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Reference Material 8536

GISP Greenland Ice Sheet Precipitation
(Hydrogen and Oxygen Isotopes in Water)

REFERENCE MATERIAL INFORMATION SHEET

Purpose: This Reference Material (RM) is a secondary reference material with known isotope ratio values for hydrogen (H) and oxygen (O) that are intermediate to VSMOW (RM 8535) and SLAP (RM 8537) [1,2]. 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 ratios of hydrogen and oxygen. The equivalent name for this RM, as used by the International Atomic Energy Agency (IAEA) and the U.S. Geological Survey (USGS), is GISP.

Description: A unit of RM 8536 consists of one ampoule containing approximately 20 mL of water.

Non-Certified Values: Although not certified, the assigned isotope-delta values for this RM, provided in Table 1 below, are at present the best estimates of the true values.

Table 1. Non-Certified Values for the Hydrogen and Oxygen Stable Isotopes of RM 8536

NIST RM Number	Name	Non-Certified Value δ^2H_{VSMOW}	Combined Uncertainty δ^2H_{VSMOW}	Expanded Uncertainty δ^2H_{VSMOW} [(a)]	Non-Certified Value $\delta^{18}O_{VSMOW}$	Combined Uncertainty $\delta^{18}O_{VSMOW}$	Expanded Uncertainty $\delta^{18}O_{VSMOW}$ [(a)]
8536	GISP	–189.7 ‰	0.9 ‰	1.8 ‰	–24.78 ‰	0.08 ‰	0.16 ‰

[(a)] RM 8536 is given with a combined standard uncertainty in addition to an expanded uncertainty value, $k = 2$, for each assigned value. The expanded uncertainty is equal to $U = ku_c$, where u_c is the combined standard uncertainty and k is the coverage factor, as defined in the ISO/JCGM Guide [3]. Non-certified values and uncertainties are given in units of per mil (‰), which is equivalent to per thousand.

Metrological Traceability: RM 8536 is a secondary reference material with known values for oxygen and hydrogen stable isotopes; it is traceable to VSMOW (RM 8535) and SLAP (RM 8537), which define the VSMOW scale.

Isotope values for hydrogen and oxygen are not traceable to the International System of Units (SI) or other higher-order reference system [3,4]. A *Traceability Exception* has been approved by the Bureau International des Poids et Mesures (BIPM) International Committee for Weights and Measures (CIPM), which states non-SI traceable isotope values "should be made traceable to materials recognized as International Standards" [4,5].

Period of Validity: The non-certified values are valid within the measurement uncertainty specified until **31 December 2032**. The value assignments are nullified if the material is stored or used improperly, damaged, contaminated, or otherwise modified.

Maintenance of Non-Certified Values: NIST will monitor this material to the end of its period of validity. If substantive technical changes occur that affect the non-certified values during this period, NIST will update this Reference Material Information Sheet and notify registered users. RM users can register online from a link available on the NIST SRM website or fill out the user registration form that is supplied with the RM. Registration will facilitate notification. Before making use of any of the values delivered by this material, users should verify they have the most recent version of this documentation, available through the NIST SRM website (https://www.nist.gov/srm).

Carlos A. Gonzalez, Chief
Chemical Sciences Division

Steven J. Choquette, Director
Office of Reference Materials

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Storage: 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 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 stable isotope calibrations 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 non-certified values in this RMIS apply only to freshly opened ampoules.

Additional Information: The distribution of RM 8536 is limited to one unit per customer per year. Users are encouraged to prepare their own standards for daily use and calibrate those standards against international reference materials. Preparation, analysis, and reporting information can be found in Appendix A.

REFERENCES

[1] JCGM 200:2012; *International Vocabulary of Metrology — Basic and General Concepts and Associated Terms*; 3rd ed.; JCGM (2012); available at https://www.bipm.org/en/committees/jc/jcgm/publications (accessed Jan 2023).

[2] Brand, W.A.; Coplen, T.B.; Vogl, J.; Rosner, M.; and Prohaska, T.; *Assessment of International Reference Materials for Isotope Ratio Analysis (IUPAC Technical Report;* Pure and Applied Chemistry, Vol. 86, pp. 425–467 (2014).

[3] JCGM 100:2008; *Evaluation of Measurement Data — Guide to the Expression of Uncertainty in Measurement* (GUM 1995 with Minor Corrections); Joint Committee for Guides in Metrology (2008); available at https://www.bipm.org/en/committees/jc/jcgm/publications (accessed Jan 2023).

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[5] BIPM Traceability Exception: Delta Value Isotope Ratio Measurements (2015); available at https://www.bipm.org/documents/20126/50116808/%5BQM%5D+Delta+value+isotope+ratio+measurements.pdf/4fe4f00a-7f3c-9683-59f2-e49a11db074a?version=1.4&download=true (accessed Jan 2023). Note that this document is a summary of Decision CIPM/104-26 from the International Committee for Weights and Measures (CIPM); *Proceedings of Session 1 of the 104th meeting: Executive Summary*; 9-10 March 2015, p. 34; available at https://www.bipm.org/utils/en/pdf/CIPM/CIPM2015-I-EN.pdf (accessed Jan 2023).

[6] Schoenemann, S.W.; Schauer, A.J.; Steig, E.J.; *Measurement of SLAP2 and GISP $\delta^{17}O$ and Proposed VSMOW-SLAP Normalization for $\delta^{17}O$ and $^{17}O_{excess}$*; Rapid Communications in Mass Spectrometry, Vol. 27, pp. 582–590 (2013).

[7] Jabeen, I.; Kusakabe, M.; *Determination of δ17O values of Reference Water Samples VSMOW and SLAP*; Chemical Geology, Vol. 143, pp. 115−119 (1997).

[8] Hut, G.; *Consultants' Group Meeting on Stable Isotope Reference Samples for Geochemical and Hydrological Investigations* (16–18 September 1985); International Atomic Energy Agency (IAEA) Vienna, pp. 1–42 (1987).

[9] Gonfiantini, R.; *Report on an Advisory Group Meeting on Stable Isotope Reference Samples for Geochemical and Hydrochemical Investigations*; IAEA, Vienna, Austria (1984).

[10] Araguás, L.; Rozanski, K.; *Interlaboratory Comparison for Deuterium and Oxygen-18 Analysis of Precipitation Samples*; Unpublished Report; IAEA, Vienna, Austria (1995).

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[12] Coplen, T.B.; *Guidelines and Recommended Terms for Expression of Stable-Isotope-Ratio and Gas-Ratio Measurement Results*; Rapid Communications in Mass Spectrometry, Vol. 25, pp. 2538–2560 (2011).

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Information Sheet Revision History: 19 January 2023 (Added metrological traceability statement and terminology section; revised δ^2H value; added expanded and combined standard uncertainties for δ^2H_{VSMOW} and $\delta^{18}O_{VSMOW}$, removed standard uncertainties, updated format; changed period of validity; editorial changes); 31 January 2012 (Separated from ROIs for 8535 and 8537; revised values for δ^2H and $\delta^{18}O$; editorial changes); 22 June 1992 (Original report issue date).

Certain commercial equipment, instruments, or materials may be identified in this Reference Material Information Sheet to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

Users of this RM should ensure that the Reference Material Information Sheet in their possession is current. This can be accomplished by contacting the Office of Reference Materials 100 Bureau Drive, Stop 2300, Gaithersburg, MD 20899-2300; telephone (301) 975-2200; e-mail srminfo@nist.gov; or the Internet at https://www.nist.gov/srm.

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APPENDIX A

PREPARATION AND ANALYSIS

Technical aspects involved in the issuance of this RM were coordinated through the NIST Chemical Sciences Division by R.A. Kraft.

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

Information that may be of use to the user: The current best value for $\delta^{17}O$ is –13.16 ‰ ± 0.05 ‰ using a $\delta^{17}O$ value of –29.6986 ‰ for SLAP [2,6]. This updates a previous value of $\delta^{17}O$ for GISP from 1997; Jabeen and Kusakabe measured a $\delta^{17}O$ value of –12.59 ‰, for GISP using a $\delta^{17}O$ value of –28.58 ‰ for SLAP [7].

Sample Preparation: GISP was prepared by W. Dansgaard, University of Copenhagen, Denmark from a sample of Greenland snow [8].

Analytical methods: The $\delta^{2}H$ and $\delta^{18}O$ values of GISP on this certificate originate from values published in IAEA TECDOC 825 in 1984, from an interlaboratory comparison. A second interlaboratory comparison was done in 1995, however those data are unpublished [9,10]. In 2007 IAEA performed a statistical re-evaluation of the two data sets combined, using an interquartile range rejection criterion to eliminate outliers [11].

Homogeneity: The isotopic homogeneity of the ampoules was assessed prior to the distribution of the samples in the interlaboratory comparison exercise. Homogeneity was within the experimental uncertainty.

REPORTING

Terminology: The terminology used here is based on the guidance given by IUPAC for isotope terminology, where stable isotope-number ratio refers to the number of atoms of one isotope relative to the number of atoms of a second isotope in the same system [2]. This is often abbreviated to stable isotope ratio. Isotope-delta value refers to the stable isotope-number ratio of a measured sample relative to the stable isotope-number ratio of a reference material (see example below). Isotope-amount ratio is numerically the same as isotope-number ratio but refers specifically to the amount (moles) of an isotope relative to the amount (moles) of another isotope in the same system [12].

Isotope-delta Values: The hydrogen and oxygen stable isotope-delta values of a measured sample reported on the VSMOW scale are defined as the difference in measured isotope-number ratio of hydrogen or oxygen in a sample relative to the isotope-number ratio of hydrogen or oxygen in VSMOW:

$$\delta^{2}H = \frac{\left[\frac{N_{sample}(^{2}H)}{N_{sample}(^{1}H)}\right] - \left[\frac{N_{VSMOW}(^{2}H)}{N_{VSMOW}(^{1}H)}\right]}{\left[\frac{N_{VSMOW}(^{2}H)}{N_{VSMOW}(^{1}H)}\right]}$$

and

$$\delta^{18}O = \frac{\left[\frac{N_{sample}(^{18}O)}{N_{sample}(^{16}O)}\right] - \left[\frac{N_{VSMOW}(^{18}O)}{N_{VSMOW}(^{16}O)}\right]}{\left[\frac{N_{VSMOW}(^{18}O)}{N_{VSMOW}(^{16}O)}\right]}$$

Normalization: By convention VSMOW is the zero point of the hydrogen and oxygen stable isotope δ-scales; δ-value for SLAP is also defined by convention and has a $\delta^{2}H$ value of –427.5‰ and a $\delta^{18}O$ value of –55.50‰. A formula

for normalizing hydrogen isotope measurement results using two laboratory standards LS1 (VSMOW or VSMOW2) and LS2 (SLAP or SLAP2) can be expressed as:

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

where the normalization factor f is:

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

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

The same formula can be used for δ^{18}O. The δ-definition above assumes $f = 1$ and does not account for scale compression.

Please note that the reporting scales for δ^2H and δ^{18}O are still referred to as the VSMOW-SLAP scales despite the exhaustion of the original supply of VSMOW and SLAP [13].

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 [14], it is recommended that:

- δ^2H values of all hydrogen-bearing substances be expressed relative to VSMOW-SLAP.
- δ^{18}O values of all oxygen-bearing substances be expressed relative to VSMOW-SLAP or relative to Vienna PeeDee Belemite (VPDB; for carbonates).
- Reporting of the relative difference of stable isotope-number ratios relative to SMOW and PDB (PeeDee Belemnite) be discontinued [13].

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