and certain of the larger values in the more highly acid solutions the lead sulfate value is considered accurate to at least 2%. For intermediate acid values the accuracy is 0.2 part per million.

It is not thought worth while to give the data on the solid phases. These data, when plotted on large triangular coördinate paper, show beyond doubt that in the solutions studied the solid phase is always the normal lead sulfate.

Our values for the solubility in pure water fall on the accepted straight line as far as the three lower concentrations are concerned. However, our value at 50° is less than that given by Mellor.[2] It is to be noted that Mellor secured this value by extrapolation. It is quite probable that hydrolysis affects the solubility at the higher temperatures. In general our data appear to fit in well with those of other investigators.

Summary

1. The solubility of lead sulfate has been determined in pure water and in sulfuric acid solutions up to 80% acid at 0, 25, 35 and 50°.
2. The solubility falls off rapidly with the addition of minute amounts of sulfuric acid. It increases again when the acid reaches a value around 70%.
3. The solid phase in equilibrium with all solutions studied was the normal lead sulfate

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF COLUMBIA UNIVERSITY, NEW YORK CITY, AND THE PALMER PHYSICAL LABORATORY, PRINCETON UNIVERSITY, PRINCETON, NEW JERSEY]

An Investigation of the Relative Abundance of the Oxygen Isotopes O^{16}:O^{18} in Stone Meteorites

BY SAMUEL H. MANIAN, HAROLD C. UREY AND WALKER BLEAKNEY

Introduction

Although terrestrial and meteoric matter have been examined quite extensively for any variations in the abundance of isotopic elements, no work on the oxygen isotopes from meteoric sources has been published. Bradley and Urey[1] give a comprehensive list of references to the literature on this general problem to the end of 1931, while Briscoe and co-workers[2] give a critical survey of the field to 1925. Of the researches published since 1930, the following on terrestrial oxygen are of immediate interest in this investigation: Naudé,[3] Babcock and Birge,[4] Mecke and Childs,[5] Smythe and Mattausch,[6] Aston,[7] Kallmann and Lasareff,[8] and Smythe,[9] also the papers on carbon isotopes by Tate, Smith and Vaughan[10] and Jenkins and Ornstein.[11] The general conclusion from the literature to date is that there is no variation in the relative abundance of the isotopes of an element in terrestrial or meteoric matter.

It is the purpose of this investigation to examine the abundance of oxygen isotopes in those stony meteorites which are said to arise in interstellar space, as deduced from their high heliocentric velocity. The source of information about the origin of meteorites at present is catalog 611, "Orbits of Great Meteors," by G. von Niessl and C. Hoffmeister.[12] Among these great meteors are the following meteorite fireballs, with the date of fall and their heliocentric velocities in km./sec.: 41, Pultusk, 1868, 56; 45, Mocs, 1882, ?; 55, Homestead, 1875, 40; 93, Burbely, 1899, ?; 147, Forest City, 1890, ?; 148, Krähenburg, 1869, 57; 155, Orgueil, 1864, 52; 166, Heschina, 1751, ?; 189, Knyahinya, 1866, ?; 506, Rochester, 1876, 44; 531, Treysa, 1916, 38; 554, Hunsrück, 1920, ?; 556, St. Michel, 1910, 60. The question marks refer to uncertain velocities which, however, are probably high.

The limiting circumsolar velocity, or parabolic velocity, is 42 km./sec. Numbers 41, 148, 155, 506 and 556 are credited with velocities greater

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(1) C. A. Bradley and H. C. Urey, *Phys. Rev.*, **40**, 889 (1932).

(2) H. V. A. Briscoe and P. L. Robinson, *J. Chem. Soc.*, **127**, 696 (1925).

(3) S. Meiring Naudé, *Phys. Rev.*, **36**, 333 (1930).

(4) H. D. Babcock and R. T. Birge, *ibid.*, **36**, 233 (1930).

(5) R. Mecke and W. H. J. Childs, *Z. Physik*, **68**, 362 (1931).

(6) W. R. Smythe and J. Mattausch, *Phys. Rev.*, **40**, 429 (1932).

(7) F. W. Aston, *Nature*, **130**, 21 (1932).

(8) H. Kallmann and W. Lasareff, *Z. Physik*, **80**, 237 (1933).

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

(10) Tate, Smith and Vaughan, *ibid.*, **43**, 1054 (1933).

(11) F. A. Jenkins and L. S. Ornstein, *Kon. Acad. Wetensch. Pro.*, **35**, 1212 (1933).

(12) G. von Niessl and C. Hoffmeister, *Wiener Denkschriften*, Vol. 100 (1925).

than this and so are presumably interstellar. Pultusk, No. 41, is undoubtedly the most reliable of all, while St. Michel, with the highest observed velocity, is probably very inaccurate (observation depends on one estimate of time of three seconds made in daylight).

Fisher[13] concludes "that the proportion of hyperbolic meteors in the von Niessl–Hoffmeister catalog is excessive and that there is a cause acting to give an over-estimate of geocentric velocities."

Although there seems to be considerable doubt regarding the reality of hyperbolic velocities, Öpik[14] has recently published some preliminary results on the velocity measurements on meteors [preliminary report by H. Shapley, E. J. Öpik and S. L. Boothroyd, *Proc. Nat. Acad. Sci.*, **18**, 71 (1932)], and finds that ten to thirty per cent. of visible meteors are hyperbolic, and that among the big meteorites, the fraction of hyperbolic objects may be expected to be of the same order of magnitude. Öpik's observations strengthen the probability of the interstellar origin of many meteorites as found by other astronomers, including the list given by von Niessl and Hoffmeister.

Our selection of the high-velocity stone meteorites has been confined to the list given above, as being the best available list to choose from. The first three meteorites selected for analysis were: 41, Pultusk; 155, Orgueil; and 556, St. Michel. Along with this set we ran a control on a terrestrial silicate rock, to which we refer as rock No. 8. In later work, we selected three more meteorites: 45, Mocs; 55, Homestead; and 189, Knyahinya. Along with this second set we ran a control on another terrestrial silicate rock, referred to as rock No. 18.[15]

Our purpose in selecting the stony meteorites for investigation in preference to the iron ones was that the former would much less likely have been contaminated by atmospheric oxygen than the iron ones, and we wished to have the total combined meteoric oxygen as representative of the source of its origin as possible. Our assumption is that these stony meteorites, during their five to ten seconds' (maximum) passage in the earth's atmosphere, have not reacted chemically, to any appreciable extent, with terrestrial oxygen, and that the total combined oxygen is representative of the oxygen at the origin of the meteorite. Crust formation and rust spots, by visual examination of our samples, show that the surfaces already have reacted with atmosphere oxygen. Hence in our work we did not use the surface crust formations.

Experimental

The first problem was to convert all of the combined oxygen of the stone meteorites over to some form which can be measured for the abundance ratio of $O^{16}:O^{18}$. Our first selection was carbon monoxide because this constituted a convenient product which could be measured by the mass spectrograph or could be converted successively to water and then to oxygen, each of which could be measured by the mass spectrograph while the water could be investigated by means of its specific gravity. After three of our meteoric samples had been worked upon and their oxygen obtained as carbon monoxide by the method described as I, the remaining three samples were subjected to another method, described as II, and their oxygen obtained as water.

Method I

Decomposition of Samples by Carbon Tetrachloride at 1000° under Reduced Pressures.—Demarçay,[16a] Quantin,[16b] Camboulives[16c] and prior workers have obtained decomposition of most metal oxides and some minerals by chlorinating with carbon tetrachloride vapor, yielding carbon monoxide, phosgene and metal chlorides. The temperatures necessary ranged between 215–580°. In the case of SiO_2[17] and silicates, however, higher temperatures (800–1000°) must be used for any appreciable amount of decomposition. In order to obviate the loss of oxygen in the form of phosgene advantage was taken of the fact that phosgene is completely decomposed into carbon monoxide and chlorine at 800° as shown by Bodenstein and Dunant[18] and Atkinson[19] and co-workers. As a temperature of 1000° is easily obtainable in a resistance wound electric furnace we decided to use this method.

Apparatus (Method I).—The general assembly of the apparatus is shown in Fig. 1. The principal parts are: still for carbon tetrachloride (a), capillary flow control

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[13] Willard J. Fisher, Harvard College Observatory Circulars, 331 (1928); 375 (1932).

[14] E. J. Öpik, *Popular Astronomy*, **41**, 71 (1933).

[15] For the chemical analyses, sources and history of the samples of the meteorites and rock Nos. 8 and 18, see S. H. Manian Dissertation, Columbia University, 1934.

[16] (a) E. Demarçay, *Compt. rend.*, **104**, 111 (1887); (b) Quantin, *ibid.*, **104**, 223 (1887); **106**, 1074 (1888); (c) P. Camboulives, *ibid.*, **150**, 175 (1910).

[17] C. Fink and C. F. Bonilla, *J. Phys. Chem.*, **37**, 1145 (1933).

[18] M. Bodenstein and Dunant, *Z. physik. Chem.*, **61**, 437 (1908).

[19] R. H. Atkinson, *et al.*, *J. Chem. Soc.*, **117**, 1410 (1920).

(b), by-pass (c) with mercury as the confining liquid, Pyrex plugs (d, d), vitreous silica combustion tube, 75 cm. long and 1.6 cm. diameter (e), porcelain boats (g) (110 × 11 × 15 mm.), cylindrical Acheson graphite rod (h), Pyrex Kjeldahl bulb (i) plugged loosely with glass wool, liquid-air traps (j, j) and the mercury manometers, McLeod gage, pumping system and receivers (not shown). The Pyrex to silica joints (d to e) were made gas tight by use of a resin (m. p. about 95°), made by heating to 190° for fifteen hours equimolal quantities of phthalic anhydride and ethylene glycol; during a run these joints were cooled by air blasts (f, f). Two receivers in parallel were used for collecting the carbon monoxide gas from each run: one, a 3-liter flask for the major bulk of the gas, and the other, a 50-cc. bulb, the gas to be used as samples for the measurements by the mass spectrograph. The purpose of the graphite rod (h) was two-fold: to reduce any small amounts of carbon dioxide to carbon monoxide and also to increase the resistance to the flow of the gases and vapors through the combustion tube.

Procedure.—Preparatory to a run, the apparatus was always cleaned in the following manner: organic compounds (carbon chlorides, see next column) were dissolved out with acetone; metal chlorides were removed with boiling cleaning mixture; films of carbon deposits were burnt out at 1000° in a current of dry air; hydrolyzed silica in the glass portions of the apparatus was dissolved out with boiling 3 *M* sodium hydroxide.

After assembling, the apparatus containing the graphite rod and porcelain boats was completely degassed at 1000°, flaming the glass parts while pumping with the mercury pump during three to five hours, and then cooling to room temperature under vacuum. The powdered meteorite charge was then quickly introduced into the porcelain boats and liquid carbon tetrachloride poured into the still.

In this series of decompositions, the reaction pressures were up to 9 cm. of mercury, equal to the vapor pressure of carbon tetrachloride at room temperature minus the pressure drops through the capillary and other parts of the apparatus. Dissolved air in the carbon tetrachloride was removed by freezing it and pumping out the system, melting the carbon tetrachloride, liberating the air and again freezing it, and pumping out the system.

The full furnace heat was turned on, and while coming to temperature the carbon tetrachloride was liquefied and the gas receivers pumped down to about 10^{-3} to 10^{-4} mm. The carbon monoxide generated by the decomposition was pumped into the receivers by an automatic Toepler pump[20] set to operate at various rates (three to five minutes per stroke of 200 cc. volume), depending on the rate of carbon monoxide generation. The duration of a decomposition was usually five to seven hours.

Purification of Chemicals

Carbon tetrachloride was of C. P. quality. It was dried over lumps of anhydrous calcium chloride and slowly distilled off as needed in an all-Pyrex still (b. p. 76.6° corrected).

Graphite.—The powdered graphite mixed with the meteorite charges was "Unctious Acheson Graphite, Grade 38" kindly supplied by the Acheson Graphite Co., New York, N. Y. Its purity was stated to be "99.9% pure graphitic carbon, made in the electric furnace at 7500°F." We degassed a quantity of it as described above at 1000° in the silica combustion tube and stored it in a paraffined glass-stoppered bottle, to be used as needed. The solid graphite rod was machined from a pure Acheson graphite electrode without an oxide core. This was degassed at 1000° between runs.

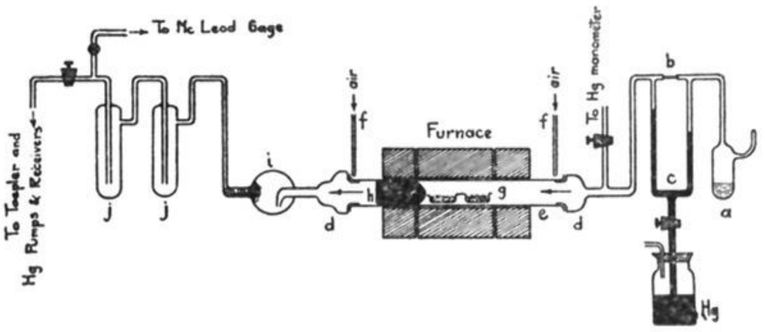

Fig. 1.—(Schematic.)

Decomposition of the Meteorites

The gases collected in the receiver in several preliminary runs using rock No. 8 were always analyzed for CO_2, O_2, CO and N_2 (by difference), in the order stated, with the following results: $CO_2 = 0.0\%$, $O_2 = 0.0\%$, $CO = 99.2\%$, N_2 (by diff.) $= 0.8\%$. The 0.8% N_2 is most likely due to a slight inleakage of air resulting from the necessary twelve to sixteen changes of connections of the Hempel buret to the various absorption bulbs.

All meteorite samples were crushed and powdered in a hard steel "diamond" mortar, and passed completely through a 50-mesh sieve; hence a large fraction of the powders was much finer than 50-mesh. The powders were then oven-dried at 110° and stored in glass vials stoppered with paraffined corks. The weighed meteorite powder and degassed "Unctious Acheson Graphite" were quickly and intimately mixed in a dry glass mortar and pestle, placed in one porcelain boat and introduced into the silica combustion tube.

In Table I the results of decompositions of the first set of three meteorites and the terrestrial rock No. 8 are summarized.

TABLE I

Meteorite	Sample, g.	Powd. graphite, g.	Duration of run, hours	CO available (from total O_2,)[a] cc.	CO actually collected,[b] cc.	Oxygen recovered as, CO, %	Press. in reaction zone, cm.
St. Michel	2.80[c]	1.05	$4^1/_2$	1610	670	41.6	6–8
Orgueil	1.15	0.63	5	634	250	39.5	8–9
Pultusk	2.51	1.00	$3^1/_2$	1375	205	14.9	2.5–4
Rock 8	2.50	1.00	5 5	1885	104[d] 132	5.5 7.0	3 3

[a] Calculated to 27° and barometric pressure. [b] Based on the pressure in the receiver of an estimated volume of 3300 cc. [c] From an initial 12-g. sample; the Orgueil and Pultusk samples used are the total weight of sample received. [d] This initial yield of 104 cc. of carbon monoxide was lost by accident.

The elements which give volatile chlorides and present in our samples to a considerable extent were Fe, Al, Mg

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[20] Donald MacGillavry, Columbia University, Ph.D. Dissertation, 1933.

Si; volatile chlorides of carbon[17] (CCl_6, C_2Cl_6, C_2Cl_4, etc.), Cl_2 and any undecomposed CCl_4 also were produced. Most of the solids condensed out around the graphite rod in the combustion tube, on the colder walls of the latter and in the Kjeldahl bulb, where the glass wool held back the larger part of them. These solids condensed as extremely fine particles on the glass wool and soon formed an impervious wall to the gas and vapor flow. This resistance was released by gently heating the solids and subliming out the metal chlorides. The residue in the boat had a fine carbon deposit on the surface and was usually caked a little, but the mass was porous and easily broken up by a spatula.

From Table I we see that the fraction of oxygen recovered as carbon monoxide was about 40% in the most favorable case and as low as 5.5% in the least favorable. The low carbon monoxide yield was probably due to two causes: the low carbon tetrachloride pressure used, and the increasing deposition of the fine carbon layer on the surface of the charge. The passage of the carbon tetrachloride over the charge at 1000° was continued for about an hour after the generation of carbon monoxide had stopped. We take this as evidence that no reaction takes place between the hot carbon tetrachloride vapors and the silica of the combustion tube and the oxygen compounds in the porcelain boat.

Method II

Decomposition of Samples by Carbon Tetrachloride at 1000° under Atmospheric Pressure.—It was thought that conducting the decomposition of the samples at higher pressures of carbon tetrachloride would increase the yield of the oxygen recovered, thereby allowing its examination in the form of water and oxygen. A new apparatus, Fig. 2, was built and the following general scheme used.

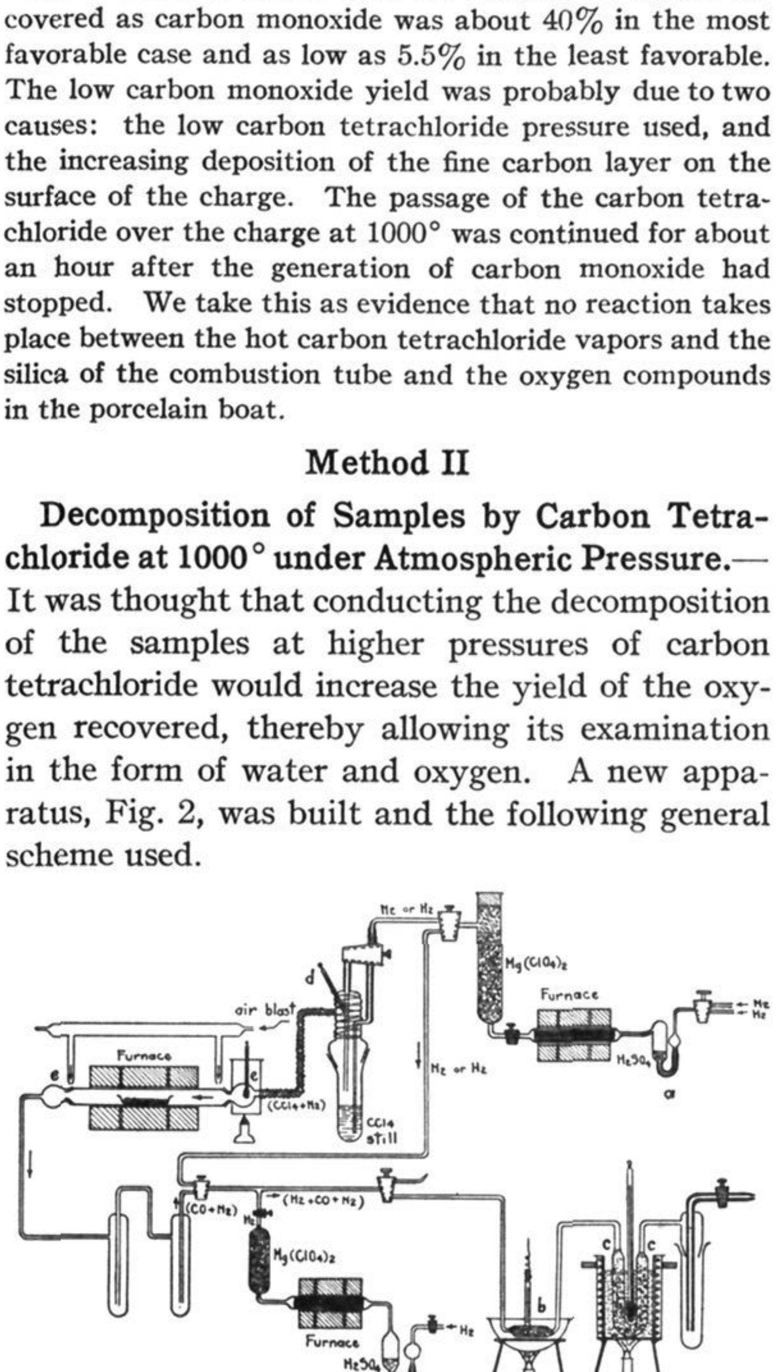

Fig. 2.—(Schematic.)

The flow of carbon tetrachloride vapors over the charge at 1000° was maintained by bubbling nitrogen through liquid carbon tetrachloride kept at its boiling point or somewhat higher by an oil-bath; the volatile reaction products were again condensed out by two liquid air traps; the carbon monoxide and nitrogen gases coming from these traps were passed into a purified hydrogen stream and thence through a supported nickel catalyst to convert the carbon monoxide to methane and water. The water formed was condensed out and the nitrogen, methane and excess hydrogen discharged through a capillary to the atmosphere.

Apparatus.—The general assembly is shown in Fig. 2. Tank hydrogen and nitrogen were purified over hot copper and dried through magnesium perchlorate. The rate of flow of the gases was obtained by means of the calibrated sulfuric acid bubble counters (a, a); the mixer and preheater (b) was a 2.5 cm. × 10 cm. bulb filled with Pyrex chips and heated to 250° by an air-bath. The Pyrex catalyst bulb (c) 18 cm. high and 2.0 cm. o. d. was heated to the desired temperature (295°) by a molten bath of potassium nitrate–sodium nitrate. It was not necessary to lubricate or seal the ground joint on the carbon tetrachloride still. The exposed portion of the still and glass tubes to the combustion tube were heated to 92° as measured by a thermometer (d) wrapped under the asbestos lagging. *The combustion tube* was of vitreous sand finished silica, 55 cm. long and 2.5 cm. diameter, and was ground on the ends to a slight bevel and ground Pyrex plugs (e, e) were made to fit on the outside. These two ground joints were made gas tight by use of the phthalic anhydride resin, and, during a run, were kept cool by air blasts. The bulb of the Pyrex joint on the entrance end of the carbon tetrachloride was heated by an air-bath in order to prevent condensation of carbon tetrachloride therein. *The combustion boats* were larger than the previous ones: the first boat of graphite was 15 cm. long, and was machined from an Acheson graphite electrode to slide loosely into the combustion tube. The second boat of silica was 150 × 15 × 12 mm.; 10-g. charges could be used easily in either of these boats. An alundum boat was found to be unsatisfactory as it reacted with carbon tetrachloride at 1000°.

Preparation and Testing of the Nickel Catalyst.—The supported nickel catalyst was prepared following the directions of Pease.[21] C. P. $Ni(NO_3)_2 \cdot 6H_2O$ adsorbed on the brick support of 8–15 mesh was ignited to the oxide in a muffle furnace at 500°; 37 g. of it was charged into the catalyst U-tube and ignited asbestos fibers placed on top. The catalyst was then reduced at 290–300° in a stream of purified hydrogen until the amount of water coming off was about 4 mg. per hour; a reduction period of twenty-four hours was required. When not in use the catalyst was kept in a hydrogen atmosphere. The height of the catalyst in the U-tube was 14 cm. with a total apparent volume of 130 cc., apparent specific volume 3.5 cc./g.

Test Runs.—The guiding conditions followed in these runs for the complete reduction of carbon monoxide by hydrogen in the presence of nickel as the catalyst according to the equation

$$CO + 3H_2 = CH_4 + H_2O$$

are those developed by Neumann and Jacob[22] for the ratio of the reactants and for the temperature of the reaction, and those developed by Medsforth[23] for the gas velocity.

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[21] R. N. Pease, THIS JOURNAL, **49**, 2783 (1927). We are indebted to Mr. C. A. Senter of the Armstrong Cork and Insulating Co., New York, N. Y., for a supply of the "Non-pariel" diatomaceous brick employed for the catalyst support.

[22] B. Neumann and K. Jacob, *Z. Elektrochem.*, **30**, 557 (1924).

[23] Samuel Medsforth, *J. Chem. Soc.*, **123**, 1452 (1923).

In these test runs hydrogen, carbon monoxide and nitrogen gases were collected and mixed in a 20-liter gasometer by displacement of water. They were then displaced by water at the desired rate, passed through a 20-cm. column of alkaline solution of pyrogallol, 15-cm. column of anhydrous calcium chloride and thence through the nickel catalyst. Carbon monoxide was generated by adding, dropwise, 85% C. P. formic acid to C. P. 95% sulfuric acid heated gently to about 100°. The carbon monoxide was not further purified.

The initial and final gases were analyzed at intervals for carbon dioxide, oxygen and carbon monoxide by absorption and for hydrogen and methane by explosion methods. Using a ratio of H_2:CO = 3.5:1, the reduction of carbon monoxide to water was complete with gas velocities up to 38 cc. per min. (N. T. P.) both without nitrogen gas and with nitrogen up to 55% of the total gas.

TABLE II

Meteorite	Sample,[a] g.	Powd. graphite, g.	Boat used	Duration of run, hours	H_1O available from total O_2 content, cc.	H_2O actually collected, cc.	Fraction of oxygen recovered as H_2O, %	Amount of liquid CCl_4 used, cc.
Rock No. 12	6.20	2.00	Graphite	5	3.41	1.5	43.8	25
Mocs	6.74	2.10	Graphite	7	2.72	1.1	40.5	25
Knyahinya	5.00	2.50	Silica	8	2.20	1.1	50.0	40
Homestead	5.01	1.54	Silica	(3 + 4)	2.04	0.6	29.5	(4 + 26)

[a] The weights of the meteorite samples are portions of the original samples received, which weighed from 5.5 to 9 g.

Procedure (Method II).—A blank run was made to show whether or not any reaction takes place between the silica of the silica combustion tube alone and the carbon tetrachloride vapors at 1000°. After cleaning out the apparatus as described under Procedure (Method I) and introducing the graphite boat containing some powdered degassed graphite, but no silicate rock, the system was swept out at 1000° by a dry purified stream of nitrogen for several hours, and the glass parts of the apparatus were well flamed in order to remove all adsorbed moisture. This was followed by a stream of hydrogen and nitrogen through the catalyst at 295° for three hours. The flow of carbon tetrachloride (20 cc.) was then started and a five-hour run made, resulting in only about 0.1 cc. of water.

Appreciable amounts of fluffy white sublimate (carbon chlorides)[17] condensed out in the tubes on the exit end of the reaction zone; simultaneously small amounts of a reddish sublimate (soluble in hydrogen chloride), probably ferric chloride, sublimed out of the tube. These sublimates formed during the first part of the experiment (first one-half to one hour), and it was during this time that the 0.1 cc. of water was formed. Thereafter no water condensed out and no further deposition of ferric chloride occurred. The above apparent slight reaction must have been due to a small amount of iron impurity left in the combustion tube, probably from the cleaning operation. The important conclusion is that the silica combustion tube is not reduced by the hot carbon tetrachloride at 1000° in these atmospheric pressure runs, thus confirming the former results obtained in the decomposition at reduced pressures.

The decompositions of the second set of meteorites and rock No. 18 were made in the same manner as the blank runs, and a summary of the results is given in Table II.

In every case the decompositions seemed to stop after the first four hours. The residue in the boats, amounting to about half of the original charge, was covered by a thin layer of carbon and, underneath it, the charge appeared to be wholly unattacked; *i. e.*, the deposited carbon layer formed a protective covering and prevented further decomposition. Apparently the fraction of oxygen recovered at this increased pressure of carbon tetrachloride to one atmosphere has not been correspondingly increased and, as suggested above, the inhibition of the reaction seems to be due to an accumulation of an impervious layer of fine carbon.

Specific Gravity Determinations

Each sample of water was vacuum distilled at room temperature, and the specific gravity determined with the results given in Table III.

TABLE III

Meteorite	Specific gravity (d_{25}^{25})
Rock No. 18	Not measured
Mocs	0.999999 ± 0.000054
Knyahinya	1.000038 ± .000008
Homestead	1.000012 ± .000001

Each value is the average of two determinations. The determinations of the specific gravity were made by means of a small Ostwald type of pycnometer made of Pyrex glass. Its bulb, of capacity 0.47 cc., had small capillary side arms, whose tips were covered with small ground caps. The pycnometer was filled with the water to a fine scratch mark on one of the side arms, viewed through a lens. The capillary tube was calibrated and its diameter was found to be 0.22 mm. All fillings of the pycnometer were made at 25.000 ± 0.002° in a thermostat.

Weighings were made to 0.01 mg. using a magnetically-damped balance and brass weights, platinum coated. The weights had recently been calibrated by Professor H. T. Beans and Mr. Robert Beans, Columbia University, and the corrections agreed to 0.01 mg. All weighings were converted to "*in vacuo*." The data taken during each weighing included the apparent weight in air, temperature inside the balance case, barometer reading and temperature of the barometer. The reduction of weighings to "*in vacuo*" and the calculations of specific gravity were done following the procedure of Reilly,[24] for which the following data were used: Wade and Merriman,[25] density of air of 50% relative humidity, the density of brass (8.40)[26] and density of Pyrex glass (2.25).[27]

Discussion of Errors and Precision

A careful consideration of the usual errors occurring in specific gravity determinations by pycnometers indicated that the largest component errors were the two weighings by the analytical balance, each apparent weight being attended by an error of ±0.02 mg. as determined by reproducibility of weighings. The total effect of each of the component errors on the specific gravity G then became $\Delta G = \pm 0.000063$.

Using 514:1 for the abundance ratio $O^{16}:O^{18}$ for terrestrial oxygen (this research) a calculation shows that the above error in the specific gravity is equivalent to a 29% error in the O^{18} abundance. From Table III we see that the differences of the specific gravity of meteoric waters from that for terrestrial distilled water are all within the experimental error and in fact are less than this error in all cases. We conclude from the densities of the water samples that within an experimental error of 29% in the relative abundance of the O^{18} isotope, the oxygen in these meteorites is of the same isotopic composition as that of terrestrial oxygen.

Abundance Measurements by the Mass Spectrograph.—The abundance of oxygen isotopes in the waters from the second set of meteorites was examined by means of the mass spectrograph on oxygen electrolytically prepared from each water sample. Two sets of measurements were made on each oxygen sample.

The electrolyses were carried out in a small cell with bright platinum electrodes at a current density of about 0.02 amp./sq. cm. For the electrolyte 30% fuming sulfuric acid was added to the water to a final concentration of 10% sulfuric acid. Air in the system was pumped out and replaced by helium purified through activated degassed coconut charcoal at liquid air temperatures. The electrolytic dried oxygen was collected over mercury and it is estimated that half of the gas was helium.

The mass spectrograph and the procedure employed in these measurements were those described by Bleakney.[28] A magnetic field of 1000 gausses was used for this oxygen work. The furnace around the spectrograph had burnt out, so that the latter could not be baked free of its initial adsorbed water. This water amounted to an appreciable fraction of the O^{18} isotope, so that an examination of the positive atomic ions O^{18+} and O^{16+} could not be utilized (interference from the $H_2^1O^{16+}$ band of mass 18). Therefore it was necessary to use the molecular ions $O^{16}O^{18+}$ and $O^{16}O^{16+}$ of masses 34 and 32, respectively.

The resolution of the spectrograph, which had been built for work on hydrogen and helium (masses up to 5) was not sufficient to separate completely the bands of the molecular ions; there was a partial overlapping of $O^{16}O^{18+}$ band by the huge $O^{16}O^{16+}$ band. In Fig. 3 is graphically represented the mass spectrum of the oxygen from Knyahinya. The abscissa (in volts) represents a mass range of 42 down to 30; the ordinates are in arbitrary units.

Therefore an accurate measure of the $O^{16}O^{18+}$ peak requires a correction for scattered background as contributed from the overlapping by the $O^{16}O^{16+}$ band. In the first set of measurements, this background correction was made by a graphical extrapolation of the left side of the $O^{16}O^{16+}$ band completely across the base of the $O^{16}O^{18+}$ peak, indicated in Fig. 3 by the dotted line, and estimating its magnitude from the base line. This background correction also includes the contribution from the $O^{16}O^{17+}$ band which is not at all resolved by this spectrograph.

For each sample of oxygen examined, a mass spectrum was first plotted to allow calculation of the background correction, and then the magnitude of the two peaks $O^{16}O^{18+}$ and $O^{16}O^{16+}$ were measured accurately by means of the electrometer. The ratio of these measured maxima was then taken for the relative isotopic abundance. With the arrangement in this spectrograph in which the second slit is wider than the first, the heights of the peaks rather than the areas under them give better results. This is because

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(24) J. Reilly, W. N. Rae and T. S. Wheeler, "Physico-chemical Methods," 1st ed., 1926, p. 324.

(25) J. Wade and R. W. Merriman, *J. Chem. Soc.*, **95**, 2174 (1909).

(26) "International Critical Tables," Vol. I, pp. 83–90.

(27) "Pyrex Laboratory Glassware," by Corning Glass Works, New York, N. Y., 1931, p. 32.

(28) Walker Bleakney, *Phys. Rev.*, **40**, 496 (1932).

nearly all of the beam goes through the second slit. If the second slit were only infinitesimal in width then the areas should be taken.

The background correction for the various samples of oxygen by this graphical method ranged from 3.7 to 8.3% of the $O^{16}O^{18+}$ peak. Considerable individual judgment is involved in this extrapolation and it is estimated that the corrections can be in error by 25%, so that its effect on the $O^{16}O^{18+}$ value is an error of 2%.

A summary of the results of the first set of abundance measurements is given in Table IV.

TABLE IV

Source of oxygen	Detns.	Av. mol. abundance ($O^{16}O^{16}$: $O^{16}O^{18}$) (uncorr.)	Corr. % of $O^{15}O^{18}$ peak, %	Corr. mol. abundance ($O^{16}O^{16}$: $O^{16}O^{18}$)	Corr. atomic abundance O^{16}:O^{18}
Rock No. 18	2	240 ± 1	7.1	258 ± 1	516 ± 2
Mocs	3	234 ± 2	5.0	246.3 ± 2.3	493 ± 5
Knyahinya	2	238 ± 2	7.5	257.6 ± 2.0	515 ± 4
Homestead					
High pressure	2	232.5 ± 4.5	8.3	253.5 ± 4.9	507 ± 10
Low pressure	2	255 ± 3	6.3	270.8 ± 3.3	540 ± 9
From $KClO_3$	4	258 ± 5.3	3.7	267.7 ± 5.5	535 ± 11

The oxygen from potassium chlorate was prepared by Dr. Wallace Lozier, of the Palmer Physical Laboratory, Princeton University, by heating potassium chlorate and manganese dioxide in a vacuum system and collecting the oxygen. The mass spectrum for this sample of oxygen indicated the presence of a considerable amount (4%) of a substance of mass 28, probably nitrogen, which of course did not interfere with our measurements.

We endeavored to make all runs at the same gas pressure approximately the same as the low pressure run on the Homestead oxygen; the Homestead high pressure is about twice that of the low pressure (about 10^{-4} mm.). Nevertheless, the gas pressures, as measured by the total $O^{16}O^{16+}$ current, did vary somewhat from sample to sample, as for example, the oxygen pressure in the Mocs run was somewhat higher, which may be the explanation for the apparent high abundance of O^{18} indicated by the results.

Omitting, for the present, the result for the Mocs oxygen and the Homestead high pressure run, we see that the maximum variation in the results is 515 to 540 or about 5%, and, since this is approximately the magnitude of the experimental error, we conclude that within an experimental error of 5% the isotopic composition of meteoric and terrestrial oxygen is the same.

With a view to improving on the precision of the above results a second set of abundance measurements was undertaken. In the above summary of results it was indicated that there seemed to be a pressure effect on the final abundance ratio. Inasmuch as the formation of the $O^{16}O^{18+}$ and $O^{16}O^{16+}$ ions is the result of a primary ionization process, it will vary linearly with pressure, while secondary ones will vary as the square of the pressure.[29] The scattered background, being the result of a secondary process, was assumed to be proportional to the square of the gas pressure. Bleakney[29] has described a method for correcting for this pressure effect and, for accurate results, it would be necessary to measure the $O^{16}O^{16+}$ and $O^{16}O^{18+}$ ion currents at several different pressures, preferably in a 5- to 10-fold pressure range and then to plot the data and extrapolate to zero pressure. With the slit width and sensitivity of the mass spectrograph available only a two-fold range of pressures could be utilized to the precision desired. Hence we decided to make the runs at two different gas

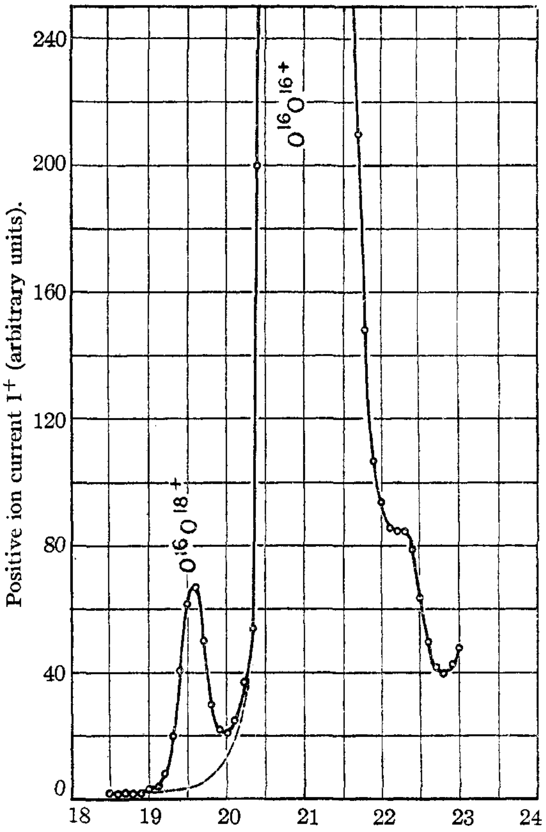

Fig. 3.—The mass spectrum for oxygen from Knyahinya meteorite.

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(29) Walker Bleakney, *Phys. Rev.*, **41**, 32 (1932).

pressures and to draw a straight line through them, extrapolating to zero pressure. Because of only two pressure runs for each sample, the correction is attended by a considerable error, estimated as about 25% of the correction, or 2% of the abundance measurement.

The results of this second set of measurements are given in Table V.

TABLE V

Source of oxygen	High pressure		Low pressure		Zero pressure	
	Runs	Mol. abundance $O^{16}O^{16}$: $O^{16}O^{18}$	Runs	Mol. abundance $O^{16}O^{16}$: $O^{16}O^{18}$	Mol. abundance $O^{16}O^{16}$: $O^{16}O^{18}$	Atomic abundance O^{16}:O^{18}
Rock No. 18	2	225 ± 1	4	233.3 ± 2	244.6 ± 2.3	489 ± 5
Mocs	2	220 ± 3	6	241.4 ± 4	263.0 ± 3.7	526 ± 7
Knyahinya		Not measured				
Homestead	3	224 ± 2	3	238.3 ± 3	257.6 ± 3.0	515 ± 6
From $KClO_3$	3	239 ± 3	2	241.5 ± 1	244.4 ± 2.7	489 ± 5

The molecular abundance at each pressure is the arithmetic average of the number of determinations indicated.

The maximum variation in the values for the different meteoric samples at the low pressure is 3.2/242 = 1.3%, while that at zero pressure is 18.6/263 = 7.0%. Because of the uncertainty attending our pressure correction, it would be more accurate in determining any variations in the isotopic abundance amongst these meteorites to compare the directly measured values at the lowest pressures than to compare those corrected to zero pressure. On this assumption the isotopic composition of these meteoric oxygens is the same as terrestrial oxygen within an experimental error of 3.4%.

Discussion

In the second set of measurements we should note that the pressure corrections in the case of the terrestrial oxygens from rock No. 18 and potassium chlorate is relatively smaller than for the meteoric oxygens. The mass spectrum curves for each oxygen obtained in the first set of abundance measurements seem to indicate a sharper resolution for the terrestrial samples than for the meteoric ones. Both of these effects mean a smaller background correction for the terrestrial oxygens, or a larger one for the meteorites. One of the possible explanations for this effect is a higher concentration of O^{17} in the meteorites. However, the differences we are discussing here are so close to the experimental error that only an accurate measurement of the abundance of the O^{17} isotope in these samples by means of a mass spectrograph, of higher sensitivity and much greater resolving power, will answer the question.

In Table VI, we compare the zero pressure atomic abundance O^{16}:O^{18} obtained in the two sets of measurements and the weighted average of all runs.

TABLE VI

Source of oxygen	First set		Second set		Weighted average
	O^{16}:O^{18}	Wt.	O^{16}:O^{18}	Wt.	O^{16}:O^{18}
Rock No. 18	516 ± 2	1	489 ± 5	1	503 ± 14
Mocs	493 ± 5	1	526 ± 7	2	515 ± 15
Knyahinya	515 ± 4	1	Not measured		515 ± 4
Homestead	540 ± 9	1	515 ± 6	2	524 ± 11
$KClO_3$	535 ± 11	1	489 ± 5	1	512 ± 23
Weighted average of all runs..........................					514 ± 7

The weight factors are based on the number of determinations entering into the various average abundance values. The weighted average 514 ± 7 for all runs includes 9 determinations on five different oxygens, 3 meteoric and 2 terrestrial. Since the error introduced by the correction method used in either set of measurements is about 2% of the abundance being measured, the total error becomes $\pm \sqrt{(2)^2 + (1.4)^2} = \pm 2.5\% \approx \pm 13$. Hence we submit the value 514 ± 13 = 514 ± 2.5% for the absolute value of the abundance ratio O^{16}:O^{18}.

Aston,[7] using his mass spectrographic method, has published the value 536 for terrestrial oxygen. Kallmann and Lasareff,[8] using a mass spectrographic method similar to the one employed in this investigation, examined the molecular ions of CO, H_2O and O_2 of terrestrial origin and report the abundance ratio O^{16}:O^{18} = 600:1, 654:1 and 640:1, respectively, with an average value of 630:1. W. R. Smythe,[9] using a positive ray method based on a different principle obtained 503 ± 10. About two years ago Bleakney (unpublished results) measured the O^{16}:O^{18} ratio in the water molecule, using the same mass spectrograph employed in the present research, and obtained the value 515 ± 20. This is a significant check of our results because of the different molecular species used in the measurements.

With the exception of the results of Kallmann and Lasareff, all of the mass spectrographic determinations agree to within about 4% with an average value of 517 ± 10, but they are definitely lower than that obtained by band spectra by Mecke and Childs,[5] 630 ± 20:1.

Abundance of O^{16} : O^{18} in the Carbon Monoxide Samples from the First Set of Meteorites.—When the above samples were examined by the mass spectrograph it was found that the resolution of the instrument was not sufficient to separate the mass spectral bands arising from the molecules $C^{12}O^{16+}$, $C^{13}O^{16+}$ and $C^{12}O^{18+}$. Although the resolving power of the instrument increases with decreasing mass of the positive ions (the spectrograph could resolve masses 32 and 34 of the molecular ions $O^{16}O^{16+}$ and $O^{16}O^{18+}$), the difficulty in the case of the carbon monoxide molecule was the presence of the C^{13} isotope to about 1%[11] of C^{12}, so that the $C^{13}O^{16+}$ ion virtually destroyed the resolution of the other carbon monoxide ions of mass 28 and 30. The $C^{12}O^{18+}$ band appeared only as a slight hump on the side of the $C^{12}O^{16+}$ peak. No further abundance measurements were made on the carbon monoxide molecule. We were also bothered here by other impurities at masses 28, 29 and 30, as shown by an initial blank run preceding the carbon monoxide measurements.

The above carbon monoxide gases were next converted to water by reduction with excess hydrogen over a supported nickel catalyst as described above. The carbon monoxide gases contained in 3-liter flasks were transferred to 300-cc. flasks and hydrogen added to 1 atmosphere pressure. (By an unfortunate accident we lost all of the carbon monoxide from the St. Michel meteorite.) The carbon monoxide was then displaced by mercury, at the rate of 9 to 10 cc. per minute, into a purified hydrogen stream, flowing at the rate of 80–85 cc. per minute, and the mixed gases passed through the nickel catalyst at 295°. In this way each of the two samples remaining yielded about 0.1 cc. of liquid water.

We tried to measure the O^{16}:O^{18} abundance on the H_2O^+ ions but the initial amount of spurious water adsorbed on the walls of the spectrograph was too large to permit any accurate measurements. No further work was done on these samples, though it is evident that there exists no large difference in the abundance ratio of these samples from that of terrestrial oxygen.

Summary

1. Two processes have been developed for the partial conversion (up to 50%) by carbon tetrachloride at 1000° of the combined oxygen of silicate rocks and stone meteorites over to carbon monoxide, and thence, by catalytic reduction with hydrogen, to water, and, by electrolysis, to oxygen gas.

2. Specific gravity measurements of the water formed have been made, showing that, within an experimental error of 29% in the O^{18}:O^{16} abundance, the isotopic composition of the oxygen from the stone meteorites Mocs, Knyahinya and Homestead is the same as that from a terrestrial granite from Stonington, Maine, and from laboratory potassium chlorate.

3. Relative abundances of the isotopes O^{18} and O^{16} in the oxygen gases were investigated by means of a vacuum mass spectrograph and the results of paragraph (2) on the same stone meteorites were confirmed and the experimental error in the atomic abundance ratio O^{18}:O^{16} was reduced to ±2.5%.

4. Examination of the oxygen from the stone meteorites Mocs, Homestead, Knyahinya and a terrestrial high silicate granite, in the form of the carbon monoxide and the water molecules, by the mass spectrograph, did not give satisfactory results because of insufficient resolving power of the spectrograph and also because of the presence of small amounts of interfering impurities in the spectrograph. We are planning to correct these two difficulties, at which time these samples of meteoric water will be examined for the abundance of the oxygen isotopes.

5. The various chemical reactions have not effected fractionation of the oxygen isotopes to within an experimental error of 2.5%.

6. The value 514 ± 13:1 is submitted for the absolute value of the abundance ratio O^{16}:O^{18} for both terrestrial and meteoric oxygen.

7. The agreement of this result with other mass spectrographic determinations is compared, and the discrepancy from the band spectra value is pointed out. The average value of the mass spectrographic determinations by the four different researches (omitting the results of Kallmann and Lasareff) is 517 ± 10.

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