OXYGEN AND HYDROGEN ISOTOPE RATIOS
IN
SEDIMENTARY ROCKS AND MINERALS

Thesis by
Samuel Marvin Savin

In Partial Fulfillment of the Requirements
For the Degree of
Doctor of Philosophy

California Institute of Technology
Pasadena, California
1967
(Submitted May 5, 1967)

ACKNOWLEDGMENTS

My sincerest thanks go to Dr. Samuel Epstein under whose direction this work was done. His encouragement and guidance throughout the course of the research are greatly appreciated.

I am grateful for valuable discussions I have had with Dr. A. L. Albee, Dr. A. J. Boucot, Mr. A. A. Chodos, Dr. H. A. Lowenstam, Dr. J. R. O'Neil, Dr. S. M. F. Shepard, Dr. L. T. Silver, and Dr. H. P. Taylor. Drs. Silver and Taylor provided advice and assistance in solving a number of experimental problems.

Samples for analysis have been generously provided by Drs. F. Birch, Jr., A. J. Boucot, V. T. Bowen, W. Broecker, E. D. Goldberg, J. J. Griffin, J. Konta, H. A. Lowenstam, T.R. McGetchin, C.C. Patterson, J. Richards, J. Schlee, and J. Trumbull.

The assistance and instruction of Mr. C. A. Bauman and Mr. E. V. Nenow in construction and maintenance of apparatus is gratefully acknowledged.

My wife, Cathleen Savin, gave valuable help in mineral separations, mass spectrometry, and preparation of the thesis.

During part of this research the writer was supported by a National Science Foundation fellowship. Research funds were provided by the National Science Foundation and

the Atomic Energy Commission.

ABSTRACT

O^{18}/O^{16} and D/H measurements were made on a variety of sedimentary rocks and minerals, with special emphasis on the fine-grained, predominantly clay mineral fraction of the sediments. The interlayer water was removed from clay minerals prior to the isotopic analyses. Precision of the measurements was generally ± 0.2 permil for oxygen and ± 0.3 percent for hydrogen. In the case of zeolites the reproducibility was less constant because of difficulty encountered in removing zeolitic water.

Listed in order of decreasing tendency to concentrate O^{18}, the sedimentary minerals for which such data are available and their approximate isotopic fractionation factors relative to water at sedimentary temperatures are:

mineral	$\alpha^{ox}_{mineral-H_2O}$	$\alpha^{hy}_{mineral-H_2O}$
quartz	1.034	
alkali feldspar	1.034	
phillipsite	1.034	
montmorillonite	1.0273	0.938
kaolinite	1.0265	0.970
glauconite	1.0263	0.926
manganese nodule	1.015	0.923

Mineral - water fractionations are related to the types of chemical bonds in the minerals.

Clay minerals which form under sedimentary conditions appear to form in isotopic equilibrium with their environments. Subsequent isotopic exchange may occur easily at elevated temperatures, but only extremely slowly at low temperatures.

Ocean sediments which are detrital in origin have isotopic compositions reflecting the fresh water origin of their clay minerals. There is no evidence for any isotopic exchange of detrital clay minerals with the marine environment in any of the ocean cores studied. (The sediments could be as old as 250,000 years as determined by ionium-thorium method.) Marine sediments which have large authigenic components are generally enriched in O^{18}, reflecting the presence of phillipsite (δO^{18} = +34 permil and montmorillonite δO^{18} = +29 permil). However, those containing a high concentration of iron and manganese oxide may be isotopically light. (A manganese nodule had δO^{18} = +15 permil.)

The isotopic compositions of the clay minerals of ocean sediments are compatible with a weathering origin for a kaolinite and a metamorphic or diagenetic origin for chlorite. Montmorillonite and illite are primarily of weathering origin but both of these minerals may have diagenetic components.

There is no evidence for any isotopic exchange of sand-sized quartz or feldspar in the sedimentary environment, and these minerals may be used as indicators of provenance in sediments. The presence of a large authigenic feldspar or quartz component may be readily detected by oxygen isotopic analysis. An authigenic feldspar had an O^{18}/O^{16} ratio ten permil greater than igneous feldspars.

Calculations have been performed to determine the effect of weathering and the formation of sediments on the isotopic composition of the hydrosphere. It is concluded that those processes could have depleted the hydrosphere 3 permil in O^{18} and enriched it 0.03 percent in deuterium through the course of geologic time.

TABLE OF CONTENTS

CHAPTER I

INTRODUCTION

1.1 Statement of the problem

Variations in the oxygen isotope ratios of rocks and minerals have been used for some time as an aid to understanding a wide variety of geologic processes. To a much lesser extent, variations in hydrogen isotope ratios have been applied to problems in the earth sciences.

A number of studies of oxygen isotope variations in sedimentary carbonates have been made by previous investigators (Epstein *et al.* (34), Degens and Epstein (26), Keith and Weber (56) and others), and these have led to a greater understanding of the geochemistry of carbonates. However, prior to the present study, only a small body of data had been obtained pertaining to the stable isotope geochemistry of non-carbonate sediments. Silverman (93) showed that oxygen isotope ratios of silicate minerals in sedimentary rocks are indicative of their modes of formation. Unweathered detrital components from igneous and metamorphic rocks generally contain less O^{18} than those which have a low temperature origin since equilibrium isotopic fractions between minerals and water usually are greater at low temperatures than they are at high temperatures.

Prior investigations have also indicated that isotopic exchange may occur in sediments which have not undergone metamorphism. Degens and Epstein (27) found that ancient fine-grained marine limestones and cherts often undergo a change of oxygen isotopic composition without showing any obvious metamorphic features.

In the present study, the O^{18}/O^{16} and D/H ratios were measured in a wide variety of sedimentary materials (rocks, minerals, and unconsolidated sediments). An attempt was made not only to establish the range of variation of isotope ratios but also to investigate the factors which determine these ratios. In particular, it was of interest to determine whether minerals which are formed under sedimentary conditions are formed in isotopic equilibrium with their environments and under what conditions they undergo isotopic exchange. An attempt was made to determine under what conditions the isotopic compositions of minerals could be used as indicators of provenance in sediments, under what conditions the isotopic compositions could be used as indicators of the environment of formation or deposition of sediments, and under what conditions the isotopic compositions could be used as indicators of the post-depositional history of the sediments in which they occur.

Finally, most sedimentary geochemical processes involving the formation of minerals result in the preferential removal of the heavy isotopes of oxygen and the light isotope of hydrogen from the hydrosphere. Using the isotopic data of the present study it was possible to refine calculations of the effect of the formation of sediments on the isotopic composition of the hydrosphere throughout geologic time.

1.2 Terminology and notation

Before embarking on a discussion of stable isotope variations in sediments it is desirable to define a few terms and symbols.

A. δ-values

All isotope ratios are reported in the δ notation. The δ-values are defined in the equations below

$$\delta\, O^{18} = \left[\frac{\left(\frac{O^{18}}{O^{16}}\right)_{\text{samp}} - \left(\frac{O^{18}}{O^{16}}\right)_{\text{std}}}{\left(\frac{O^{18}}{O^{16}}\right)_{\text{std}}}\right] \text{X } 1000$$

$$\delta\, D = \left[\frac{\frac{D}{H}_{\text{samp}} - \frac{D}{H}_{\text{std}}}{\frac{D}{H}_{\text{std}}}\right] \text{X } 100$$

Oxygen is reported as per mil deviation from the standard while hydrogen is reported as per cent deviation. In both cases the standard reported throughout this work is standard mean ocean water (SMOW), as defined by Craig (19).

B. Fractionation factors

The fractionation factors between two compounds or phases containing oxygen or hydrogen are defined by the equations

$$\alpha^{ox}_{A-B} = \frac{\left(\frac{O^{18}}{O^{16}}\right)_A}{\left(\frac{O^{18}}{O^{16}}\right)_B} \quad \text{and} \quad \alpha^{hy}_{A-B} = \frac{\left(\frac{D}{H}\right)_A}{\left(\frac{D}{H}\right)_B}$$

where A and B denote the compounds or phases. The fractionation factors are related to the δ's by the equations

$$\alpha^{ox}_{A-B} = \frac{1 + \frac{\overset{A}{\delta O^{18}}}{1000}}{1 + \frac{\overset{B}{\delta O^{18}}}{1000}} \quad \text{and} \quad \alpha^{hy}_{A-B} = \frac{1 + \frac{\overset{A}{\delta D}}{100}}{1 + \frac{\overset{B}{\delta D}}{100}}$$

C. Sedimentary and diagenetic processes

Throughout this work the terms "sedimentary" and "diagenetic" are frequently used. Sedimentary processes are those which occur at or very near the earth's surface or the sediment - water interface, such as weathering, transportation, sedimentation, precipitation from solution at or above the sediment - water interface, etc. Diagenetic processes are those which alter the sediment physically or chemically, mineralogically or isotopically after formation and burial. There is a gradation between sedimentary and diagenetic processes and between diagenetic and metamorphic processes.

CHAPTER II

HISTORICAL BACKGROUND AND PREVIOUS WORK

2.1 Early work

In the years following the discovery of the two heavy isotopes of oxygen (Giauque and Johnston (42)) and the stable heavy isotope of hydrogen (Urey, Brickwedde and Murphy (106)) a number of searches were made for variations in the O^{18}/O^{16} and D/H ratios of naturally occurring materials. Most early measurements used density techniques. The precision of these methods was generally so poor as to obscure most of the isotopic variations which occur in nature. They were sufficiently sensitive, however to detect a difference between the oxygen of the atmosphere and that of fresh waters (Dole (29), Smith and Matheson (95), and others). By the early 1940's enough carefully performed density measurements had been performed so that it was known that the oxygen of Atlantic Ocean water was richer in O^{18} than that of Lake Michigan water which was in turn richer in O^{18} than that of atmospheric water (Dole (28)), and that the oxygen of carbonates was heavier than that of "normal" waters while that of oxide minerals was the same as "normal" waters (Dole and Slobod (30)). It had also been determined that fresh waters contained less deuterium than ocean waters (Swartout and Dole (97)).

The earliest mass spectrometric attempt to measure variations in the O^{18}/O^{16} ratio of silicates was that of Manian, Urey and Bleakney (67). They extracted oxygen from granitic rocks and meteorites by reacting them with a mixture of carbon and carbon tetrachloride. The precision of the method was 2.5% and they found no significant isotopic variations.

2.2 Igneous and metamorphic rocks

Refinements in mass spectrometric techniques by Nier (75) and McKinney *et al.* (70) made available an instrument capable of measuring O^{18}/O^{16} ratios relative to a standard with a precision better than ±0.1‰. This new tool provided the impetus for the development of improved chemical techniques for the removal of oxygen from silicates and oxides for measurement in the mass spectrometer. The methods used are based either on reduction of the oxygen with carbon or on oxidation with fluorine or fluorine-containing compounds. These techniques have been reviewed by Taylor and Epstein (103), Clayton and Mayeda (15), and Garlick (39) and will not be discussed further.

Some of the results of the studies of igneous and metamorphic rocks and minerals are of importance in the present study, as they relate to the source materials for sediments. They will be reviewed here.

Baertschi (3) analyzed the oxygen in a wide variety of igneous and sedimentary rocks with a precision of 1.5‰. He found that the oxygen of the igneous rocks had an isotopic variation of only 4.5‰ and that the igneous rocks contained about 5‰ more O^{18} than Hawaiian sea water. All the igneous rocks were depleted in O^{18} relative to the sediments. Silverman (93) measured more samples with better precision and found essentially the same results. He also measured a suite of metamorphic rocks from Duchess County, New York and found a trend of decreasing O^{18}/O^{16} with increasing metamorphic grade. Taylor and Epstein (103, 104) carried out a major survey of the oxygen isotopic composition of igneous rocks and minerals. They concluded that the total variation in whole - rock analyses was only 4.5‰ . The basic rocks were lighter than the more acidic ones. Of greater significance to the present study was the finding that regardless of the igneous rock type from which a mineral was taken, its isotopic composition could be predicted within a very narrow range. Quartz was invariably the heaviest mineral ($\delta = +10.5$ ‰ relative to Hawaiian sea water) and magnetite was the lightest ($\delta = +2$‰). Feldspars fell in a range 1 or 2 permil lighter than quartz.

Metamorphic rocks have been analyzed by Silverman (93), Taylor and Epstein (103), Taylor, Albee and Epstein (100), Garlick (39), and Garlick and Epstein (40).

These investigators reported much wider variations in O^{18}/O^{16} ratios than exist in igneous rocks, and also found that the oxygen of metamorphic silicate rocks is generally heavier than that of igneous rocks. Isotopic fractionations between minerals are generally related to metamorphic grade.

Hydrogen isotope variations in igneous and metamorphic rocks have been measured by Godfrey (43) and Taylor and Epstein (101). Godfrey found a wide range of variation of D/H ratios in rocks from the Sierra Nevada and Yosemite National Park. Taylor and Epstein reported measurable D/H fractionations between coexisting minerals and suggested that there exists at least a rough correlation between fractionation and temperature. They found no relation between O^{18}/O^{16} and D/H ratios.

2.3 Waters

Virtually all weathering processes take place in the presence of water. Many of these processes include hydration reactions. In addition, most sediments are transported by water, deposited in bodies of water, and subject to cementation and diagenetic changes in the presence of either trapped or mobile ground water. It should be expected, then, that the isotopic composition of these waters would have a bearing on the isotopic composition of the sediments. There is a large body of data on the isotopic composition of natural waters, and a few of the more pertinent points will be reviewed.

Epstein and Mayeda (35) demonstrated that there was only a narrow range of oxygen isotopic composition of deep ocean waters, and they showed that fresh waters were isotopically very variable, all being lighter than sea water and having a total O^{18}/O^{16} range of about 45‰. Friedman (37) measured hydrogen isotope variations in a variety of waters, and found a linear relationship between the oxygen and hydrogen isotope ratios. Craig (20) measured the O^{18}/O^{16} and D/H ratios in a very large number of meteoric waters and showed that for nearly all samples except those from closed basins and hot springs in which evaporation was an important factor, the relationship

$$\delta D\ (\%) = 0.8\ \ \delta O^{18}\ (‰) + 1.0 \qquad (2\text{-}1)$$

was valid. This relationship depends to a large extent on the presence of both oxygen and hydrogen isotopic equilibrium during evaporation and condensation processes. It has been discussed in detail by Craig, Gordon and Horibe (21).

Clayton _et al_. (14) have shown that the waters of brines from oil fields in Michigan and Illinois do not fall on the line described by equation (2-1). They interpret their data as demonstrating oxygen isotopic exchange between meteoric water and marine carbonates in a closed system where the amount of water was small enough so that the exchange markedly changed the isotopic compositions of the waters as well as that of the minerals.

It should be expected that the isotopic compositions of most waters encountered in sedimentary processes may be described by the relationship

$$\delta D\ (\%) = 0.8 \quad \delta O^{18}\ (\%.) + 1.0$$

However, in some cases, non-equilibrium evaporation or exchange with rocks may drive the isotopic composition away from this line.

2.4 Laboratory studies of isotopic fractionations

A number of experimental studies of equilibrium oxygen isotope fractionations between minerals and water have been performed by several workers. Experimentally determined fractionation factors are shown graphically in figure 1 for the following minerals with water: quartz, feldspar, calcite, muscovite, magnetite, and phosphate.

Clayton (12) and O'Neil and Clayton (77) have shown that the logarithm of the calcite - water fractionation factor varies linearly with $1/T^2$ over a temperature range 0^oC to 750^oC. This is in accord with the theory of isotope fractionations which is discussed in Chapter 3. The high temperature data of other mineral -

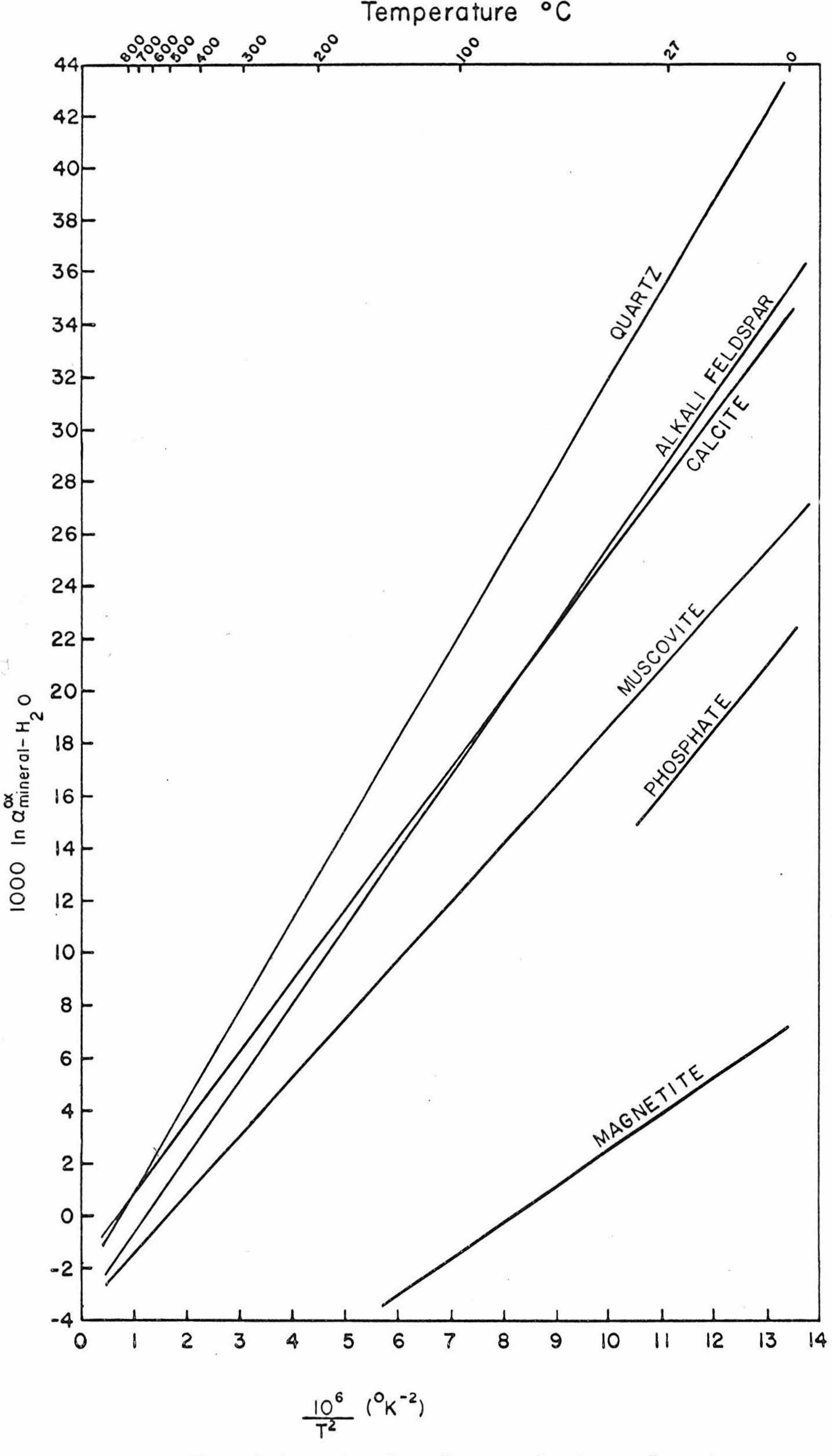


Figure 1. Experimentally determined values of mineral-water oxygen isotope fractionations factors linearly extrapolated to low temperatures

water fractionations have been fitted to curves in 1000 ln α, and $1/T^2$ by least squares methods, and these curves have been extrapolated to low temperatures. The extrapolated curves should be expected to yield at least semi-quantitative data on equilibrium fractionations under sedimentary conditions. This has been done for the quartz - water data of Clayton, O'Neil and Mayeda (16), the feldspar - water data of O'Neil and Taylor (80) and the muscovite - water data of O'Neil and Taylor (79).

O'Neil and Clayton (77) studied the magnetite - water system between 400°C and 800°C. By combining their experimental data with an observed fractionation between a magnetite chiton tooth they were able to describe the magnetite - water fractionation between 9°C and 800°C.

Longinelli (64) has measured the phosphate - water fractionation in mollusc shells grown at a range of low temperatures.

The experimental and extrapolated oxygen isotope fractionation data indicate that at low temperatures fractionations between minerals may be very large (up to 25 per mil or more). Minerals in isotopic equilibrium with most natural waters can be expected to be isotopically heavier than igneous and metamorphic minerals. Also, there is a much larger temperature dependence of fractionation factors at low temperatures than there is at high temperatures.

Preliminary experiments on hydrogen isotope fractionations in the serpentine - water system by Epstein and O'Neil (unpublished data) indicate that at temperatures of 200°C to 400°C the water is approximately 2% richer in deuterium than is the serpentine.

2.5 Sediments

The carbonates were the first group of sedimentary minerals to be studied isotopically with modern methods. In conjunction with the paleotemperature scale, McCrea(69) and Epstein *et al.* (34) developed reproducible analytical techniques for the acid extraction of CO_2 from carbonates. Epstein *et al.* (33, 34) showed that many calcite secreting organisms laid down their shells in isotopic equilibrium with the water in which they grew. They could thus be used as indicators of the temperature of the environment of growth.

Degens and Epstein (27) examined the oxygen isotopes in a large number of coexisting marine carbonates and cherts, formed throughout the range of post Precambrian times. They observed a marked trend for the oxygen of better preserved carbonates and of coexisting cherts to become lighter with increasing age. This information, combined with the fact that paleotemperatures measured in non-recrystallized fossils as old as the Permian show waters isotopically similar to those found today, led the authors to the conclusion that the older carbonates have undergone more exchange with isotopically light fresh waters than have the younger ones.

Keith and Weber (56) have produced a great mass of data on carbonates demonstrating the above relationship of δO^{18} and time, but Weber (112) interprets it as being the result of changing isotopic composition of sea water.

Only a small body of data exists on O^{18}/O^{16} variations in the non-carbonate sediments. As mentioned earlier, Baertschi (3) observed that sediments were isotopically much heavier than igneous rocks. In particular, quartzites tended to be very heavy. He interpreted this as the result of exchange of oxygen between water and the minerals under sedimentary conditions. Silverman (93) observed the same relations, but correlated the degree to which a quartzite was heavier than igneous quartz with the amount of secondary quartz it contained.

Taylor and Epstein (102) measured the oxygen in a number of soils and shales. They found that soils had a very wide range of O^{18}/O^{16} ratios and were heavier than igneous materials in most cases (+10 to +16 relative to SMOW). The isotopic ratios varied with the concentration of quartz and with the degree of weathering. The small number of shales measured were found to have a spread of O^{18}/O^{16} ratios from +14 to +18‰ relative to SMOW.

The few arkoses, meta-arkoses and quartz sandstones measured by Silverman (93), Clayton and Mayeda (15), Taylor and Epstein (102) tend to have δO^{18} between +11 and +16‰ relative to SMOW.

The range of O^{18}/O^{16} ratios in diatomites, cherts, and other forms of authigenic silica is +15 to +33‰ (Silverman (93), Degens and Epstein (27)). The heavier values presumably represent silica in or approaching isotopic equilibrium with sea water, and the lighter values are the result of various degrees of exchange with fresh waters.

In summary, the previous knowledge of the oxygen isotope variations in sediments indicates that the measured isotope ratios may be traced on a gross scale to the origins of the different minerals within a rock. Unweathered detrital components from igneous and metamorphic rocks are generally isotopically light. Minerals which have a sedimentary or low temperature origin are isotopically heavy. Of the minerals of sedimentary origin, at least calcite and amorphous silica appear to be subject to isotopic exchange with waters at sub-metamorphic temperatures.

The ranges of O^{18}/O^{16} ratios measured in sediments by previous workers are shown graphically in figure 2.

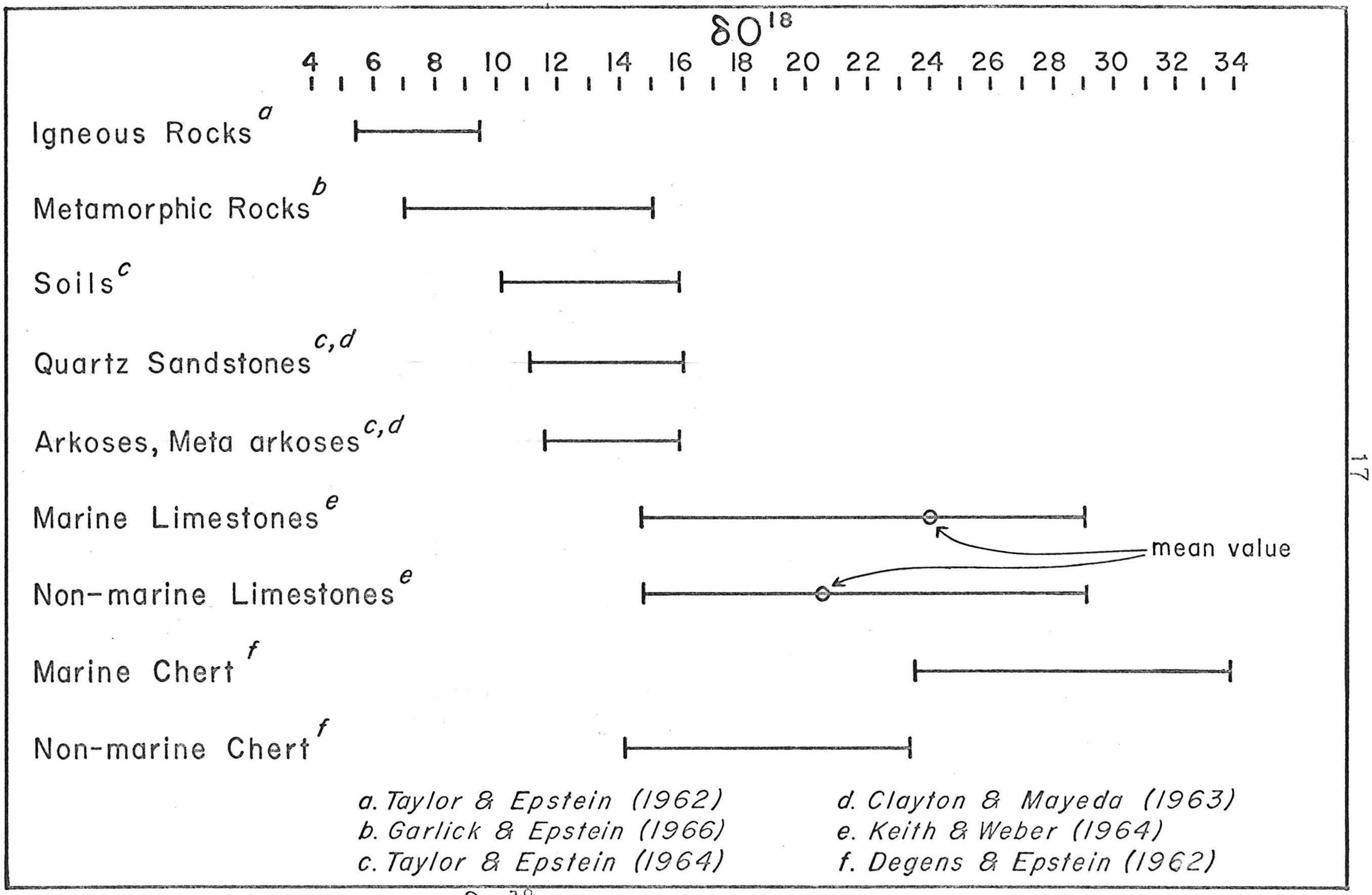


Figure 2. Ranges of δO^{18} values of rocks analyzed by previous investigators

CHAPTER III

THEORY

3.1 Introduction

In this chapter processes which could affect the isotopic compositions of minerals in the sedimentary environment are discussed. Included in the discussions are isotopic equilibrium exchange processes, kinetic isotope fractionations, and the kinetics of isotopic exchange in solids.

3.2 Isotopic equilibrium

Isotopic equilibrium can be described in terms of an exchange reaction of the type

$$a\ A_r + b\ B^*_s \quad = \quad a\ A^*_r + b\ B_s$$

where a and b are coefficients and A and B denote two compounds containing r and s atoms respectively of the isotopes being exchanged. The asterisk denotes the compound which contains the heavy isotope. As with any chemical reaction

$$a\ r = b\ s$$

We can write an equilibrium constant for the exchange reaction in the usual manner

$$K = \frac{(A^*)^a \quad (B)^b}{(A)^a \quad (B^*)^b}$$

This equilibrium constant is related to the statistical mechanical partition functions by the relationship

$$K = \frac{(Q_{A^*} / Q_A)^a}{(Q_{B^*} / Q_B)^b} \qquad (3\text{-}1)$$

where the Q's are the partition functions defined by the equation

$$Q = \sum g_i e^{-E_i/kT} \qquad (3\text{-}2)$$

where g_i is the degeneracy of the i^{th} quantum state and E_i is its energy.

A widely used treatment of isotope equilibrium was developed by Bigeleisen and Mayer (5) for the case of ideal gasses of non-interacting particles. In this treatment it is assumed that the only important contributions to the energy of the molecule result from translational, rotational, and vibrational motions and that there is no interaction between these three types of motion. The translational portion of the partition function can be treated classically at all temperatures above a few degrees Kelvin, because the energy levels are so closely spaced. Within the limits of the accuracy of the calculation, the rotational partition function also can be approximated by the classical expression at room temperature and higher except for some molecules containing hydrogen. The vibrational portion of the partition function is approximated by that of a harmonic oscillator. The partition function expressions for vibration, rotation and translation are multiplied together to obtain the complete partition function. Taking the ratio of the complete partition functions for the molecules containing the light and heavy isotopic species and simplifying the resulting expression with the Teller - Redlich relationship which relates moment of inertia, atomic and molecular weights, we get a quotient of the type

$$\frac{Q_A}{Q_A^*} = \frac{\sigma}{\sigma^*}\left(\frac{M^*}{M}\right)^{\frac{3n}{2}} \prod_j \frac{u_j^*}{u_j} \cdot \frac{e^{-u_j^*/2}}{e^{-u_j/2}} \cdot \frac{1-e^{-u_j}}{1-e^{-u_j^*}} \qquad (3\text{-}3)$$

where $u_j = h\nu_j/kT$, the σ's are symmetry numbers, M's are the atomic weights of the substituted isotopic species, and n is the number of atoms of the isotopic species per molecule which is exchanged. The equilibrium constant is obtained by calculating a similar expression for the partition functions of compound B, the second compound in the exchange reaction and then taking the ratio of the two expressions, each raised to the appropriate power, as in equation (3-1). This expression is exact, but its usefulness is limited by the assumptions that the system is an ideal gas of non-interacting particles and that the molecules are rigid rotor-harmonic oscillators. In fact, there is not complete separation between the rotational and vibrational modes and molecules are not strictly harmonic oscillators. Vibration-rotation coupling is generally ignored in calculations of this type, but the effects of anharmonicity can be significant. The vibrational partition function is often corrected by a multiplicative correction factor which is experimentally determined. For some molecules containing hydrogen, especially linear and diatomic ones, the rotational partition function cannot be approximated by the classical expression at room temperatures, and the quantum expression must be used.

Bigeleisen and Mayer (5) and Urey (105) have developed approximations to make the calculations less tedious. The chief importance of the approximations as far as this discussion is concerned is to show clearly that the logarithm of the equilibrium constant varies as $1/T$ for large values of u (low temperature or high frequency) and as $1/T^2$ for small values of u (high temperature or low frequency).

When the equilibrium constant is calculated by taking the ratios of two expressions of the type (3-3), the terms for the ratios of the masses cancel. The important terms are then those containing the frequency, or u. Of these terms, $e^{-u^*/2}/e^{-u/2}$ is a result of the difference in zero point energies of the molecules containing the isotopic species relative to the potential energy minimum of the bonds. The term $1-e^{-u}/1-e^{-u^*}$ is a result of the differences of vibrational energy levels, and the term u^*/u corresponds to the translational and rotational terms.

A large number of calculations have been made by this and similar techniques for isotopic exchange involving gases and ions in solution. Urey (105) has tabulated the results of some of these calculations and compared them with experimentally determined values where available. The agreement between the experimental and calculated values is generally quite good, especially considering that the actual systems do not always show the ideal behavior assumed in the postulates of the calculations.

The partition function ratio for liquid water may be obtained by multiplying the experimentally determined vapor-pressure ratio of the isotopic species by the calculated partition function ratio for the gas phase.

$$\frac{Q^{liq}_{H_2O^{18}}}{Q^{liq}_{H_2O^{16}}} = \frac{Q^{gas}_{H_2O^{18}}}{Q^{gas}_{H_2O^{16}}} \cdot \frac{P_{H_2O^{18}}}{P_{H_2O^{16}}}$$

where $P_{H_2O^{18}}$ and $P_{H_2O^{16}}$ are the partial pressures of the two water molecules.

McCrea (69) extended the above calculations to include the crystalline state of the calcite - water system. He considered a different set of energies and corresponding partition functions than the translational, rotational and vibrational energies used in the gas state calculations. Rather he used the internal vibrations of the carbonate ion, the vibrations of the lattice positions, and the restricted rotation of the carbonate ion within the lattice. He then calculated the partition function for the vibration of the lattice positions in terms of a Debye function which relates the vibrations of the lattice positions to the accoustical properties of the crystal. The partition function for rotation of the carbonate ion is treated as a type of vibration and calculated using an Einstein function which assumes each atom acts as an independent harmonic oscillator. Calculations performed in this way were in good agreement with the experimental values which

McCrea measured.

One more step remains in relating calculated values of the equilibrium constant to measurable quantities. The quantity which is experimentally determined is the fractionation factor, α . If we assume that the isotopes are randomly distributed through the molecules so that there is no intra-molecular fractionation and that isotopic equilibrium prevails, then, since in the exchange reaction

$$a\ A_r + b\ B_s^* = a\ A_r^* + b\ B_s$$

$$\frac{[A^*]}{[A]} = \frac{[O^{18}]^r}{[O^{16}]^r} = \left(\frac{O^{18}}{O^{16}}\right)^r$$

we obtain the expression

$$\alpha = \frac{\left(\frac{O^{18}}{O^{16}}\right)_A}{\left(\frac{O^{18}}{O^{16}}\right)_B} = \frac{\left\{\frac{[A^*]}{[A]}\right\}^{\frac{1}{r}}}{\left\{\frac{[B^*]}{[B]}\right\}^{\frac{1}{s}}} = \frac{\left\{\frac{[A^*]}{[A]}\right\}^{a\cdot\frac{1}{ar}}}{\left\{\frac{[B^*]}{[B]}\right\}^{b\cdot\frac{1}{bs}}} = K^{\frac{1}{ar}} = K^{\frac{1}{bs}}$$

It will be noted that the relationship between equilibrium constant and fractionation factor is exact only when the isotopes are randomly distributed in a particular molecule. This is generally valid to within experimental error. The greatest deviation from ideality in this sense which is of any concern here is in the reaction

$$H_2 + D_2 = 2HD$$

for which the equilibrium constant, $K = 3.26$ at 25°C rather than the ideal value of 4. As can be seen in Table 1, even this large intramolecular fractionation has little effect on the measured $(HD)/H_2$ ratio when dealing with the low abundances of deuterium normally found in nature. It could be important in highly spiked deuterium - rich systems used in experimental tracer studies. For the remainder of the present work it will be assumed that intramolecular fractionations are negligible.

TABLE 1

Effect of intramolecular fractionation on measured D/H ratio

H/D ratio	ideal $\frac{HD}{H_2}$ (K=4)	actual $\frac{HD}{H_2}$ K=3.26	percent deviation
1	2	1.806	10%
5000	$4x10^{-4}$	$4.00x10^{-4}$	< 0.1%

Because the equilibrium constant is the quotient of the two partition function ratios, each raised to the appropriate power, and because the ratios are large numbers, similar in magnitude, a very small error in the partition function ratios may result in a much larger error in the equilibrium constant and a very large error in the calculated δ-values of minerals in isotopic equilibrium. The theoretical treatments are therefore more useful in understanding the isotope fractionations observed and their temperature dependence than they are in predicting fractionation factors.

3.3 Non-equilibrium considerations

The isotopic compositions of minerals may not always be determined by processes which lead to isotopic equilibrium. Kinetic isotope fractionations are due to differences in reaction rates or translational velocities of molecules containing different isotopic species. An example of a kinetic effect which is the result of different reaction rates of isotopically substituted molecules is observed in the electrolytic decomposition of water. A kinetic effect which is the result of varying velocities of the isotopic species is found in the reaction of O_2 with a hot carbon rod to form CO_2 (Taylor and Epstein (103). Cognizance must be taken of the possibility that kinetic effects in the formation of sedimentary minerals might occur during precipitation from solution and in hydration, dehydration and other reactions in which hydrogen and/or oxygen are gained by or lost from a solid phase.

Sometimes the conditions under which a reaction occurs can preclude the attainment of isotopic equilibrium.

The rapid precipitation of calcium carbonate from aqueous solution is an example of such a case. McCrea (69) showed that calcium carbonate, when slowly precipitated, forms in isotopic equilibrium with water, but when it is precipitated rapidly its isotopic composition is that of the bicarbonate ion in solution. Under conditions of rapid precipitation there is not sufficient time for the carbonate of the solid to equilibrate with the water before it is shielded by overlying, subsequently formed layers of the crystal. While this is not a kinetic effect in the sense in which the word is used here it is an example of an effect which can cause a mineral to have an isotopic composition reflecting formation under non-equilibrium conditions.

3.4 Diffusion and kinetics of isotope exchange

The rate at which a solid attains isotopic equilibrium with its environment is governed by the rate at which the exchanging isotopes can enter, move through and leave the crystal. In some instances exchange may occur through the mechanism of solution and redeposition (O'Neil and Taylor (80)). In other instances exchange may occur by diffusion of the exchanging isotopes.

Urey *et al.* (107) considered the problem of solid state diffusion of carbonate ions in calcite in conjunction with the durability of isotope records in the calcite - water paleotemperature scale. Using questionable values for the diffusion coefficient, they calculated that at 20°C a crystal 1mm on an edge would retain 96.4 percent of its original isotopic composition relative to a new equilibrium position over a period of 700 x 10^6 years. At a temperature of 100°C this time is reduced to 64 x 10^3 years. Because these calculations suggest that solid state diffusion could be important in some diagenetic environments if not for strictly sedimentary ones, and because many of the minerals dealt with in this study are extremely fine grained, ($<10\,\mu$), the calculations for solid state diffusion will be reexamined.

Urey et al. (107) give the diffusion equation for a cube as

$$\frac{Q}{Q_o} = \frac{512}{\pi^6}\left\{\sum_{m=0}^{\infty} \frac{1}{(2m+1)^2}\, e^{-a(2m+1)^2}\right\}^3 = \frac{\left(\frac{O^{18}}{O^{16}}\right)_\infty - \left(\frac{O^{18}}{O^{16}}\right)_t}{\left(\frac{O^{18}}{O^{16}}\right)_\infty - \left(\frac{O^{18}}{O^{16}}\right)_{\text{initial}}}$$

where

$$a = \frac{D\pi^2 t}{l^2}$$

Q/Q_o = fraction of exchange left to go

t = time

D = diffusion coefficient

l = length of the edge of the cube

These writers have calculated that when a = 0.1, Q/Q_o= 0.461. Figure 3 is a graph of diffusion coefficient vs time for 53.9 percent exchange (or 46.1 percent retention of the isotopic record) for solid cubes of edges 100μ, 10μ, 1μ, and 0.1μ. This graph can be used as an aid to understanding the importance of diffusion in the solid state for fine grained minerals.

The evaluation of diffusion coefficients of oxygen and hydrogen in solids is difficult. While a few measurements are available from the rates of exchange experiments, most are calculated from electrical conductivity measurements and assumptions as to the amount of the current which is carried by the migrating species of interest.

Verhoogen (109) has calculated the diffusion coefficient for oxygen in quartz at 500°C parallel to the c axis, based on the assumption that all the current was carried by diffusing oxygen ions. His data can be extrapolated to low temperatures, but the extrapolations are fraught with uncertainties. Based on conductivity measurements in calcite and the assumptions that the carbonate ion provides one percent of the current carying species, Urey et al. (107) have calculated the diffusion coefficient for calcite. Anderson (116) has measured the diffusion of CO_2 in calcite and his results have been extrapolated to low temperatures. Garlick has estimated the diffusion

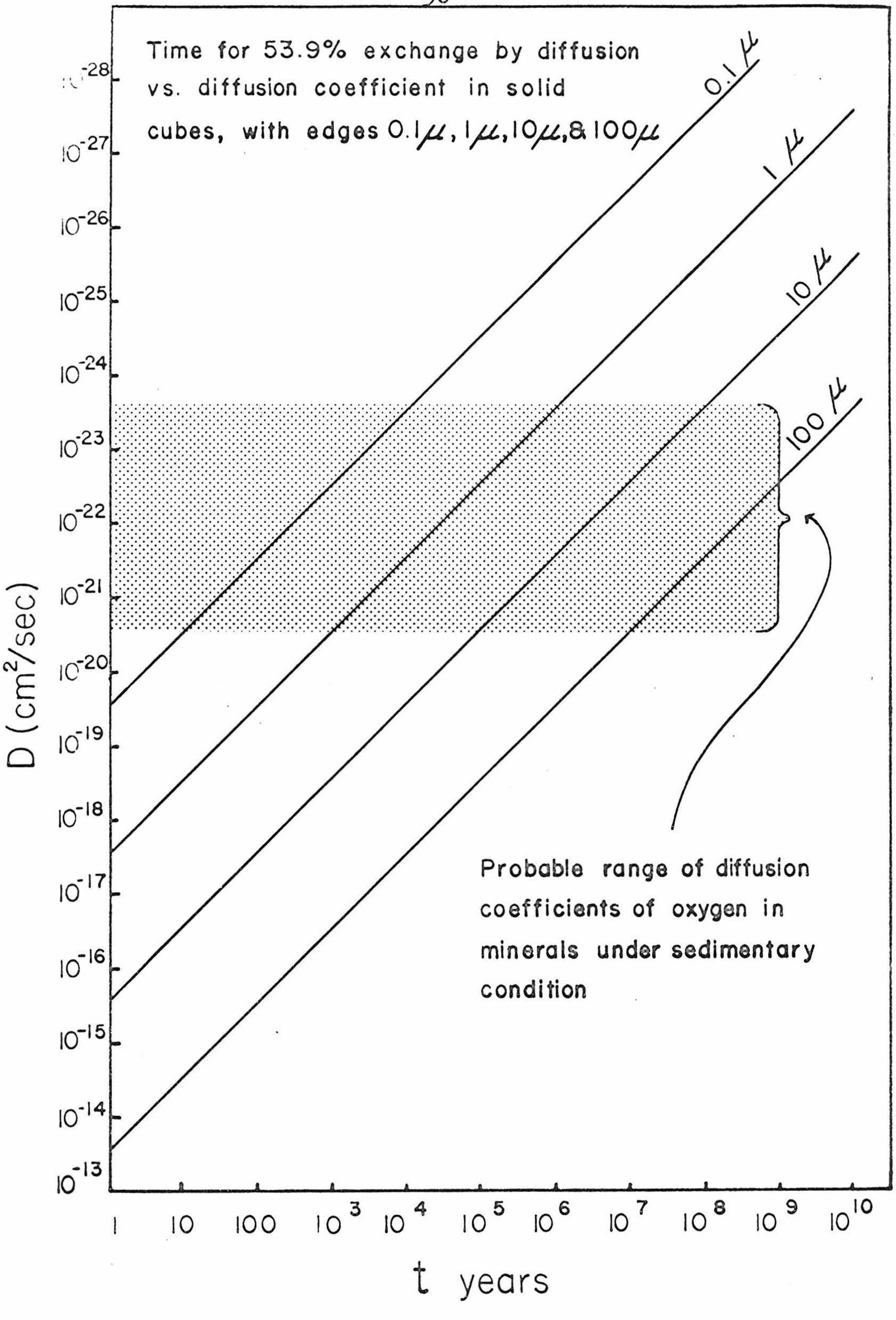


Figure 3. Time for 53.9% exchange by diffusion in solids plotted as a function of diffusion coefficient

coefficient of volcanic glass based on the amount of isotopic exchange which occurred in fine grained (0-6 μ) volcanic glass shards in a Miocene ocean sediment. The results of the above calculations are listed in Table 2.

TABLE 2

Estimated values of diffusion coefficients in minerals at low temperatures

Mineral	Postulated Diffus. species	Type of data	Temp. °C	D cm^2/sec	Ref.
Calcite	$CO_3^=$	conductivity	20	4.4×10^{-23}	Urey *et al.*
			100	4.8×10^{-20}	(107)
Calcite	CO_2	diffusion	0	3.2×10^{-23}	Anderson
			27	4.3×10^{-22}	(116)
Quartz	$O^=$	conductivity	0	1.2×10^{-23}	Verhoogen
			27	2.9×10^{-21}	(109)
Volcanic glass		exchange of natural sample	2	$\sim 10^{-23}$	Garlick (39a)

A comparison of the data of Table 2 and the theoretical lines of figure 3 for 53.9 percent diffusion shows that diffusion in the solid state cannot be dismissed as a mechanism for isotope exchange in the fine grained sedimentary minerals. Even if diffusion coefficients have been over estimated by three or four orders of magnitude this mechanism might be important in some sedimentary environments for crystals with dimensions of 10 μ or less.

A number of attempts have been made to exchange the hydrogen (and oxygen) of the hydroxyl groups in clays. (McAuliffe et al. (68), Roy and Roy (90), Halevy (51)). All of these experiments were designed to measure rates of exchange and were not capable of measuring fractionation factors. The results of the work of Roy and Roy indicate that while at room temperature the rate of exchange is very slow, at temperatures of 190°C it is noticeable in 22 days and at temperatures of 370°C it is very marked in a period of a month. These authors conclude that isotopic exchange of hydroxyl hydrogen of kaolinite should be significant even at low temperatures over geologic time.

The experimental results of the present study indicate that at temperatures of 0° to 5°C there is no isotopic exchange of hydrogen between clay minerals and water over periods of 250,000 to 500,000 years. At temperatures substantially above room temperature but below metamorphic temperatures, exchange between clay minerals and water probably occurs quite readily. However, as the data of Garlick (39a) have shown, over periods of millions of years at ocean-bottom temperatures could be significant.

CHAPTER IV

EXPERIMENTAL TECHNIQUES

4.1 Hydrogen isotope measurements

The most important hydrogen bearing minerals of sediments are the clays. In some sediments hydrous oxides and amorphous compounds may also contain significant amounts of hydrogen.

All clay minerals contain hydroxyl groups as part of the octahedral layers of the silicate framework. In addition many clays contain molecular water which occupies structural positions between the layers of the aluminosilicate framework and also contain varying amounts of adsorbed water.

The adsorbed water and the interlayer water may be removed from the clay minerals by heating to low temperatures or even at room temperature in a vacuum. The conditions necessary to remove this water are discussed in detail in section 4.5. The hydrogen of the hydroxyl groups may be evolved by heating the clays to temperatures of 800° or 900°C. At these temperatures most of the hydrogen is evolved as H_2O but some may be evolved as molecular hydrogen. As will be pointed out in a later section, the interlayer and adsorbed water were found to be labile. Because no precautions were taken during sampling, storage, and preparation of materials to prevent exchange of this water with the atmosphere, its isotopic composition as measured in the laboratory was not representative of its composition in the natural environment. It was therefore usually desired to remove the interlayer water and then to extract the hydroxyl hydrogen for mass-spectrometric measurement.

The apparatus used for the extraction of hydrogen from minerals is shown schematically in figure 4. The procedure used consists of three parts, the removal of interlayer and adsorbed water, the conversion of all the hydroxyl hydrogen to H_2O, and the subsequent conversion of this H_2O to H_2. Usually 75 to 200 mg of a finely ground sample is weighed into a quartz glass boat which is placed in the quartz glass part of the line. The line is then evacuated while heating to a temperature between 125° and $250^{\circ}C$. These temperatures have been determined to be sufficient to permit the removal of the adsorbed and interlayer water in a period of two to three hours (Section 4.5). After outgassing the sample, the stopcocks to the vacuum pump are closed, the furnaces are raised to $900^{\circ}C$, and the water evolved is collected in trap T 1. Any hydroxyl hydrogen evolved as molecular H_2 is converted to water by hot CuO placed in the furnace next to the sample boat. After heating the sample at

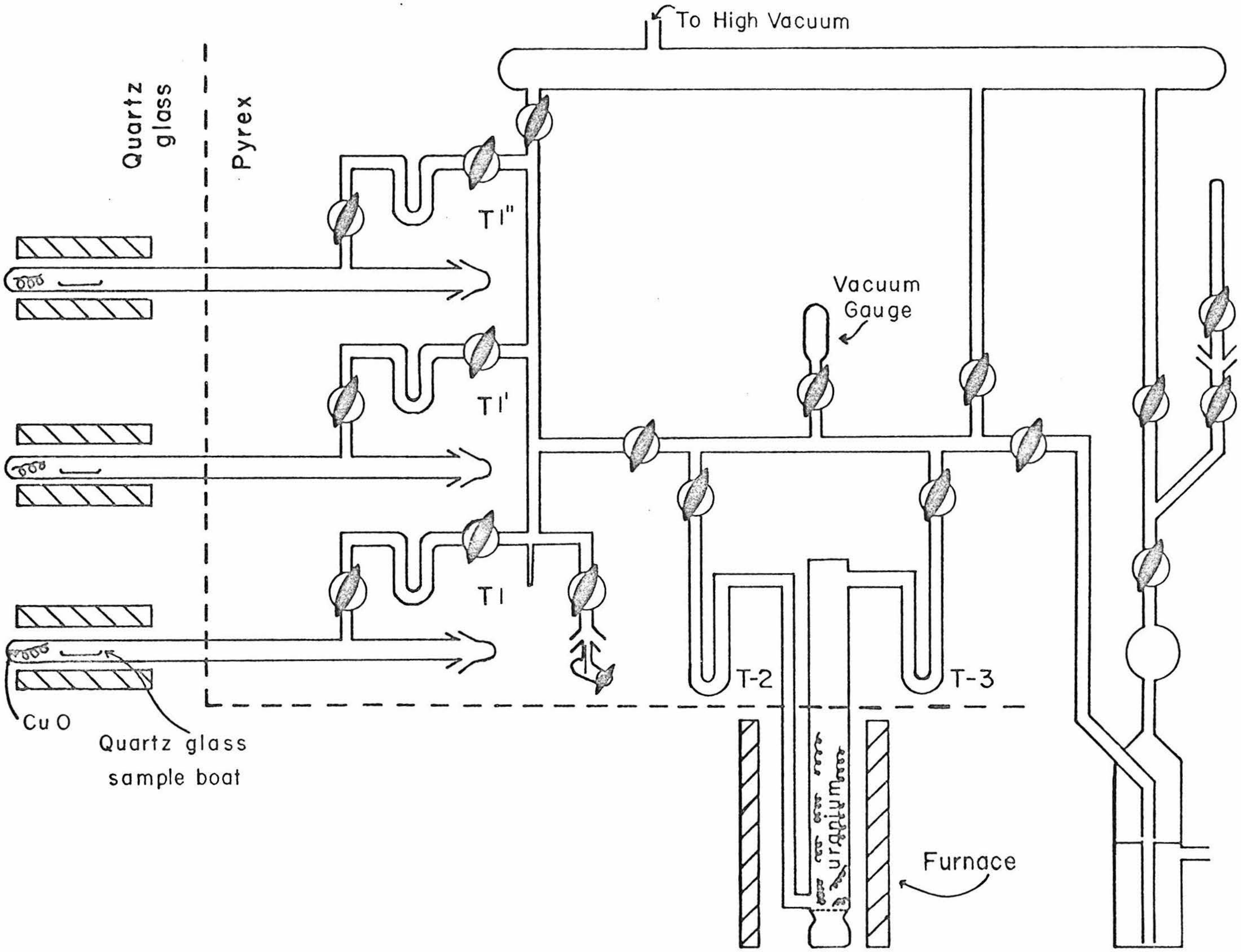


Figure 4. Apparatus used for extracting hydrogen from minerals

900°C for at least three hours, the furnace is isolated from trap T 1 by means of a stopcock. Trap T 1 is then warmed in a dry ice bath, permitting any CO_2 present to be pumped away. The water is transferred from trap T 1 to trap T 2 and allowed to warm and pass through the furnace containing uranium filings heated to 675°C. The uranium reduces the H_2O to H_2 which is pumped into the manometer by the Toepler pump. After measuring the volume of the gas it is forced into a sample tube and measured mass-spectrometrically.

The mass spectrometer used for hydrogen isotope measurements is similar to the mass spectrometer commonly used for CO_2 analyses (Nier (75), McKinney et al. (70)), with modifications because of the large relative mass difference between hydrogen and deuterium (Nier (75), Friedman (37)). An extra arm, containing the mass-2 collector is added to the mass spectrometer tube, since if the mass-3 beam is deflected 60° , the mass-2 beam is deflected 71°.

The mass spectrometer reference gas is produced from an aliquot of a distilled water sample. The isotopic composition of the reference gas is established through its relationship to a water sample, LJ-2, furnished to this laboratory by Professor Harmon Craig. Craig has determined the isotopic composition of LJ-2 to be -0.3 percent relative to S.M.O.W. The δ-value of LJ-2 relative to the mass spectrometer standard is +7.20 percent. Therefore S.M.O.W. has a δ-value of +7.49 percent relative to the mass spectrometer reference gas, or the mass spectrometer reference gas has a δ-value of -6.97 percent relative to S.M.O.W. By Craig's (19) definition, $(D/H)_{SMOW} = 1.050$ $(D/H)_{N.B.S.-1}$. N.B.S.-1 is a water standard obtainable from the National Bureau of Standards.

The working standards used in the hydrogen isotope measurements of this work were a water with a δ-value of -6.71 percent and a kaolinite sample (Wards No. 492, Langley, S. Carolina) which has a δ-value of -5.67 percent.

The water standard is introduced into the hydrogen line by means of a sealed glass capillary. The capillary is broken inside the line and converted to hydrogen as described above. Average deviation from the mean of the δ-value of the secondary standard is 0.16 percent for 18 runs as may be seen in Table 3.

Memory effect in the measurement of waters is less than one percent as may be seen by the results in Table 4. This is negligible because of the small total range of isotope ratios measured.

The reproducibility of hydrogen isotope measurements on minerals containing interlayer water is not as good as that for water analyses, as is evident from the data in Table 3. This is not surprising as the isotopic composition of the hydroxyl hydrogen of these clays may be affected if the interlayer water is not completely removed, or if there is not a sharp separation between the removal of interlayer water and the evolution of hydroxyl hydrogen.

TABLE 3

Precision of hydrogen isotope measurements

Sample	No. Runs	δ D (percent)	Average Deviation
H_2O Std.	18	-6.71	0.16
Kaolinite Langley, S.C.	10	-5.67	0.18
Montmorillonite Clay Spur, Wyo.	9	-9.92	0.30
Glauconite R-13	4	-8.63	0.38

TABLE 4

Memory effect in hydrogen isotope measurements

Run #	Sample	δ D (percent)	Memory
187	H_2O Std.	- 6.62	
188	H_2O Std.	- 6.79	
189	162-SP-25	-38.55	
190	H_2O Std.	- 7.00	<1%

4.2 Oxygen isotope measurements

Extraction of oxygen from silicate and oxide minerals for measurement in the mass spectrometer was done in most cases by a fluorine oxidation method. Occasionally bromine pentafluoride was used instead of fluorine. CO_2 was extracted from carbonates by reaction with phosphoric acid. A few water samples were analyzed using a special bromine pentafluoride technique (O'Neil and Epstein (78).

A. Fluorine and bromine pentafluoride oxidation

The fluorine oxidation technique has been described in detail by Taylor and Epstein (103). The bromine pentafluoride method has been discussed by Clayton and Mayeda (15) and by Garlick (39). For the present work a line was constructed capable of using either of these reagents (figure 5). The procedures used are essentially those of the above mentioned authors, and will be discussed only where significant variations from the published procedures were used.

When the line is used for fluorine reaction, the KBr furnace bypass valve, V-7, is kept closed. The manifold is placed in the drybox with samples to be loaded in the presence of P_2O_5 drying agent for a period of at least 24 hours prior to loading. (The significance of the drying time will be discussed in section 4.5 which

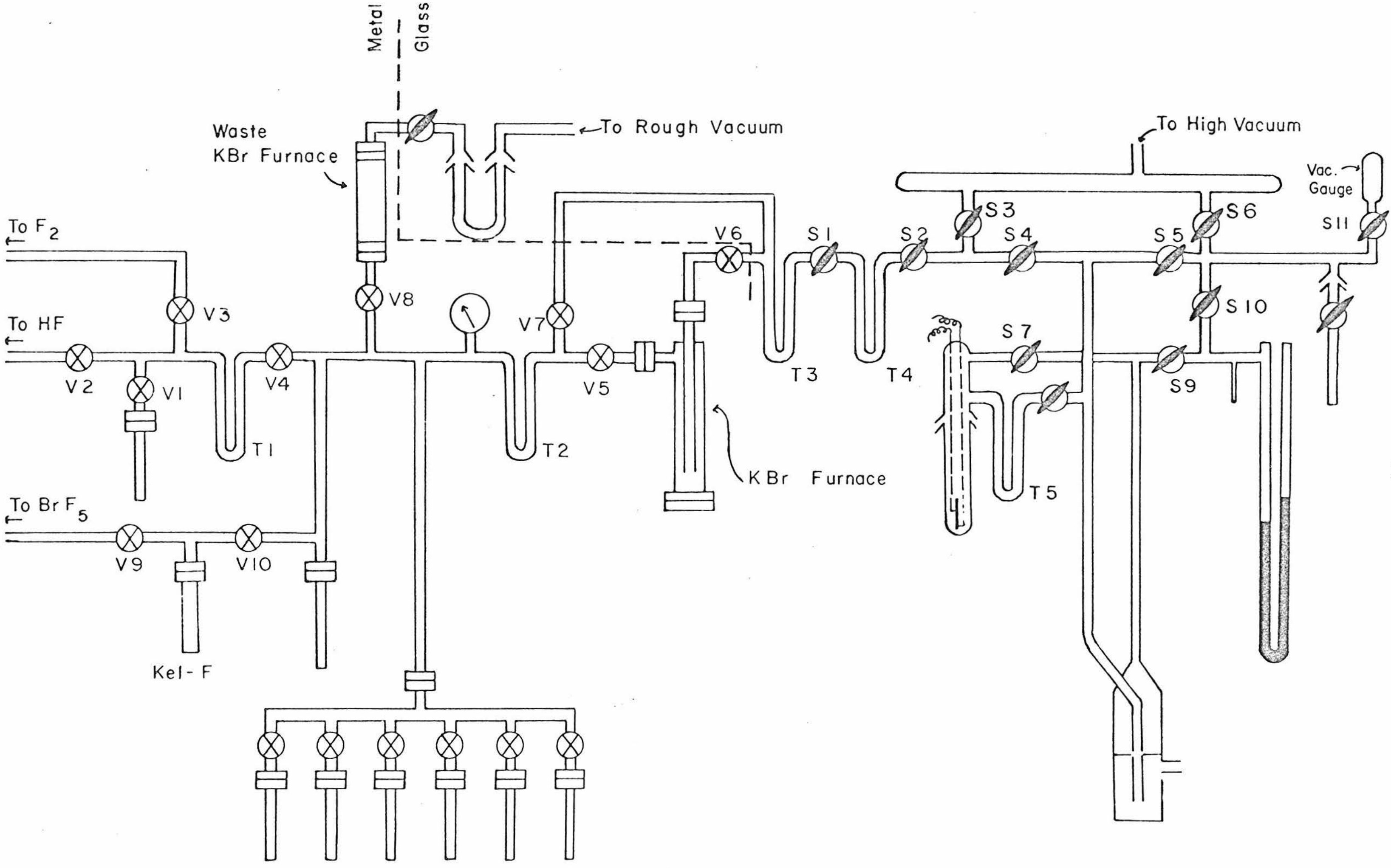


Figure 5. Fluorine-bromine pentafluoride line used for extracting oxygen from minerals

deals with the conditions of removal of adsorbed and interlayer water in clay minerals). Minerals are reacted with a 3-fold or 4-fold excess of fluorine, generally at a temperature of 475°C for silicates, but higher for oxides. After reaction, the gas passes through trap T 2, the KBr furnace and traps T 3 and T 4. After passing through these traps, the sample consists of oxygen, some nitrogen (contaminant in the fluorine), and possibly traces of untrapped halogens. It is pumped with the Toepler pump into the part of the line containing the carbon rod conversion vessel and trap T 5. Stopcocks S 8 and S 9 are closed at this time to prevent back diffusion into the metal part of the line. Carbon dioxide is trapped in trap T 5 and the conversion vessel is cooled with cold water. By the time the sample has been collected in this area of the line (about one half hour) all the oxygen should be converted to CO_2 and trapped out. The remaining gas gives the pink color of nitrogen when excited with a Tesla coil. As a precaution, at this point stopcock S 4 is closed and stopcock S 8 is opened to allow the nitrogen and any remaining oxygen to circulate over the carbon rod for ten minutes, completing the conversion of the oxygen. The nitrogen is pumped away and the volume of the CO_2 is measured in the manometer. As a precautionary measure, the CO_2 is circulated over hot mercury prior to isotopic analysis.

This step serves to remove any fluorine, bromine, or bromine pentafluoride compounds which might inadvertently escape entrapment in the liquid nitrogen traps, and was instituted to safeguard the mass spectrometer from contamination and from possible malfunction.

When bromine pentafluoride is used rather than fluorine, the KBr furnace is closed off by valves V 5 and V 6, (figure 5) and the bypass valve, V 7, is used to admit the oxygen gas into the glass part of the line. Since the BrF_5 reagent contains no nitrogen gas, the oxygen can diffuse rapidly and completely to the carbon-rod conversion vessel without the aid of a Toepler pump. The CO_2 formed at the hot carbon rod is frozen out in trap T 5. The rate of conversion can be followed by means of a thermocouple vacuum gauge.

For many minerals, bromine pentafluoride oxidation must be done at higher temperatures than fluorine oxidation. At these higher temperatures a copious coating of hygroscopic metal fluorides forms on the walls of the reaction tubes. Therefore, care must be taken to assure that the drybox is extremely dry before opening these reaction tubes used with BrF_5 to load the new samples. Otherwise, water in the drybox atmosphere will be adsorbed by these fluorides and yield contaminating oxygen in the course of the reaction.

After circulating the sample over hot mercury, its isotope ratio is measured mass-spectrometrically.

The working standard for oxygen isotope measurements is a sample of quartz from the St. Peter sandstone. The δO^{18} value of this standard was determined by Garlick (39) to be +10.95 permil, by comparison with Silverman's St. Peter sandstone (93). If this determination is in error, all reported values will have to be corrected by adding the difference between the true value and 10.95 permil.

There are long term fluctuations of over one permil in the δ-value of St. Peter sandstone measured on the mass spectrometer. This is probably due to variations in the isotopic composition of the mass spectrometer reference gas.

The isotopic composition of the mass spectrometer reference gas was checked regularly by analyzing oxygen extracted from the St. Peter sandstone standard. An aliquot of this standard was included in each set of six samples. The results of the St. Peter sandstone analyses were plotted sequentially and a smooth curve was drawn through the data. The δ-value taken from the smooth curve was assumed to be the true δ-value of St. Peter sandstone relative to the mass spectrometer reference gas. Average deviation of measured δ-values from the δ-values read from the smooth curve was 0.2 permil. The δ-value of the mass spectrometer reference gas relative to S.M.O.W.

at any time was calculated using the δ-value of St. Peter sandstone relative to the reference gas at the time of analysis of a sample.

B. Carbonate extraction

Standard methods (McCrea (69), Epstein *et al.* (34)) were used to extract CO_2 from carbonate minerals. δ-values reported are for the total oxygen of the mineral rather than merely the acid-extracted portion. The acid fractionation factors used are 1.01008 for calcite and 1.01090 for dolomite, after Sharma and Clayton (91).

C. Water extraction

A few samples of water were analyzed by oxidation with bromine pentafluoride on a line constructed for that purpose (O'Neil and Epstein (78)). Except for the manner in which the sample is introduced into the line, the procedure is similar to that described above for fluorine and bromine pentafluoride oxidation of minerals.

4.3 Mass spectrometer and other corrections

The experimentally determined isotope ratios were all corrected and reported as δ-values relative to S.M.O.W. The correction factors used are explained below

A. Hydrogen

The hydrogen mass spectrometer simultaneously measures and compares abundances of mass-2 and mass-3. The mass-3 beam consists of both HD^+ and H_3^+ ions. The H_3^+ ions are produced in the mass spectrometer source and a correction must be made for their contribution to the mass-3 signal. This correction has been described by Kirshenbaum (61) and Friedman(37). If the voltage divider resistance is denoted by R, the measured δ-value by δ_m and we define a term ΔR as being equal to R at normal operating intensities minus R when linearly extrapolated to zero beam intensity then

$$\delta_m = \frac{R\ \text{sample} - R\ \text{std}}{R\ \text{std} - \Delta R} \times 100$$

δ_m is subject to multiplicative corrections due to mass spectrometer background and leakage through the switching valves. There are also both multiplicative and additive corrections in converting the raw data to δ-values relative to the standard S.M.O.W.. The correction factors, listed in their order of application, are given below.

i. Multiplicative corrections

a.	leakage through switching valves	1.019*
b.	mass spectrometer background	1.002
c.	change of standard	0.9303
	TOTAL	0.9498

ii. Additive correction

a.	change of standard	-6.97

B. Oxygen

All fluorine - extracted samples contain a small amount of oxygen contaminant from the fluorine reagent. This blank is 9.2 μ mol of oxygen with a δ-value of +6.7 permil. The blank correction is seldom more than a few tenths of a permil and depends on both the δ-value and the size of the sample.

The mass spectrometer measures the ratio of the mass 46 beam to the mass 44 and 45 beams. Because of the presence of C^{13} and O^{17} species $\delta\left(\frac{46}{44+45}\right)$ is unequal to $\delta\ \frac{O^{18}}{O^{16}}$ which is the value of interest. The derivation of the correction factor for this correction is given by Craig (20a). If numbers appropriate to the mass spectrometer

---

*The correction factor for leakage through the switching valves was variable and was occasionally as small as 1.015.

standard are substituted into this derivation, the measured δ is denoted by δ_m and the corrected δ by δ_c, we obtain the expression

$$\delta_c O^{18} = 1.001\ \delta_m + 0.009\ \delta C^{13}$$

However, since all CO_2 samples have essentially the same carbon isotopic composition, including the quartz standard, St. Peter sandstone to which all measurements are ultimately referred, we can neglect the additive term in δC^{13} and use only the multiplicative correction 1.001. The corrections and the correction factors for oxygen are listed below in the order of their application.

i. Multiplicative

a.	C^{13} and O^{17} correction	1.001
b.	mass spectrometer background	1.018
c.	leakage through mass spectrometer valves	1.008
	TOTAL	1.027

ii. Blank correction

a. differs for each sample-material balance

iii. Multiplicative

a.	change of standard	1.024

iv. Additive

a. change of standard - variable approx. +24.5

4.4 Sample preparation and treatment

Mineral separations in coarse-grained materials were done in the usual ways, using magnetic susceptibility techniques where possible and heavy liquids where necessary. Quartz was sometimes cleaned of iron oxide coatings by heating in aqua regia and was occasionally separated from feldspar of the same magnetic succeptibility by washing for a few minutes in cold HF. This method should have no effect on the isotopic composition of isotopically homogeneous quartz and was not used on quartz which appeared petrographically to have secondary overgrowths.

Fine-grained materials were generally subject to few or no separation procedures. The processes by which the samples were prepared for analysis depended upon the nature of the particular samples and upon whether they were being prepared for hydrogen or oxygen analysis.

A. Preparation of samples for hydrogen analysis

Samples which appeared dry were ground in an agate mortar to finer than 100 mesh. They were subject to no other treatment or precautionary measures to protect them from atmospheric moisture. Samples which did not appear dry, such as fresh ocean bottom cores were allowed to dry in the air at room temperature for periods ranging from a few days to a few weeks. They were then subject to the same treatment as dry samples.

B. Preparation of samples for oxygen analysis

1. Ocean bottom sediments

Ocean core samples were subject to treatment to remove salts of sea-water, to remove carbonate minerals, and to separate them into coarse and fine fractions. The procedure followed was to place approximately 300 mg. of the sample in a glass vessel with enough acetic acid-lithium acetate buffer solution (pH=5) to dissolve all the carbonate present in the sample. The δO^{18} value of the water used to make the buffer solution was 0.0 permil. The removal of the carbonate generally took from a few hours to a few days, depending on its amount and its grain size. The clay-liquid suspension was then wet-sieved through a 325 mesh sieve into a Millipore filter. The coarse and fine-grained portions were washed thoroughly with distilled water ($\delta O^{18}=0$) and air dried. The fine grained portion generally dried into a hard cake which was broken up in an agate mortar prior to measurement of its isotopic composition.

ii. Relatively pure clay deposits

Samples of relatively pure clay deposits were ground to P 100 mesh in an agate mortar.

iii. Shales

Non-carbonate containing shales were ground in an agate mortar to pass a 200 mesh sieve. Carbonate-containing shales were subject, after grinding, to leaching in an acetic-acid--lithium acetate buffer solution, as were the ocean sediments.

C. Special considerations

It was necessary to verify that none of the mineral separation procedures used, especially leaching of the carbonate in acid solution, produced any change in the isotopic composition of the minerals. The data of Roy and Roy (90) on rates of exchange of deuterium between water and clays make it seem highly unlikely that any significant exchange could occur at room temperature even over a period of a few years. However, because of the possibility that the acid in the water could catalyze an isotope exchange reaction, aliquots of three samples were treated with buffer solutions made with waters of differing isotopic compositions. (Both waters used were isotopically lighter than the clay, but one was lighter and one heavier than the waters with which the clays may have been expected to be formed or exchanged.) The results are shown in Table 5. Kaolinite and the Green River Shale appear to be unaffected by the exchange, although analyses after treatment are not as reproducible as analyses before treatment. The montmorillonite seems to contain more O^{18} after treatment regardless of whether it was treated with the light or heavy acid solution. This probably is a result of solution of an isotopically light impurity. As a precautionary measure, however, all leaching solutions used with ocean sediments were made from waters for which $\delta O^{18} = 0$. Thus, if any exchange did take place, it would be with water of the same isotopic composition as that in which the sample had been for thousands of years.

4.5 Problem of the different types of oxygen and hydrogen positions in sedimentary minerals

It was pointed out in section 4.1 that clay minerals may contain oxygen and hydrogen both as part of the aluminosilicate lattice and as adsorbed and interlayer water molecules. Therefore, in order to make meaningful measurements of the oxygen and hydrogen isotopic compositions of clay minerals it is first necessary to determine under what conditions the adsorbed and interlayer water may be removed, whether it is possible to extract all or

TABLE 5

Effect of leaching clay minerals with acetate-acetic acid buffer solutions of different isotopic compositions

Run	Mineral	Time leached	p^H	δO^{18} of acid (per mil)	Clay δ orig.	Clay δ final	$\delta_{final} - \delta_{orig}$
22	Kaolinite	1 hr.	5	-9.87	+21.03±0.25	+22.10±0.03	1.1±0.3
24	Kaolinite	1 hr.	5	+13.20	+21.03±0.25	20.85±0.23	-0.1±0.5
25	Kaolinite	7 hrs.	5	-9.87	+21.03±0.25	21.80±0.15	0.7±0.4
11	Kaolinite	24 hrs.	3.75	-9.87	+21.03±0.25	21.53±0.19	-0.5±0.5
21	Montmorillonite	1 hr.	5	-9.87	+17.20±0.17	17.99±0.50	0.8±0.7
23	Montmorillonite	1 hr.	5	+13.20	+17.20±0.17	18.81±0.25	1.6±0.5
12	Montmorillonite	24 hrs.	3.75	-9.87	+17.20±0.17	18.33±0.36	1.1±0.6
32	Gr. R. Shale	6 hrs.	5	-9.87	+18.2 ±0.2	17.90±0.35	-0.3±0.5
33	Gr. R. Shale	6 hrs.	5	+13.20	+18.2 ±0.2	18.39±0.07	0.2±0.3

almost all of the interlayer water while removing none of the oxygen or hydrogen of the aluminosilicate framework, and whether it is possible to extract the interlayer water without causing isotopic exchange with the oxygen and hydrogen of the aluminosilicate lattice.

A number of tests were performed to answer these questions and to establish the correct analytical procedures for clay minerals. It may be concluded from these tests that over a wide range of experimental conditions almost all the adsorbed and interlayer water can be removed from clay minerals and that the small amounts of interlayer water remaining have only slight effects on the isotopic composition of the minerals.

A. Tests related to the extraction of hydrogen from clay minerals

Two series of experiments pertaining to the removal of interlayer water and the extraction of hydroxyl hydrogen from clay minerals were made using hydrogen extraction techniques. The first series was designed to determine the temperature conditions under which interlayer water and hydroxyl hydrogen were evolved from clays in a vacuum, and to determine the sharpness of the separation between the evolution of interlayer water and that of hydroxyl hydrogen. The second series of experiments, which was more closely related to routine analytical procedure, was designed to measure the effect on the isotopic composition of hydroxyl hydrogen of outgassing clays for different lengths of time and at different temperatures.

i. Experiments to determine conditions of outgassing of interlayer water

In this series of experiments clay minerals were held at a fixed temperature for an interval of 24 hours, and the water evolved during this time was collected and analyzed for hydrogen isotope ratio. At the end of the 24 hour interval the temperature of the furnaces was raised and the water evolved during the next 24 hour period was collected and analyzed. Aliquots of three samples, two montmorillonites and an illite, were analyzed in this way. Beginning with two 24 hour periods at room temperature, the temperature was raised in seven successive steps to 900°C, at which temperature all the hydrogen had been evolved. A second aliquot of one of the samples (Clay Spur, Wyoming) was heated rapidly to 130°C when first placed in the line and was subsequently treated as described above. The results of these experiments are shown in figure 6 and are compared with differential thermal analyses (D.T.A.) of the same samples by Kerr, Kulp and Hamilton (59). It may be seen in this figure that large amounts of water are evolved at room temperature, corresponding to adsorbed and interlayer water, and at higher temperatures, (beginning

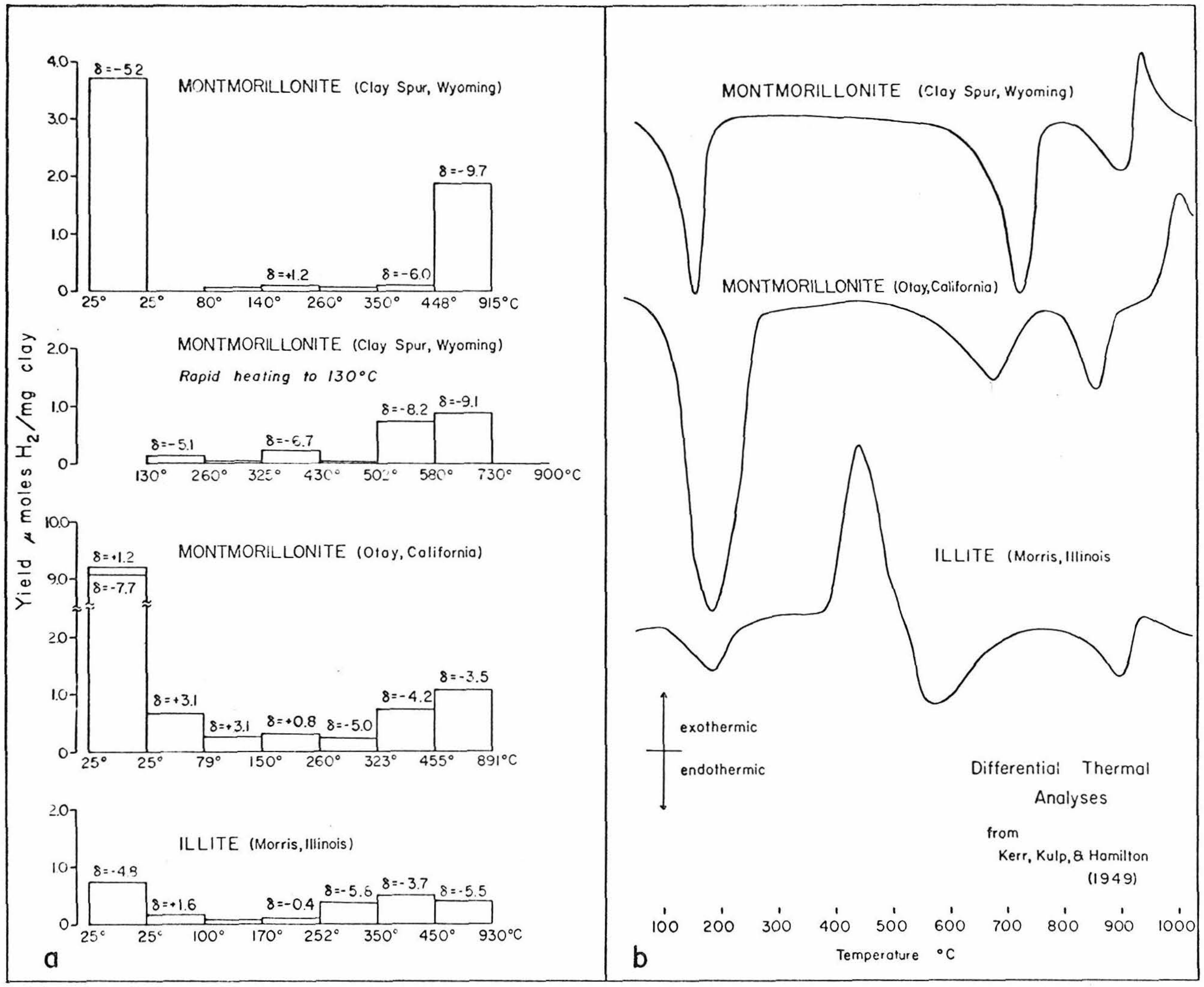


Figure 6. a) Amount of hydrogen removed from clay minerals in a vacuum at successively higher temperature ranges. Each bar represents amount evolved in 24 hours in the temperature range indicated.
b) D.T.A. curves of same samples

at 250° to 500°C, depending on the particular sample,) corresponding to the hydroxyl hydrogen. At intermediate temperatures a smaller amount of water is evolved, corresponding primarily to interlayer water which was not evolved at lower temperatures, and to a small extent to hydroxyl hydrogen liberated at lower temperatures than the bulk of the hydroxyl hydrogen.

Evidence for the origin of water evolved in the intermediate temperature range is obtained from the isotopic data. In one of the samples (Otay, Calif.) a small amount of water was evolved during the second 24 hour period, and that water was markedly richer in deuterium than was the water evolved in the first 24 hour period ($\delta D = +1.2$ vs $\delta D = -7.8$). This is undoubtedly the result of a fractionation during removal of the interlayer water, with preferential removal of isotopically lighter H_2O. This same enrichment of deuterium is observed in the water driven off between 25° and 250°C for all samples which were outgassed at room temperature. It is not observed for the sample which was outgassed by heating rapidly to 130°C. Therefore, the fractionation which may be observed during removal of interlayer water occurs only when the water is removed slowly at low temperatures. In the temperature range 250° to 350° or 450°C small amounts of water are evolved but are not deuterium rich. This water must then be from a different source than the interlayer water removed at low temperatures. The most likely source is the hydroxyl hydrogen and the oxygen partially liberated at a lower temperature than the major portion of the hydroxyl groups. This might occur if these groups were at grain edges or near crystal defects and were weakly bonded to the crystal lattice. The above explanation has some basis because a kaolinite heated in a related experiment was found to give off no water at temperatures below 125°C, 0.151μ mol/mg between 125° and 206°C, and 0.413 μ mol/mg between 206° and 340°C. Since the kaolinite contains no interlayer water and adsorbed water would probably be evolved at lower temperatures this water must have had its source in the hydroxyl groups of the mineral.

There is a correlation between the sharpness of separation of interlayer water and hydroxyl hydrogen and the sharpness of the D.T.A. peaks. This may be a function of the grain size or of the crystallinity of the samples.

ii. Experiments to determine effects of outgassing on the isotopic composition of the hydroxyl hydrogen

The analytical procedure for clay minerals involves outgassing samples at low temperatures under vacuum and then heating to high temperatures to drive off the hydroxyl hydrogen. Since the conditions of outgassing affect both the amount and the isotopic composition of the water evolved, it is necessary to examine the effects of temperature and length of time of outgassing on the measured isotopic composition of the hydrogen subsequently evolved at high temperatures.

A series of tests was made in which an aliquot of a mineral or rock sample was outgassed in the hydrogen line for a known length of time at a known temperature, and the water evolved was collected. After outgassing, the sample was heated to 900°C and a second portion of water was given off. The two portions of water were analyzed isotopically. This procedure was then repeated with another aliquot of the sample, outgassing at a different temperature and for a different length of time. These experiments were done on a montmorillonite (Clay Spur, Wyoming) and an ocean sediment (A·296·4). The isotopic compositions and amounts of hydrogen evolved under the different conditions are shown in the data of Table 6. As the data of this table shows, the temperature of outgassing has no significant effect on the isotopic composition of the hydrogen evolved at high temperature. Montmorillonite samples outgassed longer than 14 hours average a few tenths of a percent more negative in δD than those outgassed 4 hours or less. This difference is almost within experimental error. There is a scatter in the yield data for both the hydrogen evolved at low tem-

TABLE 6

Effect of outgassing temperature on the measured hydrogen isotopic compositions of outgassed water and hydroxyl hydrogen

a. montmorillonite (Clay Spur, Wyoming)

Run	Outgas T° C	Outgas Time hrs.	Outgas δD	Yield μ mol/mg	Hydroxyl δD	Yield μ mol/mg
130	25	2	-5.14	2.50	- 9.16	2.77
116	40	4	-5.43	????	-10.12	3.20
128	91	15	-5.45	2.50	-10.20	2.02
121	95	4	-7.04	1.98	- 9.88	3.30
125	147	17	-????	2.24	-10.26	2.61
122	206	4	-6.35	1.97	- 8.98	3.68
126	252	17½	-????	2.37	-10.67	2.73
127	253	15	-5.73	2.43	- 9.84	2.10
129	303	4	-5.27	2.28	- 9.68	2.24
117	344	2½	-5.46	????	- 9.88	3.08
		AVERAGE	-5.73 ±0.48	AVERAGE	- 9.87 ±0.36	

b. ocean sediment (A-296-4)

Run	Outgas T° C	Outgas Time hrs.	Outgas δD	Yield μ mol/mg	Hydroxyl δD	Yield μ mol/mg
134	25	4 3/4	-6.69	1.26	-5.67	2.84
137	25	16	-5.23	0.82	-5.37	2.77
135	150	5 1/2	-7.90	1.72	-5.90	1.95
136	265	16	-4.92	1.39	-6.05	2.10
		AVERAGE	-6.19 ±1.1	AVERAGE	-5.75 ±0.23	

perature and that evolved at high temperature, but there exists no correlation between yield and either δ-values or temperatures of outgassing.

It may also be ascertained from the data in Table 6 that no significant isotopic exchange between the interlayer water and the hydroxyl hydrogen occurs during the outgassing procedure. If such an exchange were to occur, it would be expected to be temperature dependent and would be evident in the experimental data.

As a result of these tests, the procedure adopted for hydrogen extraction throughout this work involved routine outgassing at temperatures between 100° and $250^{\circ}C$. In order to minimize systematic experimental error no effort was made to maintain constant the length of time or the temperature of outgassing or the amount of sample analyzed.

B. Tests related to the extraction of oxygen from clay minerals

The nickel vessels in which samples are reacted with fluorine to liberate oxygen become lined with an extremely hygroscopic layer of fluorides. In order to prevent the adsorption of water by this fluoride coating it is necessary to dry the reaction vessels and the samples in a drybox containing P_2O_5 prior to opening the vessels for loading. Experimentally it is difficult to subject samples to dehydration in a vacuum at elevated temperatures prior to loading them in the reaction vessels, and it is not possible to dehydrate them in the fluorine line in the reaction tubes because the fluoride coating on the tubes adsorbs any water given off by the minerals. It was therefore necessary to perform two sets of tests, one to determine the length of time necessary for a clay mineral containing interlayer water to attain a constant isotopic composition in the drybox and one to determine the amount and isotopic composition of the interlayer water remaining in the mineral after it reached a constant isotopic composition.

i. Effect of length of time clays remain in drybox on their isotopic composition

In this series of experiments six aliquots of a mineral were placed in the drybox with the reaction vessels. Each aliquot was loaded into a reaction vessel after a prescribed length of time. Then, by analyzing the samples, the effect of the time in the drybox on the measured δ-values could be observed. The results of these experiments are shown in figure 7. It may be seen from this figure that while the isotopically light atmospheric water is removed from the drybox, and quartz (P 45, R 60) reaches its final isotopic composition in only three hours, clay minerals and fine grained sediments require a much longer time. The two samples of this type which were

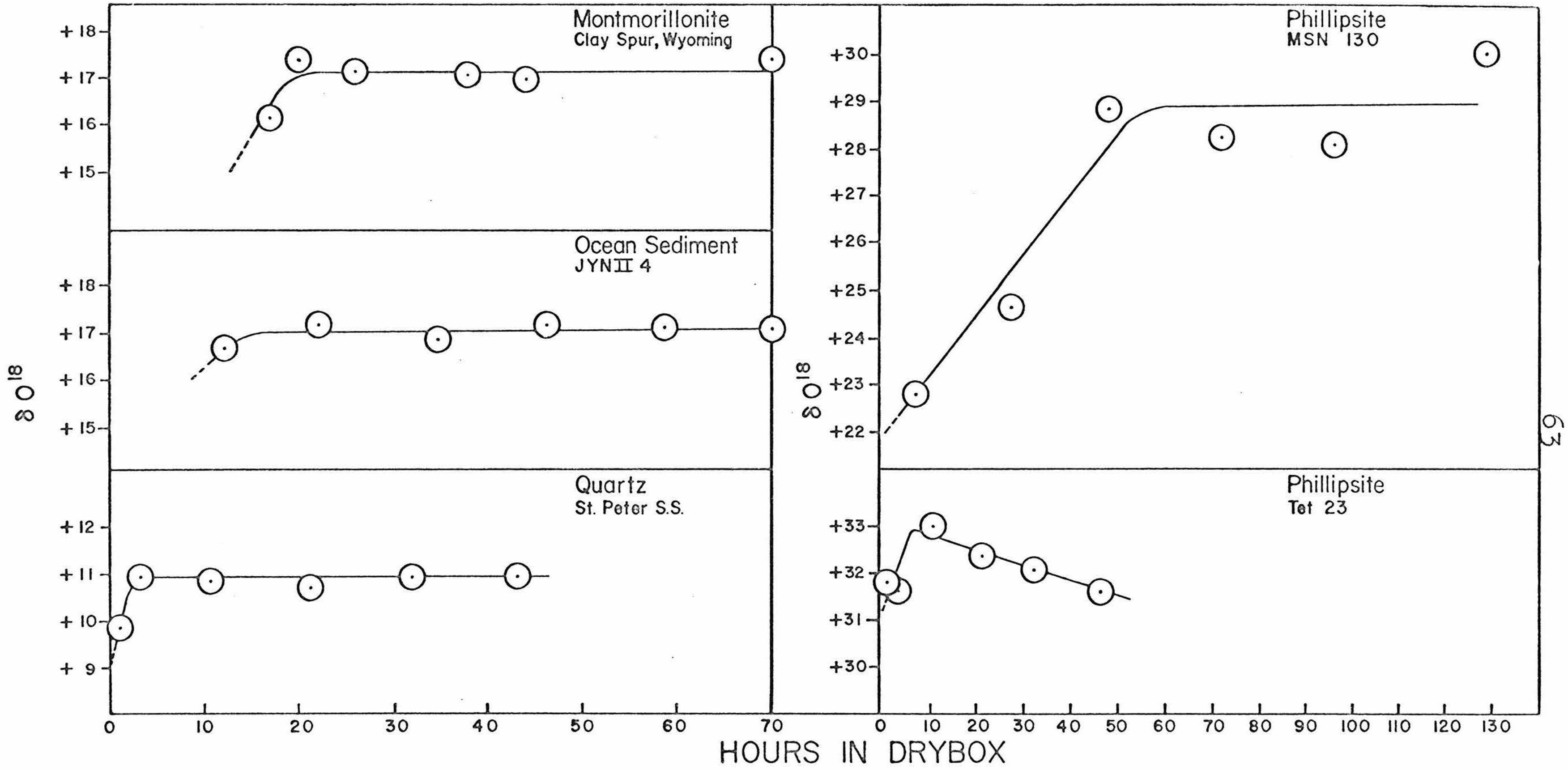


Figure 7. Relationship between length of time sample remains in drybox prior to loading in the reaction vessel and the measured δO^{18} value of the sample

studied in this way, a montmorillonite (Clay Spur, Wyoming) and an ocean sediment (JYN II-4), reached their final isotopic compositions in 20 hours or less. The longer time for the clays to reach their final isotopic compositions must represent the length of time it takes for the interlayer water to be removed from the minerals. The difference in drying time between the quartz and the montmorillonite cannot be due to differences in grain (as opposed to crystal) size, as the two samples were of approximately the same grain size.

The two phillipsite samples (zeolites) show very different behavior than the clays. The difficulty of obtaining good measurements of the isotopic composition of zeolites is pointed out by the data of figure 7. It is not surprising that clays and zeolites behave differently, as the nature of their waters of hydration is very different. Differential thermal analysis and thermogravimetric analyses of clays (Ross and Hendricks (88)) indicate that these minerals dehydrate in a single step, in a manner similar to a mono-hydrated salt. Many zeolites, however, appear to dehydrate in several steps similar to the behavior of a poly-hydrated salt. Some water is much more tightly bound than other water and it may take up to a few thousand hours for the water in the zeolites to come to equilibrium with surrounding water vapor (Milligan and Weiser (73). When this is the case it might be expected that the first water to leave the mineral in the drybox would be isotopically light. If the remaining water were isotopically heavier than the silicate and this water were finally evolved, then a curve of the type of sample Tet 23, figure 7 would be obtained. The curve for phillipsite MSN 130 is somewhat more complicated, but it, too, undoubtedly reflects slow loss of zeolitic water.

ii. Amount of interlayer water remaining in montmorillonite after 24 hours in the drybox

As was shown previously, all the interlayer water was not removed from clay minerals at room temperature in a vacuum, and the small amount remaining behind was isotopically fractionated with respect to hydrogen. Thus, it was important to determine the amount and oxygen isotopic composition of interlayer water which was not removed in the drybox. In order to do this, two montmorillonite samples (Clay Spur, Wyoming and Otay, California) were placed in the drybox, and after 24 hours, the length of time which samples are normally left in the drybox prior to loading, each montmorillonite was loaded into a specially constructed glass vessel. These vessels were sealed inside the drybox and placed on a vacuum line. The samples were heated to 250°C. The water evolved from each sample was collected and the oxygen was extracted for isotopic analysis. The results of these analyses are shown in Table 7.

As may be seen from the data of Table 7 only a small amount of interlayer water is left in the clay after 24 hours in the drybox. Its effect is to cause the δ-value of the oxygen to be too low by a few tenths of a permil, an error within or just slightly greater than normal analytical error. Because of the small magnitude of this correction it was not routinely applied to the montmorillonite data.

It may appear inconsistent that in D/H analyses clays are preheated at temperatures above 125°C to remove interlayer water while in O^{18}/O^{16} determinations the removal of interlayer water can be done at 25°C. However, a larger contamination by interlayer water can be tolerated in the case of oxygen analyses. There is six times as much oxygen as hydrogen in clays containing interlayer water, and the effect of contamination is correspondingly reduced.

In summary, it may be seen that while the separation between interlayer water and hydroxyl water is not complete with the extraction techniques used here, the errors caused in the isotopic analysis of aluminosilicate oxygen and hydrogen due to incomplete removal of the interlayer water are small compared to the effects being measured. These errors are probably never more than a few tenths of a permil for oxygen or a few tenths of a percent for hydrogen.

TABLE 7

Interlayer water remaining in montmorillonite after 24 hours in drybox

Sample	Remaining water $\left(\frac{\mu\text{mol } H_2O}{\text{mg clay}}\right)$	δO^{18} (‰)	Percent of O_2 in Sample	Correction to mineral δO^{18} (‰)
Clay Spur, Wyo.	0.102	-6.72‰	0.72%	0.2‰
Otay, Calif.	0.404	-0.88‰	3.1%	0.6‰

4.6 Exchangeability of interlayer water in clay minerals

It was pointed out in the preceding section that in clay minerals containing interlayer water, the greater portion of this water is readily removable in a drybox containing P_2O_5 at room temperature. It is also well known (Grim (50)) that given sufficient time clay minerals from which the interlayer water has been removed will become rehydrated under normal atmospheric conditions. It follows that the interlayer water is probably subject to isotopic exchange with atmospheric water vapor. If the exchange occurs slowly enough, the isotopic composition of the interlayer water might provide useful geologic information. On the other hand, if it occurs rapidly, the isotopic composition of the interlayer water would provide no useful information unless special precautions were taken in sampling and preparation to prevent its exchange.

To determine the rate of exchange of interlayer water, two beakers containing a few humdred milligrams of montmorillonite (Clay Spur, Wyoming) were placed in a closed vessel containing an atmosphere saturated with water vapor enriched in deuterium ($\delta D = +187\%$). One beaker was removed after two days and one after six days. The water evolved from each sample between 25° and $160^{\circ}C$ was collected and isotopically analyzed. The results of the analyses are presented in Table 8.

The data are sufficient to demonstrate that interlayer water may undergo exchange with a water vapor phase in a matter of days. The isotopic composition of the interlayer water cannot be expected to be controlled by any factors other than the isotopic composition of the water or water vapor in which the clay was last stored. For this reason, in routine analyses of clay minerals the interlayer water was discarded and only the hydrogen or oxygen of the aluminosilicate frameworks of the minerals was analyzed.

TABLE 8

Exchange of interlayer water in montmorillonite

(Clay Spur, Wyo.)

Exchange time	Interlayer water		Percent exchange
	orig. δD	final δD	
6 days in D-rich vapor followed by ½ hr in air	-5.2%	+108.6%	61
6 days in D-rich vapor followed by 1 wk in air	-5.2%	-3.3%	1
2 days in D-rich vapor followed by 2 hrs in air	-5.2%	+13.7%	10

4.7 Reaction of different oxygen positions in the same mineral

It was postulated by Taylor (99) and Taylor and Epstein (104) that the oxygen of the hydroxyl groups of micas contained considerably less O^{18} than the oxygen of the Si-O-Si and Al-O-Si bonds. However, no direct measurement of this effect had been made. In the present study an attempt was made by carefully controlling reaction conditions to selectively remove the hydroxyl oxygen of kaolinite without liberating the remaining oxygen, and in this manner determine the δO^{18} value of the oxygen of the hydroxyl group. Kaolinite is especially well suited to a study of this type since only one side of the octahedral layer, which contains the hydroxyl groups, is bonded to a silicon-oxygen sheet. If the OH oxygen is preferentially liberated by F_2 then extrapolation of the experimental results in the manner described below leads to a value which probably approximates the oxygen isotopic composition of the hydroxyl groups.

Several aliquots of a kaolinite (Langley, S. Carolina) were reacted with fluorine at different temperatures. There was essentially no reaction of the mineral with fluorine at temperatures up to 165°C. At temperatures of 175°C and above the percent yield was almost exactly equal to the percent of the stoichiometrically required amount of fluorine which was used. Once the mineral reaches a temperature at which reaction can occur, if there is a sufficient amount of reagent the reaction will go to completion.

In figure 8b the δO^{18} values of the oxygen liberated at temperatures above 165°C are plotted against the percent of the stoichiometric amount of oxygen released in the reaction. If all the oxygen of the hydroxyl groups is liberated prior to reaction of the remaining oxygen of the mineral, and if there are no large isotopic fractionations of the oxygen of the Si-O-Si and Al-O-Si bonds due to incomplete reaction then a line through the data of

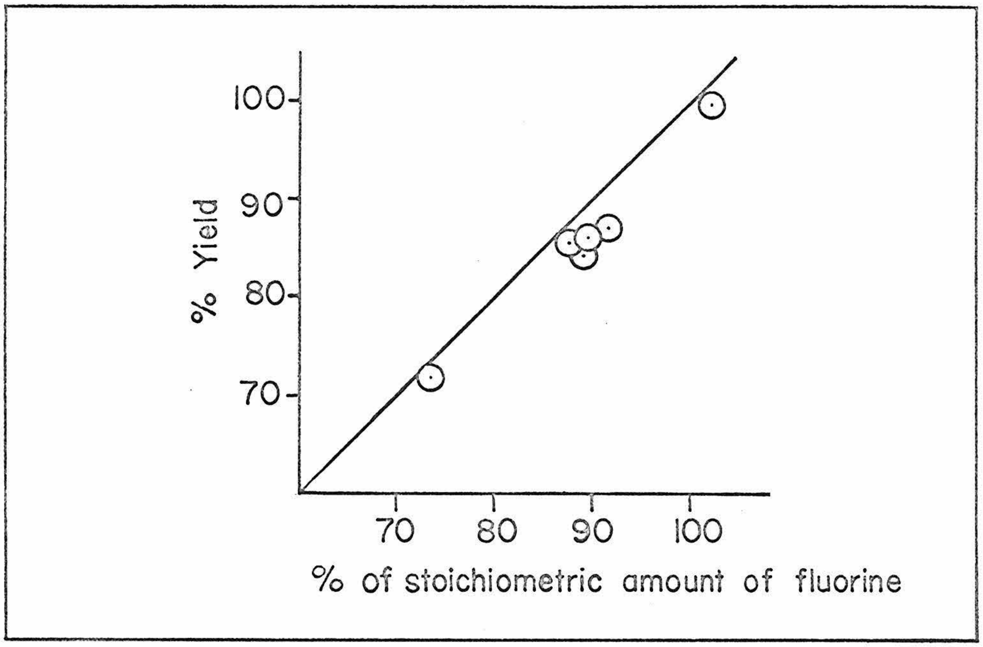


Figure 8a. Stoichiometric amount of fluorine used in reaction with kaolinite plotted against oxygen yield obtained

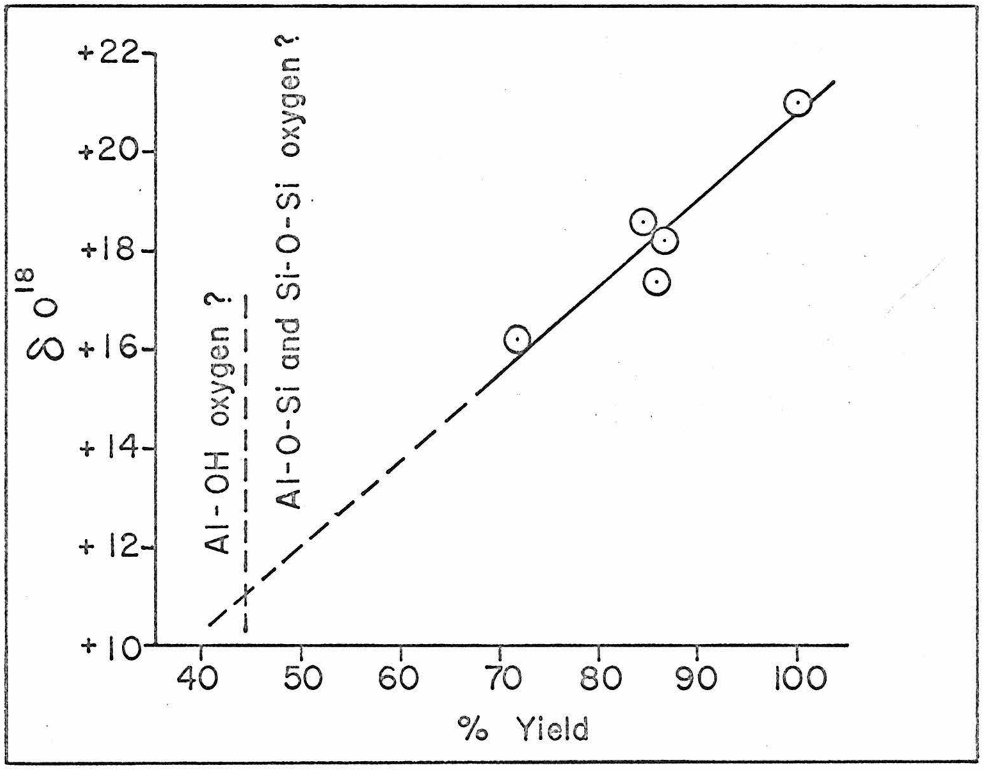


Figure 8b. Oxygen yield from incomplete reaction of kaolinite vs measured δO^{18}. The line through the data is extrapolated to 44.5% yield, corresponding to the total amount of hydroxyl oxygen in mineral

figure 8b can be extrapolated to give the oxygen isotopic composition of the hydroxyl groups. A least-squares line has been fitted to the data and is extrapolated to 44.5 percent yield, which corresponds to the yield of oxygen due to the hydroxyl groups. The isotopic composition of the oxygen of the various positions is then calculated to be:

		δO^{18}
1.	Entire mineral	+21.0
2.	Al-O-H bonds	+11.1
3.	Al-O-Si and Si-O-Si bonds (by calculations from 1 & 2)	+29.0

Thus, if the assumptions of the calculation are correct, there is a fractionation of approximately 18 permil between the isotopic composition of the oxygen in the Al-O-H bonds and that in the Al-O-Si and Si-O-Si bonds. Probably the biggest uncertainty is whether all the hydroxyl groups have been removed before the reaction of the remaining oxygen begins, and although this is likely it cannot be proven with the available data. The assumption that there is not a large isotopic fractionation between the liberated and the unreacted oxygen of the Al-O-Si and Si-O-Si bonds is justified by the fact that a straight line can be drawn through the data of figure 8b. If there were a large fractionation the data would be best fitted to a Rayleigh distillation curve. In addition, the isotopic fractionation observed by Garlick and Epstein (40) for incomplete reaction of quartz as a result of insufficient bromine pentafluoride reagent is in the opposite direction to that observed in this case.

CHAPTER V

ISOTOPIC COMPOSITION OF SEDIMENTARY MINERALS

5.1 Introduction

The bulk of the experimental work in this study consists of isotopic analyses of a large number of samples of a variety of sedimentary rock types. Where feasible, mineral separations were performed and the separated minerals were analyzed. However in many cases the fine-grained nature of the materials made separations impractical and it was necessary to perform whole rock analyses.

Analyses of mineral separates and monomineralic rocks provided information about the isotopic behavior of a number of the common minerals in sedimentary processes. With this information the isotopic behavior of polymineralic rocks may be understood. Consequently, data on pure and almost pure minerals will be presented first, followed by data on polymineralic rocks.

5.2 Isotopic composition of clay minerals

A. Analytical data and interpretation

Oxygen and hydrogen isotopic analyses were performed on a number of kaolinites, montmorillonites, and glauconites from a wide variety of areas. The results of these analyses are presented in Table 9 and are shown in figures 9 and 10 compared with the analyses of some igneous and metamorphic rocks and minerals. The measured O^{18}/O^{16} ratios of the kaolinites and bentonites have been corrected for the contribution of quartz and feldspar. The mineral percentages used in the corrections are those of Kerr et al. (60) and Konta (63). These corrections generally were between 0.1 permil and 0.3 permil. As the data of figure 9 shows, the oxygen in the clay minerals is richer in O^{18} than that of nearly all the igneous and metamorphic rocks for which data is available. In addition, the oxygen of the clay minerals is richer in O^{18} than that of almost all the igneous and metamorphic muscovites for which there are data. (These are the closest analogues of the clay minerals for which analyses are available.) While the clays as a group are rich in O^{18}, there are no large differences in the ranges of oxygen isotope ratios of the different clay minerals. Wherever there are a large number of analyses for a particular type of clay mineral there is a fairly broad spread in the value of oxygen isotope ratios. As subsequent treatment of the data will show, this spread in δ-values is due to the variety of conditions under which the minerals have formed and exchanged. The most important variables in this respect are the isotopic composition of the coexisting water and the temperature at the

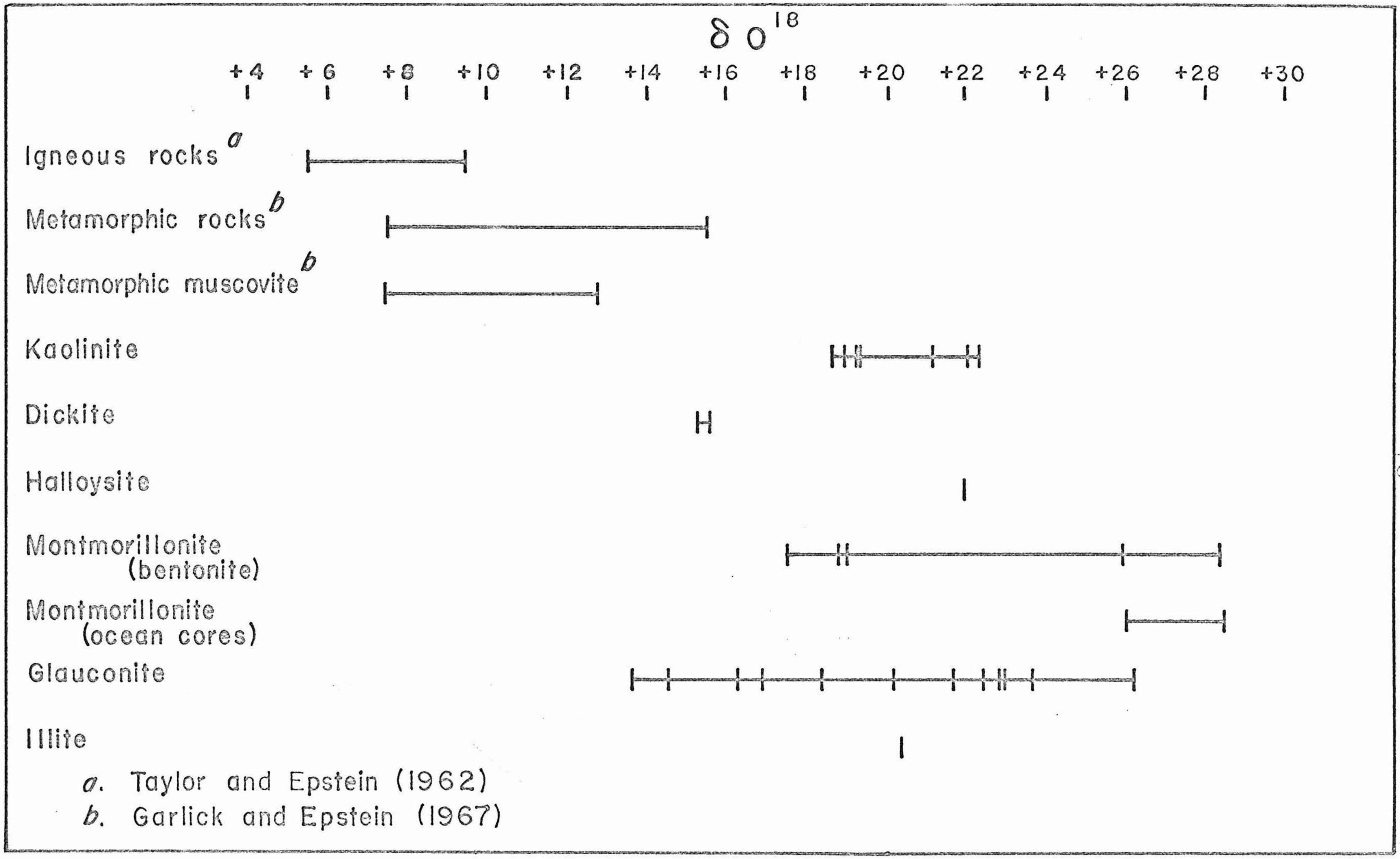


Figure 9. O^{18}/O^{16} ratios of clays analyzed in this study compared with pertinent isotopic data of previous workers

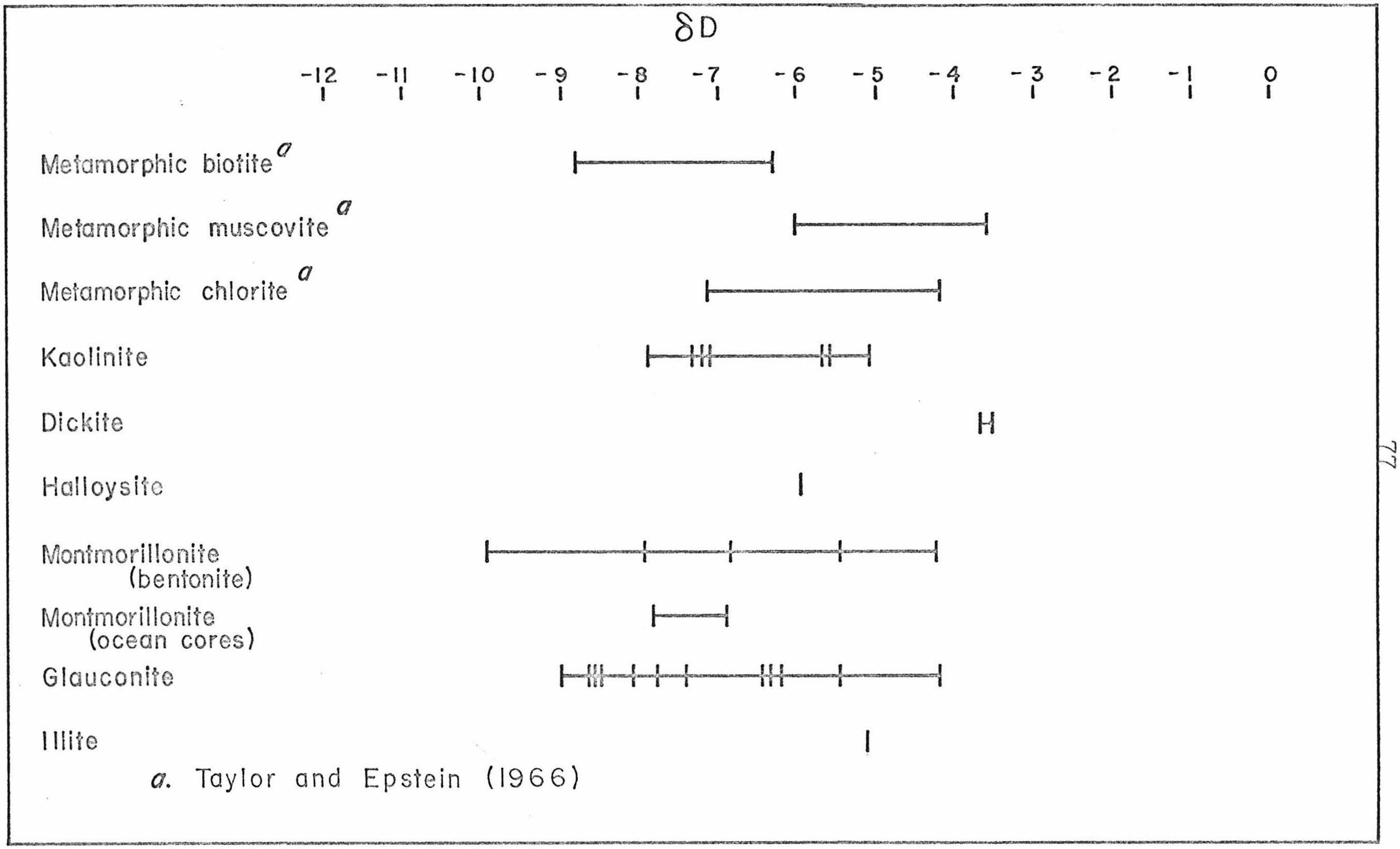


Figure 10. D/H ratios of clays analyzed in this study compared with pertinent isotopic data of previous workers

TABLE 9

Isotopic Composition of Clay Minerals

Sample	δO^{18} per mil	Av Dev	No. Runs	δD (percent)	Av Dev	No. Runs
a. Kaolinite						
Langley So. Carolina	+21.2	0.3	2	-5.7	0.2	10
Murfreesboro Arkansas	+22.4	0.3	3	-5.1	0.0	2
Bath So. Carolina	+22.1	0.1	2	-5.6	---	1
Mesa Alta N. Mexico	+18.7	0.6	2	-7.3	0.1	2
Kadan Czech.	+19.4	---	1	-7.1	---	1
Podlesi Czech.	+19.0	0.0	2	-7.2	0.1	2
Sedlec Czech.	+19.3	0.2	3	-7.9	0.3	3
b. Halloysite						
Bedford, Indiana	+22.0	0.4	2	-6.0	---	1
c. Dickite						
Kladno Zapotocky, Czech.	+15.6	0.6	2	-3.7	---	1
Horni Slavkov, Czech.	+15.3	---	1	-3.6	---	1

TABLE 9 cont.

Sample	δO^{18} per mil	Av Dev	No. Runs	δD (percent)	Av Dev	No. Runs
d. Montmorillonite (bentonite)						
Polkeville, Miss.	+28.5	0.2	2	-5.4	0.2	2
Chambers, Arizona	+19.1	0.4	7	-7.9	0.3	3
Otay, Calif.	+19.0	0.4	4	-4.1	0.1	3
Clay Spur, Wyo.	+17.6	0.2	5	-9.9	0.4	11
Little Rock, Ark.	+26.0	0.0	2	-6.8	1.0	4
e. Montmorillonite (ocean cores)						
RIS 81	+26.1	0.0	2	-7.8	0.8	2
EM7-RUN I	+28.5	1.0		-6.8	---	1
f. Illite						
Morris, Ill.	+20.5	0.5	2	-5.1	0.2	2
g. Glauconite (from ocean sediments)						
Sta 1752 (Blake Plateau)	+26.3	0.5	5	-7.4	0.2	4
Sta 1957 (L.I.Sound)	+21.8	0.0	2	-9.0	0.1	3

TABLE 9 cont.

Sample	δO^{18} per mil	Av Dev	No. Runs	δD (percent)	Av Dev	No. Runs
Sta 6941 (S.Monica Bay)	+23.8	---	1	-8.5	---	1
h. Glauconite (from rocks)						
R8-Merchantville Fm	+20.3	0.0	2	-7.8	0.5	3
R12-Marshalltown Fm	+23.0	0.5	3	-8.0	0.2	3
R13-Navesink Fm	+23.0	0.1	2	-8.6	0.2	3
R17-Hornerstown Fm	+22.5	0.3	3	-8.5	0.1	2
E53/3/14 Crawford Fm Australia	+14.6	0.3	2	-6.3	0.3	3
E53/3/15 Crawford Fm	+13.7	0.4	3	-6.2	0.8	4
E53/3/16 Crawford Fm	+18.5	0.5	4	-4.1	0.2	2
E53/3/18 Crawford Fm	+15.0	0.2	2	-5.4	---	1
E53/3/19 Crawford Fm	+16.4	0.1	2	-6.4	---	1

time of exchange or formation.

The hydrogen isotope data of the clay minerals in figure 10 show many of the features seen in the oxygen isotope diagram. One notable exception, however, is that there is no difference between the range of values for metamorphic muscovites and biotites and those of clay minerals. Furthermore, all the clay minerals are depleted in deuterium with respect to sea water. This includes a number of samples which appear to have formed in isotopic equilibrium with sea water. Thus, while $\alpha^{ox}_{clay-H_2O}$ is greater than unity at normal ocean temperatures, $\alpha^{hy}_{clay-H_2O}$ is less than unity.

A further understanding of the clay mineral isotope data demands an understanding of the variables which can affect the isotopic compositions of clay minerals. Among the more important variables are:

1. the isotopic composition of the various waters with which the clay mineral may have come in contact during and after its formation;
2. the temperature of the environment at any time during which the clay mineral was being isotopically exchanged; and
3. the nature and rate of any isotope exchange process.

The temperature sensitivity of equilibrium isotopic fractionation factors is very large at low temperatures. The temperature during most sedimentary processes is restricted to a range of approximately 0° to 25°C. Temperatures on the deep sea floor are restricted to a very much narrower range, approximately 0° to 3°C (Sverdrup, Fleming and Johnson (96)). Temperatures in shallow marine areas are more greatly influenced by the climate on adjacent land areas and may have a somewhat greater range. Diagenetic temperatures may be considerably warmer.

The isotopic composition of the waters with which a mineral reacts or exchanges are reflected in the isotopic composition of the mineral. Because clay minerals contain both hydrogen and oxygen their isotopic compositions are especially amenable to interpretation in cases where the isotopic composition of the water is unknown. This is a consequence of the interdependence of the O^{18}/O^{16} and D/H ratios in most waters.

Craig (20) has shown that most meteoric waters other than those in evaporating basins and hot springs have isotopic compositions lying near a straight line described by the equation

$$\delta D^{(\%)} = 0.8 \ \delta O^{18}_{(\text{‰})} + 1.0$$

The factor 0.8 results primarily from the ratio of the values of the fractionation factors $\alpha^{ox}_{H_2O}$ liq-vap and $\alpha^{hy}_{H_2O}$ liq-vap.

Since the O^{18}/O^{16} and D/H ratios of water are related, and since the isotopic composition of clay minerals depends in part on the isotopic composition of water, there should also exist a relationship between the oxygen and hydrogen isotope compositions of clay minerals. It can be shown that if clay minerals undergo isotopic exchange with a variety of meteoric waters under conditions such that the fractionation factors $\alpha^{ox}_{clay-H_2O}$ and $\alpha^{hy}_{clay-H_2O}$ are constant (for example, equilibrium exchange at constant temperature), then the isotopic compositions of the clays will lie along a straight line of the type

$$\delta D = A\ \delta O^{18} + B \qquad (5\text{-}1)$$

when δD is plotted against δO^{18}.
It can further be shown* that

$$A = 0.80 \times \frac{\alpha^{hy}_{clay-H_2O}}{\alpha^{ox}_{clay-H_2O}} \qquad (5\text{-}2)$$

and $$B = 800 \times \frac{\alpha^{hy}_{clay-H_2O}}{\alpha^{ox}_{clay-H_2O}} - 699\ \alpha^{hy}_{clay-H_2O} - 100 \qquad (5\text{-}3)$$

Thus, the slope of the line is determined by the ratios of the α's and its intercept is determined by the absolute values of the α's.

---

*See Appendix I for derivation.

As may be seen from equation 5-3, the intercept of the line is extremely insensitive to large variations of the fractionation factors, so that small errors in determining the intercept can result in large errors in the values of the α's. For this reason it has not been practical to calculate fractionation factors from the values of the slope and the intercept of a line through a set of analytical clay mineral data. However, if the fractionation factors can be estimated by some independent means such as from the isotopic compositions of samples which have formed in a known environment, then a line corresponding to these fractionation factors can be drawn. The positions of points corresponding to the isotopic compositions of other clay minerals relative to this line may then be used to interpret the isotopic compositions of these minerals.

If the fractionation factors are equilibrium ones it is possible to estimate the effect of an increase in temperature on the position of the line along which the isotopic compositions of the clays lie. Clay minerals concentrate O^{18} with respect to water, and the fractionation between clays and water is smaller at higher temperatures than at lower ones. As will be seen in the following sections, water concentrates deuterium with respect to clay minerals, and at sedimentary and diagenetic temperatures the fractionation between water and clay minerals probably decreases with increasing temperatures. Therefore the line corresponding to the isotopic compositions of clays in equilibrium with meteoric waters will lie closer to the line of meteoric waters at higher temperatures than at lower ones.

While the assumptions used in deriving the above equations will seldom be exactly met in natural processes, they are often fairly closely approximated. In spite of their limitations, these relationships provide a useful working model with which the oxygen and hydrogen isotope variations in clay minerals may be better interpreted.

i. Kaolinite minerals

The kaolinite group of clay minerals are chemically and structurally the simplest of all the clays. The basic structural formula of the group is $Al_2 Si_2 O_5 (OH)_4$, and generally there is little substitution of other elements in the crystal lattice. Structurally the kaolinite minerals consist of a stack of layers, each layer being built of a sheet of aluminum, oxygen, and hydroxyl groups in octahedral coordination bonded to a sheet of silicon-oxygen tetrahedra. Of the three members of the kaolinite group studied isotopically, two of them, kaolinite and dickite are almost identical, differing only by a slight modification of the stacking arrangement. The third member of the group, halloysite, differs from the other two in that between each aluminosilicate layer there is a layer of water molecules.

Kaolinite may be formed during weathering processes or by hydrothermal alteration. Halloysite has been observed to form in warm springs and also at low temperatures. Dickite is not found as a primary mineral in sediments and is chiefly associated with hydrothermal deposits. (Deer, Howie and Zussman(25))

The oxygen and hydrogen isotopic compositions of several kaolinites, dickites, and halloysites are listed in Tables 9 and 10 and plotted on a graph of δD against δO^{18} in figure 11. All the kaolinite points and the halloysite point lie near a straight line on this plot while the dickite points fall well off the line. A least-squares line through the kaolinite points has the equation

$$\delta D = 0.615\ \delta O^{18} - 19.0$$

Using equations 5-2 and 5-3, this corresponds to values of the fractionation factors of $\alpha^{hy}_{kaol-H_2O} = 0.763$ and $\alpha^{ox}_{kaol-H_2O} = 0.992$. Acceptance of these values would lead to the improbable conclusion that the waters in which all of these kaolinites formed had δO^{18} values of +19 or greater. However, a small shift in the slope of a line drawn through the center of gravity of these points would produce a large change in the calculated values of the fractionation factors. This illustrates the weakness of

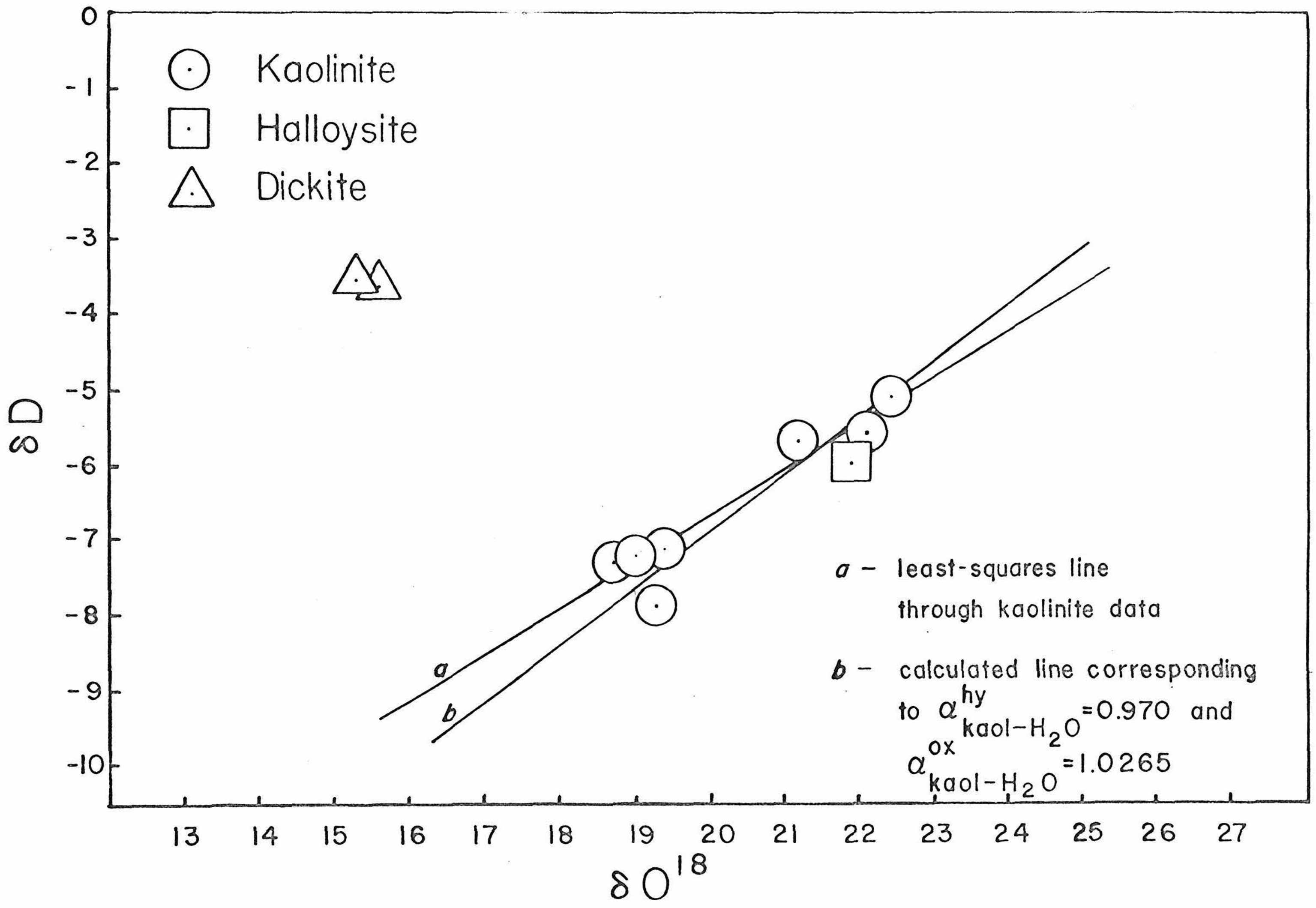


Figure 11. Graph showing relationship between δD and δO^{18} values of some kaolinites, dickites, and a halloysite

using the values of the slope and intercept of a line through the experimental data to determine the absolute values of the fractionation factors. A change in the intercept from -19 to -23 will cause a change of $\alpha^{ox}_{kaol-H_2O}$ from 0.992 to 0.026. This corresponds to a difference of approximately 34 permil in the O^{18}/O^{16} ratio of a sample of kaolinite in equilibrium with water, and represents a reversal of the direction of fractionation. It is therefore not practical to determine fractionation factors from lines drawn through the analytical data at the present time. However if the fractionation factors are estimated by an independent method a corresponding line may be drawn on a δ D vs δO^{18} plot, and this may be used to demonstrate whether or not conditions approximating constant fractionation factors obtained in a particular set of samples.

An estimate of the fractionation factors of the kaolinite - water system has been made by using the measured isotopic compositions of some of the samples and the best estimates available for the isotopic compositions of the waters with which they formed. All of the kaolinites measured in this work are of residual weathering or sedimentary origin. All have probably formed and been deposited in fresh water environments (See Appendix II for geological and petrographic descriptions of the samples.) All were collected from shallow quarries or outcrops in regions of temperate climate.

Hydrogen isotopic compositions of waters from streams and springs in areas near those from which some of the kaolinite samples were collected were measured by Friedman et al. (38). If it is assumed that the kaolinites attained their present isotopic compositions in the presence of waters of the same isotopic compositions as measured by Friedman et al., under temperature conditions similar to those which prevail today, then we are able to estimate the fractionation factors $\alpha^{ox}_{kaol-H_2O}$ and $\alpha^{hy}_{kaol-H_2O}$. This has been done in Table 10. The weaknesses of these estimates is apparent. The waters were sampled only once from each location, thereby ignoring any seasonal variations. They were sampled from streams and springs, and the isotopic compositions measured are then an average of an entire drainage basin rather than a representative sample from which the clay was taken. These effects would be expected to be smallest for the samples from the relatively low-lying regions of the southeastern United States, and greatest for the sample from the mountainous region of New Mexico. Finally, the isotopic compositions of the waters and the temperatures at the time during which exchange occurred may have been significantly different than they are now.

Keeping the above limitations in mind, the calculations in Table 10 suggest values of the fractionation

TABLE 10

Estimate of the isotopic fractionation factor in the Kaolinite - water system

Sample No.	Clay Locality	δD Kaol.	Water Locality	δD_{H_2O}	$\alpha^{hy}_{Kaol-H_2O}$	$\alpha^{ox}_{Kaol\ H_2O}$
H-1	Murfreesboro, Ark.	-5.1	Red R. Shreveport La.	-2.7[a]	.975	1.0271
			Ouachita R. Monroe, La.	-3.0	.978	1.0275
H-5	Bath, So. Carolina	-5.6	Ogeechee River Ft. McAllister Georgia	-2.1	.964	1.0261
N 11-11	Langley, So. C.	-5.7	Ogeechee River Ft. McAllister Georgia	-2.1	.963	1.0252
H-9	Mesa Alta N. Mex.	-7.3	Sulfur Spring Jemez Mtns. N. Mex.	-7.6	1.003	1.0298

a. Hydrogen isotopic composition of waters from Friedman et al (38) factors of $\alpha^{ox}_{kaol-H_2O} = 1.0265$ and $\alpha^{hy}_{kaol-H_2O} = 0.970$. These are the averages of the values for the kaolinites from South Carolina and Arkansas. The average annual air temperature in both these places is close to 18°C. A line corresponding to these fractionation factors has been drawn on figure 11.

While the kaolinite points, all of which are of sedimentary or weathering origin fall very close to a straight line, the two dickite samples lie well off the line. As was mentioned above, the difference between kaolinite and dickite is a very minor one, consisting only of a small difference in the way the aluminosilicate layers are stacked. Because of the small differences between these two minerals, their isotopic fractionation factors are probably similar or identical. If kaolinite and dickite behave similarly with respect to isotope fractionations then factors which might cause the dickite points to lie as far away from the kaolinite line as they do are temperature variations, deviation of the isotopic compositions of the coexisting waters from the line describing the isotopic compositions of meteoric waters, and incomplete isotopic exchange.

One of the dickite samples (Horni Slavkov) has been interpreted as being of hydrothermal origin, with a temperature of formation of approximately 300°C or 350°C

(J. Konta (62)). The second dickite sample (Kladno) is from a sedimentary deposit in the same region of Czechoslovakia. However, based on the fact that its isotopic composition is almost identical with the known hydrothermal dickite and the fact that almost all dickites are of hydrothermal (or at least diagenetic) origin, it is probable that the Kladno dickite is also of hydrothermal origin.

Although it is quite certain that the dickites are not in isotopic equilibrium with meteoric water at sedimentary temperatures, it is not as certain that their isotopic compositions represent isotopic equilibration at hydrothermal temperatures. The oxygen isotope fractionation factor between dickite and water can be estimated semiquantitatively either by analogy with the muscovite data of O'Neil and Taylor (79) in figure 1 or by the methods used in section 5.4. In either case, the estimated value of $\alpha^{ox}_{dickite-H_2O}$ in the temperature range 200° to 350°C is between 1.001 and 1.004. The water in equilibrium with a dickite sample with a δO^{18} value of +15.5 permil in the temperature range 200° to 350°C would therefore have a δO^{18} value between 11.5 and 14.5 permil. These δ-values are larger than have been estimated for hydrothermal waters by previous workers (Clayton and Epstein (13), Garlick and Epstein (41), Rye (117) and larger than most estimates of the O^{18}/O^{16} ratios of magmatic waters (O'Neil and Taylor (80)). It is possible that these dickites formed in the presence of unusually O^{18}-rich hydrothermal waters. However, the more attractive explanation is that the isotopic compositions of the dickites were established by either partial or complete isotopic reequilibration with waters of normal δ-values at temperatures lower than 200°C. If it is assumed that the dickite last equilibrated with water of isotopic composition between 0 and -7.4 (the calculated δO^{18} value for the nearby Podlesi and Kadan kaolinites) the temperature of last equilibration can be estimated to range between 40°C and 100°C.

The halloysite point falls quite close to the kaolinite line. This mineral differs from kaolinite in that it contains a layer of water molecules between each aluminosilicate layer. This water was removed prior to analysis, however, and it is likely that the aluminosilicate portion of the mineral behaves isotopically very similarly to kaolinite. It has been suggested that this particular specimen was deposited from solution (Kerr, Main, and Hamilton (60)). If so, it was probably formed from a low temperature solution or else underwent subsequent exchange at low temperatures.

Of all the clay mineral data, the kaolinite data show the most systematic behavior in terms of exchange with different waters under conditions of constant $\alpha^{ox}_{kaol-H_2O}$

and $\alpha^{hy}_{kaol-H_2O}$. The near constancy of these parameters is strongly suggestive that the exchange resulted in isotopic equilibrium. There is some deviation from the ideal model, however, and this may be due in part to temperature variations and in part to departures of the isotopic compositions of the waters from the straight line relationship. While kaolinite forms under a wide range of climate conditions, pure kaolinite deposits such as the ones these samples were taken from tend to be formed in zones of quite intense weathering. This weathering is favored by a mild wet climate, and so the kaolinite samples measured here were probably formed within a fairly narrow temperature range. This has simplified the interpretation of the data somewhat. The contrast between the kaolinite and dickite isotopic compositions indicated that isotopic exchange is relatively slow even on a geologic time scale, and the isotopic composition of clays in sedimentary environments may retain some memory of previous events.

ii. Montmorillonites

The montmorillonite group of clay minerals is structurally and chemically more complex than the kaolinite group. The basic building block of the montmorillonite structure is similar to pyrophyllite in that a sheet of aluminum ions in octahedral coordination with oxygen and hydroxyl groups is sandwiched between two sheets of silicon atoms in tetrahedral coordination with oxygen. The ideal formula for this structure, $Al_4\ (Si_8\ O_{20})\ (OH)_4$ is electrically neutral and is the formula for pyrophyllite, a mineral found in metamorphic rocks. Montmorillonite differs from pyrophyllite in that magnesium and iron may substitute for aluminum in the octahedral positions and to a small extent aluminum may proxy for silicon in the tetrahedral positions. Both of these substitutions result in creating a net negative charge in the aluminosilicate framework which is neutralized by exchangeable cations between the aluminosilicate layers. In addition to the cations, the space between the layers is occupied by water molecules. A typical montmorillonite formula is

$$(Na)_{0.7}(Al_{3.3}Mg_{0.7})\ Si_8O_{20}(OH)_4 \cdot n\ H_2O$$

(Deer, Howie and Zussman (25).

Montmorillonite occurs in a variety of geologic settings including hydrothermal alteration products, low grade metamorphic rocks, altered tuffs and volcanic rocks. In the present study, montmorillonites of sedimentary or low temperature origin were analyzed. All the pure and almost - pure montmorillonites analyzed were formed by the alteration of volcanic material which was deposited under fresh or marine water. Nearly monomineralic montmorillonite rocks formed in this manner are referred to as bentonites. Several bentonites from the American Petroleum Institute collection of clay mineral standards were analyzed as were two nearly pure montmorillonite samples from ocean cores provided by John Griffin and interpreted by him as being the alteration products of volcanic material on the sea floor (Griffin (118)).

The hydrogen isotope compositions of the above montmorillonites range from approximately $\delta = -4$ to -10 percent and the oxygen isotopic compositions range from about $\delta = +17.5$ to $+28.5$ permil. This large range of variation strongly suggests formation or exchange under a wide range of conditions of temperature, isotopic environment or both. The isotopic data have been plotted in figure 12 on a graph of δD vs δO^{18}. As was done in the case of the kaolinites, two lines have been drawn through the experimental data. The first of these is a least squares line through all but one of the data points. The point for the Otay, California bentonite was omitted from the calculation because it lay so far off the straight line which best fit the experimental points. In addition, 1.0 percent was added to the hydrogen values of the two samples from the deep sea cores. This was done to compensate for the fact that the isotopic composition of ocean water, when plotted on a graph of δD vs δO^{18}, does not lie on the line of natural meteoric waters (Craig (20)). The least squares line has the equation

$$\delta D = 0.33 \quad \delta O^{18} - 15.1$$

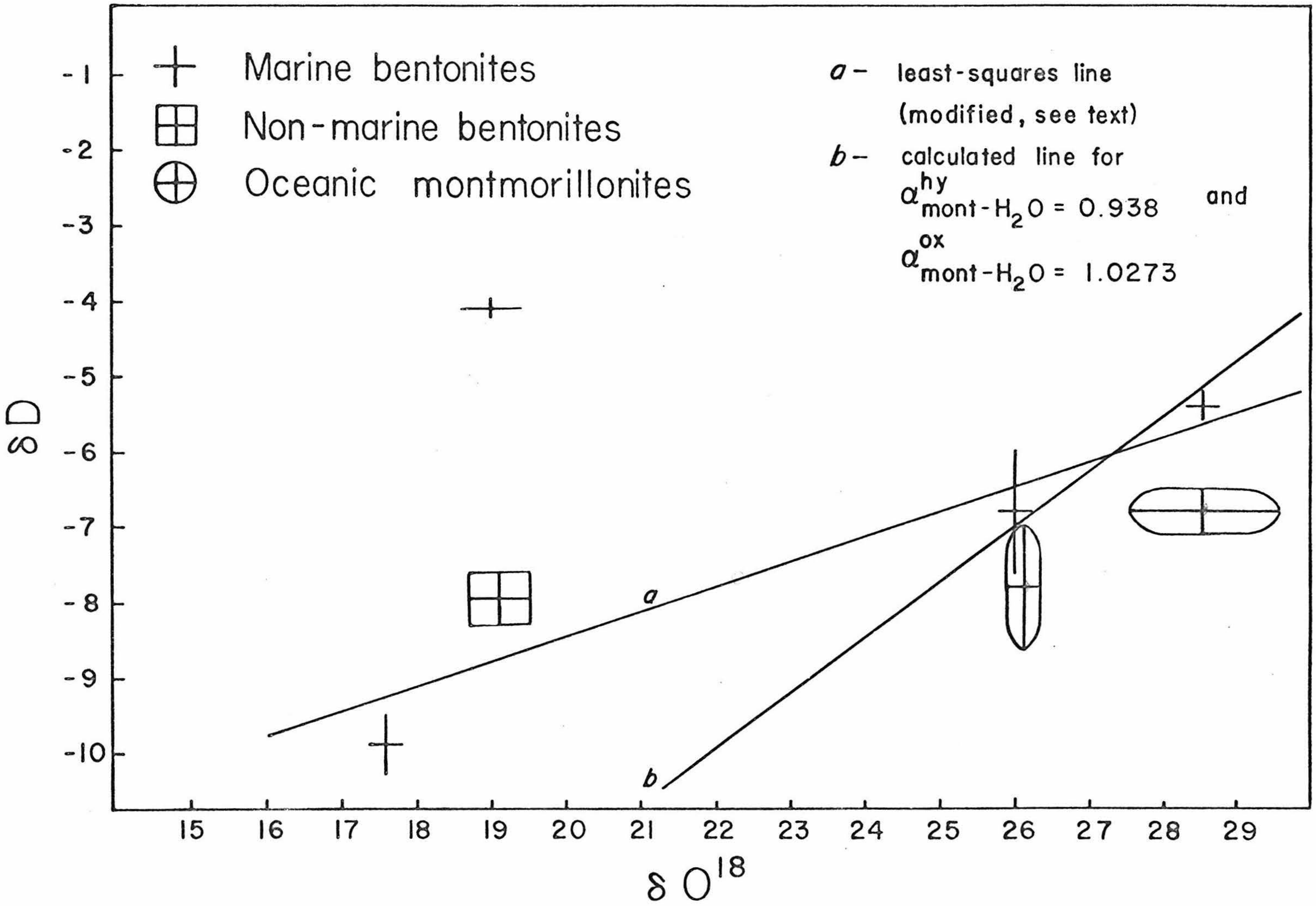


Figure 12. Graph showing relationship between δD and δO^{18} values of some montmorillonites from ocean cores and bentonite deposits.

The slope of this line is very much smaller than the slope of the line of meteoric waters. The constants of the equation correspond to values of $\alpha^{ox}_{mont-H_2O}$ and $\alpha^{hy}_{mont-H_2O}$ which are impossibly small. Therefore, the isotopic compositions of all the montmorillonite samples cannot be interpreted in terms of the simple model of exchange with meteoric waters under conditions of constant fractionation factors.

The second line on the diagram has the equation

$$\delta D = 0.73 \quad \delta O^{18} - 26$$

This line was drawn using the fractionation factors $\alpha^{ox}_{mont-H_2O} = 1.0273 \pm 0.0012$ and $\alpha^{hy}_{mont-H_2O} = 0.938$ $\pm$ 0.007. These values were estimated by taking the average of the calculated fractionation factors between sea water and the four montmorillonites richest in O^{18}. All four of these samples were taken from marine beds or ocean cores, have similar isotopic compositions, and are richest in O^{18} of all the montmorillonites analyzed suggesting that they were formed under marine conditions. The values of the fractionation factors estimated for these samples are consistent with fractionation factors estimated between other clay minerals and water, and are also consistent with the values estimated in section 5.4 on the basis of the types of chemical bonds in the mineral. These facts strongly suggest that the estimated fractionation factors are equilibrium ones.

The points corresponding to the three bentonite samples with the smallest O^{18}/O^{16} ratios fall well away from the line estimated using the isotope data for the O^{18} rich samples. Possible causes of deviation of the isotopic compositions of the minerals from this line are deviations of the isotopic compositions of meteoric waters from the ideal straight line relationship (Clayton _et_ _al_.(14) non-equilibrium formation or exchange, and variations of fractionation factors due to temperature variations or differences in the chemical compositions of the minerals.

Chemical analyses and structural formulas of all the bentonites analyzed in the present study are reported by Kerr _et_ _al_.(57). Osthaus (81) has reported analyses and structural formulas of three of the samples. The two sets of analyses are in fairly good agreement and the calculated formulas are listed in Table 11. There appears to be no correlation between chemical composition and isotopic composition of the minerals, and thus there is no suggestion that the chemical composition is responsible for the low O^{18}/O^{16} and/or high D/H ratios.

At elevated temperatures the oxygen isotope fractionation factors of clays are smaller than they are at sedimentary temperatures, and the hydrogen isotope fractionation factors are probably closer to unity. This would cause the isotopic compositions of minerals exchang-

TABLE 11

Structural Formulas of A. P. I. Standard Montmorillonites

Sample	Locality	Kerr et al (57)	Osthaus (81)
H 19	Pokeville, Miss.	$(Na_{.02}Ca_{.74})(Al_{1.49}Fe_{.08}Mg_{.53})$ $(Al_{.10}Si_{3.90}O_{10})(OH)_2$	$(Na_{0.428}K_{0.007}Ca_{0.008})$ $(Al_{1.465}Fe_{0.060}Mg_{0.489})(Si_4O_{10})(OH)_2$
H 23	Chambers, Ariz.	$(Na_{.02}Ca_{.74})(Al_{1.51}Fe_{.13}Mg_{.40})$ $(Al_{.07}Si_{3.93}O_{10})(OH)_2$	
H 24	Otay, Calif.	$(Na_{.12}Ca_{.14})(Al_{1.43}Fe_{0.3}Mg_{.64})$	$(Na_{.494}K_{.009}Ca_{.004}Mg_{.026})(Al_{1.281}$ $Fe_{0.062}Mg_{.705})(Si_4O_{10})(OH)_2$
H 26	Clay Spur, Wy.	$(Na_{.20}Ca_{.04})(Al_{1.54}Fe_{.16}Mg_{.33})$ $(Al_{.09}Si_{3.91}O_{10})(OH)_2$	$(Na_{.332}K_{.006})(Al_{1.584}Fe_{.180}Mg_{.254})$ $(Al_{.117}Fe_{.018}Si_{3.865})(OH)_2$
H 28	Little Rock, Ark	$(Na_{.01}Ca_{.10})(Al_{1.57}Fe_{.23}Mg_{.19})$ $(Al_{.09}Si_{3.91}O_{10})(OH)_2$	

ing with meteoric waters to lie on the low O^{18}/O^{16}, high D/H side of the line determined at sedimentary temperatures. The isotopic compositions of the three bentonites which fall off the line fall on the low O^{18}/O^{16} side and thus exchange at elevated temperatures could have determined their isotopic compositions. The elevated temperatures might have occurred during formation of the clays, possibly as the result of a hot volcanic ash-fall in a restricted basin or, more likely, during post-depositional exchange.

In no case may the isotopic data of the O^{18}-poor bentonites be explained by the mechanism of incomplete equilibration of a clay moved from an O^{18}-rich environment to an O^{18}-poor one at the same temperature. Figure 13 shows possible trajectories of the isotopic composition of a clay when it is moved from a marine to a fresh-water environment and undergoes isotopic exchange toward a new equilibrium value. Hydrogen atoms or hydroxyl groups would be expected to exchange more readily than the remaining oxygen of the clay, and because of this, the isotopic composition of the mineral will always lie below the line on corresponding to $\alpha^{hy}_{clay-H_2O}$ and $\alpha^{ox}_{clay-H_2O}$ on a δD vs δO^{18} plot as a result of incomplete exchange. This is not observed in the case of any of the bentonites.

The isotopic compositions of meteoric waters have a scatter of approximately one percent in the D/H ratio on either side of the line

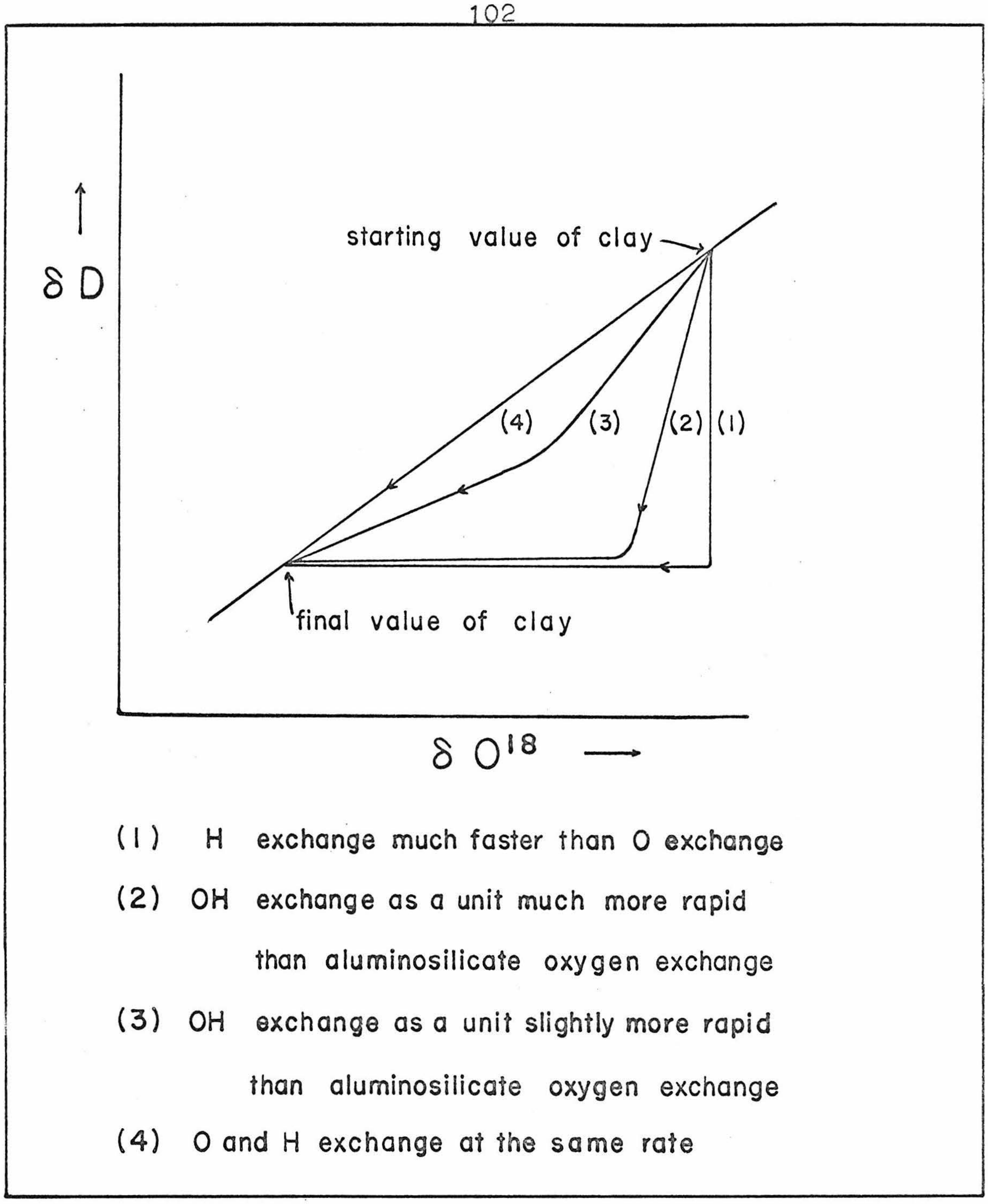


Figure 13. Possible trajectories of the isotopic composition of a clay which is originally in isotopic equilibrium with sea water and which subsequently undergoes isotopic exchange with fresh water at the same temperature.

$$\delta D = 0.8\ \delta O^{18} + 1.0$$

(Craig (20)). Thus, normal scatter cannot account for the anomalous isotopic compositions of the three O^{18}-poor bentonites. Clayton _et al_. (14) showed that marine sediments could exchange with fresh waters under some conditions, causing the water to become enriched in O^{18}. This would have the effect of causing the waters to lie below the line of normal meteoric waters and therefore clays in equilibrium with these waters would lie below the line determined for clays. However, all the O^{18}-poor clay samples lie above the line. Thus, the isotopic compositions of these samples cannot be interpreted simply as the result of equilibration with water of unusual isotopic composition.

The most reasonable interpretation of the montmorillonite data is that the four samples which are richest in O^{18} formed in isotopic equilibrium with sea water at sedimentary temperatures and did not undergo subsequent isotopic exchange, and that the three O^{18}-poor samples have undergone isotopic exchange with meteoric waters at temperatures greater than room temperature. At the same time, since there is no obvious evidence of metamorphism associated with these samples, the temperatures were not excessively high.

The data suggest that montmorillonites are readily subject to isotopic exchange at elevated temperatures, and that during exchange they attain isotopic compositions in equilibrium with their environments. With better sampling and geological and mineralogical control it may be possible to work out the details of the conditions under which exchange occurs. Isotopic compositions of clay minerals may then be able to serve as sensitive indicators of diagenetic conditions.

iii. Illite

Illite is similar to muscovite and is analogous to montmorillonite in that its basic structure is a sheet of aluminum atoms in octahedral coordination with oxygen atoms and hydroxyl groups and bonded on either side to a sheet of silicon-oxygen tetrahedra. Unlike montmorillonite, however there is very little substitution of iron or magnesium in the octahedral layer and considerably more substitution of aluminum in the tetrahedral position. As a result, there is a greater net negative charge on the aluminosilicate framework than there is in the case of montmorillonite, and there are more cations, chiefly potassium, to balance this charge. Also, unlike montmorillonite there is generally no interlayer water in the structure. Illite may be described by the structural formula $K_{1-1.5}Al_4(Si_{7-6.5}Al_{1-1.5}O_{20})(OH)_4$ (Deer, Howie and Zussman(25)).

Illite is probably the most common clay mineral in sedimentary rocks. It may form by weathering or diagenetically from kaolinite and montmorillonite. It appears to have a wide range of stability and is stable in the marine environment. Hurley et al. (54) determined, however, that illites of the ocean basins have potassium argon ages of 200 to 400 million years and must therefore be of detrital age.

In the present study only one illite sample was analyzed. This sample, of non-marine origin, was taken from the underclay of a Pennsylvanian cyclothem at Morris, Illinois. The illite has a δO^{18} value of +20.5 permil and a δD value of -5.1 percent. Because only one sample was measured, it is not possible to give a meaningful discussion on the range of isotopic variations of illites in sediments.

The point corresponding to the isotopic composition of the illite deviates by about one percent from the line estimated for the isotopic compositions of kaolinites in equilibrium with meteoric waters. It deviates by about three percent from the line estimated for a mineral with the chemical composition of illite (figure 19, section 5.4). The illite is isotopically not unlike other non-marine clays, having a δ-value similar to kaolinites. Its deviation from the line estimated for illite is not large suggesting that it could have been formed under equilibrium or near-equilibrium conditions, and adding to the general understanding of isotopic variations in clay minerals.

iv. Glauconite

Glauconite is structurally similar to illite but differs in having more iron and magnesium substituted for aluminum in the octahedral layers and less aluminum substituted for silicon in the tetrahedral layers. In many instances there is interlayering of some montmorillonitic-type "expandable layers" accounting for the presence of some interlayer water. The chemical formula for glauconite is $(K, Na, Ca)_{1.2-1.0}(Mg^{+2},Fe^{+2},Al^{+3},Fe^{+3})_{4.0}(Si_{7-7.6}Al_{1-0.4}O_{20})(OH)_4 \cdot n\,H_2O$ (Deer, Howie and Zussman (25)).

Glauconite occurs in many types of sedimentary rocks and generally forms in a marine environment. There are many cases reported in the literature, however, of glauconite and glauconitic mica having formed under non-marine conditions, so that, contrary to earlier belief (Cloud (18)), its presence can not be used as an indicator of a marine environment. Its formation probably requires a fairly restricted set of physical and chemical environmental conditions (Burst (8,9)). The concentration of expandable layers in glauconite has been found to decrease with the age of the samples, and this has been interpreted as a diagenetic effect (Hower (53)). Glauconite is thus undoubtedly stable in some diagenetic environments.

Aside from its use as an indicator of sedimentary environment, glauconite in sediments is of interest as a potassium bearing authigenic phase suitable for radiometric K^{40}/Ar dating (Wasserburg et al. (110), Evernden et al. (36), etc). Because of this particular use, it is of interest to determine what information the oxygen and hydrogen isotopic composition of glauconite can contribute to the understanding of its chemistry.

The isotopic data of the glauconite samples analyzed are shown in figure 14. There are two distinct groups of samples evident in this figure, one set richer in O^{18} and poorer in deuterium than the other. The O^{18} -rich set of samples consists entirely of glauconites formed during or since the Late Cretaceous, and none have been subject to deep burial (Owens, Minard and Blackmon (82), Emery (31)). The O^{18} -poor set of samples are from a suite of Precambrian Australian rocks and are thought to have been buried at some time during their history to depths ranging from one thousand to seven thousand feet Plumb (84). The Mesozoic and Cenozoic samples can then be considered to be more representative of glauconites forming or exchanging on or near the earth's surface under con-

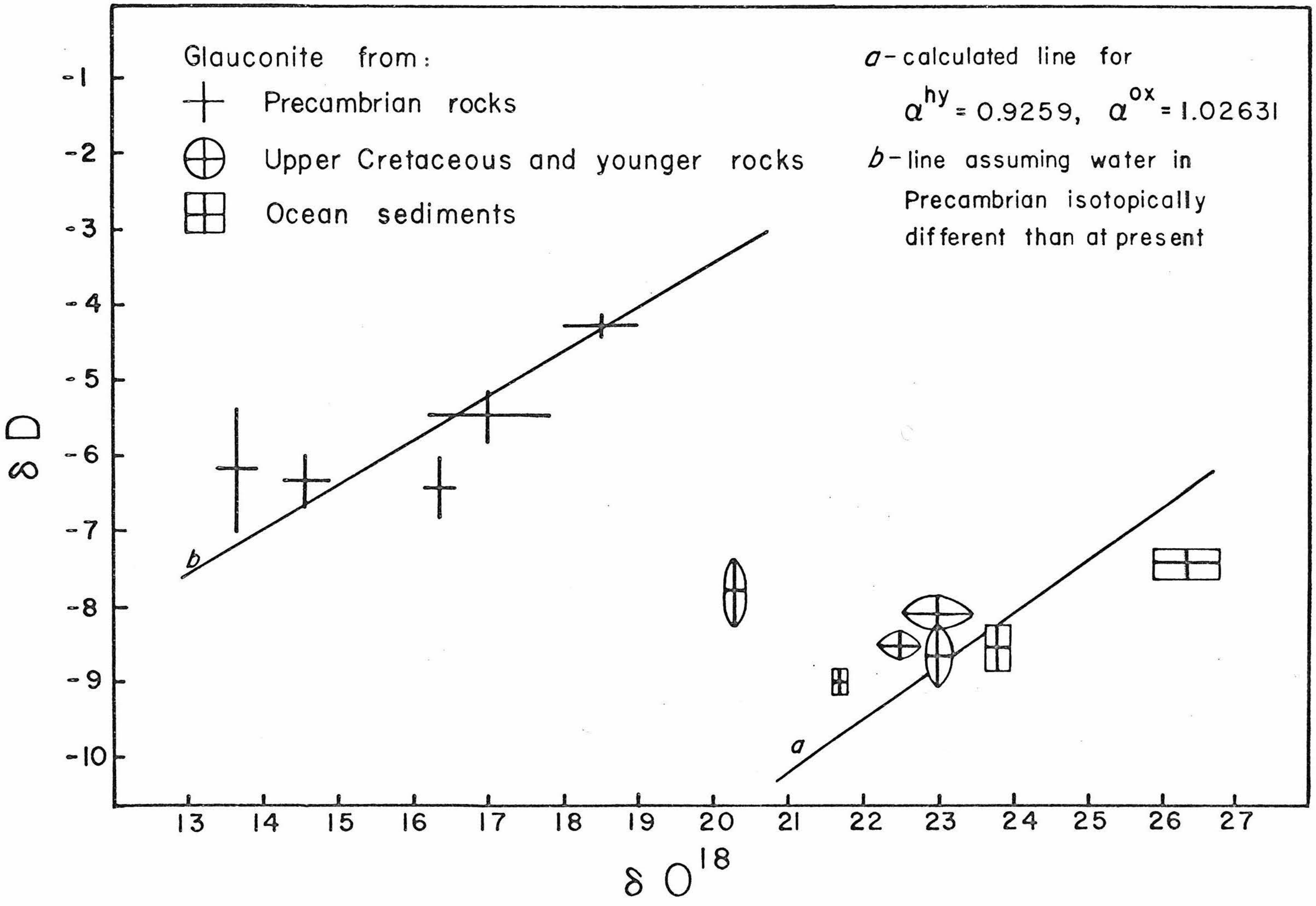


Figure 14. Graph showing relationship between δD values and δO^{18} values of some glauconites taken from rocks and ocean sediments.

ditions similar to those found at the present time.

A line corresponding to the equation

$$\delta D = .722 \quad \delta O^{18} - 25$$

has been drawn on figure 14. This line corresponds to the fractionation factors $\alpha^{hy}_{glauc-H_2O} = 0.9259$ and $\alpha^{ox}_{glauc-H_2O} = 1.02631$ which are calculated from the assumption that sample Sta 1752 has undergone complete isotopic exchange with sea water. This sample, the richest in O^{18} of all the glauconites measured, was dredged from the surface of the Blake Plateau (31° 28.7'N, 72° 290'W) in the Atlantic Ocean. A temperature of approximately 6°C prevails on the sea floor in this area (Stewart (121)). The region is swept by currents from the south containing no meltwater, so the isotopic composition of the water is probably close to 0.0 permil. It is uncertain whether this glauconite is of detrital origin from the continents or is forming <u>in situ</u> based on the available geological data (Trumbull (119)).

With only one exception (R-8), data for the remaining Mesozoic and Cenozoic glauconites lie on or very close to the line drawn, in a manner compatible with the model of exchange with fresh waters under conditions of constant fractionation factors. If this model is a valid interpretation of the isotopic compositions of these minerals, and if it is also true that they have formed under marine conditions, as interpreted by Owens, Minard, and Blackmon (82), then this is the only case where minerals formed in a marine environment can be demonstrated to have undergone isotopic exchange at sedimentary temperatures.

While the above explanation of the data is possible, there is another interpretation of the data. The isotopic compositions of the five samples which lie near the line are clustered together in a small region. It is possible that some or all of these points represent glauconites which were also in isotopic equilibrium with sea water and did not subsequently undergo isotopic exchange. If the sea water with which the samples equilibrated were diluted with isotopically light fresh water and/or the temperature of formation were warmer than for the Blake Plateau sample then the measured isotopic compositions might lie in the region in which they do. The two facts which raise the suspicion that this may actually be the case are: 1) the isotopic compositions of these samples cluster together, and it is unlikely that all of them would have exchanged completely with waters of similar isotopic compositions at similar temperatures; and 2) one of the samples (Sta 6941) was dredged from Santa Monica Bay, California and has very likely formed in sea water and remained there since formation (Emery (31)).

Factors which render plausible the proposed mechanism for obtaining the observed isotopic compositions are that all samples were formed in areas which might be diluted by meltwater, and that four of them were formed during the late Cretaceous at which time temperatures were warmer than at present.

The isotopic composition of one Tertiary sample (R-8) lies well above the line drawn. The deviation of this sample from the line can be caused by exchange with fresh water under conditions of elevated temperature.

A line of slope similar to that through the data of the younger samples may be drawn through the points representing the Precambrian samples. This line, however, is displaced considerably. One possible explanation for this displacement is that the isotopic composition of sea water may have changed since the time of formation of the samples (1390 million years ago according to potassium argon dating (Plumb (84))). If the isotopic composition of sea water were approximately 3 percent richer in deuterium and 6 permil poorer in O^{18} 1390 million years ago than at the present time then the two sets of data would be compatible. A change in the oxygen isotopic composition of sea water in this direction has been postulated by Weber (112). However, there exists another possible cause for the displacement of the isotopic compositions of the Precambrian glauconites, and that is exchange with ground water at an elevated temperature.

This appears to be a likely explanation for at least part of the observed effect since the sandstones from which the samples were taken were cemented with secondary quartz and the rocks were therefore probably subject to invasion by silica bearing solutions with which isotopic exchange might have occurred. In addition, there is a spread of five permil in the oxygen isotopic compositions of the glauconites indicating that at least some of them underwent exchange after formation. The observed range of O^{18}/O^{16} ratios is larger than seems reasonable to have occurred in marine waters in a fairly short length of time and in a fairly small area. The potassium - argon dates for these samples are the same within experimental error (Plumb (84)).

As was the case with the kaolinites, and to some extent with the montmorillonites, many of the glauconite samples appear to have formed or exchanged with natural waters under conditions of similar fractionation factors, $\alpha^{hy}_{glauc-H_2O}$ and $\alpha^{ox}_{glauc-H_2O}$. Because of the internal consistency of much of the glauconite isotope data, and the similarity of the estimated fractionation factors to those of other minerals, it can be argued that these fractionation factors represent isotopic equilibrium fractionation. It is not possible to say with certainty whether or not the O^{18} -rich samples of figure 14 have undergone isotopic exchange with fresh water at low temperatures. If they have, they are the only clay minerals studied which have exchanged in this manner.

B. Summary of clay mineral findings

The variations of the oxygen and hydrogen isotope ratios in kaolinite, illite, montmorillonite, and glauconite are relatively large. However, the isotopic variations show systematic relationships which are dependent on the conditions of formation and exchange of the clay minerals. These relationships follow the form

$$\delta D = A \quad \delta O^{18} + B$$

Clays which have undergone complete exchange with meteoric waters under conditions of constant $\alpha^{ox}_{clay-H_2O}$ and $\alpha^{hy}_{clay-H_2O}$ would be expected to lie along the curve representing the above equation.

Clays which have exchanged with water at elevated temperatures would lie above the line drawn for sedimentary temperatures. Marine clays which have subsequently undergone incomplete exchange with meteoric waters at sedimentary temperatures would be expected to lie below the line. Estimated values of the fractionation factors and the constants A and B for kaolinite, montmorillonite and glauconite are given in Table 12.

Using the above relationships it is possible to interpret the isotope data of the hydrothermal dickites and some of the bentonites and glauconites as having resulted from isotopic exchange at elevated temperatures. However, most of the clay mineral data lie along the line estimated for isotopic equilibration at low temperatures.

Most of the clays which lie above the line were originally formed under sedimentary conditions, and their isotopic compositions are indicative of the fact that post-formational isotopic exchange may occur at elevated temperatures. There is also some evidence that some of the glauconites which originally formed under marine conditions may have subsequently undergone complete isotopic exchange with fresh water at sedimentary temperatures. There is, however, no case in which such post-formational exchange at sedimentary temperatures can be unequivocally demonstrated to have occurred. Also, no evidence has been found for incomplete isotopic exchange under sedimentary conditions since no points lie beneath the lines on plots of δD vs δO^{18}. This suggests that exchange under sedimentary conditions may occur only slowly and with great difficulty.

Since clay minerals appear to form in isotopic equilibrium with their environment and since their isotopic compositions respond to changes in the environment in a predictable manner at elevated temperatures, isotopic variations should prove useful for determining conditions of formation of clay minerals and alterations during their subsequent history.

TABLE 12

Fractionation factors between clay minerals and water

Mineral	$\alpha^{ox}_{clay-H_2O}$	$\alpha^{hy}_{clay-H_2O}$	A	B
Kaolinite	1.0265	0.970	0.76	-22
Montmorillonite	1.0273 ±0.0012	0.938 ±0.007	0.73	-26
Glauconite	1.0263	0.926	0.72	-25

5.3 Isotopic composition of non-clay minerals in sediments

In addition to clay minerals, other minerals of sedimentary origin including phillipsite, potassium feldspar, quartz, hydrous silica and oxide minerals were analyzed to further understand the contribution isotope data may make to the interpretation of sedimentary processes.

A. Phillipsite

Phillipsite is a zeolite mineral which occurs on the ocean floor as an alteration product of volcanic materials by sea water (Bramlette (7)). It is the only zeolite which occurs in high concentration on the sea floor, and is one of the rare documented cases of an authigenic framework silicate forming on the sea bottom. As such, phillipsite samples taken from the ocean floor are authigenic silicates which have been formed under known isotopic and temperature conditions. They are the closest analogues to feldspars which are commonly formed authigenically at low temperatures under known conditions*

There is considerable variation in reported chemical analyses of phillipsite which can result from isomorphous substitution. Deer, Howie, and Zussman (24) list the ideal chemical composition of phillipsite as $(\frac{1}{2}Ca, Na, K)_3Al_3Si_5O_{16}\cdot 6H_2O$. This corresponds to an aluminum:silicon ratio intermediate between that of alkali and alkaline earth feldspars.

Three phillipsites from ocean core samples were analyzed for oxygen isotope ratios. The results are listed in Table 13. The oxygen of all three samples is extremely rich in O^{18}, and has an isotopic composition similar to that of dehydrated diatomite (Degens and Epstein (27)). The oxygen isotope fractionation factor between phillipsite and sea water is approximately 1.034, and is thus greater than any of the estimated clay - water fractionation factors. This is consistent with the observation that at higher temperatures framework silicates concentrate O^{18} with respect to sheet silicates (Taylor and Epstein (104)). For these reasons it is reasonable to assume that the

---

* A thorough search of the literature has yielded only one claim of a feldspar forming authigenically on the sea floor (Mellis(71) and this is not considered well documented.

analyzed phillipsites were formed in isotopic equilibrium with sea water. As was observed with the clay minerals, there is no evidence of any memory of the isotopic composition of the parent basaltic material from which the phillipsites were formed.

TABLE 13

Isotopic composition of phillipsite from ocean cores

Sample	Latitude	Longitude	δO^{18} permil	Av. dev.	No. runs
MSN 130	10°34'S	151°05'W	+33.6	.7	3
RIS 79	14°03'S	131°44'W	+34.1	1.1	4
Tet 23	15°11'N	162°25'W	+33.6	.4	2

B. Feldspar

The existence of authigenic feldspars of sedimentary or diagenetic origin has long been recognized, but the chemical and temperature conditions under which they form are not known. Stable isotope measurements can throw some light on this problem. The oxygen isotopic composition of one authigenic feldspar was measured. This sample was a secondary overgrowth of potassium feldspar on a detrital feldspar core, from the (Cambrian) Franconia Formation in Wisconsin. The isotopic compositions of rimmed grains and detrital cores were measured and the isotopic composition of the rim was then calculated using the core to rim ratio of 50:50 (±10) measured by Tatsumoto and Patterson (98) for this sample. The results are shown in Table 14. The uncertainty in the δ-value of the secondary rim results not from the isotopic measurements but from uncertainty in the core to rim ratio.

There is a striking difference of about 10 permil between the isotopic composition of the core and that of the rim. The typical igneous value for the isotopic composition of the core indicates that it did not exchange during the formation of the authigenic feldspar. A maximum temperature of formation of the rim may be estimated from its oxygen isotopic composition. The water present at the time of formation was undoubtedly meteoric in origin. The δO^{18}-value of this water was probably less than zero, or at most a few permil greater than zero. If we suppose that the O^{18}/O^{16} ratio of the water in which the feldspar precipitated was as high as +3 permil, then the temperature at which the feldspar formed can be calculated to be 110°C if we use the fractionation factor estimated from the types of oxygen bonds present in the mineral (figure 17 , section 5.4). A δO^{18}-value for the water smaller than +3 permil will give a temperature lower than 110°C. Since there is little likelihood of having the O^{18}/O^{16} ratio of the water greater than +3 permil, the 110°C temperature of formation is probably an upper limit, and implies a low temperature of formation for the secondary feldspar.

The marked difference between the O^{18}/O^{16} ratios characteristic of igneous and metamorphic feldspars and the O^{18}/O^{16} ratios of secondary or authigenic feldspars, as well as the high degree of temperature sensitivity of the feldspar - water fractionation factors, suggests that isotopic measurements of this type should be useful for evaluating the conditions of formation of authigenic feldspars. In addition, O^{18}/O^{16} measurements can aid mineralogical interpretation of sedimentary phase assemblages by indicating whether fine-grained feldspars and other minerals are of sedimentary or high temperature origin.

TABLE 14

Isotopic composition of detrital core and authigenic rim of Franconia Fm. feldspar

Sample	δO^{18} permil	Av. dev.	No. runs
Core plus rim	+13.7	0.4	3
Core only	+ 8.5	0.1	3
Rim only (by calc.)	$+18.8^{+2.7}_{-1.6}$		

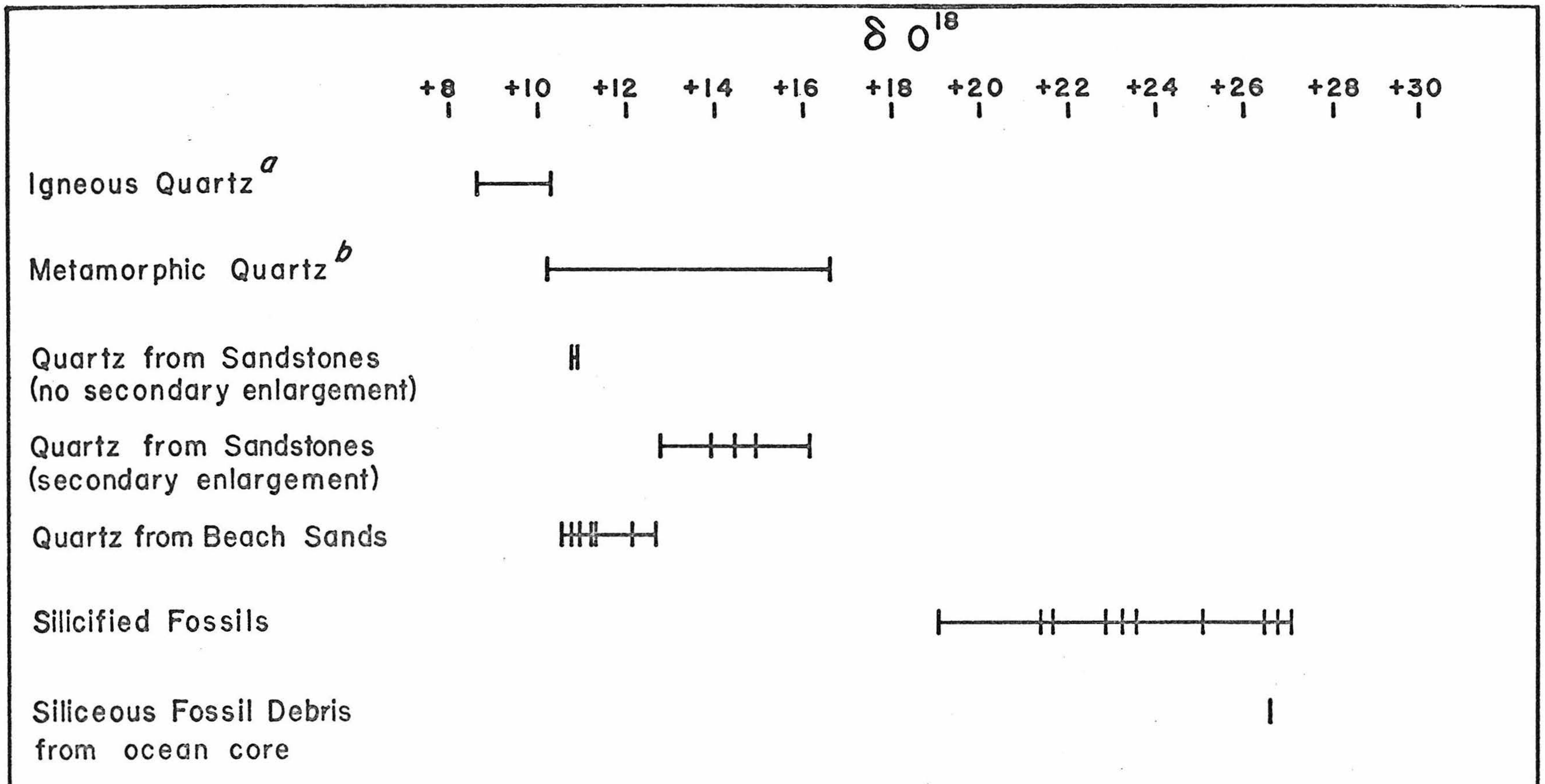
C. Silica minerals

Quartz and cryptocrystalline silica are the most abundant non-clay minerals in sedimentary rocks. While quartz in sediments is primarily of detrital origin, secondary or authigenic quartz is commonly observed. Chert, or cryptocrystalline quartz, is also a common sedimentary rock. It has been known for some time that chert and secondary quartz are richer in O^{18} than igneous quartz. Silverman (93) observed a semiquantitative correlation between the amount of secondary overgrowth and the isotopic composition of three quartz sandstones. Degens and Epstein (27) measured the isotopic compositions of a number of cherts in marine limestones and found that those richest in O^{18} had δ-values between +33 and +34 permil, similar to the isotopic compositions they measured in two dehydrated marine diatomites (+32 and +33.5 permil). This strongly suggests that the quartz - water fractionation factor at sedimentary temperatures is between 1.033 and 1.034. This value is three to nine permil lower than the extrapolated value of the high temperature experimental data of Clayton _et al_. (16) for the quartz - water system. In the present study a number of quartz samples from various sedimentary deposits were analyzed in order to see whether oxygen isotopic analyses are a useful tool for determining provenance of detrital quartz and the conditions of formation of secondary or authigenic quartz. The analytical data are shown in figure 15.

i. Oxygen isotope ratios of sand sized quartz

All sand-sized quartz samples measured, including those from ancient sandstones and modern beach deposits are slightly richer in O^{18} than that of any quartz in the igneous (non-pegmatitic) rocks analyzed by Taylor and Epstein (103). Two possibilities for this enrichment are isotopic exchange of quartz with water under sedimentary conditions, and a mixing of O^{18}-rich metamorphic quartz with igneous quartz during sedimentation.

If isotopic exchange of sand-sized quartz under sedimentary conditions were significant, a much broader spread in the range of δ-values of quartz from sandstones and beach sands would be expected. This is expecially true for the almost pure, well-rounded quartz beach sands of the southeastern United States which have undoubtedly been through a number of sedimentary cycles. Furthermore, if isotopic exchange were to occur in sand-sized quartz, it would be expected to occur from the outside and proceed inward, so that the outside of the grains would be expected to be richer in O^{18} than the cores. In the course of mineral separation, some of the samples were subject to etching in concentrated hydrofluoric acid for about 10



a. range of igneous (non-pegmatitic) quartz measured by Taylor and Epstein (1962)

b. range of quartz in regionally metamorphosed regions, after Garlick and Epstein (1967)

Figure 15. Oxygen isotopic compositions of some detrital and authigenic quartz samples from sedimentary rocks.

minutes, removing the outer layer of quartz. It may be seen from the data of Table 15 that there is no large difference in the averages of the isotopic compositions of the etched and the non-etched samples. While there is not a statistically large number of samples, the data suggest that the quartz of the beach sands is isotopically homogeneous.

The samples may be mixtures of O^{18} -poor igneous quartz with metamorphic quartz richer in O^{18}. Each sample may represent the integrated isotopic composition of quartz derived over a broad area. The beach sand quartz richest in O^{18} is from Bath, Maine, an area composed primarily of metamorphic rocks. The samples lowest in O^{18} are from La Push, Washington and Huntington Beach, California, areas for which the source rocks are primarily igneous, (although it is recognized that one or more cycles of sedimentation may have preceded deposition on the beach).

The data on sand-sized quartz suggest that the isotopic composition of quartz may be used as an indicator of provenance. The range of variation is small, but measurements may be made with great precision and should be useful for distinguishing between detrital deposits of metamorphic origin from those of igneous origin.

In computations where it is necessary to assume an isotopic composition of detrital quartz in sediments, the best value to use is generally +11.0 or +11.5 permil rather than +10 permil, the average for igneous quartz.

ii. Isotopic composition of quartz replacements of carbonate fossils

Carbonate fossils in limestones are often replaced by silica, but the mechanisms of replacement are not known. The isotopic compositions of the silica should be expected to reflect its conditions of formation. A suite of silicified brachiopods from a Devonian marine limestone of the Roberts Mountain area, Nevada , furnished by A. J. Boucot, was analyzed, and the results are shown in figure 15. All of the samples were fairly fine-grained crystalline quartz. Although the fossils were collected from a fairly small area and within a stratigraphic range of only about 1400 feet (J. Johnson (120)) there was a wide range in the values of the measured isotopic compositions (+19.1 to +27.1 permil). The data imply that these quartz samples formed at relatively low temperatures (probably not above 100°C). The large range in δ-values suggests that the processes involved in the replacement of the fossils by quartz were probably complicated. For example the variability of the δ-values could have been caused by the dehydration of amorphous silica deposited under marine conditions subsequent to the removal of the beds from the marine environment. The isotopic data would also be compatible with the silicification of the fossils in the presence of fresh water after lithification and uplift.

TABLE 15

Isotopic compositions of detrital quartz

Etched in HF		Not etched in HF	
Sample	δO^{18}	Sample	δO^{18}
<u>Beach sands</u>		<u>Beach sands</u>	
Huntington Beach, Calif.	10.6	Fernandia, Fla.	11.0
Bath, Me.	12.7	Bay St. Louis, Miss.	11.4
La Push, Wash.	10.9	S. Island, So. Carolina	11.3
		Ocean View, Va.	12.1
		<u>Sandstones</u>	
		St. Peter	10.95
		Franconia Fm.	10.9
Average	11.4	Average	11.3

iii. Isotopic composition of organic siliceous debris in an ocean core

The carbonate-free, larger than 44 μ fraction of an ocean core taken at 39°56'N, 165°32'E was composed almost entirely of the siliceous debris of organisms, primarily diatoms. The δ-value of the oxygen of this silica was +26.6 permil. This is a considerably lower value than that of dehydrated diatomite or chert thought to be in equilibrium with sea water, and the difference is probably the result of the inclusion of a large amount of water in the opaline silica. This result indicates that considerable caution must be exercised regarding the interpretation of the isotope data of hydrated silica until we have a better understanding of the nature of water associated with these minerals.

D. Oxide minerals

Oxides of iron are present in small amounts in a great many types of sedimentary rocks. However, very little is known about their isotopic behavior. O'Neil and Clayton (77) measured a δO^{18} value of +5.6 permil in a magnetite (possibly maghemite) chiton tooth which grew in a marine environment at a temperature of 9°C. The δO^{18}-value for this oxide is very much lower than the values of silicate minerals which formed at low temperatures.

In our effort to determine and interpret the isotopic composition of ocean sediments it was important to have a rough idea of the isotopic composition of the oxides of iron and manganese. Therefore a manganese nodule from the Blake Plateau in the Atlantic Ocean was analyzed for oxygen and hydrogen isotope ratios. The results are shown in Table 16. The oxygen isotope ratio, while greater than that of the magnetite tooth is still considerably smaller than that of silicates which have formed in sea water. It is recognized that the isotopic values obtained for the manganese nodule are subject to question because of the complex nature of this sample. Manganese nodules are mixtures of oxides and oxide-hydroxides of iron and manganese, and also contain molecular water. Unlike the case of clay minerals, the conditions necessary for the removal of the molecular water are not known. If some of this water were not removed, it would have a greater effect on the hydrogen results than on the oxygen results.

TABLE 16

Isotopic composition of Blake Plateau manganese nodule

	δ-value	No. Runs	Av. Dev.
O^{18}	+15.0‰	2	0.8
D	- 7.7%	3	0.3

Whole rock isotopic analyses of sediments may be affected by the presence of oxides because these minerals have low O^{18}/O^{16} ratios. It is therefore important to check for these minerals in samples in which their presence is suspected.

5.4 The estimation of isotopic fractionations between minerals and water from crystal chemical considerations

A. Oxygen isotope fractionations

Taylor and Epstein (104) showed that δ-values could be assigned to the various types of bonds associated with oxygen in igneous minerals, and that the oxygen isotopic compositions of the minerals could be approximated from a knowledge of the types of oxygen bonding they contained. Garlick (39) showed that this approach is approximately correct for a large number of minerals which have equilibrated over a range of igneous and metamorphic temperatures.

In the present study a series of calculations were made to determine if the relationships between bond types and fractionation factors could be extended to lower temperatures. Fractionation factors between various oxygen bond types and water were estimated in the temperature range 0° to 800°C. These estimated fractionation factors are shown plotted as a function of temperature in figure 16.

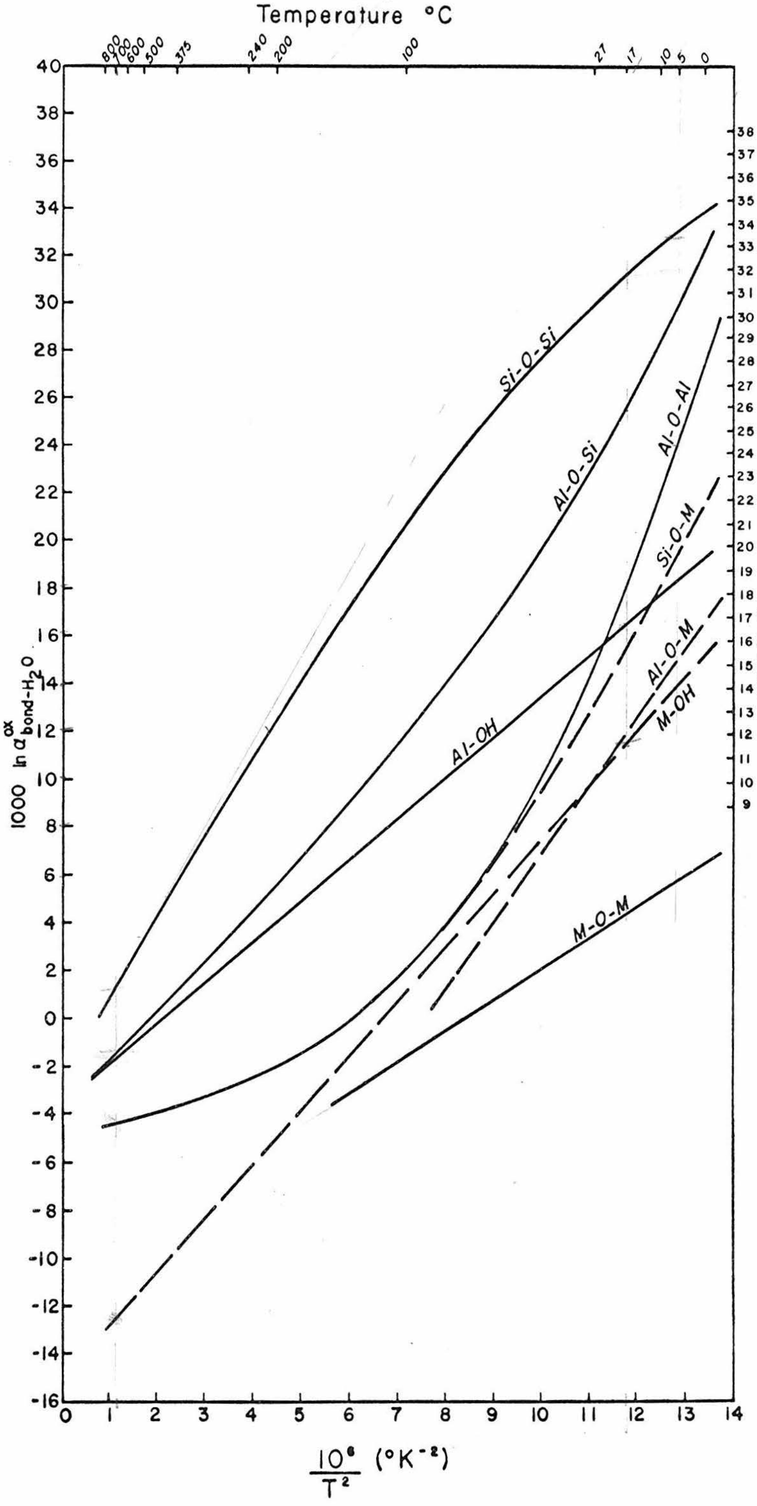


Figure 16. Estimated oxygen isotope fractionation factors between oxygen bond types and water, plotted as a function of temperature. Dashed lines indicate greater uncertainty than solid lines.

At sedimentary temperatures the estimations were based primarily on the mineral - water fractionation factors which were evaluated from the isotopic compositions of the natural samples discussed in the previous sections, but in some cases by extrapolation of fractionation factors between oxygen bonds and water at high temperatures. The high temperature values were obtained from the experimentally determined mineral - water fractionations of quartz (Clayton, O'Neil and Mayeda (16)), feldspars (O'Neil and Taylor (80)), muscovite (O'Neil and Taylor (79)), and magnetite (O'Neil and Clayton (77)), and from some of the relationships between bond types determined by Taylor and Epstein (104) and Garlick (39).

The basic assumption in the estimation of fractionation factors between oxygen bonds and water in this manner is that the fractionation for each bond is essentially independent of the presence of all other bonds in the mineral. For example, quartz is composed entirely of Si-O-Si bonds and olivine is composed entirely of Si-O-M bonds. Therefore the fractionation factor for a mineral with 50 percent of each type of bonding would have a fractionation factor with respect to water half way between the quartz - water and olivine - water fractionations.

The details of the calculations for each oxygen bond type are described below. The percentages of the various bond types in a number of minerals are listed in

Table 17.

a. Si-O-Si - water: This is identical to the quartz-water fraction. The experimental data were used at high temperatures, and the low temperature value used was 1.0335 at 7°C, corresponding to the isotopic compositions of the dehydrated marine diatomites analyzed by Degens and Epstein (27).

b. Al-O-Si - water: At high temperatures the alkali feldspar (50% Al-O-Si and 50% Si-O-Si) and alkaline earth feldspar (25% Si-O-Si, 50% Al-O-Si, 25% Al-O-Al) experimental data were used. The assumption was made that the Si-O-Si - Al-O-Al fractionation was twice the Si-O-Si - Si-O-Al fractionation. A line was determined for each of the two feldspars, and the average of these two was plotted as the Al-O-Si - water fractionation. At low temperatures the Al-O-Si - water fractionation was calculated by using the Si-O-Si - water fractionation and a value of 1.032 for the anhydrous phillipsite ($Na_3Al_3Si_5O_{16}$) - water fractionation factor at 4°C.

c. Al-O-Al - water: At all temperatures the Al-O-Al - Si-O-Si fraction was taken to be twice the Si-O-Si - Al-O-Si fractionation. This relationship was previously determined by Taylor and Epstein (104) and Garlick (39) at igneous and metamorphic temperatures.

d. Al-OH - water: At high temperatures the values for Si-O-Si, Al-O-Si and Al-O-Al were used with the

TABLE 17

Percent of various oxygen bond types in minerals

	Si-O-Si	Al-O-Si	Al-O-Al	Al-O-H	Mg-O-Si	Mg-O-Al	Mg-OH
Quartz	100						
Alkali feldspar	50	50					
Anorthite	25	50	25				
Kaolinite	33.33	22.22		44.44			
Muscovite	25	50	8.333	16.67			
Biotite	25	25			25	8.333	16.67
Montmorillonite	50	27.5		13.7	5.8		3.0
Glauconite	37.4	34.4	3.2	12.5	7.3	1.0	4.2
Chlorite	16.67	16.67		11.11	16.67	5.55	33.33
Illite	37.5	41.6	4.2	16.7			
Vermiculite	22.9	27.9	4.9	2.8	19.4	8.3	13.9
Phillipsite	35.7	53.5	10.7				

experimental muscovite - water data. The line determined for the Al-OH - water fractionation could be extrapolated linearly to the value of 1.0165 at 17°C estimated from the incomplete fluorination of the Langley, S. Carolina kaolinite (section 4.7).

e. M-O-M* - water: The magnetite - water fractionation of O'Neil and Clayton (77) was used as the M-O-M - water fractionation.

f. Si-O-M - water: At temperatures greater than 100°C the Al-O-Al - water and Si-O-M - water fractionations were assumed to coincide. At temperatures below 100°C the Si-O-M - water fractionation was assumed to be intermediate between the Si-O-Si and M-O-M fractionations.

g. Al-O-M - water: This was estimated only at low temperatures. The Al-O-M - water fractionation was assumed to be intermediate in value between the Al-O-Al - water and M-O-M - water fractionations.

h. Mg-OH - water: The biotite - water fractionation was estimated at high temperatures from the isotopic compositions of the minerals of quartz - biotite - muscovite assemblages. The Mg-OH - water fractionation was estimated from the biotite - water fractionation and the fractionations between water and the bonds listed above. The Mg-OH - water fractionation was linearly extrapolated to

---

*M refers to iron, magnesium or other divalent or trivalent atoms.

low temperatures.

In the high temperature regions where mineral - water fractionations and mineral - mineral fractionations are small, good agreement (±0.5 permil) exists between values of mineral - water fractionations calculated from the bond - water fractionations and the experimental values. At lower temperatures where fractionations are considerably larger, agreement between calculated values of the mineral - water fractionations and values estimated from the isotopic compositions of natural samples is within 3 permil for the three minerals (montmorillonite, glauconite, and kaolinite) which were not used in determining the bond - water fractionations as seen in Table 18.

TABLE 18

Mineral - water fractionation factors estimated from the oxygen bonds in minerals compared with fractionation factors estimated from the isotopic data on natural samples

Mineral	Temp. °C	$(\alpha-1)1000$ estimated from bond fractionation	$(\alpha-1)1000$ estimated from natural samples
Kaolinite	17°	23.9	26.5
Montmorillonite	4°	29.9	27.3 ±1.2
Glauconite	6°	28.5	26.3
Chlorite	4°	22.2	
Illite	4°	29.9	
Vermiculite	4°	25.6	

Considering the assumptions necessary for estimating the oxygen isotope fractionation factors from the curves of figure 16, the agreement between the values estimated in this manner and those independently evaluated from the isotopic data of natural samples is gratifying. The discrepancies between the two sets of data are probably due to a breakdown of the basic assumption of the calculation, i.e. that the fractionation factors of the minerals are linear combinations of the fractionation factors of the bonds. The success of the calculations in the cases in which they could be compared with estimates obtained by independent means indicates that the method is a useful one for obtaining semi-quantitative estimates of isotopic fractionations.

As examples of the relationship between temper- and fractionation factors at low temperatures, kaolinite - water and montmorillonite - water and alkali feldspar - water oxygen isotopic fractionations have been estimated over the temperature range 0^{o} to 150^{o}C, and are shown in figure 17. The values were based on the fractionations between the various bond-types and water over this temperature range.

B. Hydrogen isotope fractionations

The data of Taylor and Epstein (101) show that igneous biotites have lower D/H ratios than igneous muscovites, implying that Al-OH bonds are enriched deuterium

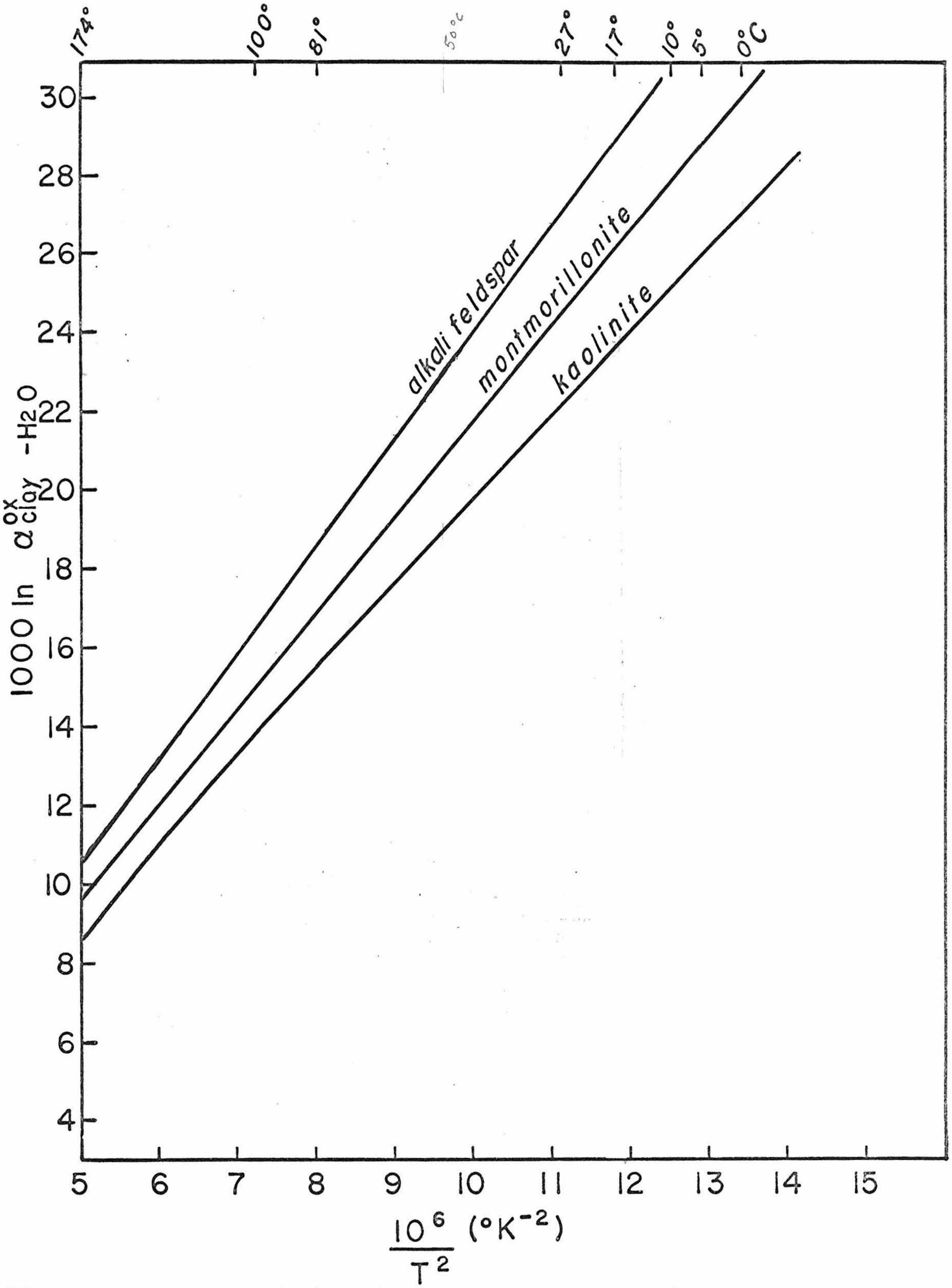


Figure 17. Estimated mineral-water fractionation factors for alkali feldspar, montmorillonite, and kaolinite as a function of temperature

relative to Mg-OH bonds at igneous temperatures. This is in accord with the results found for sedimentary minerals. Figure 18 is a graph of $\alpha^{hy}_{clay-H_2O}$ against mole percent hydrogen in Al-OH bonds for kaolinite, montmorillonite and glauconite. The chemical compositions of the minerals are average values taken from Deer, Howie and Zussman (25). The three points lie very close to a straight line which if extrapolated to 100 percent Mg-OH gives a fractionation factor of 0.79. This corresponds to a fractionation of approximately 18 percent between Al-OH bonds and Mg-OH bonds. The straight line drawn in figure 18 is based on the assumption that the mineral - water hydrogen isotope fractionations may be obtained from a linear combination of the Mg-OH water and Al-OH water fractionations.

Using the results of this section it is possible to estimate values of $\alpha^{ox}_{clay-H_2O}$ and $\alpha^{hy}_{clay-H_2O}$ for illite and chlorite under sedimentary conditions. It is then possible to plot lines on a graph of δD vs δO^{18} for the isotopic compositions of these minerals in equilibrium with natural waters. The fractionation factors for these minerals and the constants of the lines on a δD vs δO^{18} plot are listed in Table 19.

The lines calculated for chlorite and illite on the basis of chemical bonds and those calculated for kaolinite and montmorillonite on the basis of the isotopic composition of naturally occurring specimens are shown in

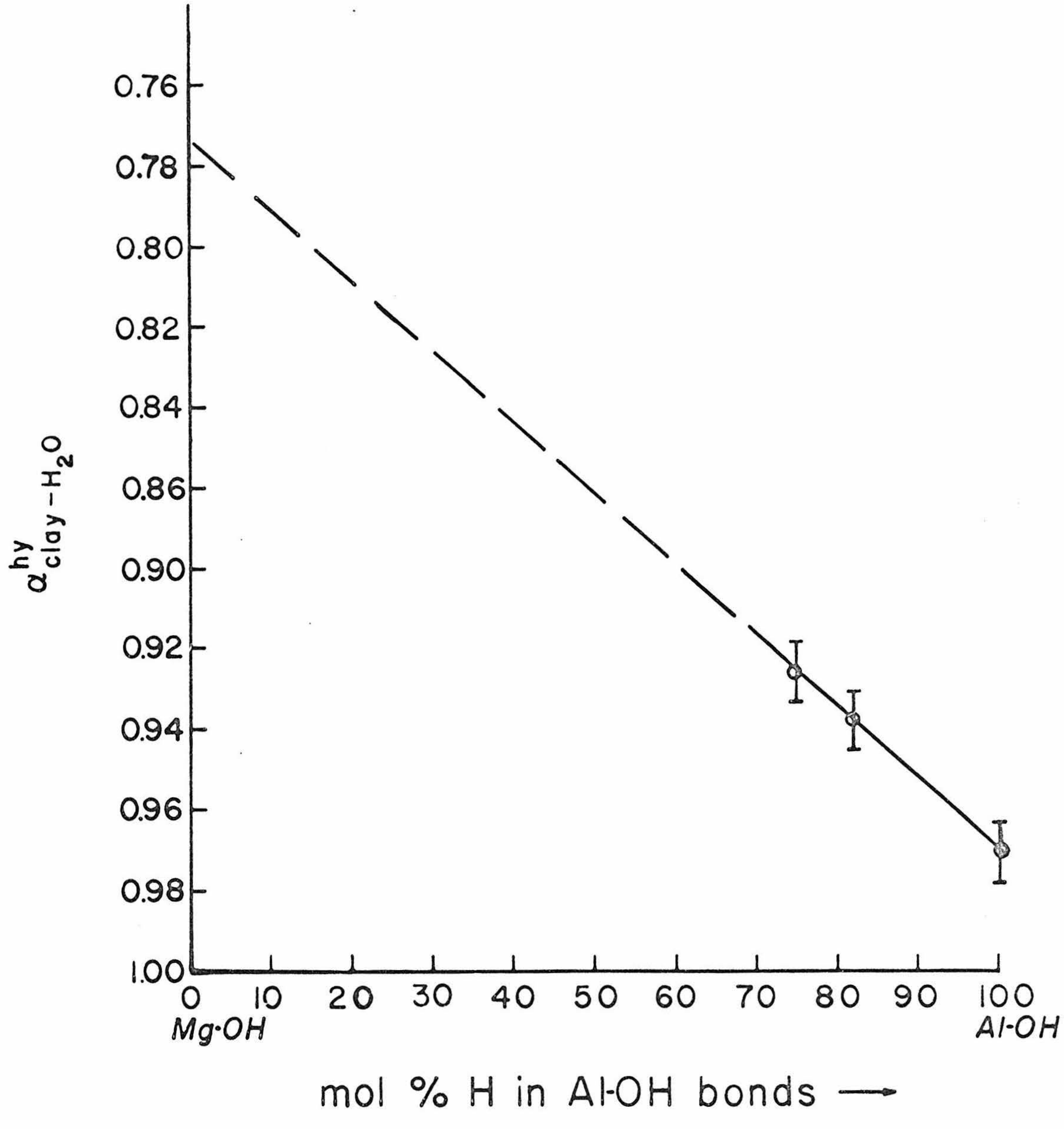


Figure 18. Hydrogen isotope mineral-water fractionation factors for kaolinite, montmorillonite, and glauconite at sedimentary temperatures as estimated from the isotopic compositions of natural samples plotted against the percentage of hydroxyl hydrogen which is in Al-OH bonds.

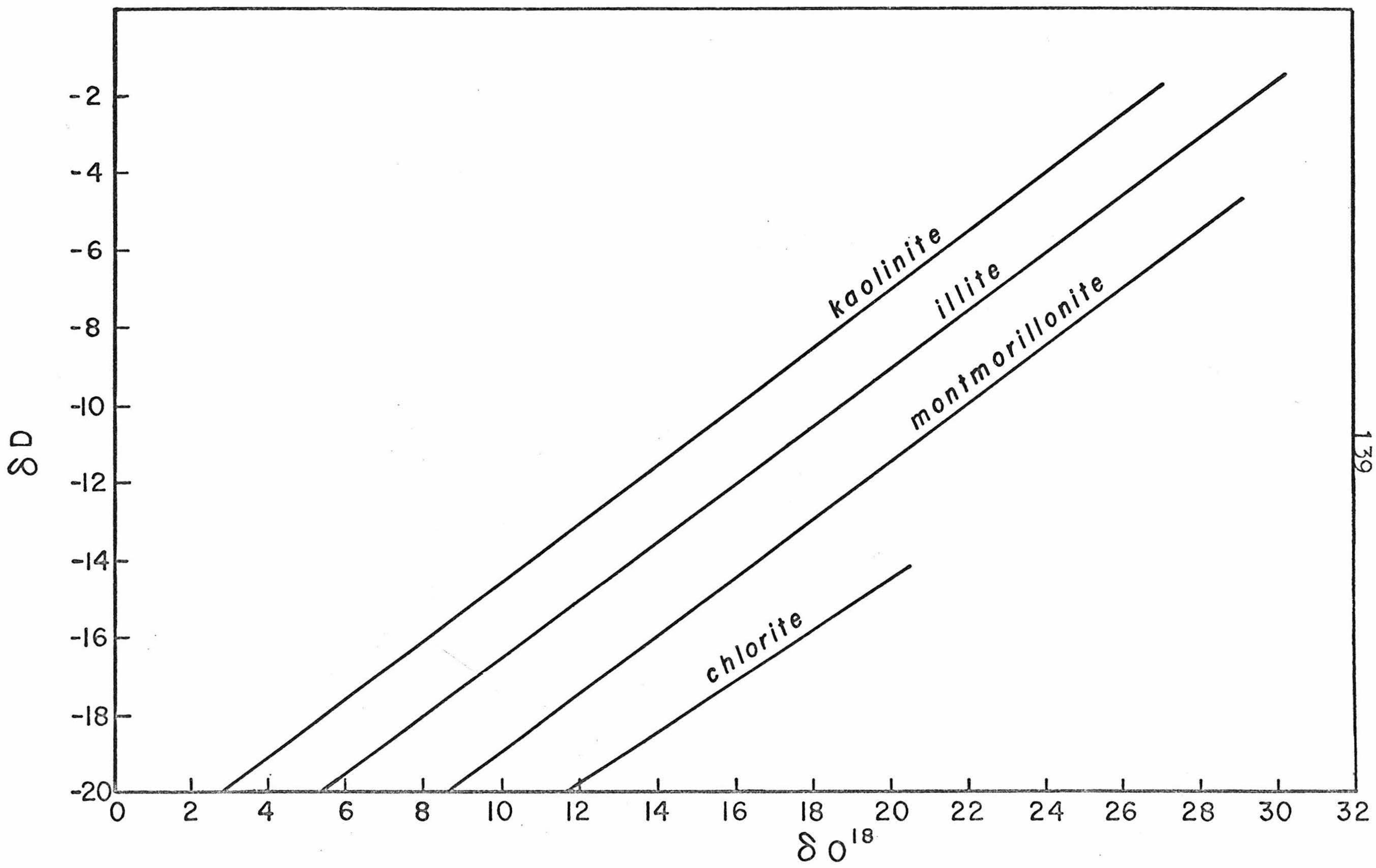


Figure 19. Estimated lines along which kaolinite, illite, montmorillonite and chlorite in equilibrium with meteoric waters would be expected to lie.

figure 19.

TABLE 19

Isotopic fractionation factors of chlorite and illite calculated on the basis of their chemical bonds

Mineral	$\alpha^{ox}_{clay-H_2O}$	$\alpha^{hy}_{clay-H_2O}$	A	B
Chlorite	1.022	0.85	0.67	-24
Illite	1.029	0.97	0.75	-24

The direction of the effect of temperature on $\alpha^{hy}_{clay-H_2O}$ may be estimated by combining the low temperature data of this study with preliminary results on the serpentine - water system by Epstein and O'Neil (122) and the results of Taylor and Epstein (101) on igneous and metamorphic rocks. Epstein and O'Neil have determined that between 200° and 400°C water concentrates deuterium with respect to serpentine by approximately two percent. Since the hydrogen of serpentine is bonded entirely in Mg-OH bonds this represents a decrease in the absolute value of the Mg-OH - water fractionation (or an increase in the value of $\alpha^{hy}_{Mg-OH-H_2O}$ relative to its value at sedimentary temperatures). Muscovite is consistently richer in deuterium than biotite. A similar effect must occur to $\alpha^{hy}_{Al-OH-H_2O}$, and the value of this fractionation factor also becomes greater at elevated temperatures than at low temperatures.

The ability to estimate isotopic fractionation factors of minerals for which there are no experimentally determined values of the α's can be valuable in interpreting isotopic measurements in natural samples. In the present study it has been possible to predict mineral - water oxygen isotope fractionations which are within three permil of values estimated from the isotopic data of the clay minerals. The effect of temperature on the α's can probably be predicted with more accuracy than the absolute values of the oxygen isotope fractionation factors. Hydrogen isotope fractionation factors between clay minerals and water are related to the amounts of magnesium and aluminum in the octahedral layers of the clays. It is hoped that the partial success obtained with calculations of this type will lead to further testing and refinement by laboratory experiments and isotopic analyses of natural samples.

CHAPTER VI

ISOTOPIC COMPOSITION OF SEDIMENTARY ROCKS AND UNCONSOLIDATED SEDIMENTS

6.1 Isotopic composition of ocean sediments

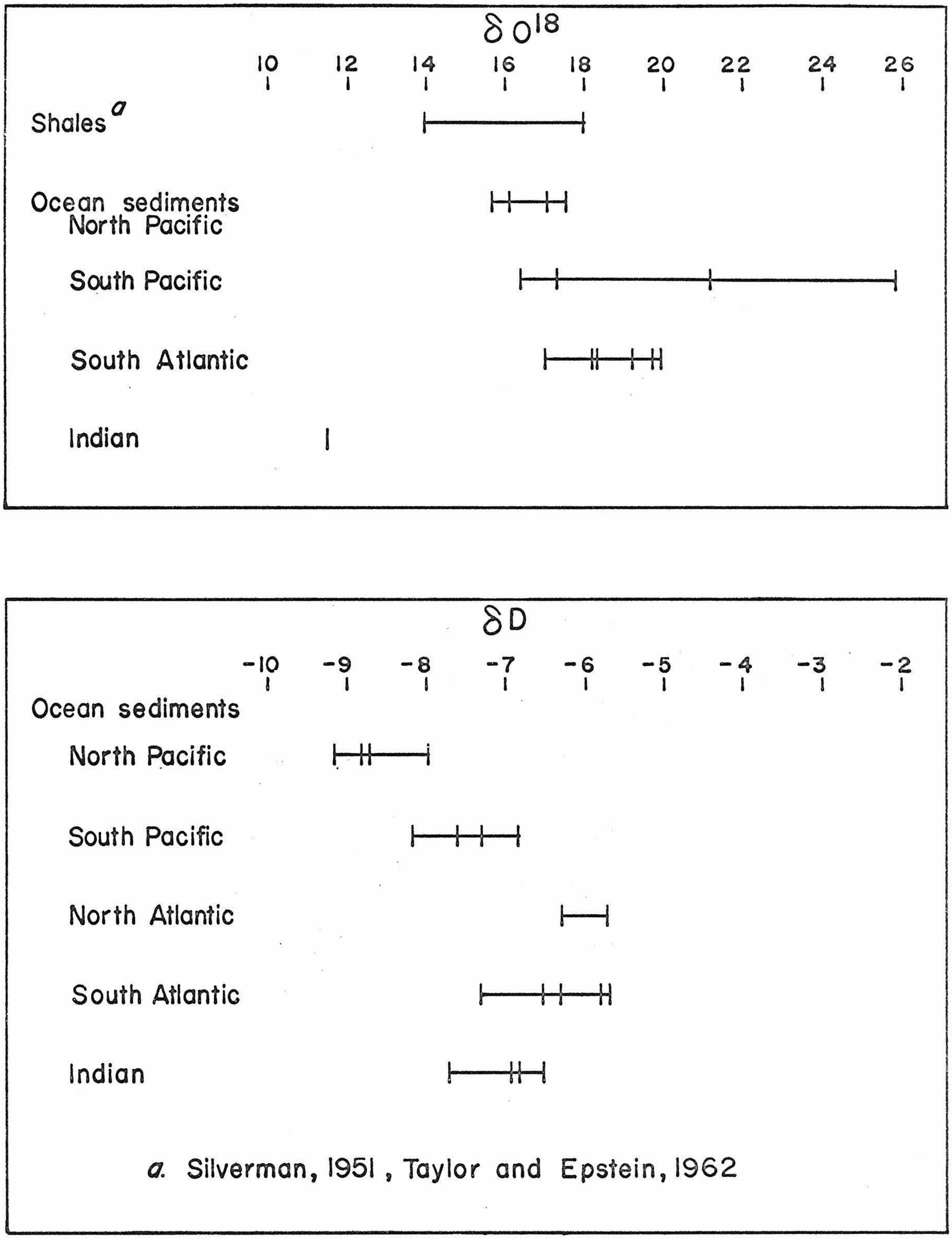
A. Introduction

Ocean sediments are of geologic interest both as the largest body of presently forming sediments and also as materials which are similar to shales in many ways. They are complex mixtures of detrital and authigenic minerals, the origins of many of which are only poorly understood. In spite of a great deal of study by a large number of scientists, many fundamental problems pertaining to the origins of a number of the minerals in the sediments and the nature of sea water-mineral interactions have not yet been solved. Oxygen and hydrogen isotope studies of sediments can provide useful information with regard to some of these problems, especially in the light of the data already presented on the isotopic variations of clay minerals, quartz, and other authigenic silicate minerals.

Isotopic analyses were performed on a number of ocean cores from the North and South Atlantic Oceans, North and South Pacific Oceans and the Indian Ocean. These were provided by the Woods Hole Oceanographic Institution, the Scripps Institute of Oceanography and the Lamont Geological Observatory. Emission spectrographic analyses for major elements were performed for many of the samples. In addition, a number of the cores were analyzed for clay mineral content (and in some cases quartz content) by Goldberg and Griffin (45),(47). The results of the isotopic analyses of the ocean sediments are presented in Table 20 and shown in figure 20. For purposes of comparison, the range of oxygen isotopic compositions of shales is included in figure 20.

B. Geographic distribution of δ-values

The geographic distributions of the isotopic compositions of the ocean sediments are shown on the map in figure 21. Iso-isotopic contours are difficult to draw due to lack of sufficient data. However a few generalizations may be drawn from these maps. In the Atlantic Ocean, samples near the equator, and especially those near the mouth of the Amazon River are richer in O^{18} than those further to the south. There is no obvious pattern of distribution of D/H ratios in the Atlantic. The sediments from the North Pacific tend to contain less O^{18} and deuterium than those from the South Pacific and the Atlantic. This isotopic distribution is related to the source of the clays and will be more fully discussed in



a. Silverman, 1951, Taylor and Epstein, 1962

Figure 20. δO^{18} and δD values measured is some ocean core samples

TABLE 20

Isotopic Composition of Ocean Sediments

Sample	Depth in core	Lat.	Long.	δO 18%	No. Runs	Av Dev	δD%	No. Runs	Av Dev.
JYN II 4[a]	10-15cm	33°04'N	174°15'W	+17.0	6	0.2	-7.9	3	0.5
JYN II 4	160-165	33°04'N	174°15'W				-8.7	2	0.1
JYN II 11	29-34	39°56'N	165°32'E	+17.5	4	0.2	-9.3	2	0.3
JYN II 20	31-36	37°04'N	148°14E	+16.1	2	0.5	-8.8	2	0.0
JYN IV 11	33-39	27°42'N	175°10'E	+15.7	3	0.1	-7.3	3	0.2
LSDA 159	98-103	33°45'S	15°00'E	+17.0	5	0.2	-7.3	4	0.5
LSDA 163	90-95	31°22'S	1°58'E	+18.2	6	0.2	-6.5	1	--
LSDA 183	10-17	19°44'S	12°55'W	+18.3	2	0.4	-4.1		
LSDA 212	24-30	6°47'N	19°18'W	+19.7	4	0.2	-5.7	2	0.3
LSDA 217	79-85	3°56'N	34°04'W	+19.9	3	0.1	-6.3	3	0.3
LSDA 223	100-108	11°34'N	44°48'W	+19.2	2	0.4	-5.8	3	0.3
MSN 121	90-95	29°35'S	158°58'W	+17.3	2	0.1	-6.8	2	0.2
RIS 42	125-130	13°11'S	84°24'W				-7.3	2	0.2
RIS 56	29-30	13°02'S	104°41'W	+21.2	2	0.4	-7.6	2	0.2
RIS 69	170-176	14°41'S	113°29'W	+16.4	2	0.0			
RIS 80	32-42	14°02'S	134°55'W	+25.9	2	0.4			

TABLE 20, cont.

Sample	Depth in core	Lat.	Long.	δO 18%	No. Runs	Av Dev	δD%	No. Runs	Av Dev
V16-75[b]	0-10	22°13'S	58°23'4	+11.5	2	0.3	-5.5	2	0.2
V16-75	50-60	22°13'S	58°23'4				-5.7	2	0.0
V16-75	200-205	22°13'S	58°23'4				-6.0	3	0.2
V16-75	700-705	22°13'S	58°23'4	+14.1	1	---	-6.0	2	0.1
V16-75	1119-1124	22°13'S	58°23'4				-5.8	2	0.4
A.296.4[c]	3½ in.	39°32'N	65°49.6'W				-5.7	3	0.2
CH.36.1	9 in.	21°08'N	65°02.5'W				-6.3	4	0.5
CH.43.4	4 in.	00°55'N	51°38'E				-6.9	2	0.1
CH.43.6	6 in.	01°38'S	53°20'E				-7.7	1	---
CH.43.18	5 in.	07°17'S	60°32'E				-6.9	2	0.8
CH.43.22	5 in.	01°02'S	61°12'E				-6.5	1	---

a. core sample numbers of the Scripps Institute of Oceanography

b. core sample numbers of the Lamont Geological Observatory

c. core sample numbers of the Woods Hole Oceanographic Institute

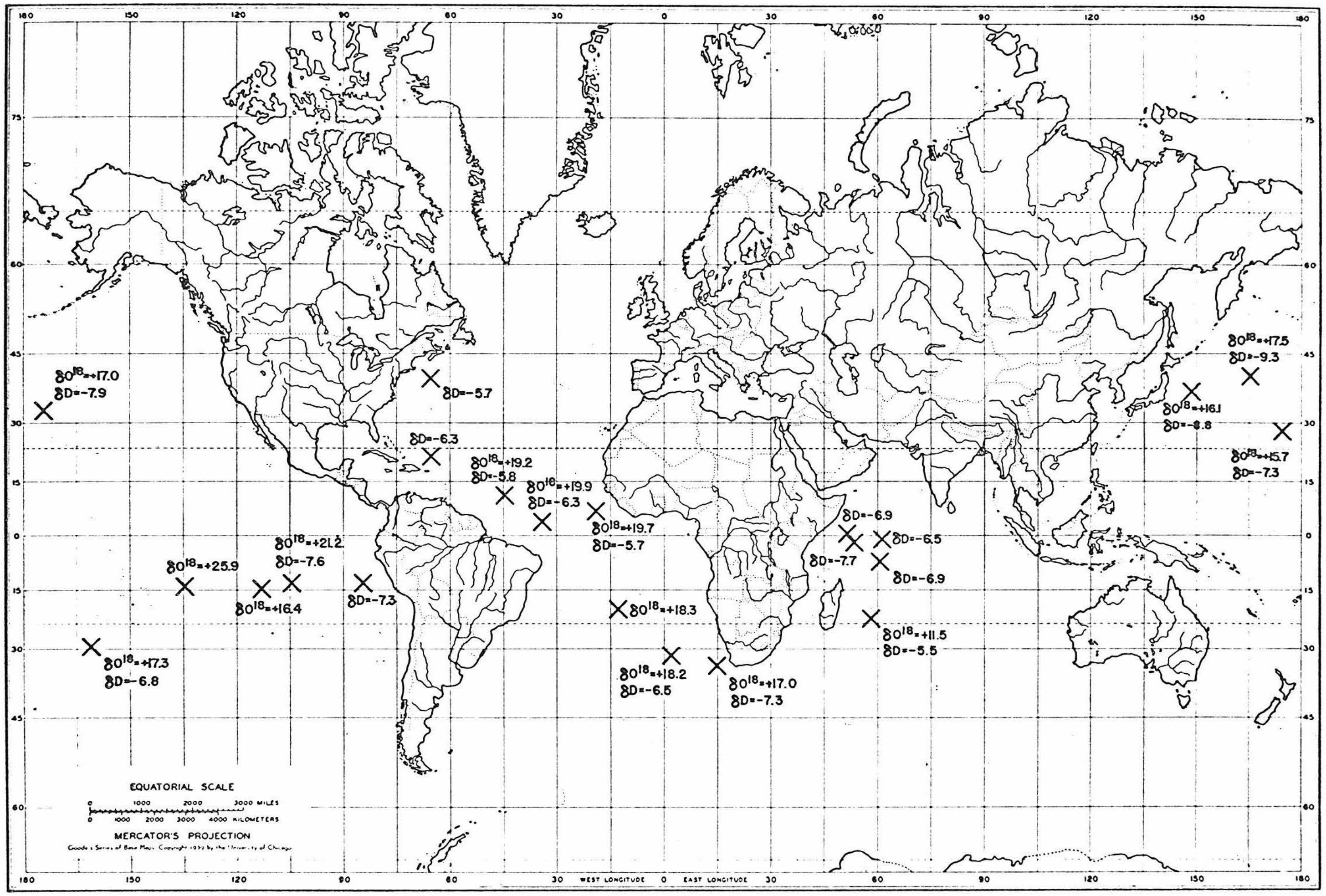


Figure 21. Locations and isotopic compositions of ocean core samples analyzed

the following sections.

C. Chemical and mineralogical analyses of the ocean cores

Emission spectrographic analyses for major elements were performed on the ocean core samples using standard techniques of the C.I.T. Geological Sciences spectrographic laboratory. Accuracy of the analyses is probably ±20 percent of the amount of the element present.

The X-ray diffraction analyses of the cores are from Goldberg and Griffin (45),(47). These analyses were made on the less-than-two micron fraction of the core and are reported normalized to 100 percent clay minerals (kaolinite, montmorillonite, illite, and chlorite). They are probably accurate to ± 10 percent of the amount of each clay present. The mineralogy of the less-than-two micron fraction can be expected to be similar to that of the less-than-44 micron fraction, which was used for the oxygen isotopic analyses. However, since montmorillonite temds to be extremely fine grained, a systematic overestimation of montmorillonite content may result from the assumption that the analyses of Goldberg and Griffin describe the mineralogy of the less-than-44 micron fraction.

Quartz contents were determined for a few of the samples by Goldberg and Griffin (45). Quartz concentrations for a number of other samples may be estimated using the data of Rex and Goldberg (87) and the data of Rex (86) as presented by Arrhenius (1).

Phillipsite was detected in some of the South Pacific samples by Goldberg and Griffin (47).

The concentration of iron and manganese oxides can be estimated from the iron and manganese concentrations determined spectrographically.

The major non-carbonate components of most ocean sediments, including those analyzed in this study, are the clay minerals, quartz, iron and manganese oxides, and sometimes phillipsite. The quartz is of detrital origin and the iron and manganese oxides and the phillipsite are authigenic. The isotopic compositions of these minerals are known from the studies of the pure mineral components discussed previously. Since in many instances the concentrations of these minerals in the sediment are also known, the contributions of each of the non-clay minerals and of the clay mineral suite to the isotopic composition of the sediment may be determined.

In calculating the contributions of the non-clay components to the isotopic composition of the sediments, it is assumed that the isotopic composition of quartz is +11.4 permil. This is the average of all the detrital quartz samples measured.

If it is assumed that the iron and manganese oxides of the sediments are chemically and isotopically similar to the manganese nodule analyzed and also that all of the manganese in the sample occurs in iron and manganese oxides then we can estimate a correction to the oxygen isotope ratio of about 0.1 percent or less for most of the samples studied. This is smaller than the experimental error and can be neglected. The correction for the hydrogen isotopic composition of the iron and manganese oxides is also small enough to neglect.

Phillipsite was found to be present in only two samples but its concentration was not determined. Corrections could therefore not be applied to these samples.

Any feldspar present was ignored in making corrections because of the lack of quantitative mineralogical data. The work of Peterson and Goldberg (83) suggests that in a few cases feldspar concentrations may be great enough to affect the δ-values of the sediments by as much as one permil.

For the majority of the samples studied, quartz was the only major non-clay component detected in large enough quantities to affect the isotopic composition significantly. The oxygen isotopic compositions of all the samples were therefore recalculated on a quartz-free basis. The isotopic compositions corrected for the contribution of quartz may be interpreted as representing the isotopic compositions of the clay fractions of the sediments, except in the cases in which the presence of phillipsite was detected or a high manganese content is noted. The latter samples are discussed as a separate group.

Pertinent chemical and mineralogical data for the ocean sediments, and the values of their isotopic compositions corrected for the contribution of quartz, are given in Table 21.

D. Discussion of the observed isotopic variations in ocean sediments

The mineralogic and chemical data of the preceding section showed that with only three exceptions the isotopic compositions of the sediments, when recalculated on a quartz-free basis, were approximately the isotopic compositions of the clay mineral suites of the sediments. The isotopic variations of these clay minerals will be discussed first, followed by a discussion of the three more complex samples (RIS 56, RIS 69, and RIS 80).

i. Isotopic compositions of clay minerals in ocean sediments

It was pointed out previously that relationships exist between the oxygen and hydrogen isotopic compositions of clay minerals formed in sedimentary environments. In figure 22 the isotopic compositions of the ocean sediment clay mineral suites are plotted on a graph of δD vs δO^{18}.

TABLE 21

Mineralogy and iron and manganese content of ocean cores

Sample	Depth in core	$<2\mu$ fraction [a]					Phillip-site observed	Wt	Wt		δO^{18} corrected for qtz
		% mont	% illite	% chlor	% kaol	% qtz		% Mn	% Fe	δO^{18}	
JYN II 4	10-15cm	14 [b]	60	17	9	14 [e]		0.45	2.8	+17.0	+17.9
JYN II 4	160-165	14 [b]	60	17	9	14 [e]		0.50	2.8		
JYN II 11	29-34	34 [b]	47	13	7	14 [e]		0.33	2.9	+17.5	+18.5
JYN II 20	31-36	42 [b]	38	15	7	14 [e]		0.24	3.0	+16.1	+16.9
JYN IV 11	33-39	25 [c]	56	11	8	14 [e]		0.50	2.6	+15.7	+16.4
LSDA 159	98-103	31 [d]	42	12	14	25 [d]		0.20	2.1	+17.0	+18.8
LSDA 163	90-95	32 [d]	42	12	14	6.5 [d]		1.0	2.9	+18.2	+18.7
LSDA 183	10-17	24 [d]	40	13	21	5.4 [d]		1.0	3.8	+18.3	+18.7
LSDA 212	24-30	16 [d]	18	14	52	11 [d]		0.32	2.9	+19.7	+20.7
LSDA 217	79-85	23 [d]	30	12	35	7.0 [d]		0.35	2.5	+19.9	+20.6
LSDA 223	100-108	24 [d]	36	12	28	10 [d]		0.37	3.5	+19.2	+20.1

TABLE 21 cont.

Sample	Depth in core	<2 μ fraction [a] % mont	% illite	% chlor	% kaol	% qtz	Phillipsite observed	% Mn	% Fe	δO^{18}	δO^{18} corrected for qtz
MSN 121	90-95	41 [b]	37	14	8	0 [e]		1.1	4.0	+17.3	+17.3
RIS 42	125-130	42 [b]	34	14	7	6 [e]					
RIS 56	25-30	No [b] clay minerals				0 [e]	yes	3.6	6.3	+21.2	+21.2
RIS 69	170-176	66 [b]	23	12		0 [e]	no	5.4	8.5	+16.4	+16.4
RIS 80	32-42	72[b]	20	8		0 [e]	yes	2.5	4.9	+25.9	+25.9

a. clay percentages in <2 μ fraction are normalized to 100% kaol+illite+montmorillonite+chlorite

b. data from Goldberg and Griffin (47)

c. values interpolated from two nearby cores

d. data from Goldberg and Griffin (45)

e. data from areal distributions of quartz given by Arrhenius after Rex (1) (86)

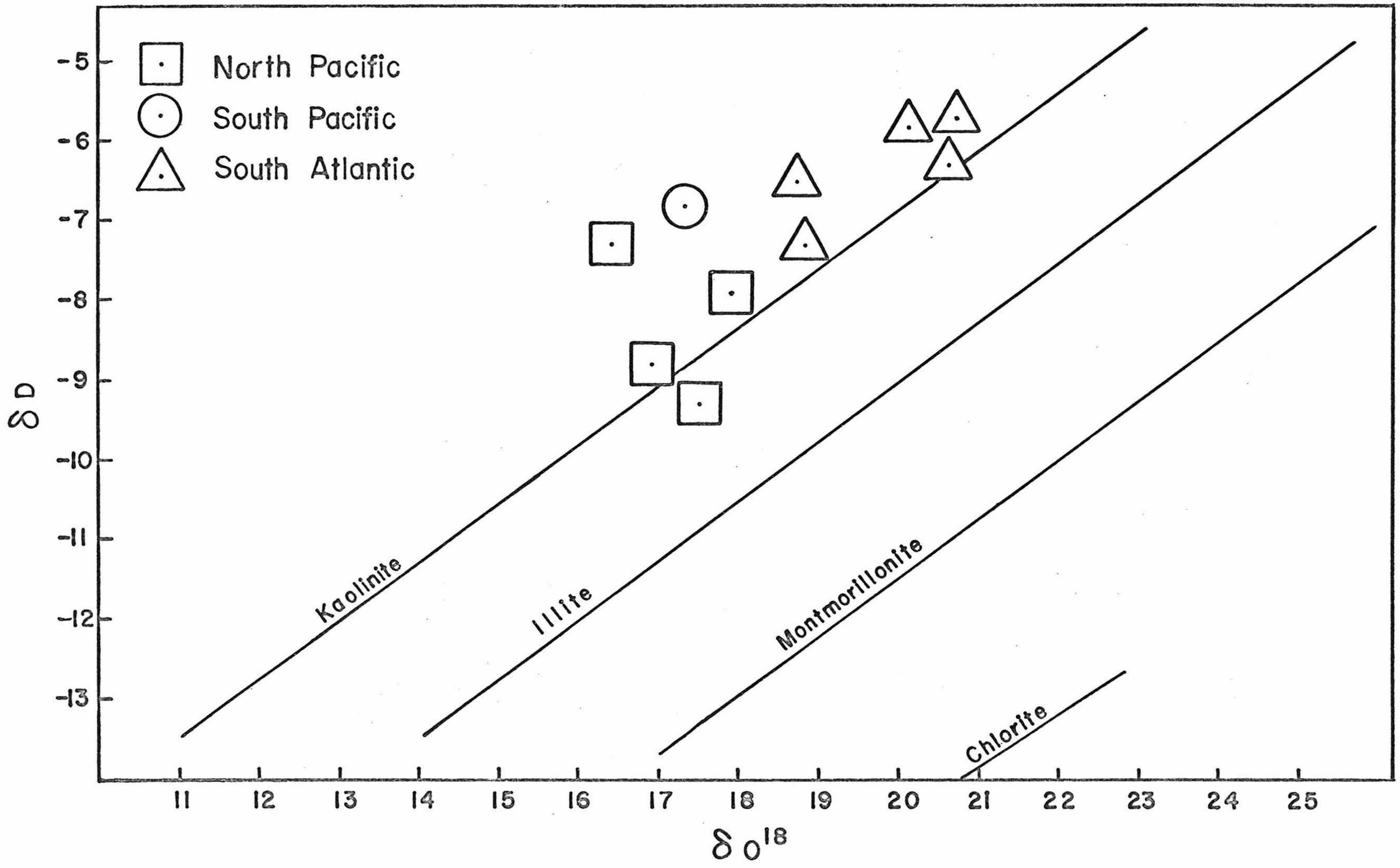


Figure 22. Relation between δO^{18} and δD values of the clay mineral suites of ocean cores

Also shown on this graph are the lines along which clay minerals formed in equilibrium with meteoric waters at low temperatures were estimated to lie. All the data points lie within a relatively narrow band which is roughly parallel to the lines calculated for the various clay minerals. This band lies almost entirely to the left (low δO^{18} or high δD) side of the kaolinite line, and completely to the left of the other clay mineral lines. The clay mineral suites of the ocean sediments cannot therefore be interpreted as being entirely composed of minerals in isotopic equilibrium with sea water or with fresh waters at low temperatures. Two possible interpretations of the data are that the clay mineral suites are mixtures of sedimentary minerals and diagenetically formed minerals which were equilibrated with water at elevated temperatures, or that the clays have incompletely equilibrated with sea water. These two possibilities can be discussed only after an examination of the relationship between clay mineralogy and isotopic composition of the ocean cores.

The X-ray determinations of clay mineral concentration in terms of weight percents have been recalculated in terms of mole percent O_2 or H_2[*] of the clay

---

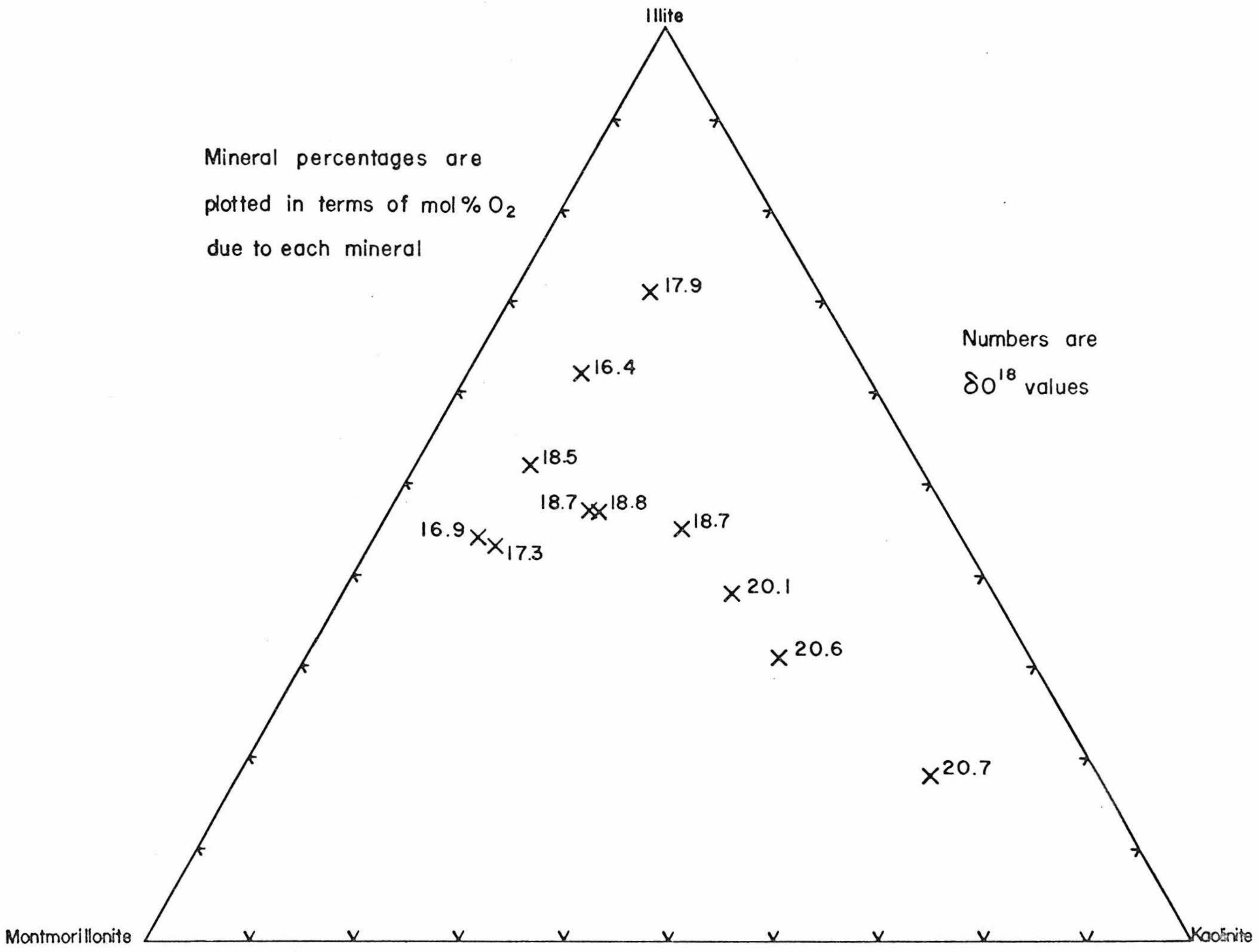
[*] Calculations were done using the formulas: Chlorite $(Fe_2Al(OH)_6)(Mg_2Al(Al_2Si_2O_{10})(OH)_2)$; Kaolinite $Al_2Si_2O_5(OH)_4$; Montmorillonite $Na_{.7}Al_2(Si_{3.3}Al_{.7}O_{10})(OH)_2$; Illite $KAl_5Si_7O_{20}(OH)_4$.

mineral suite which is contributed by each mineral. These mole percent concentrations are shown in Table 22. The mole percent of oxygen due to chlorite is almost constant within the experimental error of the determinations, and discussions of oxygen isotope variations may be simplified by treating the chlorite concentration as a constant rather than a variable. This permits the mineralogical compositions of the clay mineral suites to be plotted on a ternary diagram (actually a projection onto one face of a quaternary diagram). The percentage of hydrogen due to chlorite has a larger range of variation (13 percent of the total amount of H_2) than does the percentage of oxygen. However, the range of variation due to this mineral is smaller than that for any other mineral and in order to simplify interpretation of the data its concentration will be treated as constant. Ternary diagrams of mole percent oxygen and hydrogen of the ocean sediment due to kaolinite, montmorillonite, and illite are presented in figures 23 and 24. As may be seen from these figures, the mineralogic compositions of the sediments may be further simplified by dividing the samples into two groups each one of which can be treated as a two component system. One group has essentially constant kaolinite concentration and varying percentages of illite and montmorillonite. The second group of samples has a fixed illite-montmorillonite ratio and is variable with respect to the relative proportions of

TABLE 22

Clay mineral analyses of ocean sediments recalculated in terms of mole percent oxygen and hydrogen due to each clay mineral

	Mole percent oxygen due to:					Mole percent hydrogen due to:				
sample	montmor-illonite	illite	chlorite	kaolinite	δO^{18} (qtz free)	montmor-illonite	illite	chlorite	kaolinite	δD
JYN II 4	13	59	17	11	17.9	10	42	29	19	-7.9
JYN II 11	32	46	13	9	18.5	26	35	24	15	-9.3
JYN II 20	39	37	15	8	16.9	31	28	27	15	-8.8
JYN IV 11	24	55	11	10	16.4	19	43	21	18	-7.3
LSDA 159	29	41	12	17	18.8	22	29	20	29	-7.3
LSDA 163	30	41	12	17	18.7	22	29	20	28	-6.5
LSDA 183	23	39	13	25	18.7	15	25	20	39	
LSDA 212	14	16	13	57	20.7	7	8	16	69	-5.7
LSDA 217	21	28	12	40	20.6	13	16	16	55	-6.3
LSDA 223	22	34	12	33	20.1	14	21	17	48	-5.8
MSN 121	39	37	14	10	17.3	30	27	25	17	-6.8



Mineral percentages are plotted in terms of mol % O_2 due to each mineral

Numbers are δO^{18} values

Figure 23. Mineralogical compositions of clay mineral suites calculated in terms of mole percent O_2 due to each mineral and projected through chlorite onto one face of the illite-montmorillonite-kaolinite-chlorite diagram.

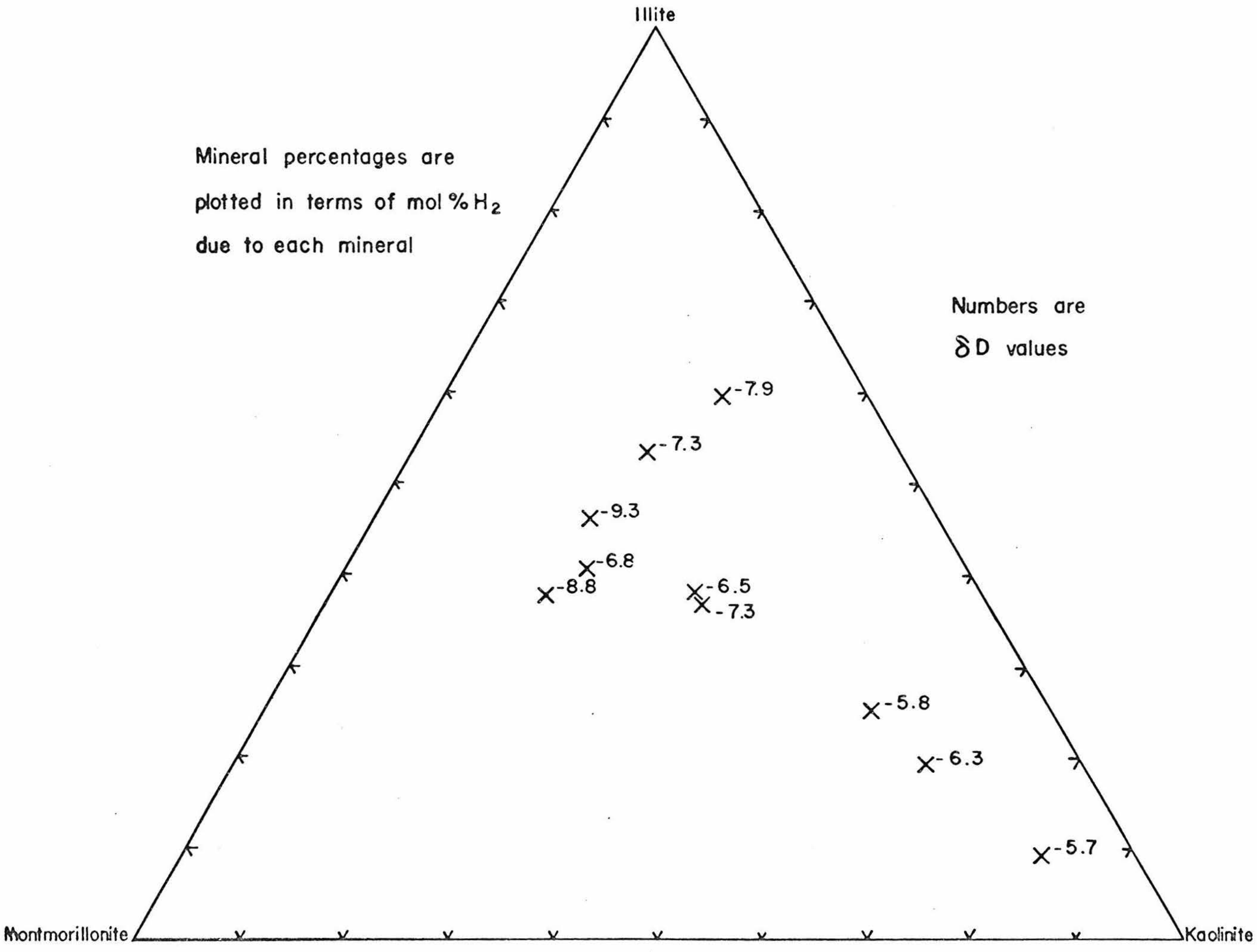


Figure 24. Mineralogical compositions of clay mineral suites calculated in terms of mole percent H_2 due to each mineral and projected through chlorite onto one face of the illite-montmorillonite-kaolinite-chlorite diagram.

kaolinite and the illite-montmorillonite mixture. Figure 25 shows the relationships between mineralogic and isotopic composition. There is a correlation between kaolinite content and both hydrogen and oxygen isotope ratios. Samples high in kaolinite are also enriched in both O^{18} and deuterium. In the constant kaolinite group of samples there is no obvious correlation between illite (or montmorillonite) concentration and isotopic composition. However the range of variation in both isotopic and mineralogic composition of these samples is small.

If it is assumed that the isotopic composition of each mineral component in a group of clay mineral suites is constant then the isotopic composition of each component may be determined by silmultaneous solution of four equations of the type

$$X_k \delta_k + X_i \delta_i + X_m \delta_m + X_c \delta_c = \delta_{\text{measured}}$$

where the X's are the mole fractions of oxygen or hydrogen due to each clay mineral, the subscripts refer to kaolinite (k), illite (i), montmorillonite (m), and chlorite (c), and the δmeasured is the experimentally determined isotopic composition of the clay mineral suite. It is not possible to find a set of unique values of the isotopic compositions of the clay minerals, the combination of which adds up to give precisely the experimentally determined isotopic composition of the clay mineral suite in the case of all the

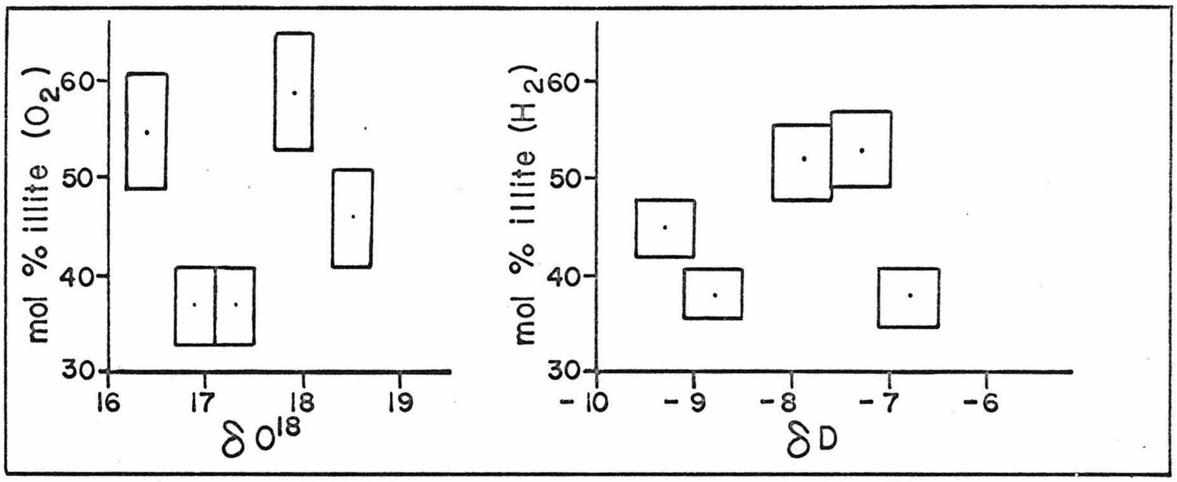


Figure 25 a. Oxygen and hydrogen isotopic compositions plotted against illite content for samples with approximately constant kaolinite content.

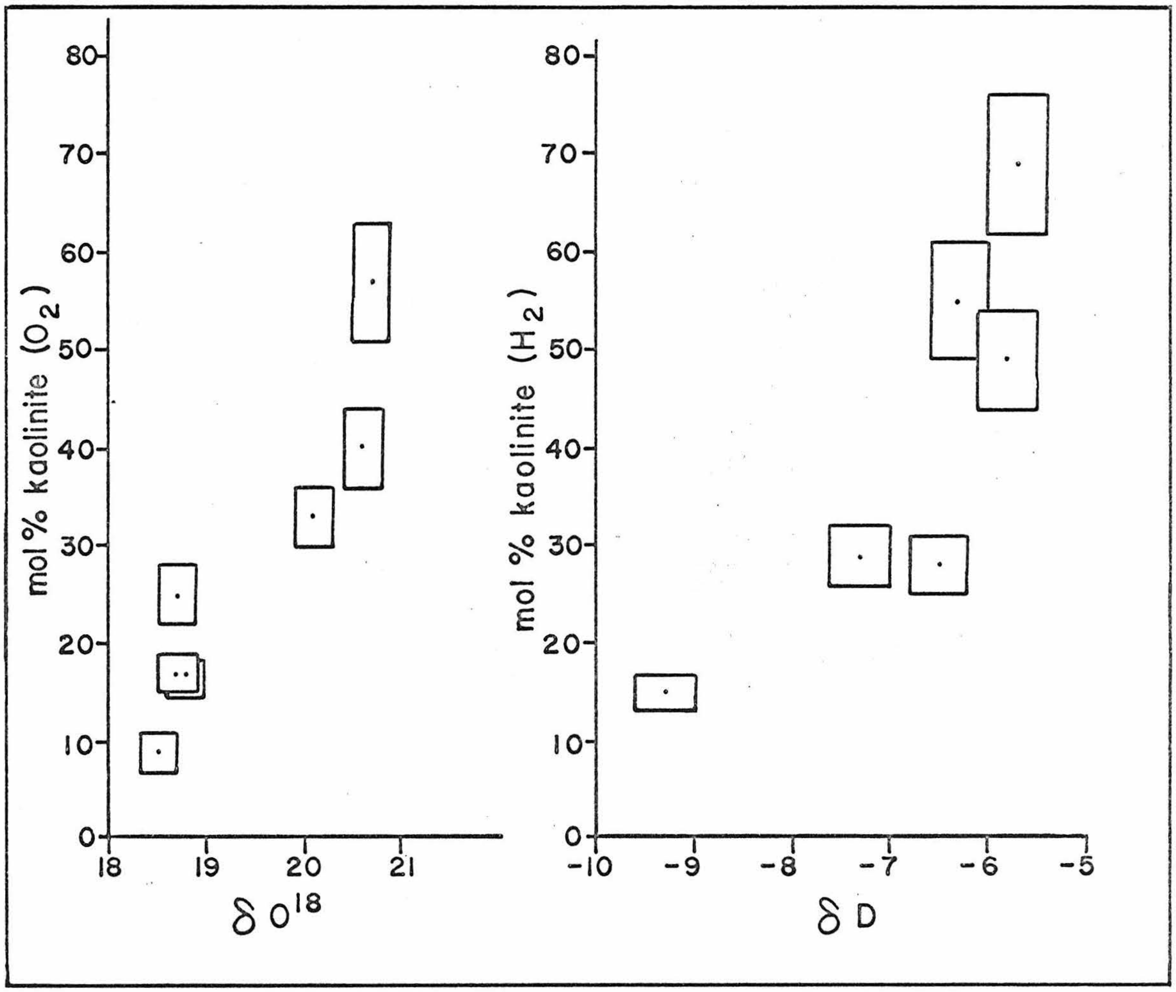


Figure 25 b. Oxygen and hydrogen isotopic compositions plotted against kaolinite content for samples with approximately constant illite: montmorillonite ratio.

sediments studied. However, by reiteration of the solutions of four equations into the equations for all of the samples, it is possible to estimate four values which will give good agreement in most cases. Figure 26 shows the measured δO^{18} values of the clay mineral suites compared with values calculated on the assumption that the δO^{18} values of the mineral components are: montmorillonite, +17.2 permil; illite, +20.8 permil; chlorite, +7.0 permil; and kaolinite, +25.0 permil. Good agreement between measured and calculated values is obtained*. Also shown in figure 26 are the measured values of δD and values calculated on the assumption that the δD values of the minerals are: montmorillonite, -11 percent; illite, -7 percent; chlorite, -10 percent; and kaolinite, -4 percent. The kaolinite δD value was chosen so as to make its isotopic composition lie on the line determined in section 5.2 for kaolinite in equilibrium with natural waters at low temperatures. All other δD values were determined so as to best fit the experimental data. Agreement between measured and calculated values of δD is good although not as good as agreement between measured and calculated values of δO^{18}. On the

---

* Agreement between measured and calculated values of δO^{18} are poor in the case of sample JYN IV 11. However, mineralogical data were not available for this sample, and its mineralogy was assumed to be the same as that for two nearby cores.

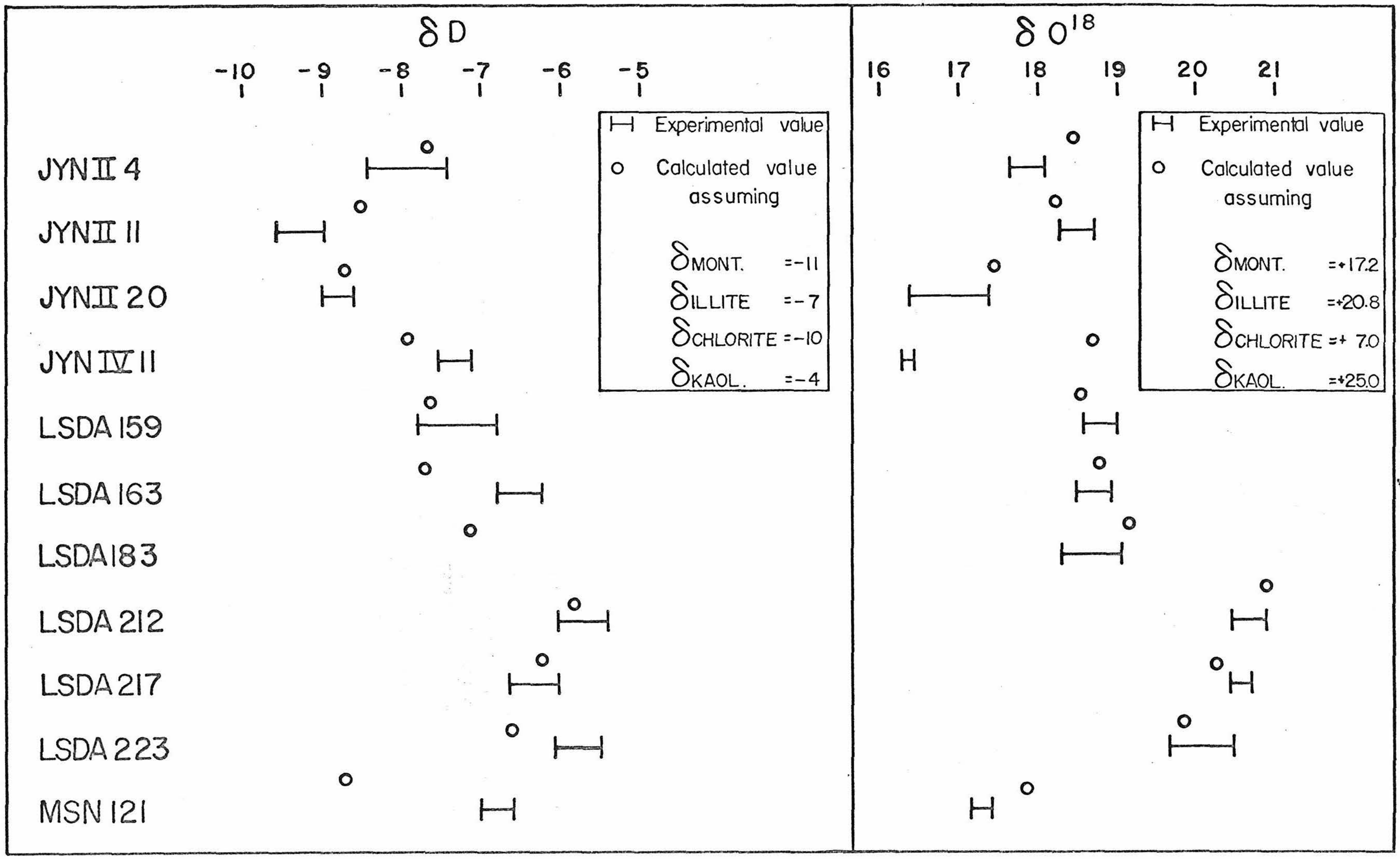


Figure 26. Comparison of the values of the oxygen and hydrogen isotopic compositions of clay minerals in ocean sediments determined experimentally and those calculated assuming constant values for the isotopic compositions of the clay mineral components.

basis of the above calculations it may be concluded that the isotopic compositions of the clay mineral components in most of the ocean sediments studied lie in the ranges indicated in Table 23, and shown in figure 27.

TABLE 23

Range of isotopic compositions of clay minerals in ocean sediments

Mineral	δO^{18}	δD
Montmorillonite	+15 to +19	-9 to -13
Illite	+19 to +23	-5 to - 9
Chlorite	+ 5 to + 9	-8 to -12
Kaolinite	+ 23 to +27	-2 to - 6

It may be seen in figure 27 that the calculated isotopic composition of illite lies close to the line estimated for illites in equilibrium with natural waters under sedimentary conditions. The calculated isotopic composition of montmorillonite lies slightly off the montmorillonite line and the calculated isotopic composition of chlorite lies far off the chlorite line.

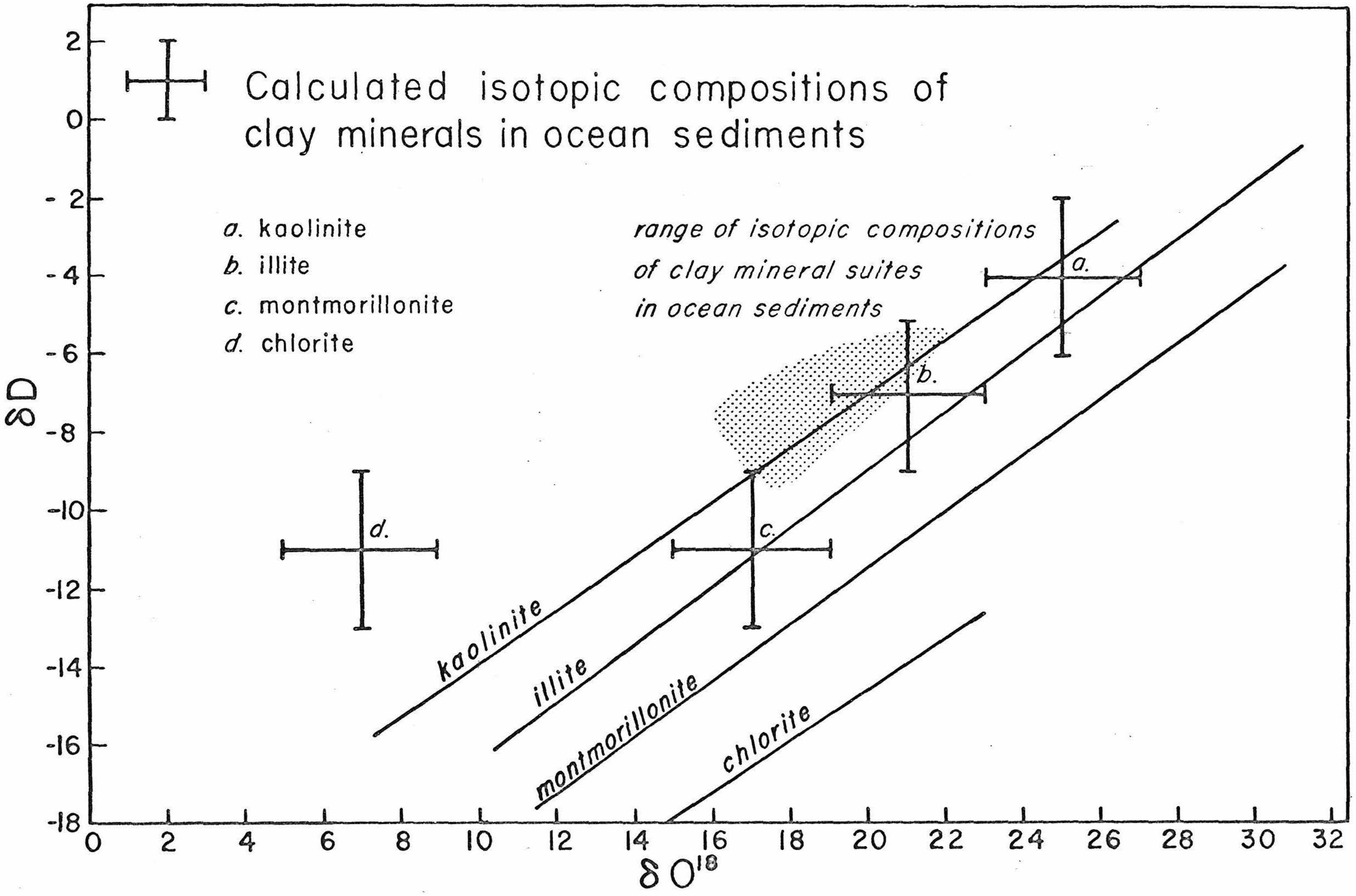


Figure 27. Experimentally determined isotopic compositions of ocean sediment clay minerals and the lines estimated for these minerals in equilibrium with meteoric waters.

a. Kaolinite

The source of the terrigenous components of ocean sediments has been discussed by many workers, including Arrhenius (1),(2), Yeroshchev-Shak (114),(115), Goldberg and Griffin (45) (46), and Biscaye (6). The high kaolinite content of the Atlantic equatorial sediments has been explained by Yeroshchev-Shak and others as originating from the tropical weathering of laterite deposits of South America and Africa. The kaolinite enters the sea through the Amazon, Congo and other rivers which flow through tropical areas to the Atlantic. The fractionation factor calculated in section 5.2 for the kaolinite water system was 1.0265 at approximately 17°C. This implies that kaolinite in equilibrium with sea water would have an oxygen isotopic composition of 26 to 28 permil depending on temperature and kaolinite forming in equilibrium with fresh waters in tropical areas would be expected to have an isotopic composition of +24 to +26 permil because the δO^{18} and δD values of tropical rains are only slightly smaller than those of rain waters. The oxygen isotopic composition of kaolinite in ocean sediments was calculated to be +25 ±2. The isotope data therefore cannot distinguish in the case of kaolinite whether the mineral obtained its isotopic composition in a fresh water or marine environment.

b. Chlorite

The chlorite of the Northern Pacific Ocean was recognized by Goldberg and Griffin (46) to have its source in Northern Canada, Alaska, and the Aleutian Islands. Biscaye (6) found high chlorite concentrations in the high latitudes of the North and South Atlantic, and concluded that the chlorite has its source in metamorphic rocks and as a weathering product in terrestrial arctic environments (Jackson (55). Based on the clay mineral distributions he observed, Biscaye found no evidence for submarine diagenesis to form chlorite as had been postulated by Griffin and Ingram (49), Powers (85) and others. The δO^{18} value of +5 to +9 permil for the chlorite found in marine sediments is in the range of the metamorphic chlorites reported by Garlick and Epstein (40). It is also in the range of values which might be expected for chlorite which equilibrated with the natural waters of temperate zones at slightly elevated diagenetic temperatures or at low temperatures with the waters of polar regions. The isotopic data for these ocean sediment chlorites give strong support to an interpretation of their origin from terrigenous sources.

As related to the δO^{18} value and the line estimated in the δD vs δO^{18} plot for the isotopic compositions of chlorites exchanged at sedimentary temperatures, the δD value of the chlorites is compatible with two origins of the mineral. First, diagenetic exchange at elevated temperatures with ground water or a metamorphic origin would result in the measured isotopic composition of the chlorites. Second, it is possible that chlorite formed at low temperatures with fresh waters but had subsequently undergone hydrogen isotopic exchange with sea water. The second possibility seems unlikely because a large fraction of the hydrogen of the chlorite occupies positions chemically and structurally similar to that of montmorillonite and illite, and montmorillonite and illite are unexchanged in sea water. In addition, the D/H ratio of chlorite in ocean sediments ($\delta = -10$ percent) is greater than the D/H ratio of hydrogen estimated for chlorite in section 5.4 ($\delta = -15$ percent). It is not possible for chlorites with low D/H ratios to exchange with sea water and attain a δ-value of -10 percent when the end point of the exchange corresponds to a δ-value of -15 percent. The chlorite of the ocean sediments is therefore probably primarily of diagenetic or metamorphic origin.

c. Illite

Illite, the most abundant clay mineral in most of the Atlantic (Biscaye (6)) and in areas of low volcanic activity in the Pacific, is probably of detrital rather than authigenic origin in the ocean basins. Hurley *et al*.

(54) measured potassium-argon ages of 200 to 400 million years on a number of ocean cores from the Atlantic Ocean. The same sediments were dated paleontologically as well as by C^{14} and Pa^{231}/Th^{230} methods as being deposited during the Pleistocene. Thus the potassium bearing phase of the sediment must be detrital. Illite is the major potassium bearing phase of the ocean sediments, and thus its detrital origin is strongly inferred. The oxygen isotopic data support the contention of the detrital origin of illite. The estimated δO^{18} value of this mineral in the sediments studied is +21 ±2. The estimated oxygen isotope fractionation factor between illite and water at ocean-bottom temperatures is approximately 1.030. Even if this is in error by as much as 3 permil, illite in isotopic equilibrium with sea water would have an O^{18}/O^{16} ratio of +27 to +30 permil and would be easily distinguishable from the illite of the ocean cores studied (δO^{18} = +19 to +23 permil). The isotopic composition of the hydrogen is similarly in accord with a terrestrial origin of the illite.

Illite is formed as a weathering product and is also formed diagenetically in sediments. The isotopic data of the ocean cores are compatible with an origin of illite by the above mechanisms. There is no evidence from the samples analyzed of any isotopic exchange of illite with sea water in the marine environment.

d. Montmorillonite

Montmorillonite can occur in ocean sediments as either a detrital or an authigenic phase. The isotopic data of section 5.2 for montmorillonites of authigenic origin on the ocean floor indicated a fractionation factor for oxygen between montmorillonite and water of approximately 1.028. Our estimates of the isotopic composition of montmorillonite from ocean core samples indicate a value between +15 and +19 permil, which is considerably lower than the O^{18}/O^{16} ratio of montmorillonite which forms authigenically on the sea floor. Montmorillonite, then, does not seem to undergo isotopic exchange in the marine environment during the length of time it existed in the marine sediment. Thus, its isotopic composition may serve as an indicator of detrital or authigenic origin.

In summary, the isotopic compositions of the clay-mineral suites of most of the ocean sediments studied may be described quite well in terms of the four component system: montmorillonite, illite, chlorite, and kaolinite, each component having an almost constant isotopic composition. The values of the isotopic compositions are generally determined by the conditions of formation in a terrestrial environment. The clay minerals do not undergo significant isotopic exchange with sea water during the time which they have been exposed to the marine environment (probably less than 250,000 years for the samples analyzed here, based on ionium-thorium dating on a number of them by Goldberg and Koide (123) and Goldberg and Griffin (45)). When the minerals of an ocean sediment are formed in situ, this may be detected by their isotopic composition

ii. Isotopic compositions of sediments containing phillipsite and high concentrations of iron-manganese oxides

Three ocean core samples from the South Pacific Ocean were omitted from the previous discussion because chemical, mineralogical and isotopic data (Table 21) showed them to be very different than the remaining samples. These samples, RIS 56, RIS 69 and RIS 80, were collected in the vicinity of the East Pacific Rise, an area of recent submarine volcanism in which the sediments are rich in weathered volcanic matter. The experimental data for the three samples from this area indicate that they are in large part authigenic, having formed by alteration of volcanic material on the sea floor. All are extremely rich in iron and manganese, and two of them contain phillipsite. In figure (28) the Fe + Mn content of a number of ocean cores as well as for phillipsite and a manganese nodule* are plotted against δO^{18}. While the Fe + Mn content of most of the samples is low and falls within a very narrow

---

* Manganese nodule analysis from Mero .

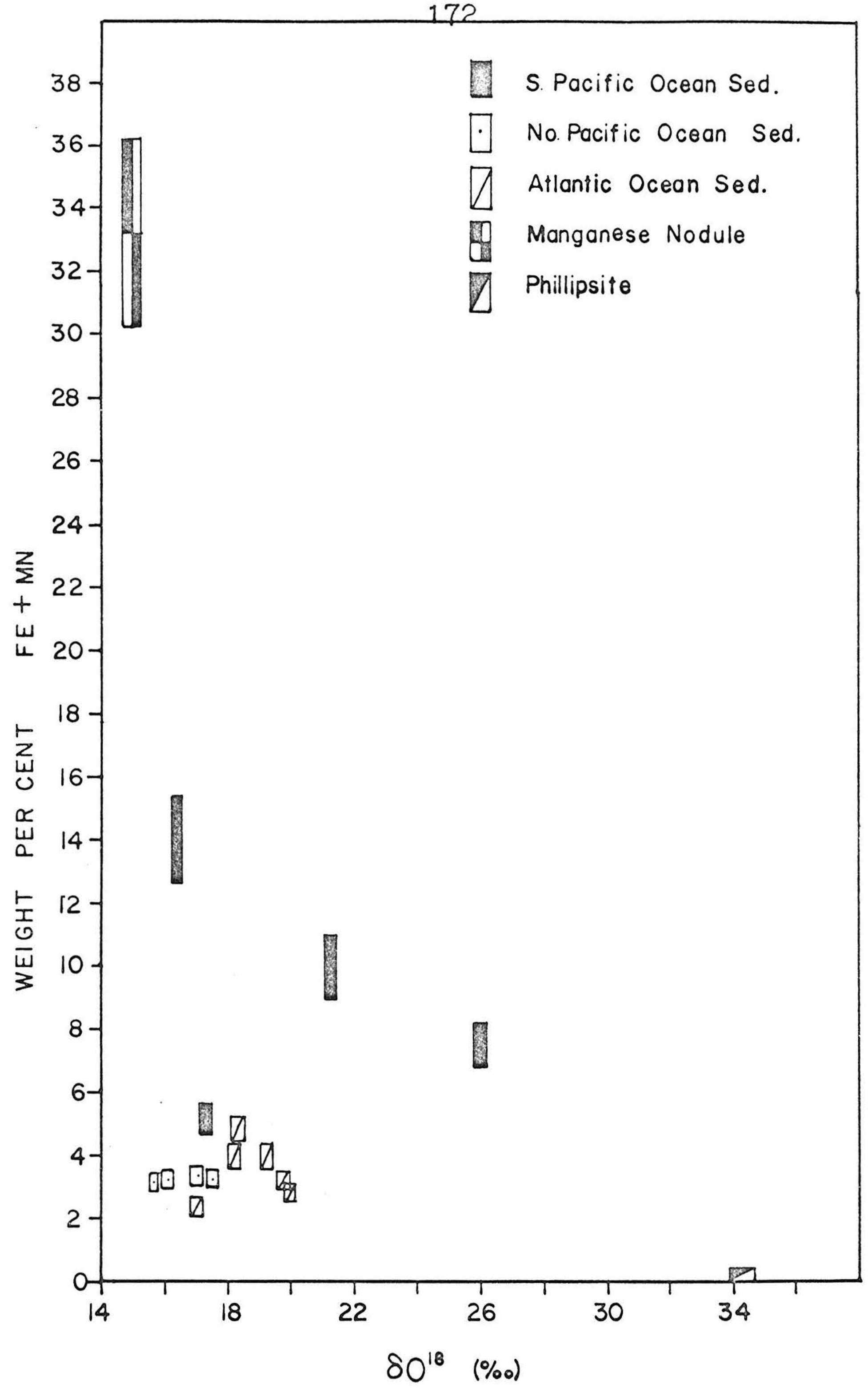


Figure 28. Weight percent iron and manganese in ocean sediments, phillipsite, and a manganese nodule plotted against δO^{18}. All ocean sediments cluster together except three South Pacific samples with large authigenic components.

range (3.5 ± 1.5 percent) the Fe + Mn content of the three anomalous samples from the South Pacific is considerably greater (7.4 to 13.9 percent). The clay mineral suites of RIS 69 and RIS 80 contain some kaolinite, illite, and chlorite, indicating they are in part detrital in origin. The positions of the three samples on the Fe + Mn vs δO^{18} diagram suggest that they are a mixture of O^{18}-poor detrital clay minerals and oxides, and O^{18}-rich phillipsite and perhaps montmorillonite of authigenic origin. It may also be seen in figure 28 that the existence of sediments with low δO^{18} values does not necessarily preclude the presence of a large amount of authigenic material. An example of such a sediment is sample RIS 69 which has a large authigenic component and a value of δO^{18} which is lower than most detrital sediments analyzed because of its high content of iron and manganese oxides. While isotopic data alone may not be able to characterize the origins of minerals in ocean sediments in all cases, a combination of isotopic, chemical, and X-ray data can shed a great deal of light on the nature of the processes by which many of the minerals in the sediments are formed.

6.2 Oxygen isotopic compositions of modern beach sands

The isotopic composition of beach sands is of interest because these materials are mineralogically similar to many which have become indurated to form sandstones.

Thus, an understanding of the isotopic composition of beach sands can serve as one of the bases for understanding the isotopic composition of sandstones and the processes involved in their formation.

Seven North American beach sands were isotopically analyzed. Samples from the southeastern United States were nearly pure quartz ($>$ 95 percent). These were cleaned in hydrochloric acid and subjected to separation on the Frantz isodynamic separator. The non-magnetic (1.4 amp., 2° side slope) fraction was analyzed for oxygen. Samples from other areas which were analyzed contained high percentages of minerals other than quartz. Whole rock "splits" of these samples were isotopically analyzed as were quartz fractions separated by magnetic and gravimetric methods followed by a brief cleaning in HF. The isotopic data are listed in Table 24. These data represent samples with broad geographical diversity and differences in mineralogy and maturity. Descriptions of the samples are given in Appendix II.

The isotopic compositions of the quartz fractions of the samples were discussed in section 5.3, and it was concluded that the O^{18}/O^{16} ratio of detrital quartz was determined by its provenance and is primarily of metamorphic and igneous origin.

The Huntington Beach, California sample contained quartz only a little heavier than igneous quartz.

TABLE 24

Oxygen isotope composition of modern beach sands

Locality	Quartz			Whole rock			Estimated quartz %	Calculated δO^{18} of non qtz. fractio
	δO^{18}	No. of Runs	Av. Dev.	δO^{18}	No. of Runs	Av. Dev.		
Huntington Beach, California	+10.6	2	0.6	+ 9.3	1	---	65±10	$+6.9^{+0.9}_{-1.7}$
Fernandia, Florida	+11.0	2	0.2					
Bath, Maine	+12.7	3	0.5	+12.1	1	---	75±10	$+10.4^{+0.4}_{-1.4}$
W. Shore, Bay St. Louis, Mississippi	+11.4	2	0.3					
South Island, So. Carolina	+11.3	2	0.6					
Ocean View, Virginia	+12.1	2	0.2					
La Push, Washington	+10.9	3	0.4	+12.5	2	0.3	50±10	$+14.0^{+0.7}_{-0.5}$

Calculation of the isotopic composition of the non-quartz fraction from the quartz and whole rock data gave a value similar to that for igneous feldspar, the most abundant mineral in the non-quartz fraction.

The Bath, Maine sample contained quartz which appeared, on the basis of its O^{18}/O^{16} ratio, to be primarily or entirely metamorphic. The isotopic composition of the non-quartz fraction was calculated to be about +10.5 permil. This fraction contained not only some feldspar but chlorite, chert, and a number of other minerals.

The beach sand from La Push, Washington is interesting in that it was the only one for which the isotopic composition of the whole rock sample was heavier than that of the quartz. This implies that the sample contained a sedimentary or metamorphic component in the non-quartz fraction. The La Push sand contained about 25 percent of what appeared to be very cloudy weathered feldspar peak and only a very weak 10 Å illite peak. Perhaps conditions under which the feldspar became cloudy and some illite formed also permitted isotopic exchange of the feldspar to occur.

It appears that in the case of beach sands as with ocean sediments, the isotopic compositions of the detrital materials are those which the minerals obtained when last they underwent some chemical alteration or isotopic exchange at elevated temperatures. The mineral may not have to be completely altered as was the case with the La Push feldspar. However, no case has been found in this study in which there is evidence that a sand-sized mineral has undergone isotopic exchange in the sedimentary environment without being accompanied by an obvious chemical alteration.

6.3 Isotopic composition of shales

Marine shales are similar in many ways to the ocean core samples which were analyzed, although they differ in rates of deposition, depth of water of deposition, depth of water of deposition and to some extent in mineralogy. Shaw and Weaver (92) have published X-ray diffraction analyses of 400 shales of Paleozoic, Mesozoic and Tertiary times and a summary of their analyses is presented in Table 25. The chief difference between these analyses and those of most of the ocean cores studied is the larger amount of quartz in the shales. There is no similar compilation of the clay mineral abundances in a large number of samples from a wide range of geologic ages. Weaver (111) has collected qualitative and semiquantitative clay-mineral data by a large number of workers. He finds a tendency for illite to be the primary clay mineral prior to the upper Mississippian, and interprets this as the result of diagenetic alteration of other clay minerals. (Most of the old illite is of the 2M variety rather than the 1M variety typical of recent sediments.) Clay mineral suites in rocks younger than upper Mississippian are more complex and appear to reflect parent material and environment of formation. Geologic periods in which there was much vulcanism tended to correspond with times in which there were greater concentrations of montmorillonite in the shales. However, as a general rule, according to Weaver, the abundances of the clay minerals in shales may be ranked as follows: illite > montmorillonite > mixed-layer montmorillonite-illite > kaolinite > chlorite.

TABLE 25

Average shale composition (wt. %) after Shaw and Weaver (92)

Mineral	Weight Percent
Quartz	30.8
Feldspar	4.5
Clay Minerals	60.9
Iron Oxides	< 0.5
Carbonates	3.6
Other Minerals	<2.0
Organic Matter	1

By assuming values of the isotopic compositions of the various mineral components we can calculate expected values for shales. If we take the isotopic composition of quartz to be +11.4 permil, that of feldspar to be +8 permil, and that of the clay mineral suite to range from +16 to +22 permil, then, using the average mineral percentages of Shaw and Weaver (92) the expected values of the isotopic composition of the carbonate-free fraction of shales would range from +14 to +18 permil. The shales measured and reported by Taylor and Epstein (102) and Silverman (93) fall within the range 14.2 and 18.2. Only two new shale measurements were made during the present study, and these were both from the non-marine Green R. formation, Green R. Wyoming. The results, presented in Table 26 are in good agreement with the shale measurements of the earlier workers.

TABLE 26

Isotopic composition of shale samples from the Green R. Fm.

Sample	δ O^{18}	No. runs	Av. dev.	δ D	No. runs	Av. dev.
GR6	+18.1	2	0.0	- 5.76	2	0.2
GR7	+19.1	3	0.7	-12.96	6	0.6

It is interesting to note that GR7 has δD of -13.0 percent. This is the lightest value measured in a sediment, and may reflect hydrogen isotopic exchange of this sample with the low-deuterium water of the area.

The isotopic composition of detrital quartz and feldspar in shales is almost certainly representative of the parent materials. The isotopic compositions of detrital clay minerals of ocean sediments were seen to be determined by the source of the clay minerals and not by the depositional environment. This is probably also true of the detrital clay minerals of shales, although in cases in which the clays have been exposed to sea water for much longer times than the clays of the analyzed ocean cores it is possible that some exchange might occur. In general, the isotopic composition of shales can not be expected to yield information as to whether the depositional environment was marine or non-marine. However isotopic analyses of separated clay minerals from shales might give information about the source of the clay minerals or the nature of any post-depositional alteration of the rocks.

CHAPTER VII

EFFECT OF FORMATION OF SEDIMENTS ON THE ISOTOPIC COMPOSITION OF THE HYDROSPHERE

The formation of minerals in the sedimentary environment results in preferential removal of the heavy isotopes of oxygen and the light isotope of hydrogen from the hydrosphere. In this chapter, the magnitude of the effects of sedimentary processes on the isotopic composition of the hydrosphere will be explored.

Based on the few available isotopic analyses, Silverman (93) estimated that the formation of sediments throughout geologic time had depleted the hydrosphere of O^{18} by 4 to 12 permil. Since that time more information has become available about the O^{18}/O^{16} ratios and the relative and absolute abundances of the various sedimentary rock types. The present work provides information on the direction and magnitude of hydrogen isotope fractionations in sedimentary minerals. It therefore seems profitable to reexamine the calculations in the light of the new data.

Material balance equations, similar in form to those used by Silverman, were the basis of the present computation. The equation used in calculating the effect of sedimentation on the O^{18}/O^{16} ratio of the hydrosphere is

$$S\ (\delta O^{18\,\text{sediments}} - \delta O^{18\,\text{igneous}}) = W\left(\begin{matrix}\text{present} & \text{original}\\ \text{oceans} & \text{oceans}\\ \delta O^{18} & \delta O^{18}\end{matrix}\right)$$

where S is the amount of oxygen in the sedimentary rocks, and is approximately equal to the amount of oxygen in all the igneous rocks which have been weathered. W is the amount of oxygen in the oceans. The data used in the calculations are given in Table 27. The assumptions and conditions of the calculation are:

1. All sediments have been formed by weathering of igneous rocks with an average δO^{18} value of +8.5 permil, or by weathering of other sediments originally formed from igneous rock. Recycling of sediments through a metamorphic cycle, accompanied by isotopic reequilibration with the mantle to an extent which would significantly alter their isotopic composition, and followed by further weathering, has been ignored.

2. The isotopic composition of the sediments formed have always been similar and have not been radically affected by possible large changes in the isotopic composition of the hydrosphere. This assumption was necessary since the value of δO^{18} for sedimentary rocks which was used in the calculation was obtained almost entirely from post-Precambrian rocks, and this period of time represents only a small portion of the time in which sedimentary rocks have

TABLE 27

Amount and isotopic composition of oxygen in sediments, weathered igneous rock, and the oceans

---

a. Wickman's estimates (113)

	kg/cm^2	Wt %O	kgO/cm^2	δO^{18}	weighted δO^{18}
shale	172	45[a]	78	16[a, d]	
sandstone	17.3	48[b]	8.3	13[a, d]	
carbonates	20	49[c]	9.8	25[e]	
all sediments			96		17
weathered igneous rock	194	48	93		

b. Goldberg and Arrhenius estimates (44)

	kg/cm^2	Wt %O	kgO/cm^2	δO^{18}	weighted δO^{18}
pelagic	23	45	10	19[a]	
carbonate	8.5	49	4	25[e]	
ss + shale	145	47	68	15[a, d]	
all sediments			82		16
weathered igneous rock	185	48	89		

c.

	kg/cm^2	Wt %O	kgO/cm^2	δO^{18}
ocean water	278	89	248	0

a present study (11)
b from Clarke used by both Wickman and Goldberg and Arrhenius
c from Wickman's abundance $MgCO_3/CaCO_3$ = 1/5.3 by weight
d Taylor and Epstein (103)
e Keith and Weber (56)

been formed.

3. The amount of oxygen in the igneous rocks which have been weathered is the same as that in the sediments.

The results of the calculations indicate that the formation of sediments has caused a depletion of O^{18} in the hydrosphere of between +2.7 and +3.3 permil depending on the values used for the amounts of the various sedimentary rock types.

The estimates of the abundances of sedimentary rocks used in these calculations were those of Wickman (113) and Goldberg and Arrhenius (44). Both of these estimates were obtained by a geochemical balance of the concentrations of elements in sea water and in sedimentary rocks. The isotopic calculations are of course only as good as the estimates of the abundances of the rock types, but as may be seen from the data of Table 27, the estimates of Wickman and of Goldberg and Arrhenius differ in a number of respects without having a large effect on the result of the present calculations. Undoubtedly the most significant variable in the calculation is the total mass of igneous rock which has been weathered. This has been agreed upon quite well by a number of separate investigators on the basis of geochemical calculations (Goldschmidt (48), 160 kg/cm^2; Engelhardt (32), 160 kg/cm^2; Goldberg and

and Arrhenius (44), 185 kg/cm^2; Wickman (113), 194 kg/cm^2). However, the weakness of geochemical balance calculations of this type is that they include the assumption that the factors controlling the concentrations of elements in sea water have been the same throughout geologic time. The residence times of most elements in the oceans are less than 10^8 years (Barth (4), Goldberg and Arrhenius (44)). Therefore, if the chemistry of the hydrosphere were greatly different 10^9 years ago than it is today, and the rate of erosion were also significantly different then, no hint of this would be found in the geochemical balance calculations.

The assumptions concerning the reworking of metamorphic material and the addition of water to the oceans through geologic time are more difficult to evaluate. If there has been considerable recycling of sedimentary material to a high degree of metamorphism with subsequent weathering, the effect will be to remove more O^{18} from the hydrosphere than was estimated in the calculation.

The figure of approximately 3 permil calculated in this work for the depletion of O^{18} from the hydrosphere is smaller than the figures of 4 to 12 permil estimated by Silverman. It is not consistent with an origin for the water from crystallizing magmatic bodies, as the δO^{18} value of water from that source is probably between +8 and +10 permil (O'Neil and Taylor (80)). If the major source of the hydrosphere is magmatic water, this would imply an underestimation by a factor of three of the amount of igneous rock which has been weathered or the existence of a large amount of recycling of sediments through metamorphism, isotopic equilibration with the oxygen of the mantle, and subsequent weathering.

If the calculations are valid and the weathering and sedimentary processes have been going on at approximately the same rate for three billion years, then the rate of change of δO^{18} since the end of the Precambrian would be only about 0.5 permil. This is only a little more than twice as large as experimental error and would be difficult to detect.

The estimation of the change in hydrogen isotope composition of the hydrosphere is done in a similar way to that of oxygen. The pertinent data are shown in Table 28. Because of the very small amount of hydrogen in rocks relative to that in the hydrosphere, the change in δD due to sedimentary processes is calculated to be 0.03 percent using Wickman's estimates of the abundance of the sedimentary rock types and even less using the estimates of Goldberg and Arrhenius. These numbers are much smaller than experimental error, so the question of any change in δD of the oceans due to sedimentary processes can be ignored. In the case of deuterium, the recycling of sediments through metamorphism would almost certainly not be a significant factor in changing the isotopic composition of the oceans.

TABLE 28

Amount and isotopic composition of hydrogen in sediments, weathered igneous rock, and the oceans

a. Wickman's estimates (113)

	kg/cm^2	Wt %H	kgH/cm^2	δ D
shale	172	0.56	0.96[ab]	-6[b]
sandstone	17.3	0.18	0.031[a]	-6[b]
carbonate	20	0.086	0.017[a]	-6[b]
all sediments			1.01	-6
weathered igneous rock	194	0.13	0.25	-6[c]

b. Goldberg and Arrhenius (44)

	kg/cm^2	Wt %H	kgH/cm^2	δ D
pelagic	23	0.56	0.13	-6
carbonate	8.5	0.18	0.015	-6
sandstone + shale	145	0.48	0.69	-6
all sediments			0.84	-6
weathered igneous rock	185	0.13	0.24	-6

c.

	kg/cm^2	Wt %H	kgH/cm^2	δ D
ocean water	278	11.1	30.8	0

a Clarke (11)
b This work
c Taylor and Epstein (101)

However, the addition of water to the hydrosphere from the interior of the earth might be expected to have a significant effect on the deuterium concentration of the oceans. Thus, if evidence were found for a change in the D/H ratio of the oceans in the course of geologic time, this would be good evidence for an increase in the volume of the hydrosphere.

The above considerations do not include possible changes in the O^{18}/O^{16} and D/H ratios of the hydrosphere due to loss of hydrogen and oxygen from the planet earth.

CHAPTER VIII

SUMMARY AND CONCLUSIONS

Oxygen and hydrogen isotope measurements have been made on a large variety of sedimentary rocks and minerals, with special emphasis on the fine-grained (predominantly clay mineral) fraction of the sediments. By means of a series of experiments in which hydrous minerals were dried in a drybox for different lengths of time or outgassed under vacuum at varying temperatures and lengths of time, it was ascertained that interlayer water could be successfully removed from montmorillonite type clay minerals prior to measurement of their oxygen and hydrogen isotopic compositions. The interlayer water was removed because it readily exchanges with atmospheric water vapor, and its analysis served no useful purpose in this study. There was no isotopic exchange between the interlayer water and the clay mineral during the outgassing procedure. The removal of water from zeolites is not as satisfactory, and δO^{18} measurements of these minerals may be inaccurate by a few permil because of the presence of some zeolitic water.

Approximate fractionation factors between sedimentary minerals and water may be inferred from the isotopic compositions of natural samples. Other mineral - water fractionation factors have been estimated from the number and kinds of chemical bonds contained in the minerals. The oxygen isotope fractionations between minerals fall in roughly the same order as do those for the igneous minerals analyzed by Taylor and Epstein (103). Framework silicates concentrate O^{18} with respect to layer silicates, and these in turn concentrate O^{18} with respect to oxides.

All hydrogen containing minerals analyzed concentrate hydrogen rather than deuterium with respect to water. Among the sheet silicates, the minerals with larger Al:Mg ratios in the octahedral sheets concentrate deuterium with respect to minerals with smaller Al:Mg ratios. Oxygen and hydrogen isotope fractionation factors between sedimentary minerals and water are listed in Table 29.

TABLE 29

Isotopic fractionation factors between minerals and water at sedimentary temperatures

Mineral	$\alpha^{ox}_{min-H_2O}$	$\alpha^{hy}_{min-H_2O}$
Quartz	1.034	
Alkali feldspar	1.034	
Phillipsite	1.034	
Montmorillonite	1.027	0.94
Illite	1.029	0.97
Kaolinite	1.027	0.97
Glauconite	1.026	0.93
Chlorite	1.022	0.85
Manganese Nodule	1.015	0.92

Consistency of relationships between oxygen and hydrogen isotope ratios of clay minerals taken from a variety of areas and having different absolute values of isotope ratios was demonstrated in a number of cases. These relationships result from exchange of clays with different meteoric waters under conditions in which the fractionation factors are constant. This strongly suggests that the fractionation factors are equilibrium ones and that clay minerals form in isotopic equilibrium with their environments. Once formed, clay minerals may undergo isotopic exchange at slightly elevated temperatures, perhaps as low as 40°C, over lengths of time which are fairly short geologically. There was no clearly demonstrable case of clay minerals undergoing isotopic exchange at sedimentary temperatures, although one possible interpretation of the data of some Upper Cretaceous glauconites analyzed is that exchange at low temperatures occurred.

Isotopic analyses of modern ocean sediment core samples indicate that the authigenic and detrital components of the sediments are each characterized by isotopic compositions determined by their mode of origin. The most important authigenic components of ocean sediments are montmorillonite, phillipsite, and iron and manganese oxides. These have isotopic compositions compatible with formation in the marine environment under isotopic equilibrium conditions. The most important detrital minerals in ocean sediments are montmorillonite, chlorite, illite, kaolinite, and quartz. Detrital montmorillonite contains as much as eight or ten permil less O^{18} than authigenic montmorillonite, and thus δO^{18} measurements can be used to distinguish between the two. The carbonate-free phases of most of the ocean sediments which are primarily of detrital origin are describable in terms of a mixture of the following components with the indicated δ-values:

	δO^{18}	δD
Quartz	+11.4	
Montmorillonite	+17	-11
Illite	+21	-7
Chlorite	+7	-10
Kaolinite	+25	-4

These values are compatible with an origin of kaolinite as a weathering product in tropical areas, of illite and montmorillonite as weathering or diagenetic minerals, and of chlorite primarily from metamorphic or diagenetic sources but possibly also containing a high latitude weathering component. There is no evidence for isotopic exchange of any of the detrital clays in the ocean cores. Some of the samples have been dated by ionium-thorium methods (Goldberg and Griffin (45)) at 250,000 years or more, indicating that isotopic exchange does not occur at ocean-bottom temperatures to a significant degree in that length of time.

The range of δ-values of pelagic sediments, which reflect the detrital origin if the minerals, is similar to that found for shales. This indicates that while isotopic composition probably cannot be used to distinguish fresh water shales from marine shales, it may be of use in studying the origin of the clay minerals in shales, and their post-depositional history.

Isotopic analyses of coarse grained detrital minerals, especially quartz and feldspar, indicate that the O^{18}/O^{16} ratios of these minerals are retained from the igneous or metamorphic environment in which they originated. Where there is no evidence of chemical reaction or secondary overgrowth, there is no evidence that these minerals have undergone isotopic exchange in the sedimentary environment. The isotopic compositions of detrital quartz and feldspar can therefore be used as indicators of provenance.

With the data of this study and others on the O^{18}/O^{16} and D/H ratios of the various sedimentary rock types, and with the available estimates of the abundances of these rock types, it has been possible to calculate the extent to which the weathering and sedimentary processes have affected the isotopic composition of the hydrosphere. These calculations indicate that changes due to these processes throughout geologic time could have made the oceans poorer in O^{18} by about three permil and richer in deuterium by only 0.03 percent. This would correspond to a very small change in δO^{18} and a negligible change in δD since the end of the Precambrian as a result of these processes.

BIBLIOGRAPHY

1. Arrhenius, G., Pelagic sediments; in The Sea, M. N. Hill, ed., Interscience Publishers, New York, pp. 655-727, (1963).

2. Arrhenius, G., Sedimentation on the ocean floor; in Researches in Geochemistry, P. Abelson, ed., John Wiley and Sons, New York, pp. 1-24, (1959).

3. Baertschi, P., Isotopic composition of the oxygen in silicate rocks; Nature 166, 112-113, (1950).

4. Barth, T. F. W., Theoretical Petrology; John Wiley and Sons, New York, 387 pp., (1952).

5. Bigeleisen, J., and M. G. Mayer, Calculation of equilibrium constants for isotopic exchange reactions; J. Chem. Phys. 15, 261-271, (1947).

6. Biscaye, Pierre E., Mineralogy and sedimentation of recent deep-sea clay in the Atlantic Ocean and adjacent seas and oceans; Bull. Geol. Soc. Am. 76, 803-832, (1965).

7. Bramlette, M. N., Pelagic sediments; in Oceanography, M. Sears., ed., Pub. No. 67, AAAS, Washington, (1961).

8. Burst, J. F., Mineral heteorgeneity in "glauconite" pellets; Am. Min. 43, 449-481, (1958).

9. Burst, J. F., "Glauconite" pellets: their mineral nature and applications to stratigraphic interpretations; AAPG Bull. 42, 310-327,(1958).

10. Callaghan, Eugene, Endellite deposits in Gardner Mine ridge, Lawrence County, Indiana; Dept. of Conservation, Div. of Geol., Bull 1, (1948).

11. Clarke, F. W., The data of geochemistry, 5th ed., USGS Bull. 770, (1924).

12. Clayton, R. N., Oxygen isotope fractionation between calcium carbonate and water; J. Chem. Phys. 34, 724-726, (1961).

13. Clayton, R. N. and S. Epstein, The relationship between O^{18}/O^{16} ratios in coexisting quartz carbonate and iron oxides from various geological deposits; J. Geol. 66, 352-373, (1958).

14. Clayton, R. N., I. Friedman, D. L. Graf, T. K. Mayeda, W. F. Meents, and N. F. Shimp, The origin of saline formation waters. I. Isotope composition; J. Geoph. Res. 71, 3869-3882, (1966).

15. Clayton, R. N. and T. Mayeda, The use of bromine pentafluoride in the extraction of oxygen from oxides and silicates for isotopic analysis; Geochim. et Cosmochim. Acta 27, 43-52 (1963).

16. Clayton, R. N., J. R. O'Neil, and T. Mayeda, Oxygen isotope fractionations between quartz and water; in preparation.

17. Cleveland, George B., Geology of the Otay bentonite deposit, San Diego County, California; Calif. Div. Mines Special Rept. 64 (1960).

18. Cloud, P. E., Physical limits of glauconite formation; AAPG Bull. 39, 484-492 (1955).

19. Craig, H., Standard for reporting concentrations of deuterium and oxygen 18 in natural water; Science 133, 1833 (1961).

20. Craig, H., Isotopic variations in meteoric waters; Science 133, 1702-1703 (1961).

20a. Craig, H., Isotopic standards for carbon and oxygen correction factors for mass-spectrometric analysis of carbon dioxide; Geochem. et Cosmochim. Acta 12, 133-149 (1957).

21. Craig, H., L. I. Gordon, and Y. Horibe, Isotopic exchange effects in the evaporation of water: 1. Low temperature experimental results; J. Geoph. Res. 68, 5079-5087 (1963).

22. Dale, T. Nelson, The commercial granites of New England; USGS Bull. 738 (1923).

23. Darton, N. H., Red beds and associated formations in New Mexico; USGS Bull. 794 (1928).

24. Deer, W. A., R. A. Howie, and J. Zussman, Rock-Forming Minerals. Vol. 4. Framework Silicates; John Wiley and Sons, New York, 435 pp. (1963).

25. Deer, W. A., R. A. Howie, and J. Zussman, Rock-Forming Minerals. Vol. 3. Sheet Silicates; John Wiley and Sons, New York, 270 pp. (1962).

26. Degens, E. T. and S. Epstein, Oxygen and carbon isotope ratios in coexisting calcites and dolomites from recent and ancient sediments; Geochim. et Cosmochim. Acta 28, 23-44 (1964).

27. Degens, E. T. and S. Epstein, Relationship between O^{18}/O^{16} ratios in coexisting carbonates, cherts, and diatomites; AAPG Bull. 46, 534-542 (1962).

28. Dole, M., The relative atomic weight of oxygen in water and in air. II. A note on the relative atomic weight of oxygen in fresh water, salt water, and atmospheric water vapor; J. Chem. Phys. 4, 778 (1936).

29. Dole, M., The relative atomic weight of oxygen in water and in air; J. Am. Chem. Soc. 57, 2731 (1935).

30. Dole, M. and R. L. Slobod, Isotopic composition of oxygen in carbonate rocks and iron oxide ores; J.Am.Chem.Soc.62, 471-479 (1940).

31. Emery, K. O., The Sea off Southern California; John Wiley and Sons, New York, 366 pp. (1960).

32. Engelhardt, W. von, Die Geochemie des Bariums; Chem. Erde 10, 187-246 (1936).

33. Epstein, S., R. Buchsbaum, H. A. Lowenstam, and H. C. Urey, Revised carbonate-water isotopic temperature scale; Bull. Geol. Soc. Am. 64, 1315-1326 (1953).

34. Epstein, S., R. Buchsbaum, H. A. Lowenstam, and H. C. Urey, Carbonate-water isotopic temperature scale; Bull. Geol. Soc. Am. 62, 417-426 (1951).

35. Epstein, S. and T. Mayeda, Variations of O^{18} content of water from natural sources; Geochim. et Cosmochim.Acta 4, 213-224 (1953).

36. Evernden, J. F., G. H. Curtis, J. Obradovich, and R. Kistler, On the evaluation of glauconite and illite for dating sedimentary rocks by the K-Ar method; Geochim. et Cosmochim. Acta 23, 78-99 (1961).

37. Friedman, I., Deuterium content of natural waters and other substances; Geochim. et Cosmochim.Acta 4, 89-103 (1953).

38. Friedman, I., A. C. Redfield, B. Schoen, and J. Harris, The variation in the deuterium content of natural waters in the hydrologic cycle; Rev. Geoph. 2, 177-224 (1964).

39. Garlick, G. Donald, Oxygen isotope ratios in coexisting minerals of regionally metamorphosed rocks; Ph.D. thesis, California Institute of Technology (1964).

39a. Garlick, G. Donald and J. R. Dymond, Oxygen-isotope exchange between volcanic glass and ocean water; (abstract) Trans. Amer. Geoph. Union 48, 236 (1967).

40. Garlick, G. Donald and S. Epstein, Oxygen isotope ratios in coexisting minerals of regionally metamorphosed rocks; Geochim. et Cosmochim. Acta 31, 181-214 (1967).

41. Garlick, G. Donald and S. Epstein, The isotopic composition of oxygen and carbon in hydrothermal minerals at Butte, Montana; Econ. Geol. 61, 1325-1335 (1966).

42. Giavque, W. F. and H. L. Johnston, An isotope of oxygen mass 18; J. Am. Chem. Soc. 51, 1436-1441 (1929); Nature 123, 318 (1929).

43. Godfrey, John D., The deuterium content of hydrous minerals from the East-Central Sierra Nevada and Yosemite National Park; Geochim. et Cosmochim. Acta 26, 1215-1245 (1962).

44. Goldberg, E. D. and G. Arrhenius, Chemistry of Pacific pelagic sediments; Geochim. et Cosmochim. Acta 13, 153-212 (1958).

45. Goldberg, E. D. and J. J. Griffin, Sedimentation rates and mineralogy in the South Atlantic; J. Geoph. Res. 69, 4293-4309 (1964).

46. Goldberg, E. D. and J. J. Griffin, Clay-mineral distributions in the Pacific Ocean; in The Sea, M. N. Hill, ed., Interscience Publishers, New York, pp. 728-741 (1963).

47. Goldberg, E. D. and J. J. Griffin, unpublished data.

48. Goldschmidt, V. M., Grundlagen der quantitativen Geochimie; Fortschr. d. Mineral., Krist. und Petrog. 17, 112-156 (1933).

49. Griffin, G. M. and R. L. Ingram, Clay minerals of the Neuse River estuary; Jour. Sed. Pet. 25, 194-200 (1955).

50. Grim, Ralph, Clay Mineralogy; McGraw-Hill, New York, 384 pp. (1953).

51. Halevy, E., The exchangeability of hydroxyl groups in kaolinite; Geochim. et Cosmochim. Acta 28, 1139-1145 (1964).

52. Herold, P. G. and G. R. Heyl, Kaolin deposits of southern Pike County; Arkansas Geol. Survey Bull. 7 (1942).

53 Hower, J., Some factors concerning the nature and origin of glauconite; Am. Min. 46, 313-334 (1961).

54. Hurley, P. M., B. C. Heezen, W. H. Pinson, and H. W. Fairbairn, K-Ar age values in pelagic sediments of the North Atlantic; Geochim. et Cosmochim. 27, 393-399 (1963).

55. Jackson, M. L., Frequency distribution of clay minerals in major great soil groups as related to the factors of soil formation; in Clays and Clay Minerals, A. Swinford, ed., Proc. 6th Nat'l. Conf., Pergamon Press, London, pp. 138-143 (1959).

56. Keith, M. L. and J. N. Weber, Carbon and oxygen isotopic composition of selected limestones and fossils; Geochim. et Cosmochim. Acta 28, 1787-1816 (1964).

57. Kerr, P. F., P. K. Hamilton, R. J. Pill, G. V. Wheeler, D. R. Lewis, W. Burkhardt, D. Reno, G. L. Taylor, R. C. Mieleuz, M. E. King, and N. C. Schieltz, Analytical data on reference clay minerals; API Project 49, Prelim. Rept. No. 7, Amer. Petrol. Inst.(1950).

58. Kerr, P. F. and J. L. Kulp, Reference clay localities--United States; API Project 49, Prelim. Rept. No. 2, Amer. Petrol. Inst. (1949).

59. Kerr, P. F., J. L. Kulp, and P. K. Hamilton, Differential thermal analyses of reference clay mineral specimens; API Project 49, Prelim. Rept. No. 3, Amer. Petrol. Inst. (1949).

60. Kerr, P. F., M. S. Main, and P. K. Hamilton, Occurrence and microscopic examination of reference clay mineral specimens; API Project 49, Prelim. Rept. No. 5, Amer. Petrol. Inst. (1950).

61. Kirshenbaum, Isidor, Physical Properties and Analysis of Heavy Water; McGraw-Hill, New York, 438 pp. (1951).

62. Konta, J., Personal communication to S. Epstein, dated June 24, 1966.

63. Konta, J., Der Rohkaolin von Sedlec bei Karlsbad; Sprechsaal für keramik glas email silikate 98, 3-12 (1965).

64. Longinelli, Antonio, Ratios of oxygen-18: oxygen-16 in phosphate and carbonate from living and fossil marine organisms; Nature 211, 923-927 (1966).

65. Lowenstam, H. A. and S. Epstein, Paleotemperatures of the post-Aptian Cretaceous as determined by the oxygen isotope method; J. Geol. 62, 207-248 (1954).

66. Mallot, Clyde A., Stratigraphy of the Ste. Genevieve and Chester Formations of Southern Indiana; The Edwards Letter Shop (1952).

67. Manian, S. H., H. C. Urey, and W. Bleakney, The relative abundance of the oxygen isotopes O^{16}/O^{18} in stone meteorites; J. Am. Chem. Soc. 56, 2601-2609 (1934).

68. McAuliffe, C. D., M. S. Hall, L. A. Dean, and S. B. Hendricks, Exchange reactions between phosphates and soils; Soil Sci. Soc. Amer. Proc. 12, 119-123 (1947).

69. McCrea, J. M., The isotopic chemistry of carbonates and a paleotemperature scale; J. Chem. Phys. 18, 849-857 (1950).

70. McKinney, C. R., J. M. McCrea, S. Epstein, H. A. Allen, and H. C. Urey, Improvements in mass spectrometers for the measurement of small differences in isotopic abundance ratios; Rev. Sci. Inst. 21, 724-730 (1950).

71. Mellis, O., Replacement of plagioclase by orthoclase in deep-sea deposits; Nature 169, 624 (1952).

72. Mero, John L., The Mineral Resources of the Sea; Elsevier Publishing Co., Amsterdam, 312 pp. (1965).

73. Milligan, W. O. and Harry B. Weiser, The mechanism of dehydration of zeolites; J. Phys. Chem. 41, 1029-1040 (1937).

74. Neumann, F.R., Origin of the Cretaceous white clays of South Carolina; Econ. Geol. 22, 374-387 (1927).

75. Nier, A. O., A mass spectrometer for isotope and gas analysis; Rev. Sci. Instr. 18, 398-411 (1947).

76. Nutting, P. G., Absorbent clays, their distribution, properties, production, and uses; USGS Bull. 928-C, 127-219.

77. O'Neil, J. R. and R. N. Clayton, Oxygen isotope geothermometry; in Isotopic and Cosmic Chemistry, Craig, Miller, and Wasserburg, eds., North-Holland Publishing Company, Amsterdam, pp. 157-168 (1964).

78. O'Neil, J. R. and S. Epstein, A method for oxygen isotope analysis of milligram quantities of water and some of its applications; J. Geoph. Res. 71, 4955-5961 (1966).

79. O'Neil, J. R. and H. P. Taylor, Jr., Oxygen isotope equilibrium between muscovite and water; in preparation (1967).

80. O'Neil, J. R. and H. P. Taylor, Jr., The oxygen isotope and cation exchange chemistry of feldspars; Am. Min., in press (1967).

81. Osthaus, Bernard, Kinetic studies on montmorillonites and nontronite by the acid-dissolution technique; Clays and Clay Minerals, A. Swineford, ed., Proc. 4th Nat'l. Conf., NAS-NRC Pub. 456, pp. 301-321 (1956).

82. Owens, J. P., J. P. Minard, and P. D. Blackmon, Distribution of clay-sized sediments in the coastal plain formations near Trenton, New Jersey; USGS Prof. Paper 424-C, 317-319 (1961)

83. Peterson, M. N. A. and E. D. Goldberg, Feldspar distributions in South Pacific pelagic sediments; J. Geoph. Res. 67, 3477-3492 (1962).

84. Plumb, K. A., Personal communication to S. Epstein, November 29, 1965.

85. Powers, M. C., Clay diagenesis in the Chesapeake Bay area; in Clays and Clay Minerals, A. Swineford and N. Plummer, eds., Nat'l. Res. Council Pub. 327, pp. 68-80 (1954).

86. Rex, R. W., Quartz in sediments of the Central and North Pacific Basins; Ph.D. thesis, University of California (1958).

87. Rex, R. W. and E. D. Goldberg, Quartz contents of pelagic sediments of the Pacific Ocean; Tellus 10, 153-159 (1958).

88. Ross, C. S. and S. B. Hendricks, Minerals of the montmorillonite group; USGS Prof. Paper 205-B, 23-80 (1945).

89. Ross, C. S. and H. D. Miser, Volcanic rocks in the Upper Cretaceous of southwestern Arkansas and southeastern Oklahoma; Am. J. Sci. 9, 113-126 (1925).

90. Roy, D. M. and R. Roy, Hydrogen-deuterium exchange in clays and problems in the assignment of infrared frequencies in the hydroxyl region; Geochim. et Cosmochim. Acta 11, 72-85 (1957).

91. Sharma, Taleshwar and R. N. Clayton, Measurement of O^{18}/O^{16} ratios of total oxygen of carbonates; Geochim. et Cosmochim. Acta 29, 1347-1353 (1965).

92. Shaw, D. B. and C. E. Weaver, The mineralogical composition of shales; J. Sed. Petrol. 35, 213-222 (1965).

93. Silverman, S. R., The isotopic geology of oxygen; Geochim. et Cosmochim. Acta 2, 26-42 (1951).

94. Slaughter, M. and J. W. Earley, Mineralogy and geological significance of the Mowry bentonites, Wyoming; Geol. Soc. Amer. Special Paper 83 (1965).

95. Smith, E. R. and H. Matheson, Difference in atomic weight of oxygen from air and from water; J. Res. N.B.S. 17, 625 (1936).

96. Sverdrup, H. U., M. W. Johnson, and R. H. Fleming, The Oceans; Prentice-Hall, New York, 1087 pp. (1942).

97. Swartout, J. A. and M. Dole, The protium-deuterium ratio and the atomic weight of hydrogen; J. Am. Chem. Soc. 61, 2025 (1939).

98. Tatsumoto, M. and C. Patterson, Age studies of zircon and feldspar concentrates from the Franconia Sandstone; J. Geol. 72, 232-242 (1964).

99. Taylor, H. P., Jr., O^{18}/O^{16} ratios in coexisting minerals of igneous and metamorphic rocks; Ph.D. thesis, California Institute of Technology (1959).

100. Taylor, H. P., Jr., A. L. Albee and S. Epstein, O^{18}/O^{16} ratios of coexisting minerals in three assemblages of kyanite zone pelitic schist; J. Geol. 71, 513-522 (1963).

101. Taylor, H. P., Jr. and S. Epstein, Deuterium-hydrogen ratios in coexisting minerals of metamorphic and igneous rocks; Trans. Am. Geoph. Union (abstract) 47, 213 (1966).

102. Taylor, H. P., Jr. and S. Epstein, Oxygen isotope analyses of tektites, soils, and impactite glasses; in Isotopic and Cosmic Chemistry, Craig, Miller, and Wasserburg, eds., North-Holland Publishing Co., Amsterdam, pp. 181-199 (1964).

103. Taylor, H. P., Jr. and S. Epstein, Relationship between O^{18}/O^{16} ratios in coexisting minerals of igenous and metamorphic rocks. Part I. Principles and experimental results; Bull. Geol. Soc. Amer. 73, 461-480 (1962).

104. Taylor, H. P., Jr. and S. Epstein, Relationship between O^{18}/O^{16} ratios in coexisting minerals of igneous and metamorphic rocks. Part II. Application to petrologic problems; Bull. Geol. Soc. Amer. 73, 675-693 (1962).

105. Urey, H. C., The thermodynamic properties of isotopic substances; J. Chem. Soc., 562-581 (1947).

106. Urey, H. C., F. G. Brickwedde, and G. M. Murphy, A hydrogen isotope of mass 2; Phys. Rev. 39, 164-165 (1932).

107. Urey, H. C., H. A. Lowenstam, S. Epstein, and C. R. McKinney, Measurement of paleotemperatures of the upper Cretaceous of England, Denmark, and the southeastern United States; Bull.

Geol. Soc. Amer. 62, 399-416 (1951).

108. Veatch, O., Kaolins of the Dry Branch region, Georgia; Econ. Geol. 3, 109-117 (1908).

109. Verhoogen, J., Ionic diffusion and electrical conductivity in quartz; Am. Min. 37, 637-655 (1952).

110. Wasserburg, G. J., R. J. Hayden, and K. J. Jensen, Ar^{40}/K^{40} dating of igneous rocks and sediments; Geochim. et Cosmochim. Acta 10, 153-165 (1956).

111. Weaver, C. E., The clay petrology of sediments; in Clays and Clay Minerals, A. Swineford, ed., Proc. 6th Nat'l. Conf., Pergamon Press, New York, pp. 154-187 (1959).

112. Weber, Jon N., The O^{18}/O^{16} ratio in ancient oceans; Geokhimiya 674-680 (1965).

113. Wickman, F. E., The "total" amount of sediment and the composition of the "average igneous rock"; Geochim. et Cosmochim. Acta 5, 97-110 (1954).

114. Yeroschev-Shak, Illite in the sediments of the Atlantic Ocean; Doklady Akad. Nauk SSSR 137, 951-953 (1961).

115. Yeroschev-Shak, Kaolinite in the sediments of the Atlantic Ocean; Doklady Akad. Nauk SSSR 137, 695-697 (1961).

116. Anderson, Thomas F., Diffusion in carbonates by isotopic exchange with carbon dioxide; (abstract) Program Geol. Soc. Amer., Ann. Mtg., p. 4 (1966).

117. Rye, Robert O., The carbon, hydrogen, and oxygen isotopic composition of the hydrothermal fluids responsible for the lead-zinc deposits at Providencia, Zacatecas, Mexico; Econ. Geol. 61, 1399-1427 (1966).

118. Griffin, J. J., personal communication, January 1965.

119. Trumbull, John, personal communication, February 1965.

120. Johnson, J., personal communication.

121. Stewart, H. B., Jr., Oceanographic Cruise Report, USC and GS Ship Explorer-1960; U. S. Dept. Commerce, Washington, 162 pp. (1962).

122. Epstein, S. and J. R. O'Neil, Hydrogen isotope fractionations in the system serpentine-water; unpublished data.

123. Goldberg, E.D. and M.N. Koide, Geochronological studies of deep-sea sediments by the ionium/thorium method; Geochim. et Cosmochim. Acta 26, 417-450 (1962).

APPENDIX I

DERIVATION OF THE EQUATION RELATING δD vs. δO^{18} PLOTS OF CLAYS EXCHANGED WITH METEORIC WATERS TO THE δD vs. δO^{18} PLOT OF METEORIC WATERS

Consider the exchange of two aliquots of a clay with two isotopically different meteoric waters under conditions such that $\alpha^{ox}_{clay\text{-}H_2O}$ and $\alpha^{hy}_{clay\text{-}H_2O}$ are constants. Then,

$$\delta^{clay}_{O^{18}} = \left[\frac{(O^{18}/O^{16})_{clay}}{(O^{18}/O^{16})_{SMOW}} - 1\right] \times 1000$$

$$= \left[\alpha^{ox}_{clay\text{-}H_2O} \times \frac{(O^{18}/O^{16})_{H_2O}}{(O^{18}/O^{16})_{SMOW}} - 1\right] \times 1000$$

$$= \left[\alpha^{ox}_{clay\text{-}H_2O}\left(1 + \frac{\delta^{H_2O}_{O^{18}}}{1000}\right) - 1\right] \times 1000 \qquad (1)$$

Similarly

$$\delta^{clay}_{D} = \left[\alpha^{hy}_{clay\text{-}H_2O}\left(1 + \frac{\delta^{H_2O}_{D}}{100}\right) - 1\right] \times 100 \qquad (2)$$

For two different clays which have undergone exchange with two different meteoric waters

$$\delta^{clay(1)}_{O^{18}} - \delta^{clay(2)}_{O^{18}} = \alpha^{ox}_{clay\text{-}H_2O}\left[\delta^{H_2O(1)}_{O^{18}} - \delta^{H_2O(2)}_{O^{18}}\right] \qquad (3)$$

Computing a similar equation for hydrogen and dividing, we obtain

$$\frac{\delta_D^{clay(1)} - \delta_D^{clay(2)}}{\delta_{O^{18}}^{clay(1)} - \delta_{O^{18}}^{clay(2)}} = \frac{\overset{hy}{\alpha}_{clay\text{-}H_2O}}{\overset{ox}{\alpha}_{clay\text{-}H_2O}} \left[\frac{\delta_D^{H_2O\ (1)} - \delta_D^{H_2O\ (2)}}{\delta_{O^{18}}^{H_2O\ (1)} - \delta_{O^{18}}^{H_2O\ (2)}} \right] \qquad (4)$$

The expression in brackets on the right hand side of equation (4) is the slope of the line of meteoric waters on a δD vs. δO^{18} plot. This is essentially a constant equal to 0.80. Thus, the expression on the left hand side of the equation, the slope of the line connecting the clay points, is also a constant. The trajectory of the clay points is therefore a straight line of the type

$$\delta D\ (\%) = A\ \delta O^{18}\ (‰) + B \qquad (5)$$

and

$$\boxed{A = 0.80 \times \frac{\overset{hy}{\alpha}_{clay\text{-}H_2O}}{\overset{ox}{\alpha}_{clay\text{-}H_2O}}} \qquad (6)$$

To evaluate B, substitute equations (1), (2), and (6) into equation (5).

$$\left[\overset{hy}{\alpha}_{clay\text{-}H_2O} \left(1 + \frac{\delta_D^{H_2O}}{100} \right) - 1 \right] \times 100 =$$

$$0.80 \times \frac{\overset{hy}{\alpha}_{clay\text{-}H_2O}}{\overset{ox}{\alpha}_{clay\text{-}H_2O}} \left[\overset{ox}{\alpha}_{clay\text{-}H_2O} \left(1 + \frac{\delta_{O^{18}}^{H_2O}}{1000} \right) - 1 \right] \times 1000 + B$$

Upon simplifying, we obtain

$$\boxed{B = 800 \frac{\overset{hy}{\alpha}_{clay\text{-}H_2O}}{\overset{ox}{\alpha}_{clay\text{-}H_2O}} - 699\ \overset{hy}{\alpha}_{clay\text{-}H_2O} - 100} \qquad (7)$$

APPENDIX II

SAMPLE DESCRIPTIONS AND GEOLOGICAL BACKGROUND

A. KAOLINITE

1. Murfreesboro,Arkansas (API Standard H 1)

This sample was collected from the Upper Cretaceous Tokio Fm. It has been interpreted by Herold and Heyl (32) as water-laid volcanic material which altered in part after deposition. Fossil plants are present.

Microscopic examination by Main in Kerr et al. (60) indicates 1 - 2 percent quartz, 1 - 2 percent orthoclase, 0.1 - 0.5 percent albite, 1 - 2 percent rutile, traces of limonite, 0.5 - 1.0 percent ferromagnesian minerals.

2. Bath, S. Carolina (API STANDARD H 5)

Sample was collected from the Cretaceous Upper Hamburg Fm. or Middendorf Fm. Veatch (108) interprets its depositional environment as non-marine but Neumann (74) interprets it as marine. Some alteration has occurred since deposition Kerr et al. (60).

Microscopic examination by Main in Kett et al. (60) indicates 1 - 2 percent quartz, 1.5 percent orthoclase, 1 - 1.5 percent limonite, 1 percent leucoxene.

3. Langley, S. Carolina (Wards No. 492)

Sample was collected a few miles from Bath, S. Carolina, and its geology is probably similar. Macroscopically it is very similar to the Bath, S. C. sample.

4. Mesa Alta, N. Mexico (API Standard H 9)

The sample was collected from the Cretaceous Dakota Sandstone. Darton (23) has interpreted it as having undergone two stages of kaolinization, one prior to deposition and one subsequent to deposition.

Microscopic examination by Main in Kerr et al. (60) indicates 1 - 1.5 percent titanite, o.5 - 1 percent limonite, traces of orthoclase, plagioclase, zircon.

5. Sedlec, Czechoslovakia (Provided by J. Konta)

The sample is a residual weathering kaolinite formed on granite. It is of Oligocene and early Miocene age and is overlain by non-marine sediments. Konta (63) gives X-ray analytical data indicating low quartz and mica content in fine grain size, and high quartz and mica in coarse grain size. Isotopic analyses were performed on several size fractions and results were extrapolated to zero percent impurities.

6. Kadan, Czechoslovakia (Provided by J. Konta)

This is of weathering origin. It was sampled 33 km NE of the Sedlec kaolinite (Konta (62)).

7. Podlesi, Czechoslovakia (Provided by J. Konta)

This sample is taken from the same area of Czechoslovakia as the Sedlec and Kadan samples and is of weathering origin (Konta (60)).

B. HALLOYSITE

1. Bedford, Indiana (API Standard H 12)

Sample was collected at Mississippian - Pennsylvanian boundary, in Chester formation. Callaghan (10) has interpreted the origin as having been deposited from solution.

Microscopic description by Main in Kerr *et al*. (60) indicates 1 - 1.5 percent sericite, 0.5 - 1 percent quartz, and traces of orthoclase, limonite and rutile.

C. DICKITE

1. Horni Slavkov, Czechoslovakia (Provided by J. Konta)

This is of hydrothermal origin. Its temperature of formation has been estimated at approximately 300 to 350°C (Konta (62)).

2. Kladno Zapotocky, Czechoslovakia (Provided by J. Konta)

The sample was taken from a sedimentary deposit (Konta (62)) from the same general region as other Czechoslovakian clays analyzed here, near Prague, about 100 miles east of Horni Slavkov.

D. MONTMORILLONITE (from ocean cores)

1. RIS 81 (Provided by J. J. Griffin)

Sample was collected in the Pacific Ocean (14°08'S, 138°06'W) in an area in which sediments are formed predominantly of volcanic material (Goldberg and Griffin (46)). Iron oxides were removed from sample by J. J. Griffin who separated the finest grained, almost pure montmorillonite fraction.

2. EM - 7 Run 1 (Provided by J. J. Griffin)

Sample was taken in experimental Mohole test site 28°58'N, 117°28'W, approximately 153 meters below sediment surface. Volcanic fragments are found in nearby sediment and basalt layer is 15 meters below sample. J. J. Griffin separated the finest grained, very pure montmorillonite fraction.

E. MONTMORILLONITE (from bentonites)

1. Polkeville, Mississippi (API Standard H 19)

Sample taken from (Oligocene) Vicksburg formation and is highly altered volcanic ash. There are marine fossils present (Kerr _et al_. (58)).

Microscopic examination by Main in Kerr _et al_. indicates 5 - 7 percent ferromagnesian minerals, 0.5 - 1.5 percent quartz, 0.5 - 1.5 percent orthoclase and traces of sericite, limonite and carbonaceous material.

2. Chambers, Arizona (API Standard H 23)

The clay appears to have formed by alteration of a volcanic tuff, transported to a lake basin in which it was altered (Nutting (76)).

Main, in Kerr _et al_. (60), notes evidence for later stage alteration, as sericite is present in veinlets. His petrographic examination indicates 2 percent ferromagnesian minerals, 1 percent quartz and traces of sericite, limonite, carbonaceous material and pyrolusite.

3. Otay, California (API Standard H 24)

Sample was collected from Pliocene marine sands with which it is interbedded. It was formed by weathering of volcanic ash. According to Cleveland (17) most of the ash was weathered prior to deposition but some was weathered after deposition. Source of volcanic ash was probably in nearby Baja, California.

Petrographic description by Main in Kerr _et al_. (60) indicates 1 - 2 percent sericite, 1 percent quartz, 0.5 - 1 percent orthoclase, and traces of limonite and ferromagnesian minerals.

4. Clay Spur, Wyoming (API Standard H 26)

Sample is very highly crystalline montmorillonite from the marine Upper Cretaceous Mowry formation. It formed by alteration of volcanic ash with a source a few hundred miles to the west (Slaughter and Earley (94).

Main, in Kerr _et al_. (60) states that corroded edges of feldspar are indicative of secondary alteration and that strain in plagioclase twins is suggestive of compression. His microscopic analysis indicates 3 percent quartz, 2 percent glauconite, 2 percent ferromagnesian minerals, 2 percent plagioclase and traces of sericite and limonite (60).

5. Little Rock, Arkansas (API Standard H 28)

Sample was collected from the marine (?) (Eocene) Wilcox formation. Ash was probably deposited in shallow water and altered in place (Kerr _et al_. (60)).

Petrographic description by Main in Kerr _et al_. (60) indicates 4 - 5 percent limonite, 2 percent quartz, 1 percent plagioclase, trace of sericite.

F. ILLITE

1. Morris, Illinois (API Standard H 36)

Sample was collected from the non-marine underclay of a Pennsylvanian cyclothem.

Petrographic description by Main in Kerr _et al_. (60) indicates 3 percent pyrite, 2 percent quartz, 2 percent sericite, 2 percent limonite, 1 - 2 percent plagioclase and trace of calcite.

G. GLAUCONITE (from ocean sediments)

1. Sta 1752 (Provided by James Trumbull)

This sample was separated from a surface sample taken by the Woods Hole Oceanographic Institution at the inner edge of the Blake Plateau in the Atlantic Ocean (31°28.7'N, 79°29.0'W). This glauconite may be detrital, originating in Tertiary rocks in the Carolinas (J. Schlee, personal communication) or it may be forming at the present time (R. Pratt, personal communication). X-ray analysis of the glauconite has not indicated the presence of any impurities.

2. Sta 1957 (Provided by James Trumbull)

Glauconite was separated from a surface sample taken in shallow water between Long Island, N. Y. and Block I., R.I. (40°21'N, 75°57'W). The glauconite is probably detrital in origin. X-ray analysis has not indicated the presence of any impurities.

3. Sta 6941 (Provided by H. A. Lowenstam)

Sample was collected in Santa Monica Bay, California. It occurs in a rock composed chiefly of glauconite pellets. It may have remained in marine waters since formation or may be detrital from some of the glauconite bearing rocks of the surrounding land area.

H. GLAUCONITE (from New Jersey Coastal Plain Upper Cretaceous and Early Tertiary Rocks (Provided by John Schlee)) .

All of these rocks were deposited in shallow water marine conditions according to Owens, Minard and Blackmon (82) .

1. R-8, Merchantville Fm. (Upper Cretaceous)
Sample was collected in Kinkora, N.J. Rock is poorly consolidated, fine grained sandstone or siltstone. Glauconite is fine sand or silt sized.

2. R-12, Marshalltown Fm. (Upper Cretaceous)
Sample was collected at Wallenford, N.J. Rock is similar in appearance to R-8. X-ray analysis of the glauconite did not indicate any impurity.

3. R-13, Navesink Fm. (Upper Cretaceous)
Sample was taken at New Egypt, N.J. Rock is similar in appearance to R-8 and R-12 but glauconite is coarse sand sized, bright green.

4. Hornerstown Fm. (Paleocene)

Sample was collected just north of New Egypt, N .J. Rock is almost entirely coarse glauconite pellets in fine glauconite matrix. The coarse glauconite was analyzed.

I. GLAUCONITE (from the Precambrian Crawford Fm. of Australia (Provided by J. Richards)).

All samples were taken from the same area on the west side of the gulf of Carpentaria. A1 contain glauconite dated by K/A at 1390 million years (L. C. Noakes, personal communication).

1. E53/3/14

A hard red sandstone. A few cracks are lined with iron oxides. Microscopic examination shows that the rock is primarily greater than 95 percent quartz. Detrital grains are cemented by secondary quartz cement. A few percent green pellets of glauconite are present. Traces of iron oxides and microcline are present. Glauconite pellets coarser than 50 mesh were analyzed.

2. E53/3/15

Macroscopically and microscopically this is almost identical to E53/3/14. Color indicates slightly smaller concentration of oxides.

3. E53/3/16

Macroscopically this is similar to E/53/3/15 but is considerably darker, indicating a higher concentration of oxides. Also, it is cut by numerous minute cracks filled with oxide minerals. Microscopically the rock differs from E53/3/14 and E53/3/15 in that much of the glauconite appears to be altered to a brownish material. In mineral separation the brown grains were hand picked from the glauconite separate and the green pellets were analyzed.

4. E53/3/18 and E53/3/19

These rocks are much finer grained than those described above. They contain a higher concentration of iron oxides and clays as well as some white mica. They are much more poorly cemented. Glauconite pellets analyzed in these rocks were from the coarser than 100 mesh fraction.

J. SECONDARY FELDSPAR

1. Franconia Formation (Provided by C. C. Patterson)

Sample was collected near Richland Center, Wisconsin and is described by Tatsumoto and Patterson (98). The feldspar grains are between 50 and 100 mesh, and consist of triclinic microcline with monoclinic euhedral potassium feldspar overgrowths. Tatsumoto and Patterson removed the secondary rims by etching with fluoboric acid. They estimated the core to rim volume ratio to be 50:50 ± 10.

K. PHILLIPSITE (Provided by J. J. Griffin)

Three finely divided phillipsites, separated from ocean core samples by J. J. Griffin were analyzed. The samples and their locations are:

RIS 79	14°03'S	131°44'W
Tet 23	15°11'N	162°25'W
MSN 130	10°34'S	151°05'W

L. BEACH SANDS (Provided by C. C. Patterson)

These samples were collected on beaches so that the finest grain size was obtained in the area between the high water mark and the water line at the time of collection.

1. Ocean View, Virginia

Sample is almost entirely quartz, mostly round and subround with a few subangular grains. Sphericity moderately high to very high, size sorting uniform, surfaces of grains generally fairly smooth.

2. South Island, S. Carolina

Sample is almost entirely quartz, subrounded to angular with a few very angular grains. Size sorting fairly poor, sphericity moderate. This sample may be a mixture of somewhat rounded, slightly frosted grains and clear-surfaced angular grains.

3. Fernandia, Florida

Sample is almost entirely quartz, moderately angular to moderately rounded. Grains are moderately spherical with a small contribution of definitely elongate grains. Size sorting is fair. There is a fair degree of frosting and surface irregularity.

4. W. Shore, Bay St. Louis, Miss.

Sample is almost entirely quartz with moderate sphericity, good sorting and moderate to well rounded grains. Frosting of grains is fairly heavy.

5. Bath, Maine

Sample is approximately 75 percent quartz. Quartz is subangular to subrounded. Sphericity is moderate. Sorting is fair to good. Frosting is heavy. Non-quartz minerals include chlorite, microcline, chert, opaque minerals, etc.

6. La Push, Washington

Sample is approximately 50 percent quartz. Quartz shows good sorting and sphericity and heavy frosting. Non-quartz minerals are primarily feldspar which is cloudy. However, X-ray analysis indicates that the feldspar has undergone only very little alteration to clay.

7. Huntington Beach, California

Sample is approximately 65 percent quartz. Quartz is a mixture of 10 percent angular, clear, unfrosted grains, 90 percent frosted subangular grains. In addition to quartz, sample contains approximately 25 percent feldspar, and 10 percent mica.

M. SHALES (Green River, Wyoming)

1. GR-6, GR-7

These are light gray shales collected along road cuts on U.S. Highway 30 1 to 2 miles east of the town of Green River. GR-6 has some secondary calcite grains. GR-7 contains many small specks of a feathery opaque mineral or carbon. Both samples are hard and appear unweathered.

APPENDIX III

SUMMARY OF ISOTOPIC RESULTS

Sample	δO^{18} permil	Av. Dev.	No. Runs	δD percent	Av. Dev.	No. Runs
a. KAOLINITE						
Langley, So. Carolina	+21.2	0.3	2	-5.7	0.2	10
Murfreesboro, Ark.	+22.4	0.3	3	-5.1	0.0	2
Bath, S. Carolina	+22.1	0.1	2	-5.6	---	1
Mesa Alta N. Mexico	+18.7	0.6	2	-7.3	0.1	2
Kadan, Czech.	+19.4	---	1	-7.1	---	1
Podlesi, Czech.	+19.0	0.0	2	-7.2	0.1	2
Sedlec, Czech.	+19.3	0.2	3	-7.9	0.3	3
b. HALLOYSITE						
Bedford Indiana	+22.0	0.4	2	-6.0	---	1
c. DICKITE						
Kladno Zapotocky, Czech.	+15.6	0.6	2	-3.7	---	1
Horni Slavkov, Czech.	+15.3	---	1	-3.6	---	1
d. MONTMORILLONITE (bentonite)						
Polkeville, Miss.	+28.5	0.2	2	-5.4	0.2	2

Sample	δO^{18} permil	Av. Dev.	No. Runs	δD percent	Av. Dev.	No. Runs
Chambers Arizona	+19.1	0.4	7	-7.9	0.3	3
Otay, Calif.	+19.0	0.4	4	-4.1	0.1	3
Clay Spur Wyo.	+17.6	0.2	5	-9.9	0.4	11
Little Rock Ark.	+26.0	0.0	2	-6.8	1.0	4
e. MONTMORILLONITE (Ocean cores)						
RIS 81	+26.1	0.0	2	-7.8	0.8	2
EM-7 RUN 1	+28.5	1.0	4	-6.8	---	1
f. ILLITE						
Morris Illinois	+20.5	0.5	2	-5.1	0.2	2
g. GLAUCONITE (from ocean sediments)						
Sta 1752	+26.3	0.5	5	-7.4	0.2	4
Sta 1957	+21.8	0.0	2	-9.0	0.1	3
Sta 6941	+23.8	---	1	-8.5	---	1
h. GLAUCONITE (from rocks of New Jersey coastal plain)						
R-8 Merchantville Fm.	+20.3	0.0	2	-7.8	0.5	3
R-12 Marshalltown Fm.	+23.0	0.5	3	-8.0	0.2	3
R-13 Navesink Fm.	+23.0	0.1	2	-8.6	0.2	3
R-17 Hornerstown Fm.	+22.5	0.3	3	-8.5	0.1	2

Sample	δO^{18} permil	Av. Dev.	No. Runs	δD percent	Av. Dev.	No. Runs
i. GLAUCONITIC SANDSTONES (from Precambrian Crawford Fm., Australia)						
E53/3/14						
whole rk.	+13.7	0.5	4			
glauconite	+14.6	0.3	2	-6.3	0.3	3
quartz	+13.9	0.5	4			
E53/3/15						
whole rk.	+13.7	0.4	3			
glauconite	+13.7	0.2	2	-6.2	0.8	4
quartz	+12.8	0.1	2			
E53/3/16						
whole rk.	+14.4	0.7	4			
glauconite	+18.5	0.5	4	-4.1	0.2	2
quartz	+14.5	0.1	3			
E53/3/18						
whole rk.	+14.8	0.5	3			
glauconite	+17.0	0.8	6	-5.4	---	1
mica	+12.0	---	1			
quartz	+15.0	0.2	2			
E53/3/19						
whole rk.	+15.3	0.1	3			
glauconite	+16.4	0.1	2	-6.4	---	1
mica	+12.9	0.4	2			
quartz	+16.2	0.4	4			
j. PHILLIPSITE						
MSN 130	+33.6	0.7	3			
RIS 79	+34.1	1.1	4			
Tet 23	+33.6	0.4	2			
k. FELDSPAR (detrital grain with secondary enlargement from Franconia Fm.)						
core plus rim	+13.7	0.4	3			
core only	+ 8.5	0.1	3			

Sample	δO^{18} permil	Av. Dev.	No. Runs	δD percent	Av. Dev.	No. Runs
l. MANGANESE NODULE (Blake Plateau)						
	+15.0	0.8	2	-7.7	0.3	3
m. BEACH SANDS						
Huntington Beach, Calif						
whole rk.	+9.3	---	1			
quartz	+10.6	0.6	2			
Fernandia, Florida						
quartz	+11.0	0.2	2			
Bath, Maine						
whole rk.	+12.1	---	1			
quartz	+12.7	0.5	3			
Bay St. Louis, Mississippi						
quartz	+11.4	0.3	2			
South Island, South Carolina						
quartz	+11.3	0.6	2			
Ocean View, Virginia						
quartz	+12.1	0.2	2			
La Push Washington						
whole rk.	+12.5	0.3	2			
quartz	+10.9	0.4	3			
n. SILICIFIED FOSSILS (Roberts Mountain Area, Nevada)						
No. 13.3	+25.1	---	1			
No. 13.1	+22.9	---	1			
No. 12.3	+19.1	0.3	2			

Sample	δO^{18} permil	Av. Dev.	No. Runs	δD percent	Av. Dev.	No. Runs
No. 12.2	+20.7	0.1	2			
No. 11.7	+27.1	---	1			
No. 11.6	+23.6	---	1			
No. 11.5	+23.3	0.5	2			
DF 3	+26.8	0.9	2			
CF 2 90'	+26.5	---	1			
o. SILICEOUS FOSSIL DEBRIS FROM OCEAN CORE						
JYN II 11	+26.6	0.8	3			
p. OCEAN CORE SAMPLES (Scripps Institute of Oceanography)						
JYN II 4 10-15 cm.	+17.0	0.2	6	-7.9	0.5	3
JYN II 4 160-165 cm.				-8.7	0.1	2
JYN II 11 29-34 cm.	+17.5	0.2	4	-9.3	0.3	2
JYN II 20 31-36 cm.	+16.1	0.5	2	-8.8	0.0	2
JYN IV 11 33-39 cm.	+15.7	0.1	3	-7.3	0.2	3
LSDA 159 98-103 cm.	+17.0	0.2	5	-7.3	0.5	4
LSDA 163 90-95 cm.	+18.2	0.2	6	-6.5	---	1
LSDA 183 10-17 cm.	+18.3	0.4	2			
LSDA 212 24-30 cm.	+19.7	0.2	4	-5.7	0.3	2
LSDA 217 79-85 cm.	+19.9	0.1	3	-6.3	0.3	3

Sample	δO^{18} permil	Av. Dev.	No. Runs	δD percent	Av. Dev.	No. Runs
LSDA 223 100-108 cm.	+19.2	0.4	2	-5.8	0.3	3
MSN 121 90-95 cm.	+17.3	0.1	2	-6.8	0.2	2
RIS 42 125-130 cm.				-7.3	0.2	2
RIS 56 29-30 cm.	+21.2	0.4	2	-7.6	0.2	2
RIS 69 170-176 cm.	+16.4	0.0	2			
RIS 80 32-42 cm.	+25.9	0.4	2			

q. OCEAN CORE SAMPLES (Lamont Geological Observatory)

Sample	δO^{18} permil	Av. Dev.	No. Runs	δD percent	Av. Dev.	No. Runs
V16-75						
0-10 cm.	+11.5	0.3	2	-5.5	0.2	2
50-60 cm.				-5.7	0.0	2
200-205 cm.				-6.0	0.2	3
700-705 cm.	+14.1	---	1	-6.0	0.1	2
1119-1124 cm.				-5.8	0.4	2

r. OCEAN CORE SAMPLES (Woods Hole Oceanographic Institution)

Sample	δO^{18} permil	Av. Dev.	No. Runs	δD percent	Av. Dev.	No. Runs
A-296-4 top 3½ in.				-5.7	0.2	3
CH-36-1 top 9 in.				-6.3	0.5	4
CH-43-4 top 4 in.				-6.9	0.1	2
CH-43-6 top 6 in.				-7.7	---	1

Sample	δO^{18} permil	Av. Dev.	No. Runs	δD percent	Av. Dev.	No. Runs
CH-43-18 top 5 in.				-6.9	0.8	2
CH-43-22 top 5 in.				-6.5	---	1
s. SHALES (Green River Formation)						
GR 6	+18.1	0.0	2	-5.8	0.2	2
GR 7	+19.1	0.7	3	-13.0	0.6	6