



# National Institute of Standards & Technology

## Report of Investigation

### Reference Materials 8535, 8536, 8537

(In cooperation with the International Atomic Energy Agency)

8535: VSMOW—Vienna Standard Mean Ocean Water ( $\delta^2\text{H}_{\text{VSMOW}}$ ,  $\delta^{18}\text{O}_{\text{VSMOW}}$ )  
8536: GISP—Greenland Ice Sheet Precipitation (Water) ( $\delta^2\text{H}_{\text{VSMOW}}$ ,  $\delta^{18}\text{O}_{\text{VSMOW}}$ )  
8537: SLAP—Standard Light Antarctic Precipitation (Water) ( $\delta^2\text{H}_{\text{VSMOW}}$ ,  $\delta^{18}\text{O}_{\text{VSMOW}}$ )

These Reference Materials (RMs) are intended to provide water samples of known isotopic composition concerning  $^2\text{H}/^1\text{H}$  and  $^{18}\text{O}/^{16}\text{O}$  isotope ratios and should be used to calibrate/check internal laboratory standards. They are distributed by NIST on behalf of the International Atomic Energy Agency (IAEA), Vienna, Austria. Each RM unit consists of 20 mL water in a sealed glass ampoule. Since only very limited quantities of these materials exist, the distribution is limited to one unit of each per three-year period of time.

The use of VSMOW and SLAP in different laboratories allows the investigators to obtain stable hydrogen and oxygen isotope ratio data which are comparable worldwide [1,2]. GISP, with its isotopic composition intermediate to VSMOW and SLAP, is considered to be a secondary reference material. For the effects of the normalized  $\delta$ -scale on GISP values, see the relevant IAEA interlaboratory comparison program reports [3,4].

**Sample Preparation:** VSMOW was prepared by R. Weiss and H. Craig of the Scripps Institution of Oceanography, La Jolla, CA. Distilled ocean water was mixed with small amounts of other water collected in the Pacific Ocean in July 1967 at latitude  $0^\circ$  and longitude  $180^\circ$  in order to adjust its isotopic composition as closely as possible to that of Standard Mean Ocean Water (SMOW) [1,2]. SLAP was obtained from a South Pole firn sample collected by E. Picciotto, Université Libre de Bruxelles, at Plateau Station, Antarctica, in 1967 [5]. GISP was prepared by W. Dansgaard, University of Copenhagen, Copenhagen, Denmark from a sample of Greenland firn [6].

**Expiration of Reference Values:** The reference values for the isotopic composition of RM 8535, RM 8536, and RM 8537 are valid **indefinitely**, provided they are handled and stored in accordance with the instructions given in this report, (see "Instructions for Use"). This certification is nullified if the SRM is contaminated, or the glass ampoule container is damaged.

**Maintenance of Reference Values:** The isotopic compositions of these RMs are monitored on a yearly basis. If substantive changes occur to the values, NIST will notify the purchaser. Return of the attached registration card will facilitate notification.

Technical coordination for these RMs was provided by R.D. Vocke, Jr., of the NIST Analytical Chemistry Division.

The support aspects involved in the issuance of these RMs was coordinated through the NIST Standard Reference Materials Program by B.S. MacDonald of the NIST Measurement Services Division.

Stephen A. Wise, Chief  
Analytical Chemistry Division

Robert L. Watters, Jr., Chief  
Measurement Services Division

Gaithersburg, MD 20899  
Certificate Issue Date: 03 March 2005  
*See Report Revision History on Last Page*

## INSTRUCTIONS FOR USE

**Storage:** It is recommended that each of these RMs be stored under normal laboratory conditions in an upright position inside the original container supplied by NIST.

**Handling:** Each RM ampoule should be used immediately after opening to avoid evaporation and isotopic exchange with atmospheric water vapor. Users are strongly advised to prepare their own internal standards for daily use and calibrate those standards against these RMs. In case not all the RM material is used up completely for the calibration after opening the glass ampoule, the remaining quantity of original RM can be transferred immediately to small, dry, glass vials with conical plastic insert caps to prevent evaporation. Each vial should be weighed immediately after closure for monitoring long-term evaporation losses by water vapor diffusion through the plastic stopper and thus to prove functionality of the material. Any quantity of a RM already used for isotopic measurements should **NOT** be used again for this purpose since the isotopic signature will have been altered during the measurement.

## PREPARATION AND ANALYSIS

**Homogeneity:** The two standards, VSMOW and SLAP, were prepared following a recommendation of an Advisory Group Meeting convened by the IAEA in 1966 [5]. VSMOW was obtained by mixing distilled ocean water with small amounts of other water and has been distributed by the IAEA since 1968. According to control analyses made by Craig, VSMOW has the same  $^{18}\text{O}/^{16}\text{O}$ -ratio as the defined SMOW, but a slightly lower  $^2\text{H}/^1\text{H}$ -ratio (0.2 ‰) that lies within the analytical measurement uncertainty of most laboratories. About 30 L of VSMOW were stored in 10 L storage flasks in the IAEA Laboratory, Vienna, Austria; an additional 20 L were stored at NIST (formerly NBS), Gaithersburg, MD. RM 8535 VSMOW, RM 8536 GISP, and RM 8537 SLAP are distributed in 20 mL ampoules. The isotopic homogeneity of the different charges and of the filling procedure have been cross-checked before distribution. These checks revealed identical values within the experimental uncertainty. In some ampoules and in one 10 L primary storage flask of the U.S. (NIST) supply of VSMOW, bright orange matter (possibly algae) had been observed. However, NIST measurements showed that, within the experimental uncertainty, the algae does not affect the isotopic composition [7].

**Normalization:** The  $\delta$ -values are stated, and should always be reported, in parts per thousand difference [‰] from the VSMOW isotope-ratio calibration standard. The adoption of VSMOW as zero of the  $\delta$  scale and of prefixed values for SLAP corresponds with the definition of the  $\delta$  value normalized on the VSMOW-SLAP scale [3]:

$$\delta = [(R_{\text{sample}}/R_{\text{VSMOW}}) - 1] \times 1000 \times f \quad (1)$$
$$f = \delta_{\text{SLAP}} / [(R_{\text{SLAP}} - R_{\text{VSMOW}}) / R_{\text{VSMOW}}]$$

where  $R$  is the measured isotopic ratio of  $^2\text{H}/^1\text{H}$  or  $^{18}\text{O}/^{16}\text{O}$ , and  
 $\delta_{\text{SLAP}}$  is the conventionally fixed  $^2\text{H}$  or  $^{18}\text{O}$  value (see Table 1).

This  $\delta$ -definition of Equation (1) coincides with the classical one [1] only if  $f=1$ , that is if the  $\delta$ -value of the measured ratio  $R_{\text{SLAP}}$ , corresponds exactly to recommended value  $\delta_{\text{SLAP}}$ .

**Recommended Reference Material Values:** Table 1 shows the recommended  $\delta^{2\text{H}}_{\text{VSMOW}}$  and  $\delta^{18\text{O}}_{\text{VSMOW}}$  values for RM 8535 VSMOW, RM 8536 SLAP, and RM 8537 GISP. The GISP value is based on the VSMOW/SLAP scale. It is the statistically evaluated result of data from two intercomparison exercises [3,16]. The “expanded uncertainty” is evaluated by multiplying the standard uncertainty with a coverage factor,  $k = 2$ , following the guidelines in NIST Technical Note 1297 [17].

Table 1. RM 8535, RM 8536, and RM 8537 Reference Values

IAEA name	NIST number	Material	$\delta^2\text{H}_{\text{VSMOW}}$ [‰]	Standard deviation [‰]	$\delta^{18}\text{O}_{\text{VSMOW}}$ [‰]	Standard deviation [‰]	Authors
VSMOW	RM 8535	water	0	0	0	0	[1,2] definition
GISP	RM 8536	water	-189.5	1.2	-24.78	0.09	this report [3,16]
SLAP	RM 8537	water	-428.0	0	-55.5	0	[3,4,8] convention

**Isotope Abundance of VSMOW:** VSMOW is the isotopic standard to which GISP, SLAP, and most other oxygen-bearing substances are compared [8]. Due to the definition of the  $\delta$  scale, the  $\delta$  value of VSMOW equals zero. Table 2 lists the absolute hydrogen and oxygen isotope abundance of VSMOW and the calculated atom percent of  $^1\text{H}$  or  $^{16}\text{O}$ , respectively. The quoted uncertainties include one of the measurements and that of the absolute values of the calibration mixtures. Values in parentheses are calculated. **NOTE:** “mass spec.” stands for mass spectrometric measurement; “FT-NMR” stands for Fourier-Transform Nuclear Magnetic Resonance.

Table 2. RM 8535 VSMOW Isotopic Abundance Values

Isotope Ratio	Isotope Ratio [10 <sup>-6</sup> ]	Standard Deviation [10 <sup>-6</sup> ]	Atom Percent of $^1\text{H}$ , $^{18}\text{O}$ and $^{17}\text{O}$ [%]	Standard Deviation [%]	Method	Authors
$^2\text{H}/^1\text{H}$	155.76	0.05	(99.984426)	(0.000005)	mass spec.	[9]
$^2\text{H}/^1\text{H}$	155.75	0.08	(99.984427)	(0.000008)	mass spec.	[10]
$^2\text{H}/^1\text{H}$	155.60	0.12	(99.984442)	(0.000012)	FT-NMR	[11]
$^{18}\text{O}/^{16}\text{O}$	2005.20	0.45	(0.20004)	(0.00005)	mass spec.	[12]
$^{17}\text{O}/^{16}\text{O}$	379.9	0.8	(0.03790)	(0.00009)	mass spec.	[13]

**Isotope Abundance of SLAP:** The oxygen and hydrogen isotope ratio scales are defined in terms of VSMOW and SLAP such that the hydrogen and oxygen composition of SLAP relative to VSMOW is -428 ‰ and -55.5 ‰, respectively. These  $\delta$  values for SLAP were conventionally fixed at the IAEA Consultants Meeting on Stable Isotope Standards in 1976, Vienna, Austria, on the basis of a data set achieved in an interlaboratory comparison [5]. Participating scientists and laboratories included in the measurement of SLAP and the reported  $\delta$  values are given in reference 14. Table 3 gives values for the absolute hydrogen and oxygen isotope abundance of SLAP, the calculated atom percent of  $^1\text{H}$  or  $^{18}\text{O}$ , and the calculated  $\delta$  values, respectively. The quoted uncertainties include one of the measurements and that of the absolute values of the calibration mixtures. Values in parentheses are calculated.

Table 3. RM 8536 SLAP Isotopic Abundance Values

Isotope-Ratio	Isotope Ratio [10 <sup>-6</sup> ]	Standard Deviation [10 <sup>-6</sup> ]	Atom Percent of $^1\text{H}$ [%]	Standard Deviation [%]	$\delta$ Value [‰]	Standard Deviation [‰]	Method	Authors
$^2\text{H}/^1\text{H}$	89.02	0.05	(99.991099)	(0.000005)	-428.5	0.1	mass spec.	[9]
$^2\text{H}/^1\text{H}$	89.12	0.07	(99.991089)	(0.000007)	-427.8	0.5	mass spec.	[10]
$^2\text{H}/^1\text{H}$	88.88	0.18	(99.991113)	(0.000018)	-428.8	1.2	FT-NMR	[11]
$^{18}\text{O}/^{16}\text{O}$	(1893.91)	(0.45)	Computed from VSMOW using $\delta^{18}\text{O} = -55.5$ ‰					

**Isotope Abundance of GISP:** The isotopic composition of GISP has been determined in two interlaboratory comparison exercises [3,16]. The reported final consensus values relative to VSMOW and normalized on the VSMOW/SLAP scale are given in Table 4. Intercalibration average values of the accepted data, standard deviation ( $1\sigma$ ) and standard uncertainty ( $1\sigma/\sqrt{n}$ ) of GISP were reported to the IAEA in 1984 and 1995. Data in first row: data within the  $2\sigma$ -range of all reported values have been accepted [5]; data in second row: values are the results of a two step statistical treatment [16]; data in third row: statistical re-evaluation of both data sets [5] and [16], interquartile rejection criterion ([16], step I.)

Table 4. RM 8537 GISP Isotopic Abundance Values

$\delta^2\text{H}$ Value [‰]	Standard Deviation [‰]	Number of Accepted Results $n$ (Reported Results)	$\delta^{18}\text{O}$ Value [‰]	Standard Deviation [‰]	Number of Accepted Results $n$ (Reported Results)	Authors
-189.7	1.1	45 (48)	-24.80	0.09	49 (52)	[3]
-189.2	1.2	19 (22)	-24.76	0.08	21 (23)	[16]
-189.5	1.2	67 (70)	-24.78	0.09	71 (75)	this report

**Information Values:** The absolute maximum density of VSMOW is  $999.975 \text{ kg/m}^3$  [18]. The tritium activity concentration of VSMOW, determined at the IAEA by direct gas counting, was  $18.5 \pm 3.6 \text{ TU}$  on 16 September 1976. The tritium activity concentration of SLAP was  $374 \pm 9 \text{ TU}$  on 16 September 1976. Both values are reported with their standard deviation ( $1\sigma$ ). The  $^{17}\text{O}/^{16}\text{O}$  ratios of GISP and SLAP have been determined in six individual measurements each [19]. The reported  $\delta^{17}\text{O}$  values [‰] on the VSMOW/SLAP scale are  $-12.71 \text{ ‰} \pm (0.03 \text{ to } 0.05) \text{ ‰}$  for GISP and  $-28.86 \text{ ‰} \pm (0.03 \text{ to } 0.12) \text{ ‰}$  for SLAP. The numbers in parentheses give the range of the standard deviation of the individual measurements. The extended uncertainty is reported to be  $\pm 0.1 \text{ ‰}$ .

## REFERENCES

- [1] Craig, H.; *Isotopic Variations in Meteoric Waters*. *Science*, Vol. 133, pp. 1702–1703 (1961).
- [2] Craig, H.; *Standard for Reporting Concentrations of Deuterium and Oxygen-18 in Natural Waters*; *Science*, Vol. 133, pp. 1833–1834 (1961).
- [3] Gonfiantini, R.; *Report on an Advisory Group Meeting on Stable Isotope Reference Samples for Geochemical and Hydrochemical Investigations*; IAEA, Vienna, Austria (1983).
- [4] Gonfiantini, R.; Rozanski, K.; Stichler, W.; *Intercalibration of Environmental Isotope Measurements: The Program of the International Atomic Energy Agency*; *Radiocarbon*, Vol. 32, No. 3, pp. 369–374 (1990).
- [5] Gonfiantini, R.; *Standards for Stable Isotope Measurements in Natural Compounds*, *Nature*, Vol. 271, pp. 534–536 (1978).
- [6] Hut, G.; *Report on the Consultants Group Meeting on Stable Isotope Reference Samples for Geochemical and Hydrological Investigations*; IAEA, Vienna, Austria (1987).
- [7] Coplen, T.; Hopple, J.; *Audit of VSMOW Distributed by the United States National Institute of Standards and Technology. Proceedings of a Consultants Meeting Held in Vienna*, 1–3 December 1993, IAEA-TECDOC-825, pp. 35–38 (1995).
- [8] Coplen, T.; *Normalization of Oxygen and Hydrogen data*, *Chemical Geology (Isotope Geoscience Section)*, Vol. 72, pp. 293–297 (1988).
- [9] Hagemann, R.; Nief, G.; Roth, E.; *Absolute Isotopic Scale for Deuterium Analysis of Natural Waters. Absolute D/H ratio for SMOW*, *Tellus*, Vol. 22, pp. 712–715 (1970).
- [10] De Wit, J.C.; van der Straaten, C.M.; Mook, W.G.; *Determination of the Absolute Hydrogen Isotopic Ratio of VSMOW and SLAP*, *Geostandards Newsletter*, Vol. 4, No. 1, pp. 33–36 (1980).
- [11] Tse, R.S.; Wong, S.C.; Yuen, C.P.; *Determination of Deuterium/Hydrogen Ratios in Natural Waters by Fourier Transform Nuclear Magnetic Resonance Spectrometry*; *Analytical Chemistry*, Vol. 52, pp. 2445–2448 (1980).
- [12] Baertschi, P.; *Absolute <sup>18</sup>O Content of Standard Mean Ocean Water*; *Earth and Planetary Science Letters*, Vol. 31, pp. 341–344 (1976).
- [13] Li, W.; Ni, B.; Jin, D.; Chang, T.L.; *Measurement of the Absolute Abundance of Oxygen-17 in VSMOW*, *Kexue Tongbao, Chinese Science Bulletin*, Vol. 33, pp. 1610–1613 (1988).
- [14] Gonfiantini, R.; *Report on the Consultants Meeting on Stable Isotope Standards and Intercalibration in Hydrology and in Geochemistry*, Vienna, 8–10 September 1976, IAEA, Vienna, Austria (1977).
- [15] Gonfiantini, R.; Stichler, W.; Rozanski, K.; *Standards and Intercomparison Materials Distributed by the International Atomic Energy Agency for Stable Isotope Analysis*; *Proceedings of a consultants meeting held in Vienna*, 1–3 December 1993, IAEA-TECDOC-825, 13–29 (1995).
- [16] Araguás, L.; Rozanski, K.; *Interlaboratory Comparison for Deuterium and Oxygen-18 Analysis of Precipitation Samples*, Unpublished Report, IAEA, Vienna, Austria (1995).
- [17] Taylor, B.N.; Kuyatt, C.E.; *Guidelines for Evaluation and Expressing the Uncertainty of NIST Measurement Results*, NIST Technical Report Note 1297 (1994 Edition).
- [18] Girard, G.; Menaché, M.; *Sur le Calcul de la Masse Volumique de L'eau* C.R. Acad. Sci, Paris, Vol. 274, pp. 377–379 (1972).
- [19] Jabeen, I.; Kusakabe, M.; *Determination of  $\delta^{17}\text{O}$  values of Reference Water Samples VSMOW and SLAP*; *Chemical Geology*, Vol. 143, pp. 115–119 (1997).

**Report Revision History:** 03 March 2005 (Extension of expiration date); 19 May 2001 (This technical revision reports changes in the reference values and establishes an expiration date); 15 October 1992 (Original report date).

*Users of this SRM should ensure that the certificate in their possession is current. This can be accomplished by contacting the SRM Program at: telephone (301) 975-6776; fax (301) 926-4751; e-mail [srminfo@nist.gov](mailto:srminfo@nist.gov); or via the Internet <http://www.nist.gov/srm>.*