6‰ relative to Canyon Diablo troilite (KAPLAN and HULSTON, 1966). Orgueil, a carbonaceous chondrite contains the isotopically lightest sulfate ( $\delta^{34}\text{S} = -1.3$ ‰ while troilite sulfur has  $\delta^{34}\text{S} = 2.6$ ‰). MONSTER et al (1965) suggested that kinetic isotope effects in a sulfur water system may be responsible for the genesis of sulfur compounds in Orgueil. However, LEWIS and KROUSE (1969) found that the oxidation of troilite by traces of oxygen or  $\text{HOOH}$  would also yield the same distribution of sulfur isotopes.

The  $\delta^{34}\text{S}$ -values of the olivine alkali basalts cluster around a mean value of + 1.3‰. Due to a higher water content of the alkali rich basalts, an oxidation of sulfur to sulfate may take place, connected with a slight enrichment of  $^{34}\text{S}$ , if the system is open for light sulfide. Granites and associated sulphides show a wider variation than the basaltic rocks. Most of the granites have small positive  $\delta^{34}\text{S}$  values,

while some have abnormally low or high  $^{34}\text{S}/^{32}\text{S}$  ratios. The idea of using sulfur isotope studies to distinguish between primary differentiated granites and secondary partially melted metamorphic rocks is probably not tenable. (Fig. 7).

Sedimentary rocks vary over a wide range of  $\delta^{34}\text{S}$  values (Fig. 7). This is because sedimentary sulfides are usually the product of bacterial sulfate reduction and dependent upon the conditions (carbon source, temperature, organism, concentration) the  $\Delta\delta^{34}\text{S}$  value for sulfides may range from 0 to  $-60^{\circ}/\text{oo}$  with respect to the source sulfate (SASAKI and KROUSE, 1969; JENSEN and WHITTLES, 1969).

Isotopic evolution of marine sulfate: Present ocean water with its large sulfate reservoir of  $4 \times 10^{19}$  moles has a fairly constant isotopic sulfur composition of nearly  $+21^{\circ}/\text{oo}$  (REES et al 1978). It is reasonable to believe that evaporite sulfates (gypsum, anhydrite) reflect the  $\delta^{34}\text{S}$  values of the ancient oceans since a small isotopic fractionation ( $\sim 1-2^{\circ}/\text{oo}$ ) occurs during sulfate precipitation (CORTECCI and LONGINELLI, 1968). Evaporite data show that the isotopic composition of the ocean has not remained constant during the geologic past. High  $\delta^{34}\text{S}$  values in the early Paleozoic and early Mesozoic with a minimum of  $11^{\circ}/\text{oo}$  in the Permian are the characteristic features. (Fig. 9). The mechanisms controlling the decrease in the Permian time and the abrupt increase at the Paleozoic-Mesozoic boundary are not clearly understood but have been interpreted in terms of competition between  $\text{CaSO}_4$  precipitation and bacterial  $\text{SO}_4^{2-}$  reductions (REES, 1970).

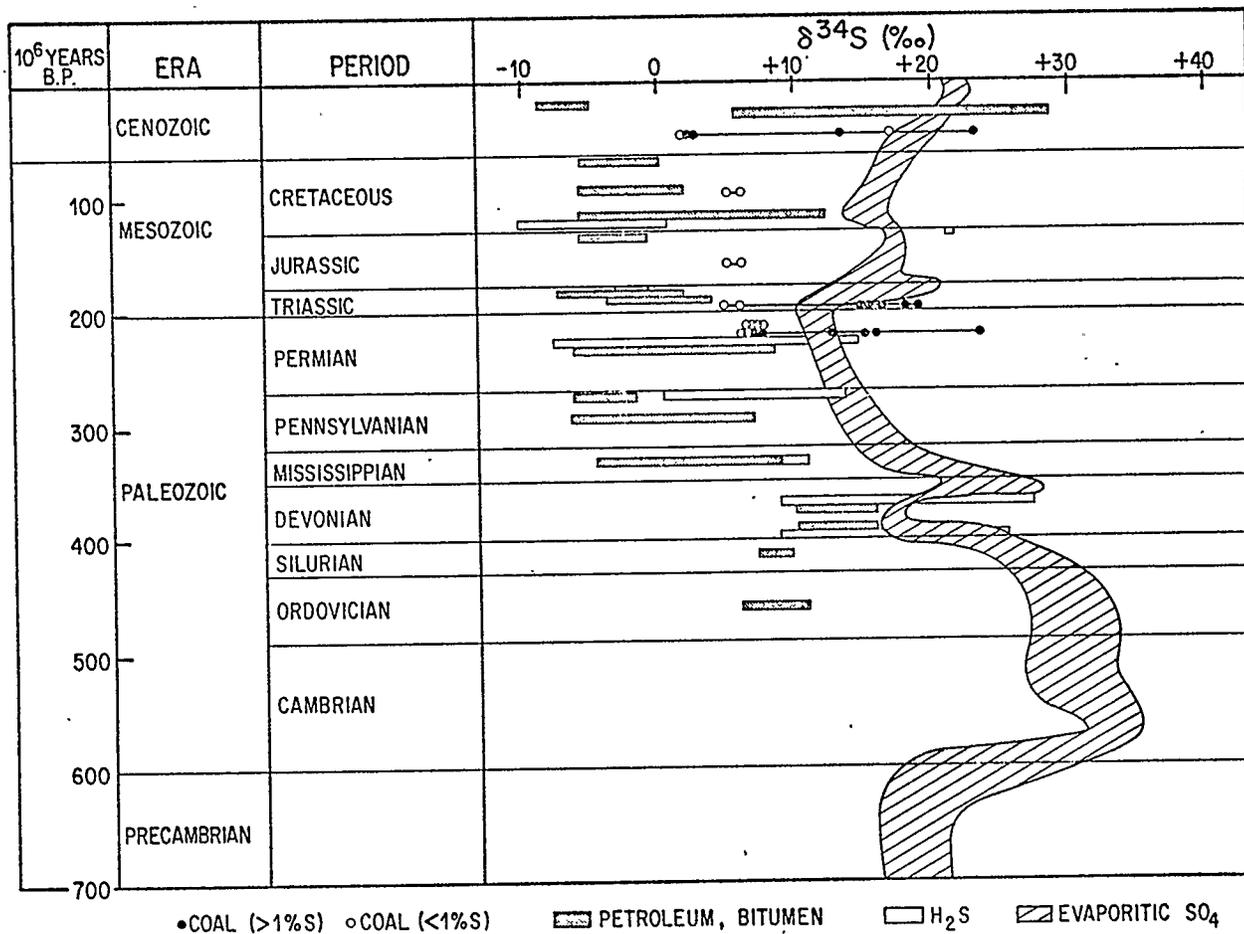


FIG. 9 Sulfur isotope abundances in fossil fuels and evaporites of different geological ages. (After KPOUSE, 1977b).

Fresh Waters: The upper boundary for fresh water is 1% salinity.

Fresh waters and non-marine evaporites differ widely in their absolute sulfur content and their  $\delta^{34}\text{S}$  values depending on the wide variety of sulfur sources of the drainage area feeding the rivers or lakes. For example, the overall  $\delta^{34}\text{S}$  variation in the Mackenzie River system of Canada is 50<sup>0</sup>/oo (HITCHON and KROUSE, 1972).

Biosphere: Sulfur of aquatic plants from a given water is slightly depleted in  $\delta^{34}\text{S}$  compared to the dissolved sulfate. The same has been observed for marine phytoplanktons and zooplanktons (MEKHTIEVA, 1971). In the case of land vegetation, it has been shown using sulfur isotopes that sulfur may be incorporated from the air as well as through the root system (KROUSE, 1977a).

Petroleum: It seems reasonable to assume that ocean water sulfate is the principal source of sulfur in petroleum. Since sea water sulfate is rapidly reduced by bacteria in the shallow muds in contact with the sea, it is very likely that it would be this reduced sulfur that would finally be incorporated in the petroleum. THODE and MONSTER (1965) found petroleum and associated  $\text{H}_2\text{S}$  to be on the average 15<sup>0</sup>/oo depleted in  $^{34}\text{S}$  as compared to related evaporites. KROUSE (1977b) reviewed recent studies and found that while shallower  $\text{H}_2\text{S}$  may be depleted in  $\delta^{34}\text{S}$  with respect to contemporaneous sea water sulfate, deeper  $\text{H}_2\text{S}$  and oil differ little isotopically from associated evaporite suggesting a thermochemical conversion with very little isotopic selectivity.

## CHAPTER 6

## OXYGEN AND SULFUR ISOTOPE GEOCHEMISTRY OF SULFATES

6.1 Variation in  $\delta^{18}\text{O}$  and  $\delta^{34}\text{S}$  in the Sulfate Ion

Consistent with the findings for sulphur isotopes, present day sea water sulfate also has a uniform oxygen isotope composition. ( $\delta^{18}\text{O}$  (SMOW) + 9.5 to + 10<sup>0</sup>/oo; RAFTER and MIZUTANI, 1967; LONGINELLI and CRAIG, 1967). This suggests that waters of the world's ocean system are well mixed. LONGINELLI and CRAIG (1967) reported that  $\text{SO}_4^{2-}$  in saline lakes and brines have  $\delta^{18}\text{O}$  values ranging from + 7 to 23<sup>0</sup>/oo SMOW. The value of the highest enrichment observed is about the same as that of atmospheric oxygen. One may conjecture that sulfate ions derived from oxidation of igneous sulfides have initially an isotopic composition near that of atmospheric oxygen, and that this composition is modified by exchange and bacterial reduction in the direction of equilibrium with water. (sec. 6.2 and 6.3).

RAFTER and MIZUTANI (1967) have measured the  $\delta^{18}\text{O}$  and  $\delta^{34}\text{S}$  of Lake Vanda, Antarctica sulphate and also the  $\delta^{18}\text{O}$  of the water. They reported that a plot of  $\delta^{18}\text{O}$  and  $\delta^{34}\text{S}$  shows that the slope is 1/4 or the  $^{34}\text{S}/^{32}\text{S}$  ratio in the sulphate is increasing four times faster than the  $^{18}\text{O}/^{16}\text{O}$  ratio. Moreover a plot of  $\delta^{18}\text{O}$  (water) against  $\delta^{18}\text{O}$  in the sulfates gives a line of slope 1/2; that is the  $^{18}\text{O}/^{16}\text{O}$  ratio in sulfate is increasing at twice the rate as in the water.

In the same paper the authors have examined barites and

observed that as  $\delta^{34}\text{S}$  values increase,  $\delta^{18}\text{O}$  values have a general tendency also to increase.

Another interesting facet of the oxygen and sulfur isotope geochemistry is the variation in the  $\delta^{18}\text{O}$  of the sulfates of ancient waters. The sulfur isotope ratios of ocean sulfates have been shown to vary with geologic age (Fig. 9). The time variation of oxygen isotopic ratios of oceanic sulfate have been reported by SAKAI (1972). For  $\delta^{34}\text{S}$  values of ancient evaporites, it is generally assumed that the minimum values would be closest to the contemporaneous oceanic sulfate. This is because the most significant sulfur isotopic fractionation in nature is involved in the bacterial reduction of sulfate and this tends to make the remaining sulfate heavy.

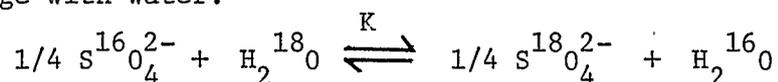
It is generally agreed that the  $\delta^{34}\text{S}$  values of the Permian ocean sulfate were uniform and the lowest of all other ages at  $\sim 10^0/00$ . SAKAI reports that the  $\delta^{18}\text{O}$  of Permian are also lowest at around  $10^0/00$ . The Tertiary sulfates, on the other hand, seem to be similar to the present sea water sulfate in both  $\delta^{18}\text{O}$  and  $\delta^{34}\text{S}$ .

SAKAI reports two Precambrian evaporites from Balmat, New York, which have much higher  $\delta^{18}\text{O}$  values than other evaporites. Except for those two, all other evaporites have  $\delta^{18}\text{O}$  values much lower than the expected equilibrium value with the contemporary ocean.

## 6.2 SO<sub>4</sub><sup>2-</sup> - H<sub>2</sub>O Exchange

The factors controlling the oxygen isotope composition of sulfate are still debatable (HOLSER et al, 1979). The oxygen is not permanently bound to the sulfate but also passes through other geochemical cycles such as the carbon cycle and the hydrological cycle. The implications of these interactions are that the oxygen isotope composition of sulfate may be affected by agents external to the sulfur cycle and that the oxygen composition can have information only back to the time of its incorporation into the sulfate ion.

The principal aspect of sulfate oxygen systematics is isotopic exchange with water.



The isotopic separation factor is

$$\alpha = \left( \frac{^{18}\text{O}}{^{16}\text{O}} \right)_{\text{SO}_4^{2-}} / \left( \frac{^{18}\text{O}}{^{16}\text{O}} \right)_{\text{H}_2\text{O}}$$

LLOYD (1967) and MIZUTANI and RAFTER (1969a) have shown that the exchange rate between water and dissolved sulfate ion is temperature and pH dependent. MIZUTANI and RAFTER (1969a) using an acid medium, .05N sulfuric acid, have determined  $\delta^{18}\text{O}(\text{HSO}_4^-) - \delta^{18}\text{O}(\text{H}_2\text{O}) \approx 1000 \ln \alpha$  at various temperatures near geothermal water temperatures. They have plotted their results which are close to LLOYD'S but deviate from UREY'S theoretical curve (1947).

If data is taken from LLOYD (1967), interpolation of a line for pH of 8.2 and extrapolation to a mean ocean temperature of 4°C gives the half time of exchange between ocean water and sulfate to be 50,000 years. To reach near isotopic equilibrium (5 half times or 97% exchange) would take 250,000 years. The effective mean lifetime

of a sulfate ion,  $\tau$ , is crudely given by the ratio of the amount of sulfate in the sea,  $4 \times 10^{15}$  tons to the annual input, some  $2 \times 10^8$  tons as calculated from river data. Thus  $\tau$  is approximately 20 million years or the residence time of  $\text{SO}_4^{2-}$  in the sea is 80 half times of exchange. Hence one would expect oceanic sulfate to be in isotopic equilibrium with ocean water. Surprisingly, this is not the case. To determine whether or not equilibrium exists in the ocean, it is necessary to evaluate the equilibrium isotope fractionation factor between dissolved sulfate and water. LLOYD (1967) has found that for oceanic sulfate to be in equilibrium with ocean water, the  $\delta^{18}\text{O}$  of the sulfate should be 38 per mil. It does not seem reasonable that such a large discrepancy ( $\delta^{18}\text{O}$  of present ocean  $\text{SO}_4^{2-}$  is  $\sim 9.7^\circ/\text{oo}$ ) from the predicted isotopic equilibrium value could be owing to uncertainty in the dissolved sulfate-water fractionation curve. Hence we conclude that oceanic sulfate and ocean water are not in oxygen isotope equilibrium. Further, if oxygen isotope exchange between  $\text{SO}_4^{2-}$  and  $\text{H}_2\text{O}$  is so slow, oxygen isotope data from  $\text{SO}_4^{2-}$  may be used to study mixing of terrestrial waters.

### 6.3 Bacterial Reduction and Oxidation

LLOYD (1967) showed that bacteria preferentially metabolize  $^{16}\text{O}$  during both sulfide oxidation and  $\text{SO}_4^{2-}$  reduction and in the oxidation of sulfide, 68% of the oxygen in the sulfate formed comes from the water and 32% comes from the air. In case of oxidation of sulfide he found  $1000(\alpha-1) = -8.7$  per mil when atmospheric oxygen was incorporated but no fractionation when water oxygen was incorporated. He found  $1000(\alpha-1) = -4.6$  per mil for  $\text{SO}_4^{2-}$  reduction.

In the bacterial reduction of  $\text{SO}_4^{2-}$ , MIZUTANI and RAFTER (1969b) report that the ratio of the  $^{18}\text{O}$  enrichment to  $^{34}\text{S}$  enrichment in the sulfates was approximately 1:4. Moreover the oxygen-sulfur isotopic ratio was found to be independent of the temperature of the experiment.

Later, MIZUTANI and RAFTER (1973) found that departures from the 1:4 ratio occurred in bacterial  $\text{SO}_4^{2-}$  reduction because the  $\delta^{18}\text{O}$  of the sulfate remaining depends on the  $\delta^{18}\text{O}$  of the water in which the sulfate is reduced. Since it is known that the rate of exchange between  $\text{SO}_4^{2-}$  and  $\text{H}_2\text{O}$  is extremely slow under the conditions of the experiment, then exchange of oxygen isotopes must have occurred between  $\text{H}_2\text{O}$  and intermediates in the reduction. For example, LLOYD (1967) has shown that  $\text{SO}_3^{2-}$  undergoes isotopic exchange with water more rapidly than  $\text{SO}_4^{2-}$  by a factor of as much as  $10^5$ .

#### 6.4 Summary and Conclusions

Evaporite data on  $\delta^{18}\text{O}$  in ancient evaporites (see sec. 6.1) and the conclusions reached in sec. 6.2 suggest that the isotopic exchange of oxygen between sulfate and water makes only a minor contribution to the  $\delta^{18}\text{O}$  values of ocean sulfate.

LLOYD (1967) proposed that the attainment of oxygen isotope equilibrium between sulfate and water is prevented by a rapid oxidation-reduction cycle of sulfur. He demonstrated experimentally that the  $\delta^{18}\text{O}$  value of the present ocean sulfate could be explained by a steady state balance between removal of sulfate by bacteria and its supply by inorganic oxidation of sulfide in marine environments. It must be pointed out that the bacterial life in the oceans is mostly concentrated in the bottom sediments and sulfate isotopic uniformity is found in all the water column. LLOYD'S steady state model implies a very fast, debatable, turnover of oceanic sulfate. LLOYD'S model requires that at least  $1/10^4$  of sulfate in the present ocean should undergo the oxidation-reduction cycle annually. Direct evidence to support such a rapid cycle is rather lacking. Furthermore, it requires widespread bacterial sulphate reduction in the bottom sediments of the oceans. The  $\text{H}_2\text{S}$  produced may spread into the overlying oxygenated water or may be partially fixed in the sediment as pyrite. The half-life of  $\text{H}_2\text{S}$  in sea water, with an  $\text{O}_2$  content of 3.8 ml/l has been estimated to be about 20 minutes at  $25^\circ\text{C}$  (OSTLUND and ALEXANDER, 1963).

LLOYD (1967) found a fractionation factor between  $\text{SO}_4^{2-}$  and water so high ( $\Delta\delta^{18}\text{O} = 38^\circ/\text{oo}$ ) at ocean water pH and  $4^\circ\text{C}$  (mean ocean temperature) that equilibrium was precluded. Moreover he estimated that attainment of 97% equilibrium would require 250,000 years. If correct, this exchange rate is slow enough to allow mixing of the oceans, and subsequent precipitation of sulfate from a batch of such equilibrated ocean water in an evaporite basin. But recent data (HOLSER et al, 1978) from interstitial waters in deep sea cores show no appreciable change in  $\delta^{18}\text{O}$  in  $\text{SO}_4^{2-}$  of interstitial waters going back to the late Cretaceous (70 million years), suggesting no appreciable exchange between  $\text{SO}_4^{2-}$  and water for times much longer than the residence time of sulfate in the sea (20 million years). This inexplicable delay in isotopic equilibration leads to the result that  $\delta^{18}\text{O}$  ( $\text{SO}_4^{2-}$ ) in the sea follows the dynamic balance of  $\delta^{18}\text{O}$  ( $\text{SO}_4^{2-}$ ) for inputs and outputs to the sea, rather than equilibrating with  $\delta^{18}\text{O}$  ( $\text{H}_2\text{O}$ ) of sea water.

HOLLAND (1973) contends that the rate of removal of sulfur from the oceans as a constituent of sulfides is a rather complicated function of a number of variables, which include the organic carbon content of marine sediments, the rate of sedimentation, the availability of iron and the sulfate content of sea water. Using a mathematical model, he evaluated the influence of the sulfur cycle on atmospheric oxygen. The results show a net gain until the upper carboniferous,

a net loss during the Upper Carboniferous and the Permian and a steady gain during the Cenozoic.

We conclude that  $\text{SO}_4^{2-}$  is apparently a very stable unit and allows little change in  $\delta^{18}\text{O}$  or  $\delta^{34}\text{S}$  once it is formed. Consequently,  $\delta^{18}\text{O}$  in sulfate minerals of evaporites is essentially a sample of  $\text{SO}_4^{2-}$  of contemporary water, which in turn is controlled by a dynamic balance of sedimentation outputs of sulfur as sulfide mud and sulfate evaporite and the erosion inputs from the weathering of sulfides and sulfates. It is still not clear why (1)  $\text{SO}_4^{2-}$  has not exchanged oxygen isotopes with  $\text{H}_2\text{O}$  over times much longer than those predicted by LLOYD'S calculations, (2) whether the best slope for  $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}$  in the bacterial sulfate reduction is 4 or substantially less and (3) whether field studies of pyrite oxidation including isotope measurement will ratify the 1:2 ratio of oxygen from the air and water proposed by LLOYD (1967).

CHAPTER 7  
EXPERIMENTAL PROCEDURES

7.1 Extraction of sulphates in water

All sulfates, whether occurring as  $\text{SO}_4^{2-}$  in water (meteoric, ocean, hydrothermal etc.) or as minerals must be extracted in the form of  $\text{BaSO}_4$  since this has been found to be the most suitable procedure for oxygen and sulfur isotope analyses.  $\text{BaSO}_4$  is then reduced by graphite to yield  $\text{CO}_2$  for oxygen isotope analyses and  $\text{BaS}$  which is further processed to  $\text{SO}_2$  for sulfur isotope analyses.

Soluble sulfates in a water sample may be precipitated as  $\text{BaSO}_4$  by employing one of the following two procedures.

Needless to say, all reagents must contain minimum amounts of sulfur.

- (A) (i) The water sample is acidified by adding a few c.c. of concentrated  $\text{HCl}$  and heated just below boiling point. Low pH prevents  $\text{BaCO}_3$  precipitation.
- (ii) 10%  $\text{BaCl}_2$  (typically 10 ml) solution is added while stirring to precipitate  $\text{BaSO}_4$ . The solution is allowed to stand overnight on a water bath.
- (iii) Completeness of precipitation is tested by adding  $\text{BaCl}_2$  solution to an aliquot of the clear supernatant and letting it stand for an hour.

- (iv) If precipitation is complete, the  $\text{BaSO}_4$  is filtered through a 541 filter paper and dried. Alternately the  $\text{BaSO}_4$  may be filtered through a millipore filter or centrifuged.

(B) An anion exchange resin column may be used. Although more time consuming, it permits extractions at lower  $\text{SO}_4^{2-}$  concentrations and produces purer  $\text{BaSO}_4$ . Anion exchange resin, Biorad AG-1-X8, 100-200 mesh is used in the chloride form.

- (i) A wad of pyrex glass wool is placed in a 10 mm I.D. glass column and 7 ml resin placed on top. The resin is best loaded by allowing it to settle freely in distilled water in the column.
- (ii) If resin is not in the chloride form, it is washed with 200 ml, 1M NaCl added at the rate of 1-2 ml/minute.
- (iii) When in chloride form, the resin is washed with 100 ml distilled water at a flow rate of 2 ml/minute.
- (iv) The water sample containing sulfate anions is passed through the resin at the rate of 1 ml/minute.
- (v) The adsorbed  $\text{SO}_4^{2-}$  is extracted by eluting with 150 ml, 1M NaCl solution at a flow rate of 1 ml/minute. This procedure also regenerates the resin for the next sample.
- (vi) 1 ml concentrated HCl is added to the NaCl eluate to acidify the solution.  $\text{BaSO}_4$  is precipitated as in (A).

Hydrous zirconium oxide  $[\text{ZrO}(\text{OH})]$  has also been used in ion exchange (CORTECCI and LONGINELLI, 1968).

## 7.2 Extraction of sulphates in rocks

Sulfates in rocks may be water soluble e.g. alabaster, gypsum, celestite, anhydrite, selenite, Glauber's salt and Epsom salt, or be insoluble principally as barite. If soluble then the rock may be taken through the processes of comminution and dissolution and thereafter,  $\text{BaSO}_4$  precipitated with an anion exchange column.

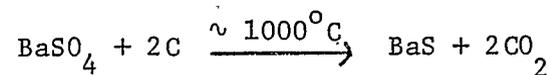
Barites may not be purified by  $\text{Na}_2\text{CO}_3$  fusion because of possible exchange of oxygen isotopes with the sodium carbonate (RAFTER and MIZUTANI, 1967). HF-HCl digestion breaks down silicates (producing gaseous  $\text{SiF}_4$ ), carbonates, and dissolves many other minerals. The following procedure is convenient for cleaning natural barites prior to graphite reduction.

- (i) The rock is ground to a very fine powder so that the acids will react thoroughly.
- (ii) 20 ml concentrated HF is added to the powder in a teflon beaker and placed on a steam bath until dry. 10 ml of 3  $\text{HNO}_3$ : 1 HCl and 1 ml  $\text{Br}_2$  are added and the mixture placed on a steam bath until dry.
- (iii) Water is added to the precipitate, stirred, and allowed to settle. The supernatant is then decanted. This is done several times until the supernatant is free from  $\text{Cl}^-$  as indicated by the addition of a drop of  $\text{AgNO}_3$  solution to the decanted solution.

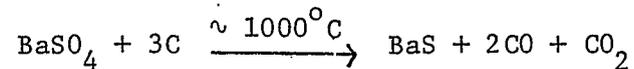
### 7.3 Graphite reduction of BaSO<sub>4</sub>

It has been found by the pioneers in the field that other forms of sulfate, like calcium sulfate, will yield undesirable gases, for instance sulfur dioxide, when heated with graphite. Barium sulfate, on the other hand, has been found very suitable for both sulfur and oxygen isotope analyses.

When heated at approximately 1000°C with very pure graphite, the following reaction takes place.



The above ideal reaction is never realized in the laboratory, and a mixture of carbon monoxide and carbon dioxide is produced.



The mixture of carbon monoxide and carbon dioxide produced is of no consequence if only sulfur isotopes are under investigation.

For oxygen isotope analyses, it is desirable to minimize CO production initially and then convert any CO produced to CO<sub>2</sub>.

RAFTER (1967) described a method for the conversion of barium sulfate to carbon dioxide for oxygen isotope analysis. 50 mg of BaSO<sub>4</sub> and about the same weight of spectrographically pure graphite were thoroughly mixed and transferred to a platinum boat. The platinum boat was heated in a quartz tube by means of a furnace which attained a temperature of 1100°C in 5 minutes. The platinum boat

is heated at  $1100^{\circ}\text{C}$  for 10 minutes. The carbon monoxide produced was converted to carbon dioxide by a high voltage glow discharge between copper electrodes. The reproducibility was reported initially as  $\pm 0.3^{\circ}/\text{oo}$  which was consequently improved to  $\pm 0.18^{\circ}/\text{oo}$  by improving the analytical methods for cleaning of barites.

SAKAI and KROUSE (1971) reported that such externally heated quartz tubes could lead to memory effects whereby the processing of one barium sulfate sample affected the following sample. Devitrified quartz tubes after prolonged usage displayed larger memory phenomena. The cause of memory effects was traced to the exchange of oxygen atoms between the carbon monoxide and the hot quartz walls. It was suggested that memory effects could be reduced by operating the electrical discharge unit throughout the reaction for continuous removal of carbon monoxide. They also designed an apparatus for internal heating by making the platinum boat the location of highest resistance in an electrical circuit.

MIZUTANI (1971) conducted similar experiments to those of SAKAI and KROUSE (1971) and reported a memory effect of about  $0.03^{\circ}/\text{oo}$  per  $^{\circ}/\text{oo}$  difference from the previous sample. His improved design with the platinum boat as the heating element is very similar to that of SAKAI and KROUSE (1971). MIZUTANI reports that 99% of the reaction at  $1000^{\circ}\text{C}$  is complete in one minute and an isotopic reproducibility of 0.1 to  $0.25^{\circ}/\text{oo}$  was achieved.

OLSON (1973) employed four DFG 35 mm. projector bulbs with parabolic reflectors to focus the rays of light onto a graphite crucible suspended within a pyrex reaction chamber. The graphite crucible, with a pin hole in the lid contained the reactants and sat on a platinum platform. Reproducibility was observed to deteriorate after a few runs with a crucible so that replacements were frequent. This method was tried in our laboratory but difficulties were encountered with contaminants in the graphite. If graphite crucibles are replaced frequently, the procedure could be expensive owing to the high cost of very high purity graphite rods. A second problem encountered was that high temperatures were not attained easily unless the lamps were pushed to higher voltages in which case lamp replacement was frequent and expensive. Finally, one could not monitor the temperature readily.

The apparatus for the present work (Plate 1) comprised a Lindberg furnace which attained a temperature of  $1000^{\circ}\text{C}$  in 40 minutes at 120V. This furnace could be slid on and off of a quartz tube 45 cm long, 24mm O.D., 12 mm I.D., and closed on one end. The thick quartz tube was necessary to sustain temperatures of the order of  $1100^{\circ}\text{C}$  under high vacuum. The length prevented heating of the apiezon grease used on the glass ground joint which connected the combustion tube to the rest of the line.

The adjoining pyrex glass line consisted, essentially, of a helical trap for the  $\text{CO}_2$  and then a conversion chamber for sparking

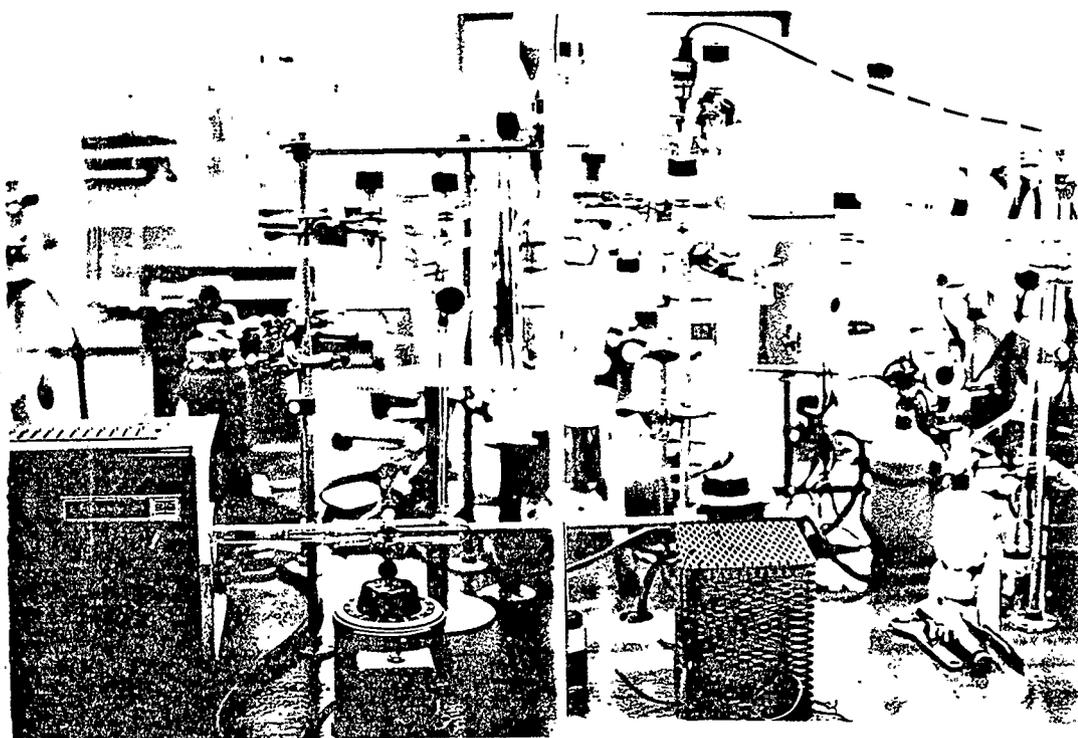


Plate 1. Line for the graphite reduction of sulfate and conversion of  $\text{CO}$  to  $\text{CO}_2$ .

CO to CO<sub>2</sub>. A manifold with attached break-seal tubes protruded as a side-arm to this pyrex line.

The conversion chamber is a 18 cm long pyrex tube connected to the main line by a 34/45 joint. Two parallel platinum foil electrodes 1 cm wide and 5 cm long are suspended 5 mm apart about midway in the tube by means of tungsten wires whose upper ends are vacuum sealed via special graded glass. A 7.5 KV transformer with maximum current output of 75 mA is connected to the tungsten leads. A 100 K $\Omega$  30 watt resistor and a 63 mA fuse are connected in series with the conversion cell across the secondary of the transformer. These components in series were mandatory because the resistance between the platinum plates varies drastically from nearly infinite (High Vac) to near zero (when sparking occurs).

The procedure for graphite reduction of BaSO<sub>4</sub> was as follows; 20 mg of BaSO<sub>4</sub> was intimately mixed with the same weight of high purity graphite in an agate mortar. This mixture was then transferred to a platinum boat 20 mm long and 6 mm in width and depth. The boat was slid inside the quartz tube till it reached the closed end of the tube. The quartz tube was then connected to the main pyrex line. The furnace was then slid so that the platinum boat was in a temperature zone of approximately 500<sup>o</sup>C. By opening the relevant valves, the quartz tube and the adjoining pyrex line were evacuated until the pressure was 5 microns. Thus all the air in the system and water vapor in the reactants was pumped out.

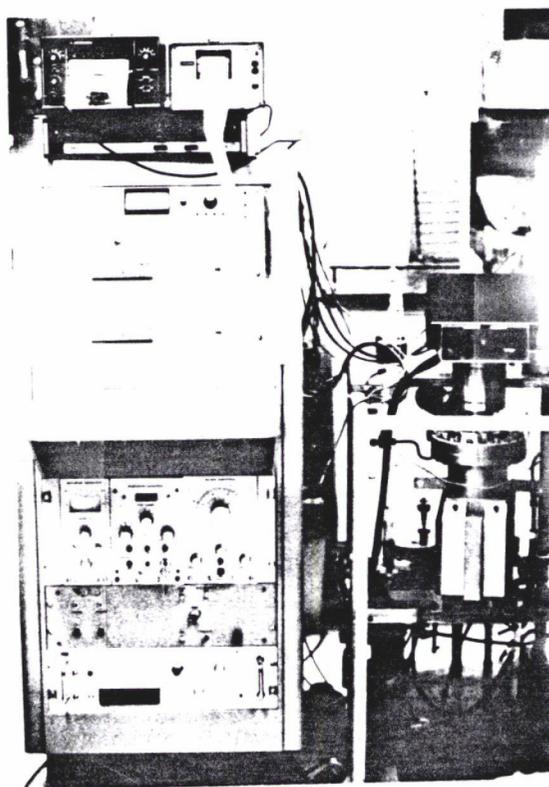


Plate 2. Micromass 602 Mass Spectrometer.

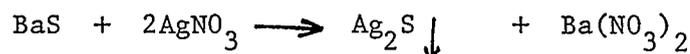
Styrofoam cups containing liquid nitrogen were placed under the helical trap and the conversion chamber. The valves leading to the vacuum line were shut and the furnace slid further so that the platinum boat was now in the hot zone at  $950^{\circ}\text{C}$ . While any  $\text{CO}_2$  produced is readily trapped by the helical trap, the production of CO can be monitored by the vacuum gauge. The helical trap preceding the conversion chamber permits continuous sparking of the CO because no  $\text{CO}_2$  will be sparked between the platinum plates. While the conversion of CO to  $\text{CO}_2$  is in progress, the temperature of the furnace is increased to  $1050^{\circ}\text{C}$  to ensure complete conversion. However, lower temperatures in the initial stages tend to diminish the amount of CO produced.

When the pressure came down to about 100 microns, it indicated that the reaction and conversion of CO to  $\text{CO}_2$  was complete. Any residual gases were air that leaked into the line or outgassed from the walls during the experiment and negligible amounts of CO left unconverted. The furnace was then slid away to cool the quartz tube and the glass line was pumped down to 5 microns. Trapped CO in the  $\text{CO}_2$  was usually minimal as checked by warming up the gases and conducting a second sparking session. The  $\text{CO}_2$  in the helical trap and the conversion chamber was frozen in a break-seal tube for mass spectrometric analysis.

#### 7.4 Conversion from barium sulfide to sulfur dioxide

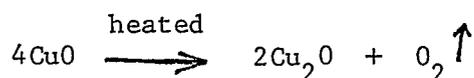
The residue of  $\text{BaSO}_4$  reduction is BaS. It is washed from the reaction boat with hot water.  $\text{AgNO}_3$  solution is then added to

solution and black  $\text{Ag}_2\text{S}$  precipitates instantly.



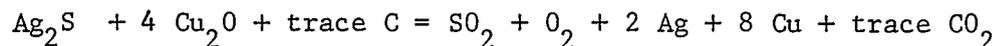
The silver sulfide is filtered and washed several times to ensure purity of  $\text{Ag}_2\text{S}$ .

The  $\text{Ag}_2\text{S}$  is then mixed with a three-fold excess of  $\text{Cu}_2\text{O}$  which is prepared before use by heating  $\text{CuO}$  at  $1000^\circ\text{C}$ .



The mixture of  $\text{Ag}_2\text{S}$  and  $\text{Cu}_2\text{O}$  is placed in a quartz ampoule, about 5 cm long, 6 mm O.D. and closed at one end.

A quartz combustion tube of approximately the same description as in 7.3 is mounted in a tubular furnace. A quartz push rod with an iron slug embedded in it is magnetically pushed to slide the ampoule within the combustion tube to a point near the edge of the furnace where the temperature is about  $400^\circ\text{C}$ . The combustion tube is then closed to the atmosphere and evacuated. When the pressure is reduced to 50 microns, the valve to the vacuum is closed and the ampoule pushed into the centre of the furnace ( $950^\circ\text{C}$ ). At this temperature the reaction is complete in five to seven minutes. A possible reaction scheme, producing a mixture of gases is shown below.



The carbon dioxide forms by the oxidation of minor organic impurities and traces of graphite in the quartz. The products are frozen in a liquid  $\text{N}_2$  trap and the  $\text{O}_2$  is pumped away. Then a liquid  $\text{N}_2$ -*n*-pentane

bath is used to retain the  $\text{SO}_2$  while traces of  $\text{CO}_2$  are pumped away because of its higher vapour pressure. The  $\text{SO}_2$  is admitted into the mass spectrometer for sulfur isotope abundance measurements.

### 7.5 Mass Spectrometry

A sample inlet system, ion source, mass analyzer, and detector are the principal components of a mass spectrometer. For gas samples, ions are formed by electron bombardment. These ions are accelerated by a high potential  $V$  and acquire kinetic energy given by

$$eV = \frac{1}{2} mv^2 \quad (1)$$

where  $e$  is the electron charge,  $v$  is the velocity and  $m$  is the mass of the ion. Hence ions of greater mass travel slower than lighter ions. This difference in velocities enables one to separate the various ions by the use of magnetic fields. When ions travel through a magnetic field at  $90^\circ$  to their velocity vector, they experience a force which is perpendicular to the magnetic flux  $B$  and the velocity.

This force  $F = Bev$  provides a centripetal acceleration of the ion (2)

so that  $mv^2/r = Bev$  or  $v = Ber/m$  (3)

Substitution from (1) gives

$$m/e = B^2 r^2 / 2V \quad (4)$$

For given magnetic flux density, heavier ions traverse a circle of larger diameter than that of lighter ions.

HERZOG (1934) developed the following equation for a magnetic field having an angle of deflection  $\phi$  for directional focussing of an ion beam entering and leaving a magnetic field at right angles to the field boundaries.

$$(a - r \cot \phi) (b - r' \cot \phi) = r^2 \operatorname{cosec}^2 \phi \text{ (Figure 10)}$$

For a  $90^\circ$  sector instrument, the equation simplifies to

$$a = r$$

The resolving power of a mass spectrometer is given as

$$R = M/\Delta M$$

where  $\Delta M$  is the difference in mass between two ions separated at mass  $M$  with less than 10% peak overlap. The theoretical resolution is given as  $R = r/w_s$  where  $r$  is the radius of curvature in the magnetic field and  $w_s$  is the width of the slit defining the ion beam as it leaves the source.

In stable isotope mass spectrometers, ion collectors are usually Faraday cups. Ion currents in the range  $10^{-9}$  to  $10^{-11}$  A are collected. These are neutralized by electrons passing through high resistances ( $10^{10} \Omega$ ) which form the input of the collector amplifiers.

The mass spectrometer used for analyzing the  $\text{CO}_2$  and  $\text{SO}_2$  for this work was based upon components of the Micromass 602 manufactured by Vacuum Generators, Micromass Ltd., Winsford, U.K. (Plate 2). The micromass 602 is  $90^\circ$  sector magnetic deflection instrument of 6 cm radius with a low resolution ( $\sim 150$ ) designed for isotope ratio

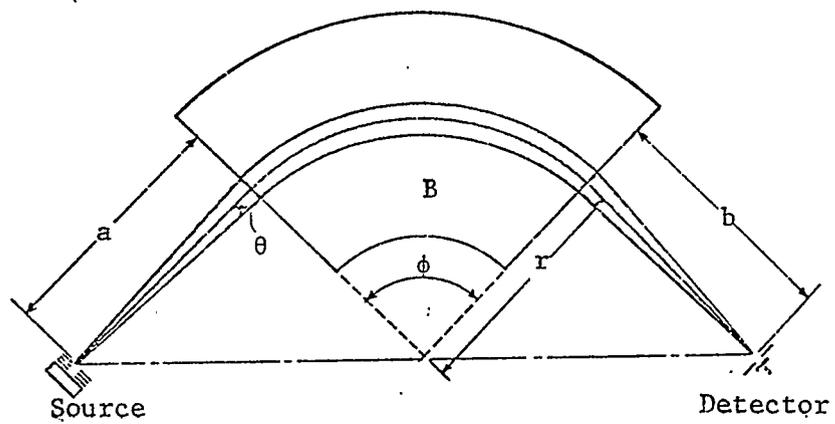


FIG. 10 90-deg. magnetic sector mass analyzer.

measurements with twin Faraday cup collectors. The collector as provided, is primarily for use in the mass range 12 to 80 where the minor isotope is of higher mass than the major isotope, e.g. CO<sub>2</sub> (<sup>13</sup>C, <sup>18</sup>O), Nitrogen (<sup>15</sup>N) and SO<sub>2</sub> (<sup>34</sup>S).

The unknown and standard gases are admitted alternately through balanced capillary leaks to the mass spectrometer source by a solenoid operated valve system which is driven by a solid state timing circuit. Whilst one gas is being analyzed the other gas is bled away to a waste line through a balanced, diffusion pumped 'bleed' system, thus ensuring stable flow conditions.

Electronics for digitizing the output voltages of the collector amplifiers were developed at The University of Calgary. An earlier system utilized a Dana 5900 5½ digit ratiometer and a Anadex printer while the current system consists of a Analogic AN5800, 16 channel multiplexer, 14 bit analogue to digital converter and a Texas Instruments 980A Minicomputer. With one mass spectrometer, four channels are used; two to detect the condition of the solenoid valve system and two for the major and minor ion currents. Software was developed by Dr. Michael R. Smith to calculate ratios of the ion currents, δ-values, and standard deviations. Standard deviations of ± 0.1<sup>0</sup>/oo are possible with this equipment.

In stable isotope analyses, corrections are necessary. These fall into two classes. In the first class are those needed because of "ion overlap" with low resolution instruments: For example, mass 66 is composed mainly of two unresolved ions <sup>32</sup>S <sup>18</sup>O <sup>16</sup>O<sup>+</sup> and <sup>34</sup>S <sup>16</sup>O<sub>2</sub><sup>+</sup>

and a correction equation is given by HULSTON (1958) as

$$\delta^{34}\text{S} = 1.09 \delta_{66} - 0.1 \delta^{18}\text{O}$$

where  $\delta_{66}$  is the measured  $\delta$  value based on the mass 66 ion current. The above equation assumes that mass 65 is not collected with the major mass 64 ion current.

In the case of  $\text{CO}_2$  analyses, correction equations have been given by CRAIG (1957) as

$$\delta^{13}\text{C} = 1.0676 \delta_{45} - 0.0338 \delta^{18}\text{O}$$

and

$$\delta^{18}\text{O} = 1.0014 \delta_{46} + 0.009 \delta^{13}\text{C}$$

Corrections in the second class are dependent upon the mass spectrometer and involve factors such as "tailing" of the major ion current under the minor ion current, "cross-talk" in the magnetic valve system, and slight mismatch in the capillaries.

The above corrections can be evaluated individually within the laboratory. This is time consuming in that they may change over time (e.g. oxygen of different isotope composition used in combusting  $\text{Ag}_2\text{S}$  to  $\text{SO}_2$ ). Therefore, it is more expedient to use two or more substandards of known isotopic composition for each element and use these to calibrate the mass spectrometer system as was done in the current studies.

## CHAPTER 8

## RESULTS AND DISCUSSION

8.1 Comparison of Techniques

In the course of developing techniques for this work, several months were spent using projector lamps to heat a graphite crucible for the  $\text{BaSO}_4$  reduction. The results were generally unsatisfactory. This was finally traced to a peculiar gaseous impurity in the graphite which was supposedly spectrographically pure. The projector lamp assembly was abandoned in favour of a quartz-tube in a furnace primarily because the former was costly in terms of bulb replacement. The latter procedure has the problem of memory effects but these were much smaller than other errors. Because of the delay in obtaining more reliable graphite, the impure material was used after heating extensively in vacuo for the bulk of the samples of this thesis.

A series of events affected performance of the digital equipment on the mass spectrometer. A lightning storm caused the TI 980A to malfunction. It was believed that this was remedied by re-reading in the programmes by paper tape. However at about this time, an electrical short also occurred in the mass spectrometer source. Although not directly connected electrically, this caused the breakdown of several FET's and I.C. chips in the controller for the solenoid valves, the digital ratiometer, printer and the Analogic analogue multiplexer A to D converter combination. Many of the samples had to be run with an older digital ratiometer with noise averaging characteristics inferior

to those of the current equipment.

As a consequence of the above, the overall reproducibility of the data is assessed at  $\pm 0.3^{\circ}/\text{oo}$  Std. Dev. Under optimum conditions using recently purchased graphite and the better electronics, reproducibilities of better than  $\pm 0.1^{\circ}/\text{oo}$  were obtained with different aliquots of the same  $\text{BaSO}_4$  samples, i.e. the graphite reductions and the isotope determinations reproduced this well. The actual processing of natural samples to yield pure  $\text{BaSO}_4$  is associated with errors greater than  $\pm 0.1^{\circ}/\text{oo}$ . It is sometimes difficult to distinguish variations introduced by the extraction techniques from the variations due to inhomogeneity of the sample.

During the course of this work, oxygen and sulfur isotope abundances were measured for  $\text{SO}_4^{2-}$  extracted from water from the following locations:

1. Calgary Bow River system and tap water.
2. Upper Hot Springs, Banff, Alberta.
3. South of Great Slave Lake, N.W.T., Canada.

The latter were part of a suite of samples made available by Dr. U. Weyer of the Hydrology Research Division of Environment Canada. Chemical data for these waters were also provided by Dr. Weyer and are summarized in Table 6.

In addition a few naturally occurring barites from Alaska were analyzed.

Since  $\text{SO}_4^{2-}$  ions may be extracted from water either via direct

TABLE 5.

 $\delta^{18}\text{O}$  Values of  $\text{SO}_4^{2-}$  Using Different Extraction Techniques

Location	Technique*	$\delta^{18}\text{O}$
Upper Hot Springs, Banff	1	+ 12.4
	2	+ 12.4
Bow River, Bowness	1	+ 3.0±0.3**
	2	+ 3.5±0.3
Bow River, Prince's Island	1	+ 3.7±0.2
	2	+ 3.2±0.1
Tapwater	1	+ 6.0±0.3
	2	+ 5.4±0.3
	3	+ 4.8±0.0
Fisher Reagent BaSO <sub>4</sub>	As supplied	+ 12.0±0.1
	After chemical "purification"	+ 12.2±0.1
Upper Hot Springs Banff, Alberta	1	+ 12.8±0.6
	2(1:10 dilution) recycled resin	+ 12.8±0.1
	2(1:3 dilution) new resin	+ 12.1

\* 1. Direct precipitation of BaSO<sub>4</sub>.

2. Ion Exchange Column.

3. Direct precipitation followed by chemical purification.

\*\* Std Deviations are for reproducibility of multiple sample preparations.

precipitation or ion exchange (see Chapter 7) a check on the techniques was made. Table 5 summarizes these data.

Fisher  $\text{BaSO}_4$  was chosen as a working standard for this investigation. After comparison with samples for which the isotope composition has been established in other laboratories, the  $\delta^{18}\text{O}$  value of this standard was chosen as  $+12.0^\circ/\text{oo}$  SMOW. With this choice, a Pacific seawater  $\text{SO}_4^{2-}$  sample was found to have a  $\delta^{18}\text{O}$  value of  $+9.8^\circ/\text{oo}$ . This compares with the range  $+9.3$  to  $+10.1$  (mean  $+9.6 \pm 0.2$ ) reported for 7 different oceanic samples by Lloyd (1966).

A substandard (Tyrrhenian seawater) from the Laboratorio Geologia Nucleare, Pisa, Italy, was found to have a  $\delta^{18}\text{O}$  value of  $+9.6^\circ/\text{oo}$  as compared to  $+9.45^\circ/\text{oo}$  quoted by that laboratory. A sample of  $\text{Na}_2\text{SO}_4$  measured as  $+14.2^\circ/\text{oo}$  at the D.S.I.R., Lower Hutt, New Zealand was found to be  $+14.5^\circ/\text{oo}$  using  $+12.0^\circ/\text{oo}$  for the Fisher  $\text{BaSO}_4$ .

Since the Fisher  $\text{BaSO}_4$  standard is very pure, chemical treatment to remove carbonates, silicates etc. should not affect the results. It is seen in Table 5 that the treated and untreated material have  $\delta^{18}\text{O}$  values of  $+12.2$  and  $+12.0^\circ/\text{oo}$  respectively. This is based on three different preparations with a reproducibility of  $\pm 0.1^\circ/\text{oo}$ .

When two water samples taken at the same time from Upper Hot Springs, Banff had  $\text{BaSO}_4$  precipitated directly or by use of an ion exchange column, the  $\delta^{18}\text{O}$  values were identical when a recycled resin was used and the sample diluted by the addition of 9 parts of distilled water. A sample diluted by adding 2 parts of distilled water and

TABLE 6. CHEMICAL AND ISOTOPIC DATA FOR WATER SAMPLES  
SOUTH OF GREAT SLAVE LAKE\*

Sample*	$E_H$ (mv)	$[Cl^-]$ (p.p.m.)	$[SO_4^{2-}]$ (p.p.m.)	$[H_2S^-]$ (p.p.m.)	Conv $SO_4^{2-}$ (%)	$\delta^{34}S$ ( $^{\circ}/\text{oo}$ )	$\delta^{18}O$ ( $^{\circ}/\text{oo}$ )
66	-310	110	1391.0	14.3	2.82	19.4	15.0
76	-400	28.0	1580.0	1100.0	66.25	24.5	13.8
77	-380	28.0	1736.0	1800.0	77.51	24.5	13.0
79	-385	32.0	1761.0	910.0	59.29	26.3	14.5
80	-360	10.0	946.0	670.0	66.63	26.2	13.6
85	-238	7.0	576.0	140.0	40.66	14.4	9.8
86	-238	13.0	601.0	220.0	50.78	15.0	8.6
87	-233	17.0	741.0	110.0	29.50	16.5	9.8
91	-190	6.0	761.0	140.0	46.12	11.9	5.2
92	-245	21.0	116.90	74.0	15.14	16.5	12.0
93	-238	37.0	1053.0	94.0	20.11	17.4	11.4
95	-240	18.0	996.0	94.0	21.01	17.0	11.0
98	-240	30.0	1111.0	130.0	24.80	18.7	11.0
101	-230	14.0	551.0	140.0	41.73	12.8	8.2
102	-220	6.0	436.0	130.0	75.67	11.7	4.4

(Table Continued)

\* $E_H$ ,  $[Cl^-]$ ,  $[SO_4^{2-}]$ ,  $[H_2S^-]$ , and percent conversion of  $SO_4^{2-}$  data have been provided by K.U. Weyer of N.H.R.I., Environment Canada. The sample numbers are those of N.H.R.I.

TABLE 6. (CONT'D)

Sample	$E_H$ (mv)	$[Cl^-]$ (p.p.m.)	$[SO_4^{2-}]$ (p.p.m.)	$[H_2S^-]$ (p.p.m.)	Conv $SO_4^{2-}$ (%)	$\delta^{34}S$ (‰)	$\delta^{18}O$ (‰)
103	-260	14.0	1095.0	76.0	16.36	16.3	11.4
105	-250	11.0	700.0	160.0	39.18	15.5	8.8
106	-260	8.0	782.0	82.0	22.82	17.7	10.4
116	-230	158.0	1062.0	160.0	29.81	18.2	12.0
117	60	5.0	313.0	2.1	1.86	17.7	11.0
118	75	362.0	1370.0	1.0	0.21	17.9	12.5
119	100	11.0	545.0	2.4	1.23	18.3	13.5
122	90	18.0	150.0	15.0	21.99	18.3	4.2
125	-10	119.0	1440.0	1.4	0.27	17.9	13.5
127	-10	16.0	1400.0	11.0	2.17	19.0	13.2
132	-35	1800.0	1400.0	7.1	1.41	17.4	5.8
137	50	94.0	724.0	1.1	0.43	20.6	12
142	110	140.0	691.00	27.0	8.92	21.3	11.2
145	110	1560.0	2050.0	1.9	0.26	18.0	12.7
147	140	58.0	1110.0	0.6	0.15	18.3	15
148	140	5.0	1250.0	0.4	0.09	17.8	14
150	-150	3.0	960.0	2.9	0.84	17.0	13.5

passed through a new resin gave a value  $0.7^{\circ}/\text{oo}$  lower.

Samples of the Bow River summarized in Table 5 were taken from the same locations but on different days (2 weeks apart). Therefore the isotopic differences may include temporal variations as well as those introduced by the different techniques. Despite this the data are consistent with the  $\pm 0.3^{\circ}/\text{oo}$  reproducibility claimed.

In the case of tap water in the laboratory, the directly precipitated  $\text{BaSO}_4$  was  $0.6^{\circ}/\text{oo}$  heavier than that obtained using ion exchange with no dilution. Chemical treatment of the directly precipitated  $\text{BaSO}_4$  however gave a value  $1.2^{\circ}/\text{oo}$  lower. In this case, samples were taken at different times and the experiments were conducted with two different  $\text{BaSO}_4$  precipitates for each condition. One direct  $\text{BaSO}_4$  precipitate was much cleaner than the other and its value of  $+5.7^{\circ}/\text{oo}$  is closer to the values obtained with the other techniques.

In summary, the different extraction techniques did not cause variations much greater than those associated with other sources of errors and one might question which value should be accepted. However, chemically cleaned precipitates and those obtained by ion exchange tended to have better reproducibility. Direct precipitates from the same water tended to vary in appearance and usually had  $\delta^{18}\text{O}$  variations near  $\pm 0.3^{\circ}/\text{oo}$ .

## 8.2 Hydrological Data and Interpretations

### 8.2.1 Upper Hot Springs, Banff

The Rocky Mountains are considered to be sedimentary rocks of Devonian age which have been folded and uplifted. Geologists have speculated that at Banff, water from Sundance Creek follows fractures down to 6000 m to the west side of Sulphur Mountain where it is heated sufficiently to rise and emerge as hot springs. The meteoric character of the water was verified by its  $\delta^{18}\text{O}$  value (KROUSE et al, 1970). On the basis of the  $\delta^{34}\text{S}$  value of the  $\text{SO}_4^{2-}$  (+ 26 $^{\circ}$ /oo), these authors also concluded that the source of  $\text{SO}_4^{2-}$  was Devonian evaporites dissolved by the percolating waters. There is a paucity of  $\delta^{18}\text{O}$  data for evaporites and it is known that the  $\delta^{34}\text{S}$  value fluctuated considerably during the Devonian (Fig. 9). Hence, one cannot make a direct comparison but the value of + 12.4 $^{\circ}$ /oo obtained in the current study falls into the range associated with the Devonian.

### 8.2.2 Springs near Buffalo River

Springs near Buffalo River, just south of Great Slave Lake (Fig. 11) ranged in  $\delta^{34}\text{S}$  value from 24.5 to 26.3 and in  $\delta^{18}\text{O}$  value from 13 to 14.5. WEYER et al (1978) have described the regional geohydrology south of Great Slave Lake. While the Caribou Mountains (Fig. 11) consist mainly of clastic Cretaceous rocks, the surrounding lowlands show outcrops of Upper and Middle Devonian calcareous, gypsiferous and other evaporitic rocks. In the lowlands between the Caribou Mountains and Pine Point, exists possibly the largest gypsum karst area in the world. Some of the large regional flow systems originate

FIG. 11 Map of region south of Great Slave Lake, N.W.T., Canada

Numbers refer to samples.

PP = Pine Point

LBR = Little Buffalo River,

SR = Salt River

BR = Buffalo River

Sample location map after WEYER et al (1978).

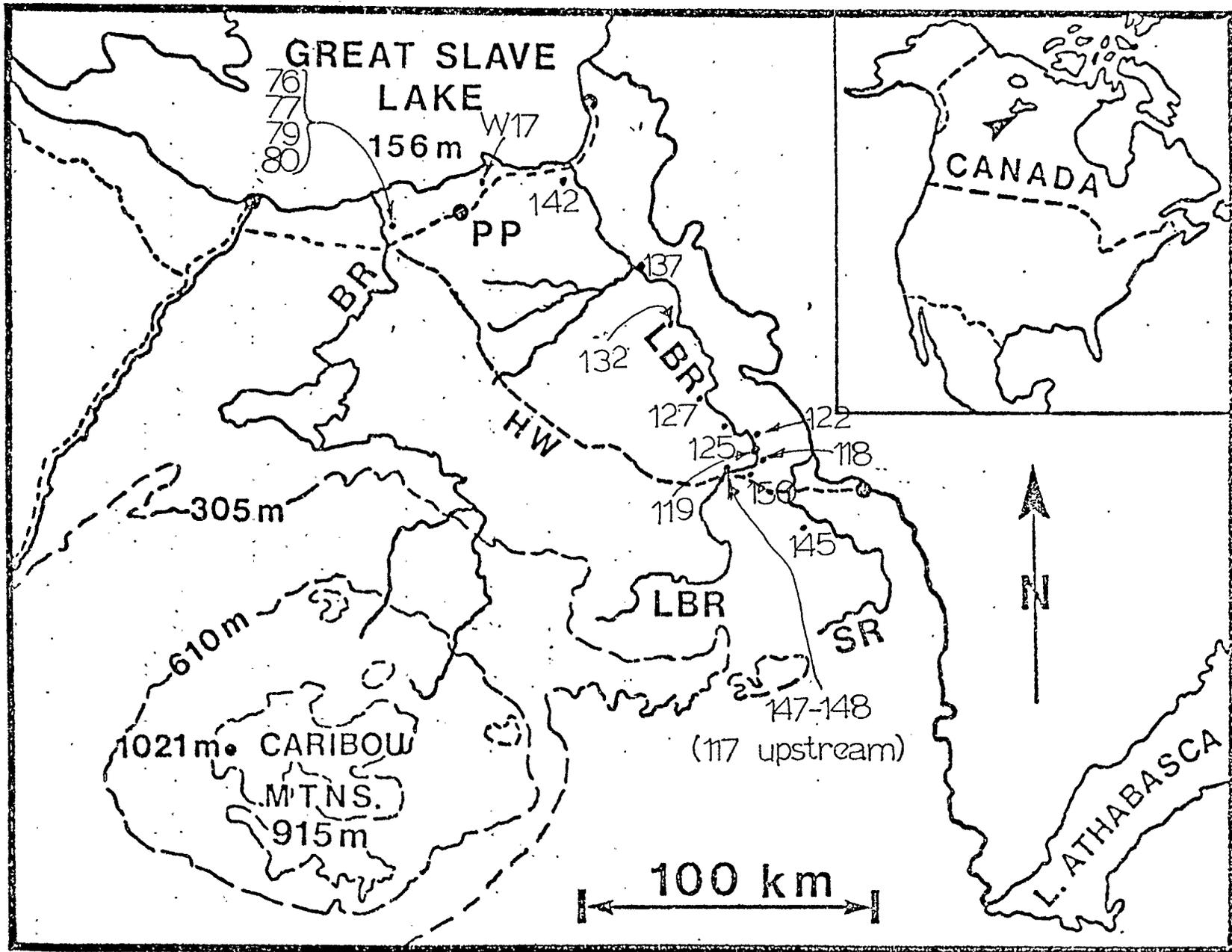


FIG. 11

in the Caribou Mountains plateau. While major groundwater discharge occurs at the shoreline of Great Slave Lake.

On the basis of the limited  $\delta^{18}\text{O}$  data for evaporites the  $\delta$ -values of the springs near Buffalo River are consistent with solution of Upper Devonian evaporites (Fig. 15).

### 8.2.3 Little Buffalo River

Although the bulk of the  $\delta^{18}\text{O}$  values for samples on the Little Buffalo River are similar to the springs on Buffalo River, the  $\delta^{34}\text{S}$  values are on the average 8‰ lower. Further, there is a trend towards higher  $\delta^{34}\text{S}$  and lower  $\delta^{18}\text{O}$  in going downstream (Fig. 11). Also compare extreme samples #150 and #142 in Table (6). Samples 122 and 132 depart markedly from this trend and have much lower  $\delta^{18}\text{O}$  values. These features cannot be identified with a single process. For example, bacterial  $\text{SO}_4^{2-}$  reduction would enrich the  $\text{SO}_4^{2-}$  in both  $^{18}\text{O}$  and  $^{34}\text{S}$ . Plots of  $\delta^{18}\text{O}$  against concentrations,  $E_{\text{H}}$ , etc. have not produced simple curves. Thus it is concluded that the variations reflect different  $\text{SO}_4^{2-}$  sources and processes over the relatively large sampling distance involving a number of feeder streams.

### 8.2.4 Pit W17

Unlike the samples discussed in Section 8.2.3, these were taken from a small area and plots of  $\delta^{18}\text{O}$  against other parameters provide reasonably simple curves.  $\delta^{18}\text{O}$  generally increases with  $[\text{SO}_4^{2-}]$  (Fig. 12) and  $[\text{Cl}^-]$  (Fig. 13). Data for describing this hydrogeologic system are incomplete as waters very high in chloride at the pit were not analyzed. Despite these limitations, it seemed interesting to

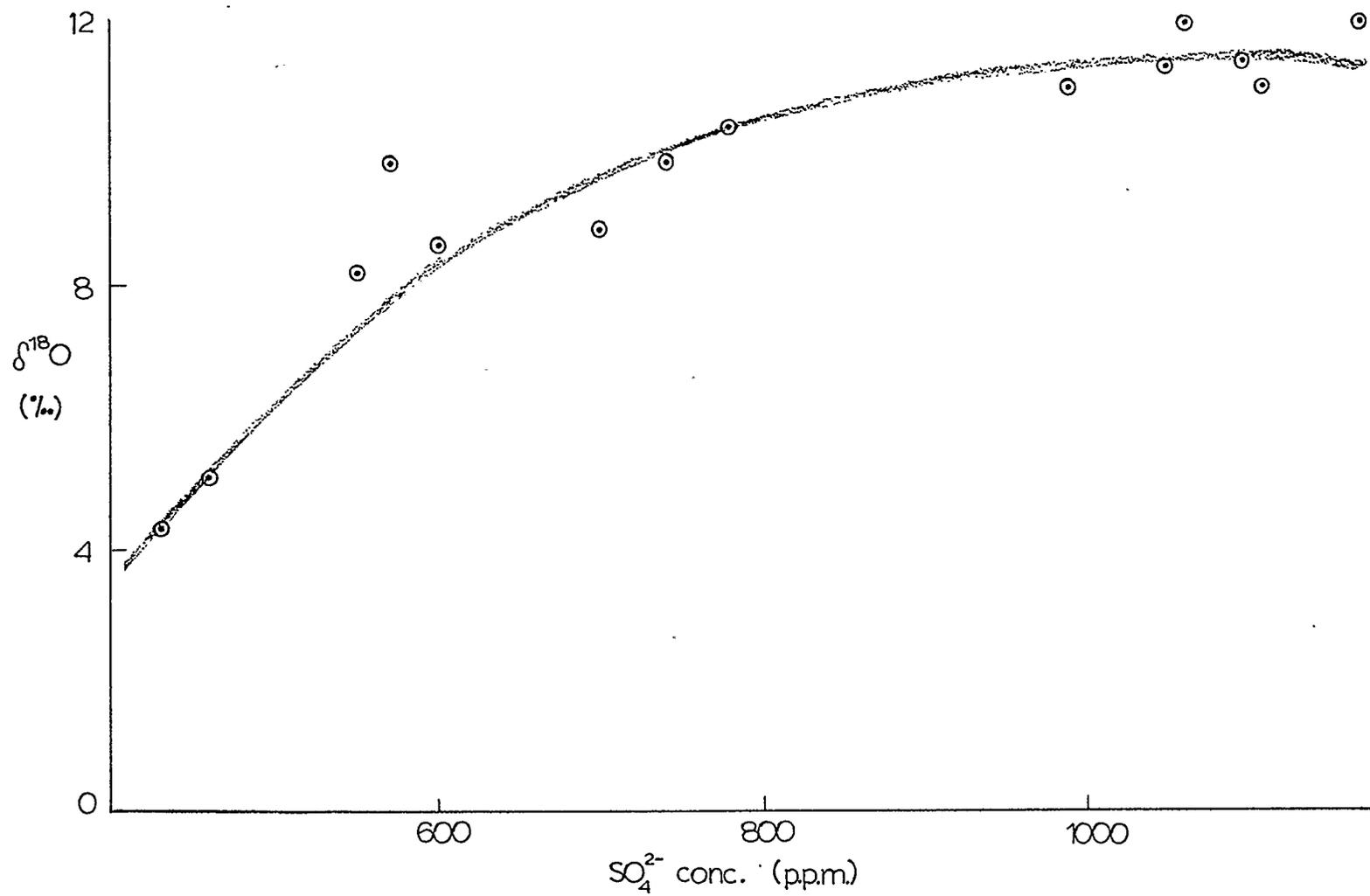


FIG. 12 Plot of  $\delta^{18}\text{O}$  versus  $[\text{SO}_4^{2-}]$  for samples from the pit.

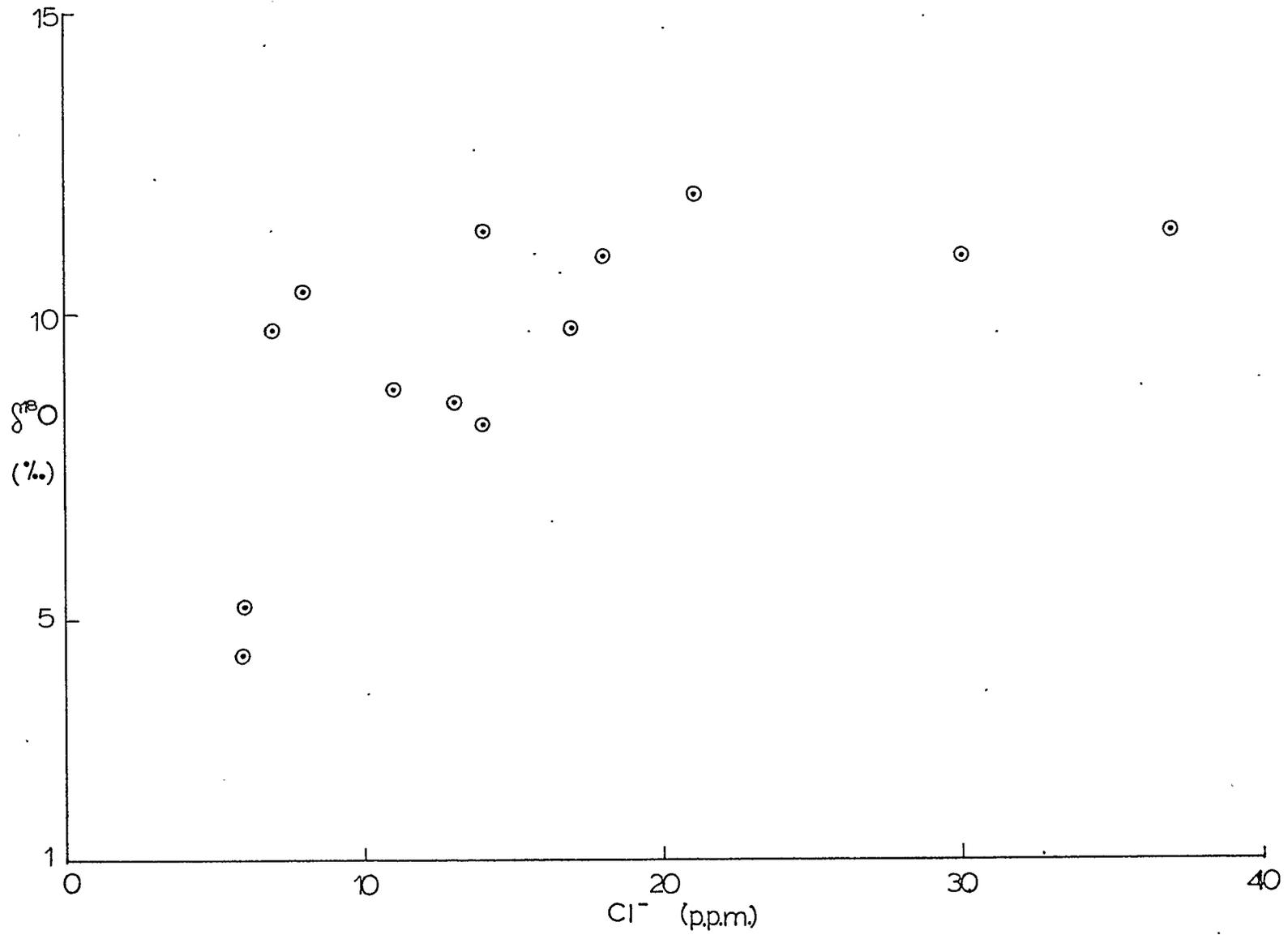


FIG. 13 Plot of  $\delta^{18}\text{O}$  versus  $[\text{Cl}^-]$  for the W17 pit samples.

subject the data to mathematical modelling. In view of Figures 12 and 13, it seemed appropriate to apply simple mixing model theory to these samples. If we assume two sources of  $\text{SO}_4^{2-}$  ions, A and B with constant  $\delta$ -values  $\delta_A$  and  $\delta_B$  and concentrations  $C_A$  and  $C_B$  then a thorough mixing of these two sources would yield  $\delta^0/\text{oo}$  for the mixture. To a first approximation,

$$C_A \delta_A + C_B \delta_B = C \delta$$

where  $C$  is the  $\text{SO}_4^{2-}$  ion concentration of the final mixture.

Moreover  $C_A + C_B = C$ . We will assume a constant  $C_A$  and a variable  $C_B$ . Hence  $C$  is a variable also.

Substituting  $C_B = C - C_A$  we obtain

$$C_A \delta_A + (C - C_A) \delta_B = C \delta$$

$$\therefore C_A (\delta_A - \delta_B) = C(\delta - \delta_B)$$

$$\therefore \delta = \frac{C_A (\delta_A - \delta_B)}{C} + \delta_B$$

Hence a plot of  $\delta$  vs  $\frac{1}{C}$  yields a straight line with a constant slope  $C_A (\delta_A - \delta_B)$  and a y-intercept =  $\delta_B$ .

Figure 14 shows the results of plotting the measured  $\delta^{18}\text{O}$  against  $[\text{SO}_4^{2-}]^{-1}$ . The plot shows a regression line with a correlation coefficient of 0.95. The y-intercept gives a  $\delta^{18}\text{O}$  value of +16.1 $^{\circ}$ /oo. This value pertains to the source which was assumed to contribute varying amounts of  $\text{SO}_4^{2-}$ .

These calculations do not allow for the possibility that  $\text{SO}_4^{2-}$  was reduced to  $\text{HS}^-$  by sulphate reducing bacteria as discussed by WEYER et al (1978). These authors used  $\text{HS}^-$  and  $\text{SO}_4^{2-}$  concentration and isotopic data to carry out balance calculations to evaluate  $[\text{SO}_4^{2-}]$  and its  $\delta^{34}\text{S}$  prior to reduction.

Unlike sulphur, there is not a product of reduction for which a  $\delta^{18}\text{O}$  value can be determined. Therefore, one cannot carry out  $^{18}\text{O}/^{16}\text{O}$  balance calculations directly. However, if  $\Delta\delta^{34}\text{S}$  and  $\Delta\delta^{18}\text{O}$  values are defined as the differences between measured  $[\text{SO}_4^{2-}]$  and initial  $[\text{SO}_4^{2-}]$  and it is assumed that they are in the ratio of 4:1 as found in some laboratory bacterial  $\text{SO}_4^{2-}$  reduction experiments, indirect calculations can be carried out. This exercise also results in a regression line (B, Figure 14) with a correlation coefficient of 0.81 and a y-intercept of + 19.9<sup>o</sup>/oo.

On the basis of the mathematical evidence alone (lower correlation coefficient for corrected data) one might question the presence of bacterial reduction. However, this is not consistent with the geochemical evidence and sulphur isotope data. One would have to find an additional source for the  $\text{HS}^-$  with  $\delta^{34}\text{S}$  values typically near - 20<sup>o</sup>/oo (WEYER et al, 1978) whereas the sulphur ore deposits have  $\delta^{34}\text{S}$  values for galena and sphalerite near + 20<sup>o</sup>/oo (SASAKI and KROUSE, 1969). Further, the  $E_{\text{H}}$  values are quite negative for all samples (Table 6), which signify a reducing environment.

Interesting questions arise in considering the two source model and  $\text{SO}_4^{2-}$  reduction. Were both  $\text{SO}_4^{2-}$  components partially reduced or

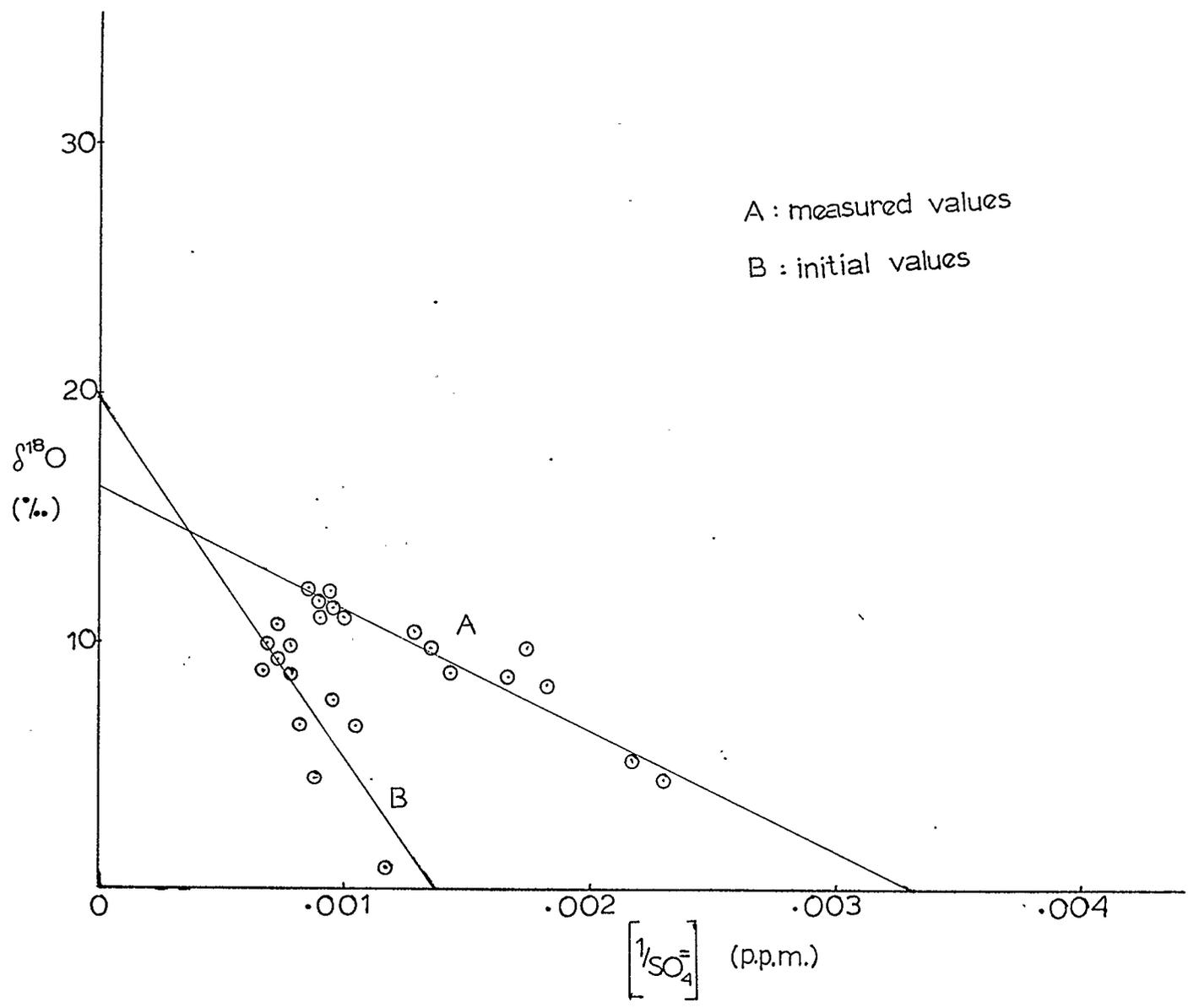


FIG. 14  $\delta^{18}\text{O}$  versus  $[\text{SO}_4^{2-}]^{-1}$  for measured and initial values.

only one? Did reduction occur prior to or after mixing? It is also possible that some  $H_2S$  escaped from solution. These factors introduce elements of unreliability into the calculations.

### 8.3 $\delta^{34}S$ versus $\delta^{18}O$ Diagram

All the data of this thesis are plotted on a  $\delta^{34}S$  versus  $\delta^{18}O$  diagram in Figure 15.

In addition to the waters, a few barite samples are also plotted. Interpretation of these data will not be pursued in this thesis since the geology of their occurrence is in the process of being described. A few Devonian evaporite data are also plotted in Figure 15 for comparison with the springs at Banff and the waters south of Great Slave Lake.

It is noted that data from different locations form distinct clusters on the plot. The data do not fit a line of slope 4 as found in some laboratory experiments or occasional terrestrial studies (RAFTER and MIZUTANI, 1967). In fact, in the case of Little Buffalo River, the slope is negative. It would be unreasonable to expect all terrestrial samples to fit such a line since sulfur and oxygen participate in distinctly different cycles in nature. Oxygen of  $SO_4^{2-}$  can exchange with oxygen of  $H_2O$ , albeit slowly. One would expect that in river systems, some oxygen in  $SO_4^{2-}$  would be derived from the air and water during oxidation processes. In subsurface environments, solution of different evaporite formations contribute a considerable range of  $\delta^{34}S$  and  $\delta^{18}O$  values and these are further altered

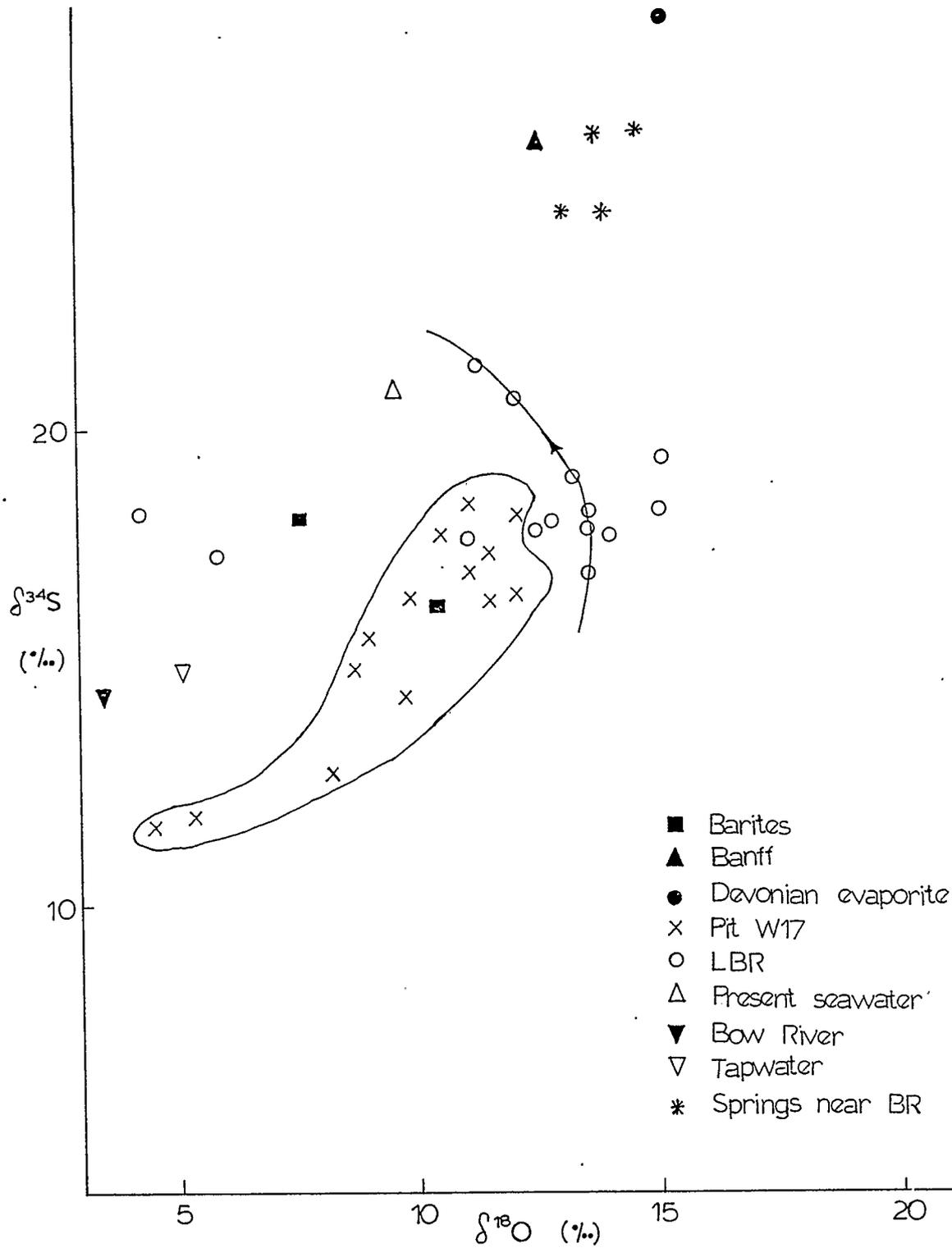


FIG. 15 Plot of  $\delta^{34}\text{S}$  versus  $\delta^{18}\text{O}$  for all samples.

by bacterial reduction. It is a consequence of all of these possibilities that the sample locations chosen for this study plot as distinct clusters on a  $\delta^{34}\text{S}$  versus  $\delta^{18}\text{O}$  diagram.

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