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30 January 1961

Standard for Reporting Concentrations of Deuterium and Oxygen-18 in Natural Waters

Abstract. A standard, based on the set of ocean water samples used by Epstein and Mayeda to obtain a reference standard for oxygen-18 data, but defined relative to the National Bureau of Standards isotopic reference water sample, is proposed for reporting both deuterium and oxygen-18 variations in natural waters relative to the same water. The range of absolute concentrations of both isotopes in meteoric waters is discussed.

In a previous report (*1*) the relationship between deuterium and oxygen-18 variations in meteoric waters throughout the world was shown. Many laboratories are measuring one or the other of these isotopes in various types of natural waters, and those workers studying O^{18} variations have more or less adopted, as a reference level for reporting enrichments, the "average ocean water" found by Epstein and Mayeda in the first precise work on O^{18}/O^{16} ratios in natural waters (*2*).

Deuterium analyses, however, occur in the literature relative to at least six different "working tap water" standards. In the previous report (*1*) the data presented for both isotopes showed how important it is to obtain data on both D and O^{18} variations in the same water samples, and it therefore seems that a common deuterium standard, preferably the same water as the O^{18} standard, should be adopted for consistency. The data shown previously (*1*) indicate that tap waters from various countries could easily differ by as much as 15 percent in the D/H ratio, and for many reasons it appears to be desirable to have an ocean water standard for reporting geochemical data.

For this purpose, the same set of ocean waters chosen by Epstein and Mayeda to give their "average ocean water" for O^{18} data was analyzed for the D/H ratio along with the samples described previously (*1*). These waters, taken from depths of 500 to 2000 m in open ocean areas where no direct dilution by continental runoff or glacial melt water could occur, were grouped by Atlantic, Pacific, and Indian Ocean samples, and equal volume composites were made from each set and analyzed relative to the laboratory working standard.

No single sample of "average ocean water" which could be circulated widely for analysis actually exists. Oxygen-18 data have generally been tied to the Epstein-Mayeda scale by analysis of various carbonate samples, requiring special techniques for preparation of 100 percent H_3PO_4, and so on. However, in the course of the present work it was found that both the D and O^{18} data on the set of ocean waters analyzed could be very simply specified in terms of the National Bureau of Standards isotopic reference sample No. 1, a distilled water sample of large volume intended for cross-check circulation to mass spectrometric laboratories (*3*). After consultation with various laboratories it was decided to define a "standard mean ocean water" (SMOW) in terms of the National Bureau of Standards reference sample 1, such that

$$D/H\ (\mathrm{SMOW}) \equiv 1.050\ D/H\ (\mathrm{NBS\text{-}1})$$
$$O^{18}/O^{16}\ (\mathrm{SMOW}) \equiv 1.008\ O^{18}/O^{16}\ (\mathrm{NBS\text{-}1})$$

and to report isotopic data for both isotopes as per mil enrichments relative to the defined SMOW (*4*), thus tying the standard to a sample readily available for world-wide distribution.

The isotopic analyses of the composite ocean water sets made from the samples used by Epstein and Mayeda are shown in Table 1, in which the O^{18} data are averages for each set taken from their paper (*2*) with slight corrections later found necessary (*5*). The deuterium analyses are those I made, and all data have been calculated relative to SMOW, so that

$$\delta = [(R_{\mathrm{sample}}/R_{\mathrm{SMOW}}) - 1] \times 1000$$

is the per millage enrichment in either isotopic ratio *R*, relative to SMOW. The analytical precision has been described (*1*).

These data indicate that, within the limits of analytical precision and geographical variation, SMOW as defined above provides a consistent and convenient zero reference level for reporting isotopic enrichments and is an adequate average for the Epstein-Mayeda O^{18} data on "average ocean water." Clearly it will be a long time before the actual mean ocean composition is known; the designation "standard" indicates that SMOW is an arbitrary mean value based on the Epstein-Mayeda oxygen scale but defined in terms of an actual water reference standard, the NBS-1. The δO^{18} value of the Chicago PDB-1 carbonate standard (CO_2 from reaction with 100 percent H_3PO_4 at 25°C) is +0.22 per mil on the SMOW scale (*6*).

Table 1. D/H and O^{18}/O^{16} enrichments of the Epstein-Mayeda "average ocean water" set and other samples, in per millage relative to SMOW. Numbers in parentheses after ocean names indicate number of samples in each set.

Sample	δD (per mil)	δO^{18} (per mil)
Atlantic (6)	− 0.7	+ 0.14
Pacific (11)	+ 0.9	+ 0.04
Indian (2)	+ 0.1	− 0.07
NBS-1	− 47.60	− 7.94
NBS-1A	−183.3	−24.33

Table 1 also shows the NBS-1 data as defined versus SMOW, and the value obtained for the NBS-1A secondary water standard. The D/H enrichment of NBS-1A relative to NBS-1 is found to be −142.5 ± 2.5 per mil (*3*). Horibe and Kobayakawa found a value of −141.3 ± 2.3 per mil (*3, 7*) in good agreement. Their data yield an absolute D concentration for SMOW of 157 ± 1 atomic parts per million (ppma), based on direct calibration with enriched standards. I analyzed five water samples which had been measured previously for absolute D content by Kirshenbaum (*8*); this comparison gives a D concentration of 159 ± 2 ppma for SMOW. We may therefore take the absolute D content of SMOW as 158 ± 2 ppma, corresponding to a D/H ratio of 1/6328.

Absolute O^{18} concentrations, based on data obtained by Nier and me, have been given for standards including the NBS-1 water (*5*). From these data the O^{18} concentration in SMOW is found to be 1989.5 ± 2.5 ppma, corresponding to an O^{18}/O^{16} ratio of $(1993.4 \pm 2.5) \times 10^{-6}$.

In the previous paper (*1*) the relation between δD and δO^{18}, expressed as per millage enrichments relative to SMOW, was found to be linear in the majority of meteoric waters, obeying the equation

$$\delta D = 8\,\delta O^{18} + 10$$

By using the absolute concentrations for SMOW as given above, the atom fractions of D and O^{18} are found to be related in meteoric waters by the expression

$$X_D = 0.6359\,X_O - 1105.6$$

when the atom fractions are given in atomic parts per million. This relation is approximately obeyed by ocean waters also, but does not hold for lakes having high ratios of evaporation to outflow.

The total variations in meteoric waters are about 360 per mil for deuterium and about 48 per mil for oxygen-18, relative to the concentrations in SMOW. This variation in D content corresponds to a variation of about 6 ppm in density, while the O^{18} variation corresponds to about 11 ppm in density. Thus the total density variation in meteoric waters produced by these isotopes is about 17 ppm, of which about 65 percent is due to O^{18}. The atomic weight variations in hydrogen and oxygen in these waters are about 5.7×10^{-5} and 1.9×10^{-4} atomic mass units respectively.

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18 January 1961

Effect of Low Concentrations of Carbon Dioxide on Photosynthesis Rates of Two Races of Oxyria

Abstract. Alpine plants of *Oxyria digyna* have higher apparent photosynthesis rates at various carbon dioxide concentrations than arctic, sea-level plants of the same species. The ability to utilize carbon dioxide effectively at low concentrations may be involved in the survival of plants at high elevations.

The volumetric concentration of atmospheric carbon dioxide in parts per million varies little with altitude (*1*). On the other hand, the partial pressure of CO_2 in the atmosphere decreases with altitude and with lowered total atmospheric pressure. As Decker (*2*) has pointed out, diffusion of CO_2 into a leaf is a function of CO_2 pressure. This has led to the suggestion (*2, 3*) that the altitudinal gradient of CO_2 pressure may be an important factor in the zonation of plant species on high mountain ranges.

Since any possible effect of low CO_2 pressure on alpine plant metabolism would be difficult to detect in the complex of environmental factors operating under field conditions, it is necessary to test this hypothesis under controlled conditions. In the laboratory, Decker (*4*) measured the effects of different CO_2 concentrations (in parts per million) on apparent photosynthesis rates of plants from a lowland (elevation, 150 feet) clone of *Mimulus cardinalis* Dougl. and of a hybrid between this clone and a high elevation (10,700 feet) form of *M. lewisii* Pursh from the Sierra Nevada Range of California. The results of his experiments showed no consistent differences between the two clones in apparent photosynthesis rates at different CO_2 concentrations and, thus, yielded no support for the hypothesis.

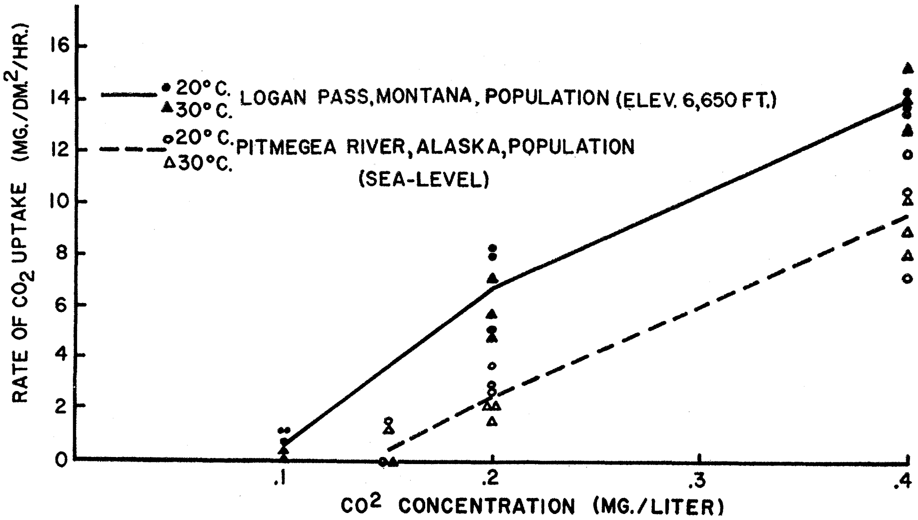

Fig. 1. Apparent photosynthesis rates of *Oxyria* leaves at low CO_2 concentrations. Points are averages of two to four determinations on a single plant.

In our experiment we used plants of *Oxyria digyna* (L.) Hill, a wide-ranging, arctic-alpine herbaceous species whose photosynthesis rates are relatively well known (*5, 6*). The sea-level race was from the northern coastal plain of Alaska at the mouth of the Pitmegea River (68°56′N), while the alpine race was from Logan Pass, Montana (48°42′), at an elevation of 2027 m. The plants were all the same age (4 months), grown from seed (*7*) under controlled conditions of continuous photoperiod and alternating 12.5°C and 1.5°C thermoperiods of 12 hours each. Apparent photosynthesis rates were measured with an infrared gas analyzer by the techniques described by Mooney and Billings (*6*). Two to four determinations were made at 20° and at 30°C on single attached leaves of three plants from each race under 1850 ft-ca of light. As in Decker's method, the plant was allowed to reduce the CO_2 in the dry air system from above 0.4 mg/lit. down to the compensation concentration, which was usually between 0.1 and 0.2 mg/lit. Results are expressed as averages of milligrams of CO_2 uptake per square decimeter of one leaf surface per hour; they are shown in Fig. 1.

Throughout the entire range of CO_2 concentrations at which apparent photosynthesis was measured, the plants from the alpine race were clearly more effective in fixing CO_2. Moreover, the compensation concentrations of the alpine race were not reached until near or below 0.1 mg of CO_2 per liter. None of the plants of the sea-level race had any apparent photosynthesis at this low CO_2 concentration, which approximates the CO_2 tension at an altitude of 12,200 m. Even at a concentration of 0.4 mg/lit., which approximates the CO_2 tension at 3000 m, plants of the sea-level race were only about 70 percent as effective photosynthetically as those of the alpine race.

While there was a slight tendency for plants of both races to be more effective at 20° than at 30°C, there was no clear-cut effect of temperature on apparent photosynthesis and compensation concentration as observed by Decker in *Mimulus*.

The data presented here appear to give substance to the hypothesis that low CO_2 pressures may limit the upward distribution of plants of certain species and races on high mountain ranges (*8*).

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8. This work has been supported as a part of a grant (G 3832) from the National Science Foundation, Environmental Biology Program, for which we express grateful appreciation.

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