

AN EXAMINATION OF WATER FROM VARIOUS NATURAL SOURCES FOR VARIATIONS IN ISOTOPIC COMPOSITION

By Edward W. Washburn and Edgar R. Smith

ABSTRACT

The densities of samples of water from various natural sources have been measured in an effort to detect differences in isotopic composition. Small differences have been found in the following cases: After the removal of all non-aqueous constituents, the water of the ocean, of the Dead Sea, and of Great Salt Lake is denser than pure normal water by about 2, and the water of crystallization of native borax tetrahydrate, kernite ("rasorite"), by about 7 parts per million. The sap water from a young willow tree was heavier than normal water by 2.8 and the water produced by burning the dry wood was heavier by 5.4 parts per million.

A differential pycnometer method for measuring differences in density with a precision of 1 part in 1,000,000 is described.

CONTENTS

	Page
I. Introduction	305
II. A differential method of measuring differences in density	306
III. The samples of water examined	309
IV. Discussion	311
V. Summary	311

I. INTRODUCTION

Following the discovery that upon electrolysis of water the residue is enriched in the H^2 isotope of hydrogen,¹ it was found that the density, index of refraction, freezing point, boiling point, and vapor pressure of water thus changed in isotopic composition undergo corresponding changes^{2 3} and furthermore, that fractional distillation^{4 5} and adsorption⁴ effect changes in the isotope ratio. It therefore appeared reasonable to expect that some isotopic fractionation of water may be taking place in nature during certain life processes, such as diffusion through animal membranes and transpiration through the leaves of plants, and may have occurred to a considerable extent

¹ E. W. Washburn and H. C. Urey, Proc. Nat. Acad. Sci., vol. 18, p. 496, 1932.

² E. W. Washburn, E. R. Smith, and M. Frandsen, Jour. Chem. Physics, vol. 1, p. 288, 1933.

³ G. N. Lewis and R. T. Macdonald, Jour. Am. Chem. Soc., vol. 55, p. 3057, 1933.

⁴ E. W. Washburn and E. R. Smith, Jour. Chem. Physics, vol. 1, p. 428, 1933.

⁵ G. N. Lewis and R. E. Cornish, Jour. Am. Chem. Soc., vol. 55, p. 2616, 1933.

throughout past ages by such physical processes as the slow evaporation of inland seas. It also seemed possible that some fractionation of the hydrogen isotopes might have occurred during the formation of coal deposits and of petroleum.

The relative abundance of the H^2 isotope in hydrogen from a few natural sources, namely, water from the crater of Mount Kilauea, water from an obsidian, Devonian water, and helium-bearing natural gases, has been determined by spectroscopic comparison with ordinary laboratory distilled water without the detection of any differences.⁶

The density of water has been found to be quite sensitive to variations in isotopic composition⁷ and in this work water from a variety of natural sources has been investigated for such variations by means of measurements of density.

II. A DIFFERENTIAL METHOD OF MEASURING DIFFERENCES IN DENSITY

The method used for determining small differences in density has been outlined briefly in a previous paper.⁷ However, it is believed that the precision, simplicity of manipulation, and probable value of the method for other purposes⁸ warrant a more complete description.

Two silica pycnometers very closely the same in size and weight, and of the shape shown in figure 1, are used. The capillary stem of each has a reference mark less than 0.01 cm in thickness, made with a diamond point, and the volume per unit length of the capillary is determined with an accuracy of 0.1 percent by calibration with mercury. The volume of each pycnometer up to the reference mark is determined with an accuracy of 0.1 percent by weighing empty, filling with distilled water to any suitable height in the capillary, as read with a cathetometer while the pycnometer is in a water thermostat, again weighing, and applying a correction for the volume of water in the capillary above the mark.

In making a measurement of the difference in density between a given sample and normal water, the first pycnometer is filled with normal water and the second with the sample, to any suitable heights in the capillaries. The filling is conveniently done with a fine silver capillary and the aid of a low vacuum line, as illustrated in figure 2. The pycnometers are then placed side by side, with their ground stoppers loosely in place, in a thermostat containing distilled water and having front and back of plate glass. After thermal equilibrium is attained, the height of the meniscus above the reference mark in each capillary is read with the cathetometer. The pycnometers are next taken out of the bath, wiped dry, placed on opposite pans of a balance with their stoppers tightened in place, and the difference in their weights is determined. After the weighing, they are emptied and refilled so that the first pycnometer now contains the sample water and the second contains normal water. Again they are placed in the thermostat in the same positions as before and the capillary heights recorded. They are again taken out, dried, placed on the

⁶ C. A. Bradley and H. C. Urey, *Phys. Rev.*, vol. 40, p. 889, 1932.

⁷ E. W. Washburn, E. R. Smith, and M. Frandsen, *B. S. Jour. Research*, vol. 11, p. 453, 1933.

⁸ For example, the measurement of partial molal volumes in dilute solutions.

same balance pans and the second difference in weight determined. The expression for the difference in density is obtained as follows:

Let P_1 = weight of pycnometer no. 1.

P_2 = weight of pycnometer no. 2.

V_1 = volume of pycnometer no. 1 to the reference mark.

V_2 = volume of pycnometer no. 2 to the reference mark.

D = density of sample investigated.

D_o = density of normal water.

$\Delta V_1'$, $\Delta V_1''$, $\Delta V_2'$, $\Delta V_2''$ = volume of water above the reference mark in the capillary of pycnometer no. 1 in the first and second fillings and pycnometer no. 2 in the first and second fillings, respectively.

m_1 = difference in masses after the first filling.

m_2 = difference in masses after the second filling.



FIGURE 1.—Silica pycnometer.

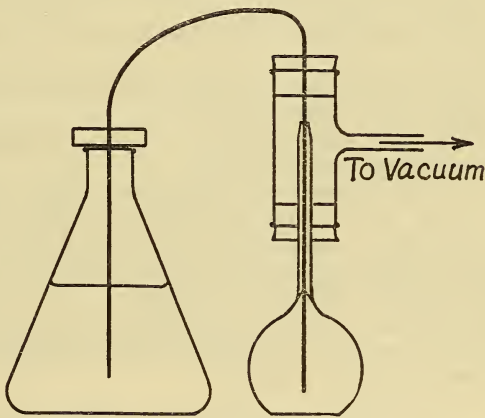


FIGURE 2.—Device for filling pycnometer.

If no. 1 is always placed on the right hand pan of the balance,

$$P_2 + V_2D + \Delta V_2'D = P_1 + V_1D_o + \Delta V_1'D_o + m_1 \quad (1)$$

$$P_2 + V_2D_o + \Delta V_2''D_o = P_1 + V_1D + \Delta V_1''D + m_2 \quad (2)$$

Subtracting equation (2) from equation (1) and rearranging gives

$$(V_1 + V_2)(D - D_o) = (m_1 - m_2) + (\Delta V_1'D_o - \Delta V_1''D) - (\Delta V_2'D - \Delta V_2''D_o)$$

Since this method is used only for the measurement of small differences in density, where $D - D_o < 0.001$, the equation can be written

$$D - D_o = \frac{(m_1 - m_2) + D_o[(\Delta V_1' - \Delta V_1'') - (\Delta V_2' - \Delta V_2'')]}{V_1 + V_2} \quad (3)$$

For most of the measurements made during this investigation a bulb volume of about 50 cm³ and a capillary diameter of about 0.1 cm were found suitable. For a precision in $D - D_o$ of one part in one million with pycnometers of this size, a convenient distribution of precision in the measurements is:

1. The temperature of the stirred water in the thermostat is held constant to within 0.01° , for with extreme fluctuations of the thermostat temperature less than 0.01° , the lag in the pycnometers is sufficient to maintain them constant to within 0.002° .

2. The capillary heights are read to 0.001 cm.

3. The weighings are made to 0.03 mg.

It is advantageous to adjust the capillary heights to make the correction $(\Delta V_1' - \Delta V_1'') - (\Delta V_2' - \Delta V_2'')$ small and thus avoid the necessity for a very precise calibration of the capillaries. It is to be noted that:

1. The dry weights of the pycnometers are not required.

2. The pycnometers are so closely alike that effects of varying humidity are balanced.

3. The temperature of the thermostat need not be accurately known but should be constant and uniform while the pycnometers are in the bath.

4. The effect of barometric and hydrostatic pressure on the capillary heights is balanced.

5. The (negligible) evaporation past the ground glass stoppers is balanced.

6. The silica bulbs show no measurable temperature hysteresis over the temperature range involved.

7. The small effect of dissolved air is balanced and it is not necessary to prepare air-free water.

8. The correction for air buoyancy affects only the difference of the differences, $(\Delta V_1' - \Delta V_1'') - (\Delta V_2' - \Delta V_2'')$, in the capillary volumes and with proper adjustment of the heights is negligible.

9. No unusual apparatus or particular skill is required for measurements precise to 1 part in 1 million.

The data of a typical experiment, the determination of $D - D_0$ for a sample of water prepared from Kernite, native borax tetrahydrate, are shown in tables 1 and 2.

TABLE 1.—*Cathetometer readings for the first filling*

No. 1 filled with normal water			No. 2 filled with the sample water		
Meniscus	Graduation mark	Capillary height	Meniscus	Graduation mark	Capillary height
75.651	70.866	4.785	75.774	70.658	5.116
75.656	70.869	4.787	75.777	70.658	5.119
75.650	70.867	4.783	75.773	70.657	5.116
75.654	70.868	4.786	75.773	70.657	5.116
Average.....		4.785 cm	Average.....		5.117 cm
Avg deviation.....		0.0013	Avg deviation.....		0.0013

TABLE 2.—*Cathetometer readings for the second filling*

No. 1 filled with the sample water			No. 2 filled with normal water		
Meniscus	Graduation mark	Capillary height	Meniscus	Graduation mark	Capillary height
75.439	70.864	4.575	75.249	70.653	4.596
75.438	70.865	4.573	75.248	70.656	4.592
75.440	70.864	4.576	75.249	70.653	4.596
75.438	70.864	4.574	75.249	70.654	4.595
Average.....		4.575 cm	Average.....		4.595 cm
Avg deviation.....		0.0010	Avg deviation.....		0.0013

The calculation of $D - D_o$ is made as follows:

Difference in weight after first filling, $m_1 = 3.79463$

Difference in weight after second filling, $m_2 = 3.79111$

$$m_1 - m_2 = 0.00352 \text{ g}$$

$$(\Delta V_1' - \Delta V_1'') = (4.785 - 4.575)0.00843 = 0.00177$$

$$(\Delta V_2' - \Delta V_2'') = (5.117 - 4.595)0.00861 = 0.00449$$

$$(\Delta V_1' - \Delta V_1'') - (\Delta V_2' - \Delta V_2'') = -0.00272 \text{ cm}^3$$

$$-0.00272 D_o = -0.00271 \text{ g}$$

$$D - D_o = (0.00352 - 0.00271)/112$$

$$= 0.000,0072 \text{ g/cm}^3, \text{ or } 7.2 \text{ ppm.}$$

III. THE SAMPLES OF WATER EXAMINED

The water obtained or prepared from each source, after appropriate preliminary treatment such as distillation for the removal of salts or refluxing with strong alkaline permanganate to destroy large amounts of organic matter, was purified by (1) distillation from alkaline permanganate, (2) distillation from dilute phosphoric acid, (3) simple distillation, rejecting first and last portions in each distillation. Laboratory distilled water, used as the normal water for comparison, was subjected to the same treatment. The source of this water was the Potomac river. Lamb and Lee,⁹ who have made precise measurements of the density of normal water purified by methods similar to those used by us, found that the densities of different lots of such water differed by less than one part per million.

A description of the samples and the experimental results follow. Where it is stated that a sample was found to be of normal density, it is meant that the density is not different by more than one part in one million from that of normal water at 25 C.

1. Water prepared from cows' milk had the same density as normal water.

2. Water prepared from slaughter-house blood was found to be of normal density.

3. Thirty liters of laboratory distilled water were reduced to 225 ml by transpiration through growing plants (cowpeas and willows). After purification, this final residue had the density of normal water. In a second experiment involving practically the same volume change but at a greater transpiration rate, with the growth of willows, no difference was found.

4. A sample of brine from approximately the 60-foot level of Searles Lake was supplied by the American Potash & Chemical Corporation, Trona, Calif. Searles Lake is subject to spring and winter rains so that no large effect due to evaporation was expected. No density difference was found.

5. Dr. Bernard N. Moore supplied a sample of water from the Salton Sea, collected about 5 miles south of Travertine Point. This water was found to be of normal density.

6. The Intermountain Experiment Station of the Bureau of Mines, Salt Lake City, Utah, supplied a sample of water from Great Salt Lake collected at a point where it was not diluted by the immediate entry of fresh water. Two determinations with intermediate redistil-

⁹ A. B. Lamb and R. E. Lee, *Am. Chem. Soc.*, vol. 35, p. 1681, 1913.

lation gave values of $D-D_0$ equal to 2 and 3.4 parts per million, an average of 2.7 ± 0.7 ppm.

7. Surface water from the Dead Sea collected at a point 5 or 6 miles from the mouth of the River Jordan was obtained through the American Consular Service, Jerusalem, Palestine. The results of three measurements were 1.5, 2.2, and 2.7, with an average of 2.1 ± 0.5 ppm. for $D-D_0$. The water was redistilled between the second and third measurements.

8. Dr. Paul Bartsch supplied a sample of ocean water taken 3,000 meters below the surface, (lat. $19^{\circ}13' N.$, long. $65^{\circ}16' W.$). It had a salinity of 34.88 parts per thousand, as determined by Dr. R. C. Wells. This water was found to be denser than normal water by 2 ppm.¹⁰

9. Two species of native borax crystals, kernite, the tetrahydrate ("rasorite"), and the decahydrate ("tincal") were obtained from the Pacific Coast Borax Co., Kramer Station, Hinkley, Calif. The results of two measurements, with intermediate distillation, on the water obtained from a single large crystal of kernite were 7.2 and 6.6 ppm heavier than normal water. To check this interesting discovery, water from a different lot of smaller broken crystals of kernite was measured and found to be 6.7 ppm heavier than normal. The average of the three determinations is 6.8 ± 0.2 ppm. The water from the "tincal" crystals however, exhibited no difference in density from normal water.

10. Water prepared by M. Frandsen of this laboratory by combustion of a sample of dry anthracite coal was found to be of normal density.

11. Water prepared by Frandsen by burning natural propane with commercial oxygen was also found to be of normal density.

12. Water prepared by M. Frandsen, from the sap content of branches and leaves of a young willow tree, was found to be 2.8 ppm heavier than normal water (two determinations with intermediate distillation, 2.8 and 2.8).

13. Water prepared by M. Frandsen, by combustion (in dry oxygen) of the dry wood and leaves from the above experiment, was found to be 5.4 ppm heavier than normal water (two determinations, 5.5 and 5.2).

14. The possibility of fractionation by a selective action of iron on dilute acid was tested by examining a sample of water prepared from pickling acid, furnished by John A. Roebling's Sons Co., Roebling, N.J. No effect was found.

15. Any process involving the electrolytic separation of hydrogen from an aqueous solution would be expected to increase the density of the residual water. Newell and Ficklen¹¹ have reported density increases of from 20 to 640 parts per million in samples of water from nine chromium plating baths. As a matter of interest, water from two chromium plating baths in use at the United States Bureau of Engraving and Printing was tested. One sample was found to be heavier than normal water by 2 and the other by 5 parts per million.

¹⁰ The first determination on the ocean water indicated a density excess of not more than 1 ppm. Having learned that Gilfillan (Jour. Amer. Chem. Soc., March 1934) working at O C had found a density excess of 2 ppm for ocean water, we repeated our measurements and obtained results which confirmed his determination.

¹¹ I. L. Newell and J. B. Ficklen, Jour. Am. Chem. Soc., vol. 55, p. 2167, 1933.

IV. DISCUSSION

In this investigation the only natural sources of water found to have an isotopic composition differing appreciably from normal were (1) those which have been subjected to evaporation over many centuries, and (2) the sap water of a willow tree and the water obtained by burning the dry wood. The water of crystallization of native borax (kernite) probably represents almost the last portion of water left from the complete evaporation of an inland sea. The existence of a natural source of hydrogen having an isotopic ratio differing from normal by more than 0.0001 appears improbable.

V. SUMMARY

A search has been made for natural water having an isotopic composition differing from normal. Purified samples of water prepared from milk, blood, the residue from the transpiration and growth of plants, sap from a willow tree, brine from Searles Lake, the Salton Sea, Great Salt Lake, the Dead Sea, ocean water, water of crystallization of native borax, water from the combustion of anthracite coal, of willow wood, and of propane, have been tested by a differential density method, which is described. Water from the ocean, from Great Salt Lake, and from the Dead Sea is heavier than normal water by two parts per million. The water of crystallization of native borax tetrahydrate (kernite) is heavier by seven parts per million. The sap water from a young willow tree was heavier than normal water by 2.8 and the water produced by burning the dry wood was heavier by 5.4 parts per million. No differences were found for the other samples.

WASHINGTON, January 15, 1934.