National Institute of Standards & Technology

Report of Investigation

Reference Material 8536

GISP Greenland Ice Sheet Precipitation

(Hydrogen and Oxygen Isotopes in Water)

This Reference Material (RM) is a secondary reference material with known isotope-number ratios for hydrogen (H) and oxygen (O) that are intermediate to VSMOW2 (RM 8535a) and SLAP (RM 8537). It is intended to be a control for working standards that have been calibrated to the VSMOW-SLAP (Vienna Standard Mean Ocean Water-Standard Light Antarctic Precipitation) δ-scales for isotope-number ratios of hydrogen and oxygen. While the values for this RM are reference values, its widespread use permits comparability of data from different laboratories. A reference value is a non-certified value that is the best estimate of the true value; however, the value may reflect only the measurement precision and may not include all sources of uncertainty [1]. The equivalent name for this RM, as used by the International Atomic Energy Agency (IAEA) and the U.S. Geological Survey (USGS), is GISP. A unit of RM 8536 consists of one ampoule containing approximately 20 mL of water.

Table 1. Reference Values[(a)] for the Relative H and O Isotope-Number Ratios of RM 8536

RM Number	IAEA Name	$10^3\,\delta\,^2H_{VSMOW\text{-}SLAP}$	Standard Uncertainty $10^3\,\delta\,^2H_{VSMOW\text{-}SLAP}$	$10^3\,\delta\,^{18}O_{VSMOW\text{-}SLAP}$	Standard Uncertainty $10^3\,\delta\,^{18}O_{VSMOW\text{-}SLAP}$
RM 8536	GISP	–189.5	0.1	–24.78	0.01

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

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

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

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

Expiration of Value Assignment: RM 8536 is valid, within the measurement uncertainty specified, until **31 December 2020**, provided the RM is handled and stored in accordance with instructions given in this Report of Investigation (see "Instructions for Handling, Storage, and Use"). The report is 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) will facilitate notification.

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Report Revision History on Last Page

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The technical aspects involved in the issuance of this RM were coordinated through the NIST Analytical Chemistry Division by R.D. Vocke, Jr.

Support aspects involved in the issuance of this RM were coordinated through the NIST Measurement Services Division.

INSTRUCTIONS FOR HANDLING, STORAGE, AND USE

Storage and Stability: The original, unopened ampoules of RM 8536 should be stored at ambient temperature in the dark. The unused fractions of this RM should be discarded 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.

Use: GISP is intended as a calibration check of working standards that are normalized to the VSMOW-SLAP scale.

Distribution: The distribution of GISP (RM 8536) is limited to one unit per year. Users are strongly advised to prepare their own standards for daily use and calibrate those standards against the international reference materials VSMOW2 (RM 8535a) and SLAP (RM 8537).

PREPARATION AND ANALYSIS

Sample Preparation: GISP was prepared by W. Dansgaard, University of Copenhagen, Denmark from a sample of Greenland firn [3].

Isotope-Number Ratios in GISP: The δ^2H and δ^{18}O isotope-number ratios of GISP were derived from two interlaboratory comparison exercises. After eliminating outliers, the average δ^2H and δ^{18}O values of the screened data together with their standard deviations and standard uncertainties were reported to the IAEA in 1984 and 1995 [5,6]. The results of those two studies are listed in the first two rows of Table 2. The δ^2H and δ^{18}O isotope-number ratios listed in the third row are a statistical re-evaluation of both data sets combined, using an interquartile range rejection criterion to eliminate outliers. The values in this last row are the values for GISP presented in Table 1.

Table 2. RM 8536 GISP Isotopic Abundance Values

δ^2H Value [‰]	Standard Deviation [‰]	Number of Accepted Results, *N* (Reported Results)	δ^{18}O Value [‰]	Standard Deviation [‰]	Number of Accepted Results *N* (Reported Results)	Source
–189.7	1.1	45 (48)	–24.80	0.09	49 (52)	[5]
–189.2	1.2	19 (22)	–24.76	0.08	21 (23)	[6]
–189.5	1.2	67 (70)	–24.78	0.09	71 (75)	see text

Information Values: The [$N(^{17}O)/N(^{16}O)$] ratio of GISP has been measured [7]. The average δ^{17}O value, normalized to the VSMOW/SLAP scale, is –12.71 ‰. The expanded uncertainty for this measurement is ± 0.1 ‰.

Homogeneity: The isotopic homogeneity of the ampoules was checked before distribution of the samples in the interlaboratory comparison exercise. These checks gave identical values within experimental uncertainty.

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 [3]. A general formula for normalizing hydrogen isotope measurement results using two laboratory standards LS1 (VSMOW2) and LS2 (SLAP) can be expressed as:

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

where the normalization factor f is:

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

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

Similar formulae are used for δ^{18}O.

The δ-definition of Eq. (1) is identical to the one in conventional use 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_{SLAP}.

Please note that the reporting scales for δ^2H and δ^{18}O are still denoted and referred to as the VSMOW-SLAP scales in spite of the exhaustion of the original supply of VSMOW [8]. Therefore in Eq.1 and Eq.2, the measured values for the new international measurement standards VSMOW2 and SLAP are entered for LS1 and LS2. The data are then normalized to the VSMOW–SLAP scale using VSMOW2 and SLAP. Of course, the standard uncertainties of VSMOW2 and SLAP 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 [9]. It is recommended that:

- δ^2H values of all hydrogen-bearing substances be expressed relative to VSMOW-SLAP on a scale where $\delta^2\mathrm{H}_{\mathrm{SLAP}} = -427.5$ ‰;
- δ^{18}O values of all oxygen-bearing substances be expressed relative to VSMOW-SLAP or relative to VPDB (for carbonates) on a scale such that $\delta^{18}\mathrm{O}_{\mathrm{SLAP}} = -55.5$ ‰ or $\delta^{18}\mathrm{O}_{\mathrm{NBS19}} = -2.2$ ‰, respectively;
- the reporting of the relative difference of stable isotope-number ratios relative to SMOW and PDB (PeeDee Belemnite) be discontinued [10].

REFERENCES

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Users of this RM should ensure that the Report of Investigation in their possession is current. This can be accomplished by contacting the SRM Program: telephone (301) 975-2200; fax (301) 926-4751; e-mail srminfo@nist.gov; or via the Internet at http://www.nist.gov/srm.