Pure & Appl. Chem., Vol. 66, No. 2, pp. 273–276, 1994.
Printed in Great Britain.

INTERNATIONAL UNION OF PURE
AND APPLIED CHEMISTRY

INORGANIC CHEMISTRY DIVISION
COMMISSION ON ATOMIC WEIGHTS AND
ISOTOPIC ABUNDANCES*

REPORTING OF STABLE HYDROGEN, CARBON, AND OXYGEN ISOTOPIC ABUNDANCES

(Technical Report)

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Reporting of stable hydrogen, carbon, and oxygen isotopic abundances (Technical Report)

Abstract—To eliminate possible confusion in the reporting of isotopic abundances on non-corresponding scales, the Commission on Atomic Weights and Isotopic Abundances recommended at the 37th General Assembly at Lisbon, Portugal that (i) $^{2}H/^{1}H$ relative ratios of all substances be expressed relative to VSMOW (Vienna Standard Mean Ocean Water) on a scale such that $^{2}H/^{1}H$ of SLAP (Standard Light Antarctic Precipitation) is 0.572 times that of VSMOW, (ii) $^{13}C/^{12}C$ relative ratios of all substances be expressed relative to VPDB (Vienna Peedee belemnite) on a scale such that $^{13}C/^{12}C$ of NBS 19 carbonate is 1.00195 times that of VPDB, and (iii) $^{18}O/^{16}O$ ratios of all substances be expressed relative to either VSMOW or VPDB on scales such that $^{18}O/^{16}O$ of SLAP is 0.9445 times that of VSMOW.

COMMENT

Abundances of stable hydrogen, carbon, and oxygen isotopes in geochemical and environmental studies are generally expressed in parts per thousand (‰ or per mil) difference from a standard. Thus, for the oxygen isotopic composition of a sample x, we have

$$\delta^{18}O \text{ (in ‰)} = \left[\frac{\left(\frac{^{18}O}{^{16}O} \right)_x}{\left(\frac{^{18}O}{^{16}O} \right)_{Standard}} - 1 \right] 1000.$$

The standard may be an actual reference material or a hypothetical material whose isotopic abundance is set by assigning an isotopic composition to an existing reference material.

Irregularities concerning the choice of the standard have arisen for hydrogen, carbon, and oxygen isotopes (refs. 1 & 2). Friedman and O'Neil (ref. 1) point out that some laboratories are "tied" to each other by acceptance of the δ values of certain comparison materials. The situation for the SMOW (Standard Mean Ocean Water) standard has become increasingly aggravated. The SMOW standard was originally a hypothetical water sample with abundances of stable hydrogen and oxygen isotopes similar to those of average ocean water (ref. 3). Its abundances of stable hydrogen and oxygen isotopes were defined in terms of NBS 1 water distributed by the U.S. National Bureau of Standards (now National Institute of Standards and Technology):

$$(^{2}H/^{1}H)_{SMOW} = 1.050(^{2}H/^{1}H)_{NBS\ 1}$$

and

$$(^{18}O/^{16}O)_{SMOW} = 1.008(^{18}O/^{16}O)_{NBS\ 1}.$$

Subsequently, H. Taylor and S. Epstein of the California Institute of Technology used a hypothetical standard that they also called SMOW and defined it by assigning a $\delta^{18}O$ value of +15.5‰ to their laboratory reference material, a sample of Potsdam Sandstone (ref. 1). Thus, their oxygen isotope scale is defined by

$$\delta^{18}O_{\text{Potsdam Sandstone/SMOW}} = +15.5‰.$$

‰ = parts per thousand

Additionally, the International Atomic Energy Agency (IAEA) distributed a water sample they named SMOW. This sample was near (but not the same) in isotopic composition to the original SMOW defined in terms of NBS 1 water. Thus, there are three independent usages of SMOW that we observe today, leading to three differing $^2H/^1H$ and $^{18}O/^{16}O$ abundances with the same name. The IAEA recognized the dilemma of naming a reference water as SMOW and subsequently changed the name to VSMOW (Vienna Standard Mean Ocean Water). Furthermore, they recommended that abundances of hydrogen and oxygen isotopes of all materials (except marine carbonates) be expressed using VSMOW rather than SMOW (refs. 2, 4 & 5). However, these recommendations have not received wide distribution and may be unknown to numerous producers of data on abundances of oxygen and stable hydrogen isotopes, particularly in the rapidly expanding fields of environmental and climate studies.

A second standard is used for reporting abundances of oxygen isotopes of marine carbonates and is named PDB (Peedee belemnite). Because the supply of this material is exhausted, some laboratories have "tied" themselves to each other by adopting $\delta^{18}O$ values of various carbonate reference materials. The IAEA recognized the potentially serious problem that oxygen isotopic scales in different laboratories might not correspond. They recommended that abundances of oxygen isotopes of carbonates be expressed relative to VPDB (Vienna Peedee belemnite) by adopting a $\delta^{18}O$ consensus value of $-2.2‰$ for NBS 19 carbonate relative to VPDB at a meeting in 1983 in Vienna (ref. 2). Thus,

$$\delta^{18}O_{\text{NBS 19/VPDB}} \equiv -2.2‰.$$

This satisfactory solution has had only limited distribution and is seldom used.

Because PDB is also the standard for carbon, a similar problem exists for reporting abundances of carbon isotopes. The IAEA provided a solution to reporting of carbon isotopic data on non-corresponding scales by recommending that carbon isotopic results of all materials be expressed relative to VPDB by adopting a $\delta^{13}C$ value of $+1.95‰$ for NBS 19 carbonate relative to VPDB:

$$\delta^{13}C_{\text{NBS 19/VPDB}} \equiv +1.95‰.$$

This value was adopted by consensus (ref. 2). Again, this viable solution has had little distribution and is seldom employed.

The δ^2H and $\delta^{18}O$ values of VSMOW lie closer to the upper end of the range of abundances of ^2H and ^{18}O of naturally occurring materials. By recommending δ^2H and $\delta^{18}O$ values of a reference material close to the lower end of the range of abundances of ^2H and ^{18}O of naturally occurring materials, the IAEA effectively normalized these scales. The IAEA selected a water sample from Antarctica and gave it the name SLAP (Standard Light Antarctic Precipitation). Three absolute isotope-ratio measurements of VSMOW and SLAP (refs. 6, 7 & 8) suggested a δ^2H value of $-428‰$ for SLAP relative to VSMOW. The $^{18}O/^{16}O$ ratio of SLAP has not been determined and a consensus $\delta^{18}O$ value of $-55.5‰$ of SLAP relative to VSMOW was adopted in 1976 (ref. 4). Also agreed to was the value $\delta^2H_{\text{SLAP/VSMOW}} \equiv -428‰$. The result of normalization was that coherence between δ^2H and $\delta^{18}O$ results reported by different laboratories increased dramatically (ref. 4).

The Commission on Atomic Weights and Isotopic Abundances at the 37th General Assembly in Lisbon, Portugal, (ref. 9) discussed the reporting of isotopic abundances and recommended that:

(1) δ^2H values of all hydrogen-bearing substances be expressed relative to VSMOW on a scale such that $\delta^2H_{\text{SLAP/VSMOW}} \equiv -428‰$;

(2) $\delta^{13}C$ values of all carbon-bearing substances be expressed relative to VPDB on a scale such that $\delta^{13}C_{\text{NBS 19/VPDB}} \equiv +1.95‰$;

(3) $\delta^{18}O$ values of all oxygen-bearing materials be expressed relative to VSMOW or relative to VPDB, defined by $\delta^{18}O_{\text{NBS 19/VPDB}} \equiv -2.2‰$, on a scale such that $\delta^{18}O_{\text{SLAP/VSMOW}} \equiv -55.5‰$; and

(4) reporting of isotopic abundances relative to SMOW and PDB be discontinued.

The reader should remember that δ values are not additive when converting from one scale to another, but are determined by the relation (*e.g.*, a relation for oxygen)

$$\delta^{18}O_{a/VSMOW} = \delta^{18}O_{a/b} + \delta^{18}O_{b/VSMOW} + 10^{-3}\delta^{18}O_{a/b}\delta^{18}O_{b/VSMOW}.$$

This relation should be kept in mind in the case of hydrogen where δ values of several hundred occur; thus, the last term in the equation above may reach a value of several tens.

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APPENDIX A; SOURCES OF REFERENCE MATERIALS

Reference materials VSMOW, SLAP, and NBS 19 may be obtained from:

Standard Reference Materials Program
Room 204, Building 202
National Institute of Standards and Technology
Gaithersburg, Maryland 20899
USA

Request RM8535 for VSMOW water.
Request RM8537 for SLAP water.
Request RM8544 for NBS 19 carbonate.

or

International Atomic Energy Agency
Section of Isotope Hydrology
P.O. Box 100
1400 Vienna, Austria