National Institute of Standards & Technology

Report of Investigation

Reference Material 8535a

VSMOW2 Vienna Standard Mean Ocean Water 2

(Hydrogen and Oxygen Isotopes in Water)

This Reference Material (RM) is an international measurement standard [1] that defines the zero of the VSMOW-SLAP (Vienna Standard Mean Ocean Water-Standard Light Antarctic Precipitation) δ-scales for isotope-number ratios of hydrogen (H) and oxygen (O). The equivalent name for this RM, as used by the International Atomic Energy Agency (IAEA) and the U.S. Geological Survey (USGS), is VSMOW2. A unit of RM 8535a consists of one ampoule containing approximately 20 mL of water.

Table 1. Reference Values for the Relative H and O Isotope-Number Ratios of RM 8535a

IAEA Name		Expanded Uncertainty		Expanded Uncertainty
	$10^3\ \delta\,^2\mathrm{H}_{\text{VSMOW-SLAP}}$	$10^3\ \delta\,^2\mathrm{H}_{\text{VSMOW-SLAP}}$	$10^3\ \delta\,^{18}\mathrm{O}_{\text{VSMOW-SLAP}}$	$10^3\ \delta\,^{18}\mathrm{O}_{\text{VSMOW-SLAP}}$
VSMOW2	0.0	0.3	0.00	0.02

Reference Values for the Relative Difference in Isotope-Number Ratios: The differences in measured isotope-number ratios of stable hydrogen isotopes [$N(^2\mathrm{H})/N(^1\mathrm{H})$] and stable oxygen isotopes [$N(^{18}\mathrm{O})/N(^{16}\mathrm{O})$] are reported as $\delta^2\mathrm{H}$ and $\delta^{18}\mathrm{O}$ values, respectively. The relative difference in isotope-number ratios for hydrogen and oxygen are defined as:

$$\delta^2\mathrm{H} = ([N\,(^2\mathrm{H})_{\text{sample}}\,/N\,(^1\mathrm{H})_{\text{sample}}] - [N\,(^2\mathrm{H})_{\text{VSMOW-SLAP}}\,/N\,(^1\mathrm{H})_{\text{VSMOW-SLAP}}]) \,/\, [N\,(^2\mathrm{H})_{\text{VSMOW-SLAP}}\,/N\,(^2\mathrm{H})_{\text{VSMOW-SLAP}}]$$

$$\delta^{18}\mathrm{O} = ([N\,(^{18}\mathrm{O})_{\text{sample}}\,/N\,(^{16}\mathrm{O})_{\text{sample}}] - [N\,(^{18}\mathrm{O})_{\text{VSMOW-SLAP}}\,/N\,(^{16}\mathrm{O})_{\text{VSMOW-SLAP}}]) \,/\, [N\,(^{18}\mathrm{O})_{\text{VSMOW-SLAP}}\,/N\,(^{16}\mathrm{O})_{\text{VSMOW-SLAP}}]$$

VSMOW-SLAP refers to the Vienna SMOW-SLAP δ-scales, which are defined by assigning $\delta^2\mathrm{H}$ and $\delta^{18}\mathrm{O}$ values of 0 ‰ to VSMOW2 (RM 8535a) and values of –427.5 ‰ ($\delta^2\mathrm{H}$) and –55.50 ‰ ($\delta^{18}\mathrm{O}$) to measurements of SLAP2 (RM 8537a) for the purpose of normalizing stable hydrogen and oxygen isotope measurements (see "Normalization") [2-4].

Expiration of Value Assignment: **RM 8535a** is valid, within the measurement uncertainty specified, until **31 December 2020**, provided the RM is handled in accordance with instructions given in this Report of Investigation (see "Instructions for Handling, Storage, and Use"). The reference values are nullified if the RM is damaged, contaminated, or otherwise modified.

Maintenance of RM: NIST will monitor this RM over the period of its validity. If substantive technical changes occur that affect the value assignment before the expiration of this report, NIST will notify the purchaser. Registration (see attached sheet or register online) will facilitate notification.

Technical aspects involved in the issuance of this RM were coordinated through the NIST Chemical Sciences Division by R.D. Vocke, Jr.

Support aspects involved in the issuance of this RM were coordinated through the NIST Office of Reference Materials.

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INSTRUCTIONS FOR HANDLING, STORAGE, AND USE

Intended Use: The international measurement standard VSMOW2 is a calibration reference material that, when used together with SLAP2 (RM 8537a), provides water standards with reference values of their relative difference in $^2H/^1H$ and $^{18}O/^{16}O$ isotope-number ratios that define the VSMOW–SLAP δ-scales. A third reference material, GISP (Greenland Ice Sheet Precipitation, RM 8536), is also available to check the calibration of internal laboratory standards when using VSMOW2 and SLAP2. These three materials are available from the International Atomic Energy Agency (IAEA, Vienna, Austria) and from the National Institute of Standards and Technology (NIST, Gaithersburg, MD).

Distribution: The distribution of RM 8535a (VSMOW2) is limited to one unit per year. As an international measurement standard, this RM, together with SLAP2 (RM 8537a), is intended to calibrate working standards and allow investigators to produce δ^2H and $\delta^{18}O$ data that are comparable worldwide [5,6] on the VSMOW–SLAP scale. Users are strongly advised to prepare their own standards for daily use and calibrate those standards against these international reference materials.

Storage and Stability: The original unopened ampoules of RM 8535a should be stored at ambient temperature in the dark. The unused fractions of this RM should be discarded immediately after opening due to the strong possibility of evaporative losses causing significant isotope fractionation. Furthermore, aliquots of this RM should not be used for repeated calibrations by repeated stable isotope measurements using water/CO_2 equilibration devices over multiple days due to isotopic exchange with the applied gas and resulting shift of the isotopic composition of the material during the preparation process. The reference values in this Report of Investigation apply only to freshly opened ampoules.

Absolute Isotope-Number Ratios in VSMOW2: No absolute isotope-number ratios have been determined for VSMOW2. As the isotopic composition of this material is very close to that of VSMOW (RM 8535), the published absolute isotope-number ratios of RM 8535 provide a good estimate of the absolute isotope-number ratios in VSMOW2 [7-11]. These values are listed in Table 2 of the Reports of Investigation for Reference Materials 8535, 8536, and 8537 [12]. The isotopic values are the same as those recommended by the Bureau International de Poids et Mesures (BIPM) for isotopic corrections to the definition of the kelvin temperature scale in 2005 [13].

Information Values: The $\delta^{17}O$ value of VSMOW is zero by consensus, just as its $\delta^{18}O$ value is zero by consensus. The $\delta^{17}O$ value of VSMOW2 was measured and compared with that of VSMOW [14] and is identical within an uncertainty of about ± 0.03 ‰. Additional measurements were conducted by Y. Lin at the University of Chicago (Chicago, Illinois, USA) in 2007 comparing VSMOW2 and SLAP2 with VSMOW and SLAP, respectively. These measurements confirmed their equivalence within an uncertainty of about ± 0.05 ‰ for both cases [15].

The tritium activity concentration of VSMOW2, determined at the IAEA by direct gas counting, was 3.5 TU $\pm$ 1.0 TU (tritium unit) on 06 July 2007. The reported uncertainty is one standard deviation. Information values cannot be used to establish metrological traceability.

Sample Preparation: The decision to produce a new international measurement standard, VSMOW2, to replace VSMOW came from a recommendation of a Consultants Group Meeting convened by the IAEA in December, 1996. VSMOW2 was prepared at the IAEA Isotope Hydrology Laboratory in 1999 from three fresh water samples: one from Lake Bracciano located near Rome, Italy (R. Gonfianini, G.-M. Zuppi), another from Lake Galilee, Israel (E. Adar), and a third from a well located near Cairo, Egypt (F. Hussein). These raw water samples were selected because they were close to the isotopic composition of VSMOW and could be mixed in appropriate proportions to give an isotopic composition nearly identical to the original VSMOW. The δ^2H of one of these raw materials had to be adjusted by about 6 ‰ to allow the production of about 300 liters of VSMOW2. This adjustment was performed via a modified platinum catalytic exchange reaction using the diffusive exchange of hydrogen gas between membrane-separated compartments containing the raw water and deuterated water. This approach avoided changing the $\delta^{17}O$ and $\delta^{18}O$ values of the raw material. The final mixing was performed after measuring the isotopic composition of the raw water in five selected laboratories: IAEA Isotope Hydrology Laboratory, Vienna, Austria (M. Gröning); USGS Reston Stable Isotope Laboratory, Reston, Virginia, USA (T.B. Coplen); Center for Isotope Research, Groningen, Netherlands (H.A.J. Meijer); GFZ Isotope Hydrology Laboratory, Neuherberg, Germany (W. Stichler); and University of East Anglia Isotope Hydrology Laboratory, U.K. (P. Dennis). Altogether, 300 liters of VSMOW2 were prepared by gravimetrically mixing the three water samples in a specially constructed storage container. Initially 5000 glass ampoules were filled with 20 mL of VSMOW2 each. The remaining portion of about 200 liters remains in the original container for ampouling when needed.

Homogeneity: A random selection of 27 ampoules was taken from the first production run of 5000 ampoules to assess the homogeneity of the mixed waters and any effects resulting from the filling procedure. Multiple

measurements were taken of each ampoule over one to two days, and the resultant data were used to evaluate the analytical reproducibility. The differences between the average of all the data and the individual ampoule means were used to estimate the degree of homogeneity within the sampled population. The between-ampoule variability was also calculated by single-factor ANOVA analysis [16,17]. The homogeneity uncertainty contribution of the mixed waters to the total uncertainty of measurements between ampoules was found to be negligible, less than 0.004 ‰ for $\delta^{18}O$ and less than 0.07 ‰ for δ^2H. The largest uncertainty component in the uncertainty budget was a consequence of the limited number of measurements that could be made on water from any one ampoule.

Characterization and Value Assignment: The δ^2H and $\delta^{18}O$ reference values for VSMOW2 came from a characterization study directly comparing VSMOW2 and VSMOW, thereby minimizing the resulting uncertainty of the value assignment processes. The characterization was carried out by three isotope hydrology laboratories: the USGS laboratory in Reston, Virginia, USA, the Center for Isotope Research, University of Groningen, Netherlands, and the IAEA Isotope Hydrology Laboratory, Vienna, Austria. For both δ^2H and $\delta^{18}O$, the mean value and the combined standard uncertainty are the result of combining all measurements from the three laboratories. The combined standard uncertainties include contributions from the upper limits for the inhomogeneity between bottled glass ampoules and the residual biases of the mean values. The results of this study suggest that the $\delta^{18}O$ value and the δ^2H value of VSMOW2 are identical to those in VSMOW, within measurement uncertainty. The combined standard uncertainty associated with the δ^2H and $\delta^{18}O$ reference values of VSMOW2, as provided in Table 1, should be included in any uncertainty analysis of measurement results when VSMOW2 is used as a calibrator. Note that the δ-values of the predecessor material, VSMOW, had no associated uncertainty as those values were defined as the zeros of the respective δ-scales.

Normalization: The δ-values for hydrogen and oxygen, when measured in samples, are presented as parts per thousand differences (per mill; ‰) from the VSMOW δ-value normalized with the defined SLAP δ-value. The adoption of VSMOW as the zero point of the δ-scale and of a fixed SLAP δ-value by convention corresponds to the normalization of δ-values on the VSMOW-SLAP scale [2]. A general formula for normalizing hydrogen isotope measurement results using two laboratory standards LS1 (VSMOW2) and LS2 (SLAP2) can be expressed as:

$$\delta^2H_{sample,cal} = \delta^2H_{LS1,cal} + \left(\delta^2H_{sample,WS} - \delta^2H_{LS1,WS}\right) \times f \qquad (1)$$

where the normalization factor f is:

$$f = \left(\delta^2H_{LS2,cal} - \delta^2H_{LS1,cal}\right) \Big/ \left(\delta^2H_{LS2,WS} - \delta^2H_{LS1,WS}\right) \qquad (2)$$

where $_{ws}$ denotes measurements made versus a transfer gas (working standard),
$_{cal}$ denotes calibrated measurements made versus the VSMOW–SLAP scale, and
$\delta^2H_{LS1,cal}$ and $\delta^2H_{LS2,cal}$ are the conventionally fixed δ^2H values for VSMOW2 and SLAP2 or those of calibrated laboratory working standards.

Similar formulae are used for $\delta^{18}O$.

The δ-definition of Eq. (1) is identical to the one in conventional use [9] if and only if $f = 1$, that is if no scale compression occurs and the δ-values measured on a given instrument correspond exactly to the recommended values for δ_{VSMOW2} and δ_{SLAP2}.

Please note that the reporting scales for δ^2H and $\delta^{18}O$ are still denoted and referred to as the VSMOW-SLAP scales in spite of the exhaustion of the original supply of VSMOW and SLAP [18]. Therefore in Eq. 1 and Eq. 2, the measured values for the new international measurement standards VSMOW2 and SLAP2 are entered for LS1 and LS2. The data are then normalized to the VSMOW-SLAP scale using VSMOW2 and SLAP2. Of course, the standard uncertainties of VSMOW2 and SLAP2 isotopic values have to be included in any uncertainty budget.

Reporting of Stable Isotope δ-Values: The following recommendations are provided for reporting the relative difference of hydrogen and oxygen stable isotope-number ratios using the δ-notation modified from Coplen [19], it is recommended that:
- δ^2H values of all hydrogen-bearing substances be expressed relative to VSMOW-SLAP on a scale where $\delta^2H_{SLAP2} = -427.5$ ‰;
- $\delta^{18}O$ values of all oxygen-bearing substances be expressed relative to VSMOW-SLAP or relative to Vienna PeeDee Belemite (VPDB; for carbonates) on a scale such that $\delta^{18}O_{SLAP2} = -55.5$ ‰ or $\delta^{18}O_{NBS19} = -2.2$ ‰, respectively;

- the reporting of the relative difference of stable isotope-number ratios relative to SMOW and PDB (PeeDee Belemnite) be discontinued [20].

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