of the values shows that the free energy of formation of calcium disilicate is the same whether the solid arises from the monomer or dimer forms; it would appear, therefore, that there is only one disilicate which may be formed indifferently from one or the other of the anions. The disilicate is intrinsically 2.6 times as soluble as the monosilicate. The ion product in range III is less than $K_{S.P.}$ for either $Ca_2H_2Si_2O_6$ or $Ca(H_3SiO_4)_2$, as is proper.

In view of the consistent rapid approach to equality of the CaO/SiO_2 ratio in solid and in solution, and the closeness of the ratios in invariant range IV, it is likely that calcium disilicate dissolves congruently in the next less-alkaline univariant range and is the last remaining compound. No hydrated silicate richer in silica than the disilicate is known in nature.

Summary

Hydrated calcium silicates are gelatinous. The effects to be expected from this in a phase rule study are discussed briefly.

Measurements were made of the ratio of CaO to SiO_2 in the solid phase, and of the concentrations of CaO and SiO_2 in solution at 30.2°. Equilibrium and reversibility were tested for.

Four phase ranges were distinguished; in two of these the concentrations were invariant. Adsorption of CaO by the solid phases occurred throughout. The compositions of the hydrated compounds, deduced from considerations of adsorption isotherm and solubility product constant, were: (1) $CaO{\cdot}SiO_2$ (CaH_2SiO_4), (2) $3CaO{\cdot}4SiO_2$ ($Ca_3(HSi_2O_6)_2$), (3) $CaO{\cdot}2SiO_2$ (indifferently either $CaH_2Si_2O_6$ or $Ca(HSiO_3)_2$). The invariant concentrations for the mixture of (1) and (2) were: 3.09 millimoles CaO/l. and 0.090 millimole SiO_2/l. and for the mixture of (2) and (3), 0.900 millimole CaO/l. and 0.931 millimole SiO_2/l.

The assumed exclusive presence of the simple ions $SiO_3^{=}$ and $HSiO_3^{-}$, or in the more rational and preferred orthosilicate terminology, $H_2SiO_4^{-}$ and $H_3SiO_4^{=}$, was inconsistent with the existence of the only alternatives of $Ca(H_3SiO_4)_2$ or any reasonable double compounds of the latter with CaH_2SiO_4. It was necessary to assume therefore that association took place in the dilute alkaline solutions. The postulate of two sets of silicate ions, based on an association equilibrium between $H_3SiO_4^{-}$ and $H_2Si_2O_6^{=}$, led to reasonable and concordant results. The association constant, solubility product constants, and one of the ionization constants, were calculated to a known precision. A high tendency toward association is evidenced.

COLLEGE PARK, MD. RECEIVED AUGUST 18, 1939

[CONTRIBUTION FROM THE PHYSICAL CHEMICAL RESEARCH LABORATORY OF NORTHWESTERN UNIVERSITY]

Isotopic Composition of Oxygen in Carbonate Rocks and Iron Oxide Ores

BY MALCOLM DOLE AND ROBERT L. SLOBOD[1]

Introduction

In recent years the isotopic composition of oxygen in various natural substances has been the subject of a number of investigations beginning with the research of Manian, Urey and Bleakney,[2] who studied stony meteorites and terrestrial silicate rocks. Unfortunately, after these workers had performed the difficult task of recovering the oxygen from these rocks by reaction with graphite and carbon tetrachloride vapors at 1000°, their methods of isotopic analysis were too inaccurate to demonstrate any significant differences between the various samples of oxygen; thus their specific gravity determinations of 0.47 cc. of water were accurate only to $\pm 63\ \gamma$[3] or 29% in the O^{18} abundance ratio while their more accurate mass spectrographic abundance measurements had for their average error 2.5%, which is equivalent to 6 γ. They found no significant variations in the isotopic composition of the oxygen between the stony meteorites and terrestrial silicate rocks, and they concluded that the absolute value of the abundance ratio O^{18}/O^{16} is 0.973/500. In a slightly more accurate mass spectrographic investigation of this abundance ratio in the oxygen from the thermal decomposition of

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[1] University Fellow, 1937–1938.

[2] S. H. Manian, H. C. Urey and W. Bleakney, THIS JOURNAL, **56**, 2601 (1934). This paper contains many references to earlier investigations concerning possible variations in the abundance of isotopic elements in meteors.

[3] The symbol refers to excess density of sample over that of normal water in parts per million; a negative value of γ means that the sample of water is lighter than normal. In this paper we shall take purified Lake Michigan water as being our standard of normal water.

lead dioxide, Smythe[4] obtained 0.994/500. Since both of these values are within the experimental error equal to the rounded-off ratio 1/500, we shall adopt the latter for the calculations of this paper.

Urey and Greiff[5] estimated the statistical mechanical partition functions for the molecular species CO_2^{16}, CO_2^{18}, H_2O^{16}, H_2O^{18}, from which they calculated that if carbon dioxide gas is brought into equilibrium with liquid water at 0°, the O^{18} isotope will concentrate in the gas phase until its abundance ratio becomes 1.046/500 or $+10.3\ \gamma$. Weber, Wahl and Urey[6] checked this prediction experimentally. Urey and Greiff calculated also the isotopic exchange equilibrium constants for many other reactions, but the carbon dioxide–water equilibrium is the one of interest to us here. A relatively large variation in the oxygen isotope ratio in natural substances was first demonstrated by one of us,[7] who found that if the oxygen isotope ratio O^{18}/O^{16} in Lake Michigan water is taken as 1/500, then that of atmospheric air is 1.029/500 or $6.6\ \gamma$. This abnormality in the distribution of the heaviest oxygen isotope may be caused by the equilibrium

$$O_2^{16} + 2H_2O^{18}\ (g) \rightleftharpoons O_2^{18} + 2H_2O^{16}\ (g) \qquad (1)$$

being set up in the stratosphere at −50° under the action of the ultraviolet light from the sun, or it may be due to the isotopic exchange equilibrium existing on the surface of the earth

$$2H_2O^{18}\ (l) + CO_2^{16}\ (g) \rightleftharpoons 2H_2O^{16}\ (l) + CO_2^{18}\ (g) \qquad (2)$$

followed by the irreversible reaction

$$CO_2^{10}\ (g) + H_2O^{0}\ (l) \xrightarrow{\text{chlorophyll}} (HCHO^{6.6})_x + O_2^{6.6} \qquad (3)$$

as suggested by Greene and Voskuyl.[7] In Eq. (3) the superscripts on the oxygen symbols represent the value of γ for each sample of the element.

Since the exact or average temperature at which reaction (2) takes place is unknown at the present time and since the extent of irreversibility of reaction (3) is also unknown, we cannot state definitely the mechanism giving rise to the greater abundance of O^{18} in the atmosphere. We are inclined, however, to the theory postulated by Greene and Voskuyl, because it is believed by geologists that all our atmospheric oxygen arose through the agency of the photosynthesis reaction. The theory of Greene and Voskuyl is also substantiated in part by the work of Morita, Goto and Titani,[8] who decomposed cane sugar in the presence of deuterium-free hydrogen, obtaining thereby 73% of the oxygen of the sugar in the form of water whose density could be measured. They found that the average γ-value of the water obtained in this way was $4.6\ \gamma$ ($6.6\ \gamma$ was predicted by Greene and Voskuyl assuming no exchange of the sugar oxygen with the oxygen of water); if the oxygen of the sugar had been obtained entirely from water, its γ-value would naturally have been zero.

Continuing the study of oxygen isotope abundance ratios, we decided to investigate carbonate rocks and iron oxide ores, not only because of the interest in these important rocks and because of the ease in recovery of the oxygen in the form of water, but also because ores precipitated during widely different geologic eras could be obtained, thus making it possible to study the isotopic composition of the oxygen as a function of age. There was the additional possibility that some inferences might be drawn from the data concerning the origin of the oxygen in the rocks; *i. e.*, whether the oxygen came from water or from the air.

Part I. Carbonate Ores

Experimental

Density Measurements.—The most sensitive method of detecting slight variations in oxygen isotope ratios is the well-known totally submerged float method. The chief improvement adopted by us in this research was the use of a platinum resistance thermometer to measure the temperature of floating equilibrium of the float. In the first measurements a fairly large cylindrical quartz float, volume 10 cc., which balanced at 29.9° was used, but although this float was more sensitive than the smaller, 1 cc. Pyrex float used later, see Fig. 1, and did not have to be corrected for expansion with rise of temperature, we abandoned it in favor of the Pyrex "swimmer" which reached floating equilibrium at 25.0°; because the latter was not "pressure sensitive" and because the smaller size of the float enabled us to reduce from 60 to 15 cc. the volume of water actually used in the density measurement. In Fig. 2 we illustrate the velocity of the quartz swimmer as a function of depth of immersion; naturally a pressure correction had to be applied for each measurement, not only for

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(4) W. R. Smythe, *Phys. Rev.*, **45**, 299 (1934).

(5) H. C. Urey and Lotti J. Greiff, THIS JOURNAL, **57**, 321 (1935).

(6) L. A. Weber, M. H. Wahl and H. C. Urey, *J. Chem. Phys.*, **3**, 129 (1935).

(7) M. Dole, THIS JOURNAL, **57**, 2731 (1935); *J. Phys. Chem.*, **4**, 268, 778 (1936). For a recent accurate measurement of this effect see J. A. Swartout and M. Dole, THIS JOURNAL, **61**, 2025 (1939). Morita and Titani, *Bull. Chem. Soc. Japan*, **11**, 403 (1936), independently discovered the same effect and it has been confirmed by C. H. Greene and R. J. Voskuyl, THIS JOURNAL, **58**, 693 (1936); W. H. Hall and H. L. Johnston, *ibid.*, **58**, 1920 (1936); T. O. Jones and N. F. Hall, *ibid.*, **59**, 259 (1937); E. R. Smith and H. Matheson, *J. Research Natl. Bur. Standards*, **17**, 625 (1936).

(8) N. Morita, K. Goto and T. Titani, *Bull. Chem. Soc. Japan*, **11**, 695 (1936); *ibid.*, **13**, 99 (1938).

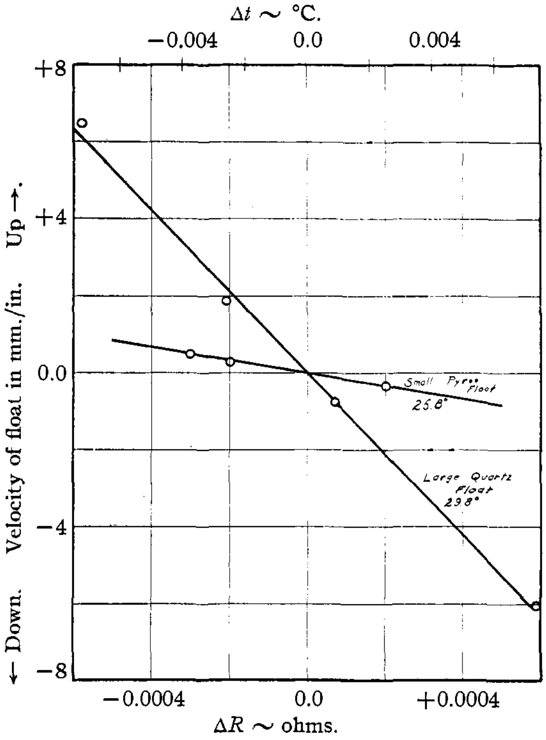

Fig. 1.

the weight of water above the float, but also because of variations in barometric pressure from day to day. In all the calculations of density obtained from the velocity readings on the Pyrex swimmer, the expansion of the latter with rise of temperature was corrected for by taking 9.6 × 10^{-6} as the volume coefficient of expansion of Pyrex. The density of a large sample (300 cc.) of standard water

TABLE I

TEMPERATURE OF FLOATING EQUILIBRIUM OF PYREX FLOAT

Date	Temp., °C. (variation from mean)	Δγ	Barometric pressure, mm.
11/15/38	+0.0001	+0.03	752.2
11/16/38	− .0008	− .19	736.2
11/17/38	− .0005	− .13	739.4
11/21/38	+ .0006	+ .16	745.7
11/22/38	+ .0003	+ .06	756.9
11/23/38	+ .0008	+ .19	757.2
11/29/38	− .0003	− .06	745.0
12/ 1/38	+ .0006	+ .16	...
12/ 2/38	0	0	745.9
12/ 3/38	− .0006	− .16	740.0
12/ 6/38	− .0014	− .35	740.0
12/ 9/38	− .0003	− .06	739.0
1/16/39	+ .0011	+ .28	752.3
1/17/39	− .0009	− .22	746.5
1/18/39	− .0019	− .47	741.8
1/19/39	+ .0001	+ .03	745.5
1/23/39	− .0009	− .22	745.9
2/ 6/39	+ .0009	+ .22	737.7
2/ 7/39	+ .0011	+ .28	748.8

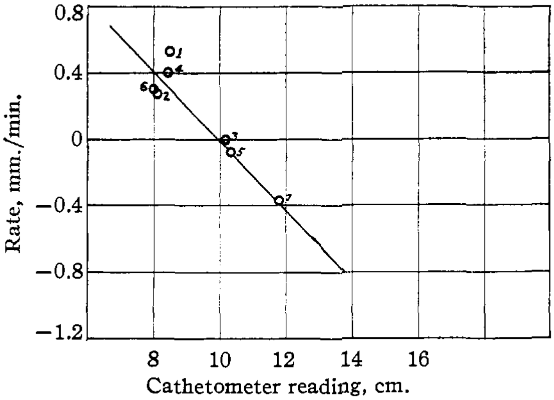

Fig. 2.—Velocity of float as function of position in water.

was compared with that of a 300-cc. sample of a light water, using both the Pyrex and quartz floats. All samples of water, both the standard and the light water, were purified and distilled in exactly the same way. With the Pyrex float the light water gave a γ-value of −12.9 while −12.8 γ was obtained with the quartz float; thus, despite the different floats, temperatures and correction factors employed in the two comparisons, the results were identical within the experimental error of 0.1 γ.

Most of the density measurements using the Pyrex float were made during a three-month interval; the data of Table I indicate that no significant change in the temperature of floating equilibrium of the Pyrex swimmer in the standard water occurred during this period (the samples of standard water were taken from the same large stock of laboratory distilled water). Furthermore, no pressure dependence of the floating temperature is indicated and in the nineteen measurements recorded, only four give results deviating from the mean by more than 0.22 γ. The average fluctuation is 0.17 γ. Apparently the small 1 cc. cylindrical Pyrex swimmer is a satisfactory float.

Occasionally it was found necessary to clean the Pyrex float with a warm solution of mixed concentrated nitric and sulfuric acids.

The wooden box containing the Mueller bridge of the platinum resistance thermometer was housed in a larger wooden air constant temperature bath, lined with two layers of $^3/_4$-inch (2-cm.) celotex, whose temperature was maintained constant at 30° to a few hundredths of a degree. The platinum thermometer of 20 ohms resistance (at 0°) could not be immersed directly into the water under investigation because the electric current flowing through the thermometer during a measurement caused too great a heating effect in the small sample of test water, although a two-volt rather than a six-volt battery was used as the source of bridge current. The platinum thermometer was therefore placed in the inner bath of the constant temperature water-bath whose outer bath temperature was controlled by the usual mercury–toluene thermostat, relay, heating and cooling coils arrangement. The temperature of the outer water-bath which fluctuated about ±0.002° was varied at will by a screw mechanism on the contact wire of the thermostat; the temperature of the inner bath through which water slowly circulated from the outer bath varied about ±0.0002° while the temperature of the test water remained even more constant. The constancy of the temperature of the inner bath can be judged from the data plotted in Fig. 2 (the number by each circle indicates the order in which the observations were made) where the maximum variation from the straight line corresponds to a fluctuation in temperature of 0.0001° (except for the first measurement, which was probably taken before temperature equilibrium was reached).

The velocity of the float was observed and measured with a travelling telescope, millimeter scale and stop watch. By taking measurements both on the slightly hotter and slightly colder sides of the temperature of floating equilibrium, the latter could be interpolated quite accurately from a plot of the observed velocities and temperatures such as illustrated in Fig. 1. We believe that the actual density measurements were obtained with an error less than $\pm 0.1\ \gamma$, and that our chief sources of error were contained in the chemical reactions used in liberating the oxygen from the rocks and in the process of purifying and distilling the impure condensates from the reduction experiments.

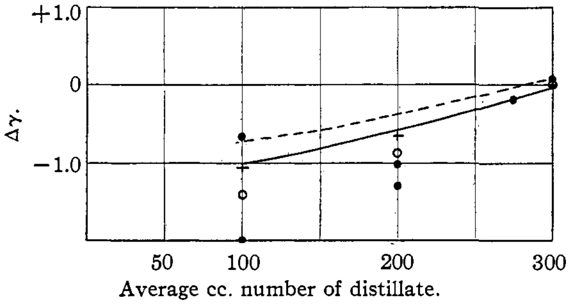

Fig. 3.—Change in water density on distillation: ○, standard water; +, sample (C) of D-free water; ●, sample (B) of D-free water.

Purification and Distillation of Water Samples.—The more accurate density measuring apparatus required much more careful preliminary treatment of the water than that used in our previous investigations. As Greene and Voskuyl[9] have recently stated, "It should be remembered that a number of successive distillations are usually made in the purification of samples of water so that although the change in density caused by a single distillation is small, the total change occasioned by the purification may be significant. The fact that this change in the case of deuterium-free water is different from and less than the change with ordinary water must also be taken account of in determinations of the deuterium-protium ratio by the method of densities." We adopted the following procedure in the treatment of the 300-cc. samples in the first case (when using the large quartz swimmer) and the 40 cc. samples in the second case. The 300-cc. samples of water were placed in a 500-cc. Pyrex distilling flask, and completely distilled from alkaline permanganate through a two foot (61-cm.) 30 mm. Pyrex tube packed with copper oxide and heated to 550°. All the water was distilled in this purification step to avoid any isotopic fractionation; the copper oxide column effectively prevented any permanganate solution spray from contaminating the condensate. The sample was then distilled from acid permanganate in a flask fitted with a bulb spray trap through a block tin condenser. The middle 100-cc. fraction was used in the density determination. To check the density measurements, the entire sample, including the 100 cc. rejected initial and end fractions, was redistilled as before. By recombining the various distillation fractions, the accumulation of errors due to repeated isotopic fractionation was prevented. The treatment of the 49-cc. sample was similar except that the bulb spray trap was steam-jacketed to prevent additional fractionation in the column, and the various glass connections and the glass to block-tin joints were made tighter since it was found that no water could be lost during the distillations without isotopic fractionation errors entering in. The sample taken for analysis consisted of the eleventh to the twenty-fifth cc. of the forty cc. sample, and the distillation rate was adjusted to a speed of one cc. per minute. The 15 cc. middle fraction was out-gassed with a water pump for one minute at 35° with continuous shaking, and allowed to stand in the constant temperature bath for half an hour before making the float velocity observations.

The standard Lake Michigan water taken from the large stock of laboratory distilled water was purified and distilled in exactly the same way as the test samples. We discuss below the question of the density differences between our standard water and the water used by other investigators.

Several experiments were performed to test the isotopic fractionation of the water in our distilling apparatus. For this purpose large (450-cc.) samples were used, the first 50 cc. of water to be distilled was rejected, the next three 100-cc. portions were separately collected and their densities measured. The 500-cc. distilling flask was equipped with a steam-jacketed spray trap and the water condensed in a block-tin condenser. Sample A (represented by the open circles in Fig. 3) was the standard water, Sample B (closed circles of Fig. 3) was nearly deuterium-free water whose oxygen was air oxygen, and Sample C was water that resulted from two electrolytic fractionations to remove the deuterium, γ-value equal to -16 (represented by crosses in Fig. 3). Changes in density only are plotted in Fig. 3, the curves being adjusted vertically to coincide at the density of the third 100-cc. portion whose density, theoretically, should be nearly identical with that of the water before distillation. The dotted line in Fig. 3 represents the changes in density to be expected on the basis of one theoretical plate in the case of D-free water and the solid line, the density changes for normal water. These calculations were made using the Rayleigh distillation formula and the fractionation factors adopted by Greene and Voskuyl.[9] The observed changes are within a few tenths of a part per million of the theoretical; in one case the distillation of D-free water produced smaller changes in density than the normal water, as expected, but in the case of Sample B the density changes were larger and fluctuated more. Evidently this last distillation was not carried out in the same manner as the other two; perhaps the water was actually impure so that the γ-values of Fig. 3 represent a change in the purity of the water. In the dis-

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[9] C. H. Greene and R. J. Voskuyl, THIS JOURNAL, **61**, 1342 (1939).

tillations of the 40-cc. samples we calculate that the 15-cc. distillate was 0.58 γ lighter than normal in the case of the standard water and 0.41 γ lighter than the original sample in the case of D-free water. The difference between the changes in the two distillations, 0.17 γ, is negligible in view of the experiments to be described. We conclude that an uncertainty of about ±0.2 γ results from isotopic fractionations on distillation in our experiments.

Reduction of the Carbonate Ores.—Most of the carbonate ore experiments were performed on Grenville marble from the Gouverneur Marble Quarry, Gouverneur, N. Y. The Grenville formation is one of the oldest geologic deposits, with a reputed age of 1.2 billion years. Niagara dolomite and Pennsylvania limestone of the La Salle formation, about 0.5 billion year old, and clam shells of recent origin also were investigated. All of these carbonate samples were supposed to be laid down from large bodies of water (oceans); we did not investigate any carbonate rocks precipitated from fresh water. Some synthetic barium carbonate made in the following way was also studied. Five liters of water whose oxygen came from the air were prepared and in this water anhydrous barium chloride was dissolved. Carbon dioxide also containing atmospheric oxygen was obtained by burning charcoal in dry, carbon dioxide-free air. After passing the gases from the charcoal combustion over hot copper oxide and calcium chloride, they were then mixed with ammonia and passed into the barium chloride solution contained in several absorption vessels connected together in series. Barium carbonate was precipitated, the nitrogen and some of the ammonia sweeping out through the absorption system. When the last absorption bottle showed traces of the carbonate, the process was stopped, the barium carbonate filtered off, and the filtrate returned to the absorption bottles. The barium carbonate was dried at 160°, the water vapor being condensed and added to the filtrate. In this way barium carbonate was prepared containing oxygen of known isotopic composition provided no fractionation of the oxygen isotopes occurred in the precipitation. We discuss this point below.

The natural carbonate rocks were broken up in a rock crusher to pebble size and treated in two different ways to eliminate the oxygen. The easiest method to accomplish this consists in the treatment of the rock with hydrochloric acid, followed by reduction of the carbon dioxide evolved with hydrogen over a nickel catalyst to methane and water. A large quantity of the rock was placed in a tall Pyrex tube and 6 *N* hydrochloric acid dropped on the rock at a constant rate using a constant head device. The apparatus was so arranged that the spent acid and calcium chloride solution could automatically siphon off. After the evolved carbon dioxide had been passed through a glass wool spray and dust trap and through a drying chamber, it entered the electrically heated catalyst chamber along with practically D-free hydrogen with the hydrogen–carbon dioxide volume ratio slightly in excess of four to one. The catalyst was pumice supported nickel heated to 280–300°. The water resulting from the reduction was condensed in a water condenser and the last traces frozen out in a dry ice–acetone trap. The yield was about 90% of the theoretical, assuming the rock to be pure calcium carbonate.

Since the exact isotopic composition of the hydrogen was not known, although it was nearly D-free, the methane resulting from the reduction was burned with air over hot copper and the density of the resulting water determined.

From isotopic fractionation considerations this method of winning the oxygen is not entirely satisfactory since the acid treatment leaves one third of the carbonate oxygen in the calcium chloride solution, thereby giving rise to the possibility of isotopic fractionation. To measure the extent of this uncertainty several samples of Grenville marble were pyrolyzed in iron tubes at high temperatures (from 800–1000°), the thermally evolved carbon dioxide stored over glycerol in 50-liter acid bottles, and later reduced to water and methane as in the acid treatment. The efficiency of the thermal decomposition method was about 80%.

All the data collected in the carbonate rock research are presented in Tables II and III.

TABLE II

DENSITY DATA OBTAINED IN PRELIMINARY EXPERIMENTS

No. of sample	Description of water	γ
1	Lake Michigan water	+0.35
2	Lake Michigan water	+ .32
3	Lake Michigan water	+ .44
4	Tank No. 1 CO_2 in large excess reduced with tank H_2	−4.92 −4.73
5	Tank no. 1 CO_2 reduced with tank H_2 in stoichiometric proportion	−3.77 −3.61
6	Water from combustion in air of CH_4 from expt. 5	−4.98 −5.30
7	Tank H_2 combined with air O_2	−6.39 −6.26
8	Tank no. 2 CO_2 reduced with excess D-free H_2	−8.59 −8.69
9	Water from combustion in air of CH_4 from expt. 8	−8.56 −8.69
10	Water from combustion in air of D-free H_2 similar to that used in expt. 8	−8.69 −8.65

Discussion

We must first consider the density of the standard water we have chosen as a reference in relation to purified Lake Michigan water, and in relation to standard waters selected by other investigators. In this research we made one density measurement on three samples of purified Lake Michigan water with the results given in Table II, 1, 2, and 3. The average of these data, 0.37 γ, indicates that the laboratory distilled water is slightly lighter than the purified lake water, but in another research more recently performed,[10] Mr. J. A. Swartout could detect no difference between the two waters greater than ±0.1 γ. In Mr. Swartout's research more than one density measurement was made on each sample, so that

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[10] J. A. Swartout and M. Dole, THIS JOURNAL, **61**, 2025 (1939).

TABLE III

DENSITY DATA OBTAINED IN CARBONATE EXPERIMENTS

Expt.	Description of water	γ	Av. γ	γ from CH_4 combustion	Correction to bring H_2 to normal	γ due to O_2 alone
11	Acid treatment of Niagara dolomite	−5.65 −6.11	−5.9	.....	+15.0	9.1
12	Acid treatment of Pennsylvania limestone	−5.2	−5.2	− 9.3	+15.0	9.8
13	Acid treatment of clam shells	−5.08 −4.92	−5.0	− 8.81 − 9.01	+15.2	10.2
14	Acid treatment of clam shells cleaned in boiling NaOH solution	−5.14	−5.1	− 7.9	+15.0	9.9
15	Acid treatment of Grenville marble	−5.65 −6.11	−5.9	− 9.92 − 9.62	+15.0	9.1
16	Acid treatment of Grenville marble	−5.91 −5.75	−5.8	− 8.46 − 8.60	+15.1	9.3
17	Special acid treatment of Grenville marble	−5.38 −5.12	−5.3	−10.11 −10.05	+15.2	9.9
18	Grenville marble pyrolyzed at 1000°	−7.34 −7.25	−7.3	− 8.90 − 7.98	+15.0	7.7
19	Grenville marble pyrolyzed at 1000°	−6.55 −6.67	−6.6	− 7.76	+14.6	8.0
20	Grenville marble pyrolyzed at 1000°	−5.59 −5.84	−5.7		+15.0	9.3
21	Grenville marble pyrolyzed at 1000° (diluted)	−3.61 −3.29	−3.45 (−6.9)	− 8.11 − 8.11	+15.1	7.8
22	Grenville marble pyrolyzed at 800° (diluted)	−4.06 −4.22	−4.1 (−5.6)		+15.0	9.4
23	Grenville marble pyrolyzed at 800°	−6.61 −6.64	−6.6		+14.6	8.0
24	Acid treatment of synthetic barium carbonate	−6.39 −6.83	−6.6	− 7.95 − 8.49	+14.9	8.3
25	Acid treatment of synthetic barium carbonate	−6.04 −5.75	−5.9	− 8.14 − 7.82	+14.6	8.7
26	Acid treatment of special barium carbonate	−9.6	−9.6	− 8.59 − 8.53	+15.2	5.6

we consider his results more reliable. In any case the difference is so slight that we shall consider it negligible.

It is more difficult to demonstrate the relation between our standard and standards used in other researches. Greene and Voskuyl[9] found that Cambridge, Massachusetts, tap water is 0.61 γ lighter than Lake Michigan water, Hall and Jones[11] found that Lake Mendota (Madison, Wisconsin) water is 0.3 γ lighter than Lake Michigan water, but Greene and Voskuyl found Lake Mendota water to be +0.16 γ heavier than Lake Michigan water. Greene and Voskuyl found the density of purified ocean water taken one mile off shore at Gloucester, Mass., to be 1.8 γ greater than their standard while we found[10] water taken 45 miles off shore at Gloucester to be 1.7 γ heavier than our standard. If we correct this measurement to the Greene and Voskuyl standard, we obtain +2.3 γ for the density of ocean water which agrees with the value found by Greene and Voskuyl for ocean water taken about 200 miles East of Cape Race, Newfoundland (Lat. 45° 13′ N.; Long. 49° W.). Incidentally this last water could hardly be considered as coming from the "Mid-Atlantic" and must consist very largely of arctic current water. From this point of view there seems little reason to believe that water from 45 miles off Gloucester should be different from Greene and Voskuyl's "Mid-Atlantic" water; hence we conclude that we should apply the correction of −0.6 γ to bring our standard water into coincidence with Greene and Voskuyl's standard. However, in an earlier publication Greene and Voskuyl[7] give +6.0 γ as the density of water containing normal hydrogen and atmospheric oxygen whereas our new result recently published[10] would be +7.0 γ instead of 6.6 γ if to the latter we applied a correction of 0.4 (two-thirds of 0.6 γ, which would be the contribution due to oxygen isotopic fractionation). Because

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(11) N. F. Hall and T. O. Jones, THIS JOURNAL, 58, 1915 (1936).

of these conflicting lines of evidence we shall leave unsettled for the time being the exact difference between Cambridge, Mass., tap water and Lake Michigan water.

The difference in γ-values for water samples 4 and 5 of Table II indicates that the carbon dioxide should be reduced with hydrogen in excess while the data for samples 6 and 7 indicate that D-free hydrogen should be used in the catalytic reduction. Experiments 8, 9, and 10 prove clearly that the use of D-free hydrogen is justified and that the method of hydrogen analysis by combustion of the unused hydrogen and methane produced in the catalytic reduction is sound.

In Table III are collected all the density data obtained in the carbonate experiments. For some inexplicable reason the first density measurements of the water from the methane combustions gave too low results since water made from air and containing no deuterium has for its minimum density, $-8.9\ \gamma$; yet in some of the experiments listed in Table III we found $-9.9\ \gamma$ and $-10.1\ \gamma$. Toward the end of this research, the reduction of the carbon dioxide from the acid treatment of the Grenville marble was repeated and the density of the water formed in the reduction and in the methane combustion carefully redetermined with the results given under experiment no. 16 of Table III. The density of the water obtained from the reduction of the carbon dioxide agreed well with that obtained in the first experiment, no. 15 of Table III, thus indicating that the early results on the water from the carbon dioxide reduction were correct, but the density of the water from the methane combustion was different from the earlier figure, yet entirely reasonable and close to the expected value. For this reason we have disregarded the early data on the densities of the water from the methane combustion and estimated the correction to be applied to bring the hydrogen of the water to normal from the later more accurate results. If the hydrogen were completely D-free, the correction would be $-15.5\ \gamma$[10]; all the corrections used in Table III are within one part per million of this figure.

The last column of Table III contains the values of the excess density over normal water of the water containing the oxygen under consideration and normal hydrogen. First of all it is interesting to note from experiments 11 through 16 that no significant difference (*i. e.*, any difference greater than 1 part per million) exists between the isotopic composition of the oxygen in the oldest rocks (Grenville marble) and the youngest (clam shells). We can make the tentative conclusion, therefore, that there has been no change in the isotopic composition of the oxygen in the oceans (from which these rocks were precipitated) over a period greater than a billion years. We must assume in making this last statement that the oxygen at present in the rocks is identically the same oxygen that was originally in the rocks when they were first laid down. Nier and Gulbransen[12] have recently similarly demonstrated in a mass-spectrographic study of the carbon isotopes in Grenville carbonates and clam shells that no apparent change in this ratio has occurred during a period of 1.2 billion years.

From Table III it is evident that a slight difference exists between the data obtained in the acid treatment of the rocks and in the thermal decomposition. The average value of γ for the acid treatment on the Grenville marble (omitting no. 17) is $9.2\ \gamma$ whereas the thermal decomposition of the Grenville marble gave $7.9\ \gamma$ as the average difference in density omitting the data obtained in experiments 20 and 22 in which some of the carbon dioxide liberated was lost. In experiment 17 the Grenville marble was decomposed with hydrochloric acid made by dissolving anhydrous hydrogen chloride in water made from the oxygen of the air. This experiment was performed to see whether the isotopic composition of the oxygen in the water of the acid solution influenced in any way the isotopic ratio of the oxygen in the liberated carbon dioxide, but as the results indicated very little effect was noted; increase in the density of the water due to the oxygen by $6.6\ \gamma$, changed the final results for experiment 17 by only $0.7\ \gamma$. The reason for the absence of any pronounced effect here is the rapidity with which the carbon dioxide is evolved, insufficient time being allowed for equilibrium with water to be attained. Since no measurable fractionation of the oxygen isotopes at the high temperatures of the thermal decomposition is to be expected, we can accept the thermal decomposition result, $7.9\ \gamma$, as giving the true oxygen isotope ratio, 1.034/500, in the carbonate rocks.

The difference between 9.2 and 7.9, or $1.3\ \gamma$, must be explained by the isotopic fractionation which takes place when the carbonate is decomposed by the acid. Whether fractionation also

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(12) A. O. Nier and E. A. Gulbransen, THIS JOURNAL, **61**, 697 (1939).

occurs at the time of the precipitation of the carbonate was tested by studying the synthetic barium carbonate made in two ways. In experiments 24 and 25, the carbonate was precipitated by adding carbon dioxide made from oxygen of the air to water made from oxygen of the air. If, on liberation of the carbon dioxide, no isotopic fractionation had taken place at any step in the process, the γ-value of the water obtained by the carbon dioxide reduction should be equal to 6.6, but the value 8.5 was found, Table III. This difference, 1.9 γ, is slightly greater than the value 1.3 γ mentioned above, but it is sufficiently close to it to conclude that a greater fractionation of the oxygen isotopes occurs when the carbonate ion decomposes than when it forms. Some barium carbonate was also prepared by adding carbon dioxide containing oxygen of the air to normal water. In this case one would expect the density of the water resulting in experiment 26 to be $^1/_3$ (6.6 + 6.6 + 0), or 4.4 γ. Actually 5.6 γ was found, or 1.2 γ greater than expected. This also agrees well with the difference, 1.3 γ, found between the results of the acid and thermal treatments of the carbonate.

Having reached the conclusion that the oxygen isotope fractionation probably occurs mainly when the carbonate is decomposed rather than when it is precipitated, it is possible and of interest to suggest a mechanism to explain the excess value of the atomic weight of oxygen in the rocks. When carbon dioxide is brought into equilibrium with water, the heavier isotopes of oxygen concentrate in the carbon dioxide phase, the fractionation factor for the O^{18} isotope being 1.047 at 0° and 1.039 at 25° as Urey and Greiff have calculated.[5] When this carbon dioxide dissolves in ocean water whose oxygen is 1.2 γ heavier than Lake Michigan water, the calcium carbonate precipitated should contain oxygen whose γ-value (when converted to water) is the average of the oxygen in the water and in the carbon dioxide. Thus at 0° we have for the carbon dioxide a γ-value equal to 11.5 and for the water, 1.2 γ, the average being $^1/_3$ {2(11.5) + 1.2} or 8.2 γ. At 25° a similar calculation yields 7.0 γ as the theoretical value for the oxygen in the carbonate rocks. Unfortunately no measurements have been made of the γ-value of the oxygen in atmospheric carbon dioxide and we do not know the average temperature to use in calculating the fractionation factor; however, our experimental result, 7.9 γ, is slightly less than that calculated for 0°, and thus agrees with the theory reasonably well.

Part II. Iron Oxide Ores

Experimental

Composition of the Ores.—The iron ores studied were classified geologically as follows: first, a sample from the Soudan mines in the Vermillion range representing an ore of the Keewatin period, 1.5 billion years old; second, a Middle Huronian iron ore from the Mesabe range (Biwabik iron formation), 1.0 billion years old; third, a Silurian iron ore of the oölitic type from Clinton, N. Y., 375 million years old; and fourth, another Silurian ore of the same age, also from Clinton, containing small fossils. Since the data obtained in the case of the last two ores made us suspect that they might contain carbonates whose oxygen would probably be quite different in isotopic composition from the oxygen of the iron oxide, the ores were analyzed with the results given in Table IV.

TABLE IV

COMPOSITION OF SILURIAN IRON OXIDE ORES IN PER CENT.

	H_2O	Fe	Ca	CO_2	Residue unreactive to acid
Oölitic	1.4	34.2	7.29	8.1	16.2
Fossil	1.2	23.9	13.25	28.7	7.0

The Keewatin ore contained no detectable water, but 450 g. of the Middle Huronian ore evolved 20 cc. of water (4.4%) on being heated to red heat in a slow stream of nitrogen. No detectable carbonate was present in either the Keewatin or Middle Huronian ore.

Reduction of the Ores.—All the ores were reduced in Pyrex tubes heated to 600° in an electric furnace; the hydrogen used was practically deuterium-free, and the water formed was first condensed in a water condenser and then the last traces frozen out in a dry-ice-acetone trap. The reduction usually lasted from thirty to sixty hours.

Purification of Samples and Density Measurements.—In all of the iron ore experiments the water distillation and density measurement technique was exactly the same as that described in Part I of this paper. The data are collected in Table V where the last column gives the final corrected γ-value for the oxygen in the ores.

Discussion

From experiments 1, 2, and 3 it is evident that the oxygen in the iron oxide of the Keewatin and Middle Huronian ores has the same isotopic composition as the oxygen in water, within the experimental uncertainties, but the data are not accurate or conclusive enough for us to state whether the oxygen corresponds to the oxygen of ocean water or to that of fresh (rain) water. Probably the former is the case since the average of the three reductions is +0.9 γ, fairly close to +1.2 γ, which is the value for the oxygen in ocean water. In expt. 3, 83.5% of the ore was reduced,

TABLE V

DATA OBTAINED IN THE ISOTOPIC ANALYSIS OF IRON ORES

Expt.	Type of ore	Ore, g.	Water obtained, cc.	Density of water		Correction for hydrogen	Density of water due to oxygen
1	Keewatin	400	51	−13.80	−13.67	+14.9	+1.2
2	Middle Huronian	450	61	−13.57	−13.57	+15.2	+1.6
3	Middle Huronian	310	87.5	−14.7	−14.7	+14.6	−0.1
4	Silurian (oölitic)	350	46	−11.62	−11.43	+15.0	+3.5
5	Silurian (fossil)	345	41	−10.06	−10.06	+14.6	+4.5

assuming it to be pure hematite, so that one might be inclined to give greater weight to the result for this experiment, yet we can think of no reason why a partial reduction of the ore at red heat should favor one or the other of the isotopes. We can conclude definitely, however, that the Keewatin and Middle Huronian ores contain very little, if any, oxygen which was in the atmosphere before being bound to the iron. The conclusion of the geologists that these ores were formed by precipitation from water seems to be completely substantiated.

The presence of the carbonates in the Silurian ore may have been responsible for the greater density of the water obtained on reduction of these ores by virtue of either of the following sets of reactions

$$\begin{aligned} CaCO_2 &\xrightarrow[\text{heat}]{} CaO + CO_2 \\ CO_2 + 2H_2 &\longrightarrow 2H_2O + CH_4 \end{aligned} \tag{4}$$

$$\begin{aligned} FeCO_3 &\xrightarrow[\text{heat}]{} FeO + CO_2 \\ FeO + H_2 &\longrightarrow Fe + H_2O \end{aligned} \tag{5}$$

since the oxygen in the carbonate ores is heavier than normal. Of reactions (4) and (5) the latter seems the more probable as ferrous oxide would be reduced more readily than carbon dioxide, yet we estimate that some carbon dioxide must have been reduced to give a total of 41 cc. of water which is more than complete reduction of all the iron oxides present would yield. We conclude that enough water was formed from the oxygen of carbonates in both the fossil type and oölitic type experiments to account for the small excess in observed density.

Acknowledgments

We are greatly indebted to the Alexander Dallas Bache Fund of the National Academy of Sciences for a grant with which the platinum resistance thermometer and accessory equipment was purchased, as well as to Northwestern University for a grant from its research fund. We wish to thank Mr. J. S. Brown of the St. Joseph Lead Company for going to the trouble and expense in providing us with several large sections of Grenville marble, and particularly do we wish to thank Professor C. H. Behre, Jr., and other members of the Department of Geology and Geography at Northwestern for aid in procuring geologic samples and for many helpful suggestions.

Summary

1. Improvements in density measuring apparatus have been developed and applied to the isotopic analysis of oxygen in carbonate rocks and iron oxide ores.

2. A study of Grenville marble, Niagara dolomite and Pennsylvania limestone and clam shells, all carbonates of widely different geologic age, reveals no significant difference in the isotopic composition of the oxygen in the rocks as a function of age.

3. The oxygen of the Grenville marble when liberated as carbon dioxide with acid and reduced with hydrogen gives water 9.2 p. p. m. heavier than normal, but when the carbon dioxide is driven out of the rock thermally, the resulting water is only 7.9 p. p. m. heavier. The difference in these two data is attributed to the isotopic fractionation which takes place when the carbonate ion is decomposed by acid.

4. The observed value of 7.9 p. p. m. can be explained quantitatively with the aid of the isotopic exchange equilibrium theory of Urey and Greiff.

5. The oxygen in iron ores of the Keewatin and Middle Huronian ages does not differ significantly in its isotopic composition from that of oxygen in normal water, the slight excess density observed in the experiments on the oölitic and fossil type Silurian ores is probably due to the presence of carbonates in the ores.

EVANSTON, ILL. RECEIVED OCTOBER 30, 1939