

IAEA Analytical Quality in Nuclear Applications Series No. 63

# Certification Report on Value Assignment for the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ Stable Isotopic Composition in the Water Reference Material GRESP (Greenland Summit Precipitation)

**IAEA**

International Atomic Energy Agency

CERTIFICATION REPORT ON VALUE  
ASSIGNMENT FOR THE  $\delta^2\text{H}$  AND  $\delta^{18}\text{O}$   
STABLE ISOTOPIC COMPOSITION IN THE  
WATER REFERENCE MATERIAL GRESP  
(GREENLAND SUMMIT PRECIPITATION)

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IN THE WATER REFERENCE MATERIAL GRESP (GREENLAND SUMMIT PRECIPITATION)

IAEA, VIENNA, 2021

IAEA/AQ/63

ISSN 2074-7659

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Printed by the IAEA in Austria  
March 2021

## FOREWORD

A primary goal of the IAEA's activities relating to reference products for science and trade is to assist Member States in the use of stable isotope and radioisotope analytical techniques to understand, monitor and protect the environment. Through its Environment Laboratories, the IAEA provides reference materials to laboratories as a key measure for calibration and quality assurance worldwide. The Terrestrial Environment Laboratory, part of the IAEA Environment Laboratories, provides assistance to Member State laboratories in maintaining and improving the reliability of analytical measurement results, in carrying out stable isotope analysis, and in assessing environmental level radionuclides and trace elements. In the field of stable isotope ratio analysis, the Terrestrial Environment Laboratory provides more than forty different reference materials for various applications covering mainly the stable isotopes of hydrogen, carbon, nitrogen, oxygen and sulphur.

In all ecosystems, water supports all life functions. Understanding the details of its origin, availability, behaviour and movement is of the utmost importance for understanding these ecosystems. The use of stable isotopes as tracers of water origin and of its possible vulnerability to pollution is of primary importance for many scientific studies.

The reliability and comparability of the analyses performed by laboratories in this context are crucial for a meaningful interpretation of any sample data, for management of the environment, and for taking decisions on policy or at an administrative level. Comparability of measurement results can be achieved only when the results are traceable to conventionally agreed standards, such as to the established  $\delta$ -value scales and the corresponding reference materials for relative stable isotope ratio measurements.

The IAEA has supported such scientific investigations since the 1960s by providing basic support through analytical networks like the Global Network of Isotopes in Precipitation and associated databases, and in its international role of providing reference materials for stable isotope measurement and calibration in laboratories worldwide. As custodian of the isotope measurement scales and their realization by primary reference materials, the IAEA has a fundamental role in the application of such methods worldwide. The two most important reference materials produced by the IAEA are VSMOW2 (Vienna Standard Mean Ocean Water 2) and SLAP2 (Standard Light Antarctic Precipitation 2), which are used to realize the  $\delta$ -value scales. Further quality control materials are used by laboratories to verify proper calibration with these two materials.

This publication describes the production of the certified reference material GRESP (Greenland Summit Precipitation) for use as a quality control material. The reference material GRESP was produced following the applicable international ISO standards and characterized by laboratories with demonstrated competence. The IAEA officer responsible for this publication was M. Gröning of the IAEA Environment Laboratories.

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## 1. INTRODUCTION

Thousands of laboratories worldwide are performing analyses of the stable isotopic composition of elements for a large variety of scientific applications, ranging from hydrology, geology and climate studies to agriculture, biology or medicine. These laboratories may develop and validate new analytical methods, study the adherence to legislative rules or provide services to other organizations. Because of the needs to base scientific conclusions on valid and internationally comparable data, it is indispensable to ensure the quality of measurement results produced by each laboratory.

The Terrestrial Environment Laboratory (TEL) of the IAEA's Environment Laboratories has the programmatic responsibility in aiding Member States' laboratories in maintaining and improving the reliability of analytical measurement results, for stable isotopes, radionuclides and trace elements. This is an important part of the IAEA's Subprogramme of Reference Products for Science and Trade. TEL accomplishes it through the provision of suitable certified reference materials, validated analytical procedures, training in the implementation of internal quality control, and through the evaluation of measurement performance by the organization of worldwide and regional inter-laboratory comparisons and proficiency tests. Especially the task of the production of reference materials represents an important benchmark for improving the quality of laboratory performances worldwide, and this helps in assessing the validity of analytical methods in the IAEA's Member States.

The international ISO/IEC 17025 standard for testing laboratories [1] indicates that competent laboratories should use appropriate reference materials to demonstrate the traceability of their measurements. The measurement scheme for the production of new stable isotope reference materials implies the use of suitable internationally available reference materials for calibration at an appropriate low uncertainty level, as for example available from the IAEA. For general application of stable isotope ratio measurements, the use of appropriate valid reference materials is also needed. This consists of an unbroken chain of comparisons of results, all having stated uncertainties. In case of  $\delta$ -scale measurements of stable isotope ratios, laboratory measurements are traceable back to the scale defining calibration materials as provided by the IAEA. This ensures the long-term comparability of measurements worldwide.

For the elements hydrogen and oxygen, the two international measurement standards used to calibrate all relative stable isotope ratio measurements are named VSMOW2 (Vienna Standard Mean Ocean Water 2) and SLAP2 (Standard Light Antarctic Precipitation 2) [2, 3]. The isotopic ratios of these two materials span almost the total range of isotopic compositions of natural water samples on earth. All stable isotope ratio measurements for hydrogen and oxygen performed worldwide are thus directly or indirectly calibrated versus these two international measurement standards, which have replaced the previously available water reference materials VSMOW and SLAP in the year 2006.

Further stable isotope reference materials provided by the IAEA are used to ensure this traceability chain back to VSMOW2/SLAP2 for different compounds or to verify it by quality control measurements [4].

Quality control procedures are commonly based on the analysis of certified reference materials to assess reproducibility and measurement bias within laboratories. By using certified reference materials (CRM) for method validation, laboratories can demonstrate that their measurement results are traceable, or that they are globally comparable. GRESP is a quality control CRM to check the calibration by VSMOW2/SLAP2 and is therefore a cornerstone for the proper implementation of relevant regulations for quality control and laboratory accreditation.

TEL provides suitable CRMs for stable isotope analyses, including the international measurement standards VSMOW2 and SLAP2 defining the hydrogen and oxygen isotopic  $\delta$ -scales, and by offering further reference materials used to propagate the calibration to other compounds and to check the successful calibration.

In this context, for water stable isotope measurements, beside the use of international measurement standards, further materials are made available to check the calibration. A water sample of intermediate isotopic composition is very useful as a quality control material.

The first such reference material, named GISP (Greenland Ice Sheet Precipitation) and characterized for its hydrogen and oxygen stable isotopic composition, was provided by W. Darnsgaard, University of Copenhagen, Denmark in 1977 from Greenland [5]. It was available for about 35 years and was used to check the successful calibration of the  $\delta^2\text{H}$ - and  $\delta^{18}\text{O}$ -scales in a laboratory, as realized with the calibration materials VSMOW and SLAP and later since the year 2006 with their replacements VSMOW2 and SLAP2. The supply of GISP was exhausted in 2012.

Already in 2007, the preparation of a replacement for GISP had started. That replacement material originated from higher altitude snow from Greenland, and is named GRESP (Greenland Summit Precipitation), to reflect its origin from the scientific Greenland Summit Station. However, in contrast to VSMOW2 and SLAP2, no attempt at all has been made for GRESP to obtain a similar isotopic composition than for its predecessor material GISP.

The work presented in this report refers to the characterization and certification of the hydrogen and oxygen stable isotopic composition ( $\delta^2\text{H}$  and  $\delta^{18}\text{O}$ ) of GRESP as a CRM. Due to the long timespan since its preparation, several independent instruments were used for its careful characterization by many hundreds of analyses over time, including heterogeneity tests and long-term stability testing. This CRM has been produced to take over the function of a quality control material for checking the calibration of laboratory equipment using VSMOW2 and SLAP2, and therefore to satisfy the quality control demands and necessities of laboratories dealing with environmental and water analyses.

The reference material GRESP was produced following the applicable ISO Guide 34:2009 and its recent replacement ISO 17034:2016 [6, 7]. The material was characterized by laboratories with demonstrated analytical competence. Uncertainties of the certified values were calculated in compliance with the Guide to the Expression of Uncertainty in Measurement (GUM) [8] including uncertainty contributions related to possible heterogeneity and the characterization process.

## 2. METHODOLOGY

### 2.1. THE $\delta$ -SCALES TO REPORT RELATIVE ISOTOPE RATIO DIFFERENCES

The  $\delta$ -values are stated in this certification report as parts per thousand difference (per mill; ‰) from the VSMOW  $\delta$ -value normalized with the defined SLAP  $\delta$ -value. The adoption of VSMOW as zero point of the  $\delta$ -scale and of a fixed SLAP  $\delta$ -value by convention corresponds to the normalization of  $\delta$ -values on the VSMOW – SLAP scale [9]. A general formula can be expressed with two laboratory standards LS1 and LS2, which would correspond to VSMOW2 and SLAP2 in a calibration exercise, to calibrate an unknown sample. For hydrogen, the formula is:

$$\delta^2\text{H}_{\text{sample,cal}} = \delta^2\text{H}_{\text{LS1,cal}} + (\delta^2\text{H}_{\text{sample,WS}} - \delta^2\text{H}_{\text{LS1,WS}}) \times f \quad (1)$$

with the normalization factor  $f$  being

$$f = (\delta^2\text{H}_{\text{LS2,cal}} - \delta^2\text{H}_{\text{LS1,cal}}) / (\delta^2\text{H}_{\text{LS2,WS}} - \delta^2\text{H}_{\text{LS1,WS}}) \quad (2)$$

where

the subscript “WS” denotes measurements performed versus an isotope mass spectrometer transfer gas (working standard) or as derived by an optical laser spectrometry instrument, the subscript “cal” denotes calibrated measurements performed versus the VSMOW–SLAP  $\delta$ -scale, and  $\delta^2\text{H}_{\text{LS1,cal}}$  and  $\delta^2\text{H}_{\text{LS2,cal}}$  are the calibrated isotopic values of reference materials or calibrated internal laboratory standards LS1 and LS2 used for calibration, in this particular case the conventionally fixed  $\delta^2\text{H}$  values for VSMOW2 and SLAP2.

This  $\delta^2\text{H}$ -value definition in Eq. (1) coincides with the classical one reported in [9] only if  $f = 1$ , that means if no scale compression occurs and the  $\delta$ -values measured with the used instrument correspond exactly to the recommended values  $\delta^2\text{H}_{\text{VSMOW2}}$  and  $\delta^2\text{H}_{\text{SLAP2}}$ .

A corresponding formula is to be applied for  $\delta^{18}\text{O}$ .

Please note that the reporting scales for  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  are still denoted and referred to as VSMOW–SLAP scales, despite the exhaustion of supply of VSMOW and SLAP and their replacement by the two new international measurement standards VSMOW2 and SLAP2 [2]. Therefore, in the formulae (1) and (2) above, the measured values for the new international measurement standards VSMOW2 and SLAP2 have to be entered for LS1 and LS2 instead of those of VSMOW and SLAP, as well as the corresponding calibrated  $\delta^2\text{H}_{\text{SLAP2}}$  value for SLAP2 instead of the one for SLAP.

By using this procedure, all data using VSMOW2 and SLAP2 for calibration are still reported on the original VSMOW–SLAP scale. The assigned standard uncertainties of VSMOW2 and SLAP2 isotopic values must be included in any uncertainty propagation together with other uncertainties derived from measurements of the unknown sample and of measurements of the reference materials used, to calculate the combined standard uncertainty for the isotopic value of a sample.

The following paragraph recommends on proper data reporting using  $\delta$ -values.

The following recommendations are provided for reporting of the relative difference of hydrogen and oxygen stable isotope amount ratios using the  $\delta$ -notation modified from [10]. It is recommended that:

$\delta^2\text{H}$  values of all hydrogen-bearing substances be expressed relative to the VSMOW-SLAP scale with  $\delta^2\text{H}_{\text{VSMOW2}} = 0 \text{ ‰}$ , so that  $\delta^2\text{H}_{\text{SLAP2}} = -427.5 \text{ ‰}$ ;

$\delta^{18}\text{O}$  values of all oxygen-bearing substances be expressed relative to VSMOW-SLAP (with  $\delta^{18}\text{O}_{\text{VSMOW2}} = 0 \text{ ‰}$ ) or relative to VPDB (mainly for carbonates, defined by  $\delta^{18}\text{O}_{\text{NBS19-VPDB}} = -2.2 \text{ ‰}$ ), on a scale such that  $\delta^{18}\text{O}_{\text{SLAP2}} = -55.5 \text{ ‰}$ .

## 2.2. PREPARATION OF THE MATERIAL

In the planning phase it was decided to replace the reference material GISP (Greenland Ice Sheet Precipitation) by a material with an isotopic composition in the same isotopic range. Due to the origin of GISP, looking for a similar material in Greenland was an obvious choice.

Therefore, in the year 2007, contacts were established with the administration of the scientific research station Greenland Summit Station located on top of the Greenland ice shelf to obtain large quantities of water for the preparation of a new reference material for the next decades to come.

In the year 2008, over 400 litres of water were filled at the Greenland Summit Station in 20 plastic canisters of 20 litres each. The water was prepared from melted snow supplying this scientific research station with drinking water. The water was then shipped from the Summit Station to Thule, Greenland, at no cost to the IAEA, and the grateful appreciation of this fact goes to the scientific administration of the Summit Station and the US National Science Foundation. The containers were then further transported to the IAEA in Vienna.

In 2009, at the IAEA Isotope Hydrology Laboratory (IHL) all water was transferred into a palette tank and was intensively mixed for 15 hours. Due to the low conductivity and the low contamination origin of the samples no further treatment or purification step was deemed necessary. 300 litres were then filled into a specially designed stainless-steel tank [11], a tank type as already used for storage of other water reference materials like VSMOW2 and SLAP2. At that time the new material was provisionally named “GISP2” (Greenland Ice Sheet Precipitation 2), under which name all further experiments and provisional measurements were carried out. Only before its final release the new reference material was renamed to “GRES P” (Greenland Summit Precipitation) to avoid confusion with the isotopically different former reference material GISP, and to avoid a name collision. The remaining 130 litres of the water were filled into another smaller tank, which was used in the IAEA Isotope Hydrology Laboratory as an internal laboratory water standard “std13”.

Subsequently in the same year, about 4600 glass ampoules (20 mL each) were directly filled from the stainless-steel tank, immediately flame sealed, and then sterilized in larger batches for 8 hours at 105 °C in a large oven. The oven sterilization constituted at the same time an individual leak test for each ampoule. The filling had been done by attaching a 20mL dispenser directly to the slightly pressurized steel tank. Each ampoule was first flushed with argon, then filled by the dispenser with 20 mL water at a continuing argon flushing flow, and then immediately sealed in a manual ampoule sealing device with all ampoules being consecutively numbered. The whole filling and sealing process lasted less than one minute per ampoule. This excluded any significant evaporation of the water during the filling process and ensured isotopic similarity of sealed water ampoules.

In 2015, further additional 4000 smaller glass ampoules each containing 4 mL of GRESP water were filled and flame sealed from the original container in a similar manner as before. These smaller amounts per ampoule should support emerging applications like infrared laser spectrometry needing only limited amounts of this reference material per calibration

measurement. All these ampoules were similarly sterilized as in the previous case for 8 hours at 105 °C. The remainder of the water is kept in the original stainless-steel tank.

A first set of isotopic ratio analyses from bulk samples and ampoules was performed at the Isotope Hydrology Laboratory during the years 2009 and 2010, mainly by cavity ringdown infrared laser spectroscopy (Picarro L1102-i WS-CRDS water isotopic analyser), and partially by dual inlet isotope ratio mass spectrometry (Finnigan Delta+) using a water-gas equilibration method.

In 2010, within a restructuration of responsibilities at the IAEA, all stable isotope reference materials were transferred to the Terrestrial Environment Laboratory (TEL) in Seibersdorf, Austria, which since then has been responsible for the distribution of all existing IAEA reference materials. During the next years, the work was delayed by the necessary creation and establishment of a new stable isotope laboratory at the Terrestrial Environment Laboratory, and in 2011 and 2013 a second set of isotopic measurements by cavity ringdown laser spectroscopy had been performed (Picarro L1102-i) using equipment from a sister laboratory in Seibersdorf, the IAEA Soil and Water Management and Crop Nutrition Laboratory (SWMCNL).

A third set of isotopic characterization measurements was then performed in 2016/2017 using another cavity ringdown laser spectroscopy instrument of SWMCNL (Picarro L2130-I) for the 4mL and 20 mL ampoules, as well as for the remaining bulk material.

The water reference material GRESP is now made available to the public in two different options, either as one flame sealed glass ampoule containing 20 mL, or as a set of four smaller flame sealed glass ampoules containing 4mL each.

### 2.3. INVOLVED LABORATORIES

The calibration measurements were performed consecutively in two different IAEA laboratories due to the shift of responsibility for stable isotope reference materials: First during 2009/2010 in the IAEA Isotope Hydrology Laboratory; and later on during the years 2011, 2013 and 2016/2017 in the IAEA Terrestrial Environment Laboratory by using equipment of the IAEA Soil and Water Management and Crop Nutrition Laboratory, with the support of these other IAEA laboratories being warmly acknowledged.

It was decided to focus on numerous analyses using a single instrument in one laboratory to optimise the assessment of inhomogeneity. Over time, three different cavity ringdown infrared laser spectrometers were used from three IAEA laboratories. Only very few further confirmation measurements were performed in external laboratories.

In each of the three characterization campaigns, hundreds of individual measurements were performed on GRESP or closely related materials on individual and independent measurement runs and over extended time periods. All measurements were performed following best practices for calibration and quality control of measurements using the same evaluation method [12] to ensure consistent results.

Additional validation measurements were performed at the Isotope Hydrology Laboratory using a Finnigan Delta+ dual inlet stable isotope mass spectrometer with self-designed water/gas equilibration unit, as well as using different infrared laser spectrometers (Los Gatos Research DT-100 Liquid Water Isotope Analyzer). Further on, the Stable Isotope Laboratory of the Environmental Research Centre UFZ Leipzig, Germany, performed further validation measurements with a high temperature pyrolysis continuous flow mass spectrometer.

## 2.4. GENERAL MEASUREMENT SCHEME USED

The large majority of all measurements were performed by water stable isotope infrared laser spectrometry. This general method developed over the last 15 years is especially suitable for stable isotope analysis of pure water samples (like the IAEA reference materials). Due to the very low volume needed for individual injections (2 $\mu$ L), it allows repeated analysis even for materials with limited available quantities. This allows for several repetitions of analysis from the contents of each ampoule, improving the resulting data quality. In the available infrared laser spectrometry systems,  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  are analysed simultaneously for each injected sample.

In this study most  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  analyses were performed using three different Picarro water stable isotope infrared laser spectrometers via autosampler syringe-controlled injection of 2 $\mu$ L of a sample [13]. The analyses were performed on samples contained in small 2mL volume glass vials with a septum cap. The used autosamplers could hold up to 108 individual vials. In all cases, eight consecutive injections and measurements were performed for each vial.

For sample preparation out of glass ampoules, its whole water contents was first transferred into a suitable number of vials for subsequent analysis, with typically 1 mL contents, or in some tests with 0.5 mL or 2 mL contents. The septum vials had been tested to cause no isotopic drift of contained water for storage periods of several weeks. The same vial filling amounts were used for ampoules containing either GRESP water or VSMOW2 and SLAP2 calibration materials. Further laboratory standards or bulk samples used in this project were transferred into vials from tightly closed glass bottles tested previously and found suitable for long term storage to avoid any water evaporation and isotopic change over time.

The measurement sequence for each analytical run using infrared laser spectrometry was carefully designed according to its main purpose (calibration, inhomogeneity study, comparability tests).

In general, during the analytical assessment run of an ampoule, four or more vials were evenly distributed over a sequence run to avoid effects of isotopic drifts with time on data interpretation. A sequence run always contained a first initialization sample to prime and stabilize the measurement system, which was disregarded for any evaluation. Typically, a calibration set (VSMOW2, Quality Control, SLAP2) was measured several times and interspersed with longer sets of unknowns (mainly GRESP ampoules); this scheme was repeated and finished by a calibration set (see Fig. 1). The set of calibration standards typically contained several vials of VSMOW2, followed by quality control samples, and then by several vials of SLAP2. Intermediary laboratory standards (QC or others) were placed in between standards to avoid too large isotopic changes between consecutive vials to minimize memory effects. The number of vials with unknowns between calibration sets depended on experience with the analytical stability of the system, and it included interspersing unknowns from independent ampoules to be tested.

A symmetrical distribution of individual vials and sample positions was aimed for, to minimize the influence of potential instrument drifts or time effects on the final results (see Fig. 1).

Such a run sequence consisted of 40 to 70 vials with a total measurement time between two and four days for complete analysis (with 9 minutes needed per single injection, so nearly 1.5 hours for 8 injections per vial). As the used vial septum proved sufficiently tight to prevent isotopic drifts, the longer measurement time posed no problem. Even for designed homogeneity tests the full calibration scheme was still applied to enable a full calibration and increase the statistical significance of measurement data.

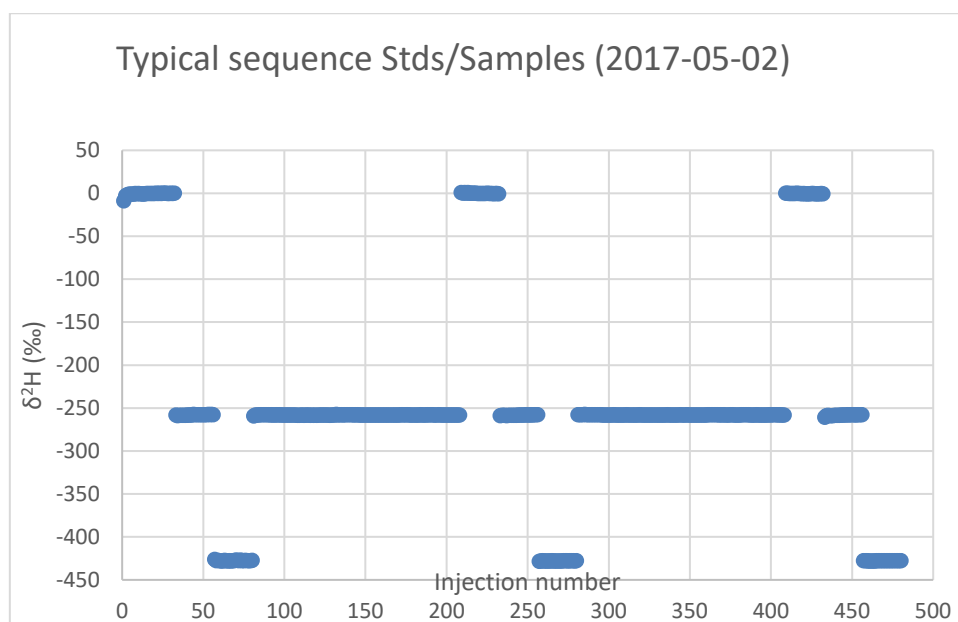


FIG. 1. A typical sequence of measurements of standards and unknowns to test heterogeneity between 4mL ampoules (here 480 injections of 60 individual samples). Three calibration blocks at beginning, middle and end of sequence (VSMOW2, Quality Control, SLAP2) show injected standards (Quality Control here is GRESP from 20mL ampoules). Between the calibration blocks, two long sequences of measurements from four individual ampoules of GRESP (4 mL) in shuffled mode are shown.

The data evaluation in all cases and for all instruments at the IAEA was performed with the Excel macro-spreadsheet based SICalib calibration program, developed at TEL for stable isotope data evaluation and integrated uncertainty calculation [12], available for free download [14]. Memory and drift corrections for all measurements were applied therein. The use of a consistent calibration process with calculation of combined standard uncertainties for each measurement enabled the use of a weighted means approach for combining these results obtained over long periods in a meaningful manner. This facilitated data handling for thousands of measurements as designed for this project.

## 2.5. INHOMOGENEITY ASSESSMENT

A key requirement for any certified reference material is the equivalence of its reference parameters at all its prepared individual ampoules/units. For reference materials in liquid form and careful handling, normally the complete homogeneity of all the material can be assumed. Despite that assumption and due to the necessary longer time periods to prepare all ampoules, extensive inhomogeneity tests were carried out on the prepared GRESP ampoules and the GRESP bulk material in order to assess a potential heterogeneity from the filling/sealing process of glass ampoules and to estimate any related uncertainty contribution for the ampoules, to fully ensure the suitability as a certified reference material.

The isotopic data measured from subsamples of each ampoule within one measurement day were compiled to derive the average measurement repeatability and standard error for each individual ampoule. These data were compared with the absolute bias between ampoules and standard error of ampoule means to estimate the effect of possible isotopic heterogeneity between ampoules as a residual of respective variances.

As an additional approach, the “between-bottle” inhomogeneity was calculated by single factor ANOVA analysis [15–17].



## 2.6. STABILITY STUDY

GRES P was analysed over an exceptionally long testing period of nine years before its release. It involved analyses taken from two independent bulk storage tanks (300 litres and 130 litres) at different times, as well as analyses from 20 mL ampoules covering the whole time span as well as analysis of 4 mL ampoules as produced in 2015. From the mean values of test portions analysed at different times, no difference in isotopic composition was observed. Besides, hermetically sealed glass ampoules guarantee the integrity of water against evaporation which is known as the major alteration mechanism. Biological activity in ampoules as another possible mechanism was prevented by sterilization of the ampoules (105 °C for >6 hours). A complication in this long-term stability study was the change of used instrumentation with time, which unfortunately could not directly be compared to each other (see in section 3.3).

## 2.7. CHARACTERIZATION

The  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  reference values for GRES P (see Table 4 below, section 3.4) were derived from characterization measurements in direct calibration with VSMOW2 and SLAP2 under repeatability conditions carried out in the years 2009-2011, 2013 and in 2016-2017 using mainly three laser spectrometry systems using the same analytical method (Picarro Inc., two Water Isotope Analyzers of type L1102-i and one of type L2130-i) in IAEA laboratories (Isotope Hydrology Laboratory and Terrestrial Environment Laboratory/Soil and Water Management and Crop Nutrition Laboratory).

These data were validated by additional measurements using a dual inlet isotope mass spectrometry system (Finnigan DeltaPlus with water-gas equilibration system) and three further Infrared laser Spectrometry systems (LGR Water Isotope Analyzers) in the IAEA Isotope Hydrology Laboratory, and a high temperature pyrolysis continuous flow mass spectrometer system at the Environmental Research Centre UFZ, Leipzig, Germany.

Numerous independent measurements were performed over time by the laser spectrometry systems and the dual inlet mass spectrometry system in the Isotope Hydrology Laboratory by measurements on the bulk material (“std13”) stored in a separate barrel. Further bulk measurements from the GRES P large barrel were performed in 2017 in the Terrestrial Environment Laboratory.

As an additional semi-independent approach for the assessment of the isotopic composition of GRES P, mixtures of two well-known internal laboratory standards were used, which had been carefully calibrated and isotopically checked over a period of one decade. They were gravimetrically mixed in such proportions to provide three water samples with isotopic values close to that of GRES P with nominal  $\delta^2\text{H}$  isotopic differences of +10 ‰, 0 ‰ and -10 ‰, respectively. The direct measurement of these samples and GRES P can exclude the occurrence of any scaling effects (no large isotopic differences during measurements), and they include additional independent previous calibration values obtained over one decade of laboratory measurements.

### 3. RESULTS AND DISCUSSION

#### 3.1. RESULTS OF INHOMOGENEITY STUDY

GRESF was bottled in quantities of either 20 mL or 4 mL in flame sealed glass ampoules.

The study of a potential “between-unit” inhomogeneity was performed twice, once for the 20 mL ampoules, and in a second assessment for the 4 mL ampoules with parallel assessment of further 20 mL ampoules and the bulk material. Samples were selected in each case by a random number generation from the pool of all prepared and consecutively numbered ampoules.

The homogeneity of 33 individual 20 mL (“large”) ampoules selected out of the initially produced 4600 ampoules has been investigated in 2010 by repeated stable isotope analysis using infrared laser spectrometry. From these measurement data of the year 2010 no inhomogeneity component could be attributed to, as the reproducibility within individual ampoules (“within-unit”) was larger than the combined effect of bias and reproducibility between ampoules, both for hydrogen and oxygen (Table 1).

In 2017 in a second homogeneity assessment, forty 4 mL (“small”) ampoules of the 4000 produced ampoules have been investigated by stable isotope analysis with infrared laser spectrometry, together with the analysis of thirteen 20 mL ampoules and additional comparison with results from one larger water sample taken from the bulk storage container.

The uncertainty contribution of a possible inhomogeneity between ampoules was found to be at very small levels of around  $\pm 0.019$  ‰ (4 mL) and  $\pm 0.013$  ‰ (20 mL) for  $\delta^{18}\text{O}$  and insignificant level (4 mL) and  $\pm 0.22$  ‰ (20 mL) for  $\delta^2\text{H}$ . For  $\delta^{18}\text{O}$  analyses of the bulk sample no possible inhomogeneity should be detected at all, however a residual of  $\pm 0.22$  ‰ was detected for  $\delta^2\text{H}$  of the bulk samples. In this respect it is to be noted that a residual inhomogeneity was now detected for large ampoules, while none was detected for  $\delta^2\text{H}$  of small ampoules (Table 1).

This provides a strong indication that these calculated data are rather subject to random effects and to observed performance variability of the used instrument at different measurement runs, than being the consequence of any real significant inhomogeneity between ampoules, both for small as well as for large ampoules..

As an independent approach, the between-ampoule inhomogeneity (“between-bottle”) was calculated by single factor ANOVA analysis [15] for all measured data of the year 2017. The method and its application is not explained here in detail, see [15–17]. By ANOVA analysis no residual inhomogeneity component could be detected, therefore supporting the statement above on insignificant inhomogeneity between the ampoules (Table 1).

Obtained results of the inhomogeneity studies are presented in Table 1.

TABLE 1: RESULTS OF THE INHOMOGENEITY STUDIES.

	Bias and ese (between amp.)	Repeatability (within amp.)	Inhomogeneity (residual diff.)	n	Bias and ese (between amp.)	Repeatability (within amp.)	Inhomogeneity (residual diff.)
	$\delta^2\text{H}$ (‰)				$\delta^{18}\text{O}$ (‰)		
20mL amp. & std13	0.16	0.27	0*	43	0.027	0.041	0*
4mL amp.	0.14	0.14	0*	40	0.037	0.032	0.019
20mL amp.	0.27	0.16	0.22	13	0.027	0.024	0.013
Bulk	0.28	0.17	0.22	5	0.030	0.041	0*
by ANOVA	0.10	0.13	0*	105	0.011	0.021	0*

\* Not quantifiable due to negative argument under the square root

**Note:** For  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$ , columns 2 and 6 represent the sum of absolute bias and estimated standard error (ese) between ampoule measurements, and columns 3 and 7 represent the calculated repeatability within ampoules. Squaring these values and taking the square root of columns 2-3 and 6-7 provide the deducted residual inhomogeneity component in columns 4 and 8 for  $\delta^{18}\text{O}$  and for  $\delta^2\text{H}$  (all data as absolute values in ‰). “n” denotes the number of ampoules tested (respective number of vial-means considered for ANOVA analysis). First data row is from year 2010, all other data from 2017. “amp.” denotes “ampoules”.

### 3.2. RESULTS FOR STABILITY STUDY

TABLE 2: RESULTS FOR GRESP STABILITY STUDY.

	year	average	Estimated standard error (2 sigma level)	n	average	Estimated standard error (2 sigma level)	n
		$\delta^2\text{H}$ (‰)			$\delta^{18}\text{O}$ (‰)		
Bulk	2010	-258.24	0.49	6	-33.397	0.039	6
	2011	-257.90	0.43	6	-33.403	0.028	6
	2013	-257.84	0.25	3	-33.390	0.023	3
	2017	-257.24	0.53	5	-33.394	0.072	5
std13	2009	-257.22	0.31	13	-33.358	0.029	13
	2010	-258.14	0.53	7	-33.426	0.028	7
	2013	-259.00	n.a.	1	-33.450	n.a.	1
T-Ampoules (20 mL)	2010	-258.41	0.15	33	-33.442	0.021	33
	2017	-257.47	0.29	15	-33.365	0.025	15
F-Ampoules (4 mL)	2017	-258.04	0.42	43	-33.397	0.046	43

**Note:** Annual averages and their estimated standard errors (ese) from daily means of isotope analyses for GRESP bulk material (taken out of the large storage tank), for “std13” (same water as GRESP stored in a different tank) and F- and T-ampoules (four ml and twenty ml contents). “n” denotes number of daily means used to calculate the average. Three different instruments using all the same cavity ringdown infrared laser spectrometry technique had been used for assessments in the years 2010/11, 2013 and 2017.

The yearly averages of data produced for bulk samples (“B”), “std13”, large 20 mL ampoules (“T”) and small 4 mL ampoules (“F”) (given in Table 2, Figure 2 and Figure 3) have been used to check for isotopic drift effects with time. To be noted is the change in instrumentation used during different years.

The data of Table 2 are displayed graphically in the two plots of Figure 2 for  $\delta^2\text{H}$  and Figure 3 for  $\delta^{18}\text{O}$ .

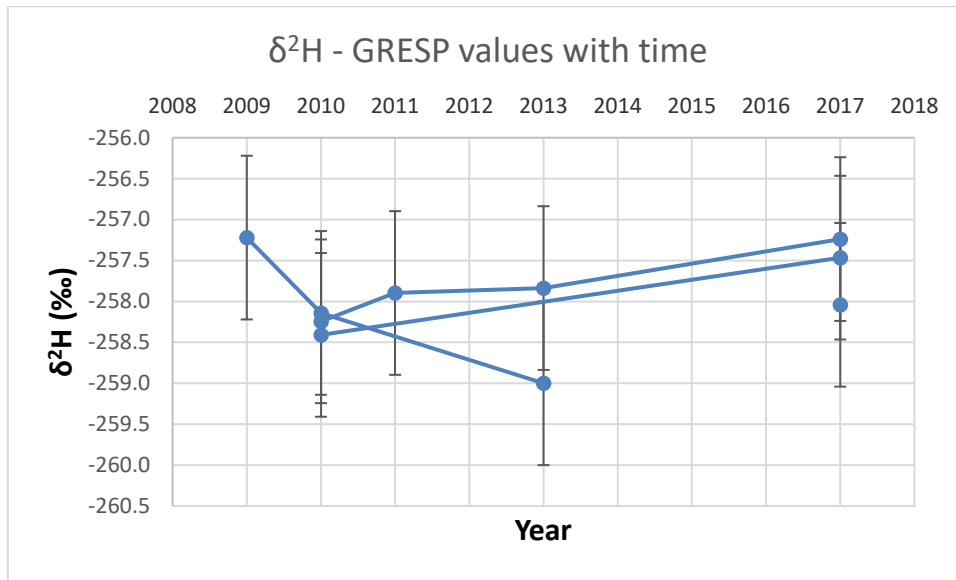


FIG. 2. Isotopic  $\delta^2\text{H}$  composition of GRESP with time measured from bulk tanks and T ampoules, including additional data for std13 for the period 2009-2013 (all data from Table 2).

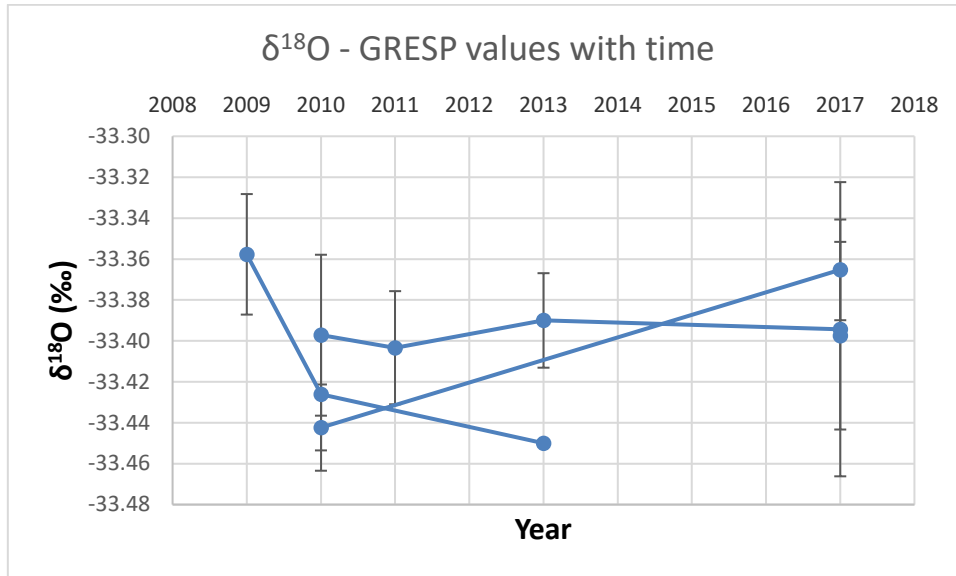


FIG. 3. Isotopic  $\delta^{18}\text{O}$  composition of GRESP with time measured from bulk tanks and T ampoules, including additional data for std13 for the period 2009-2013 (all data from Table 2).

Overall, for the whole data set and the eight-year period covered, no time trend is visible for the isotopic composition of GRESP within the uncertainty of mean values. The slope for the whole data set with time is close to zero and insignificant. Rather, changes in instrumentation used for analyses (e.g. mass spectrometry in 2009, laser spectrometry thereafter) and possible biases of instruments contribute to the data scatter and to apparent isotopic changes with time. There is no physical explanation for an isotopic change towards more negative delta values with time.

Within measurement uncertainties, no significant time effect on the isotopic composition of GRESP in storage containers could be deduced, hence stability is assumed. The monitoring of isotopic stability of GRESP in ampoules will be continued.

### 3.3. ASSIGNED VALUES AND THEIR UNCERTAINTIES

For both  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$ , the calculated mean value and the calculated combined standard uncertainty are based on all measurements performed in the two IAEA laboratories using three independent Picarro laser spectrometers.

All data were calibrated directly versus VSMOW2 and SLAP2 as measured in the same analytical run and checked by GISP or internal quality control materials. Combined standard uncertainties were calculated from results of measurements performed under repeatability conditions. Contributions are included from evaluated upper limits for the inhomogeneity between bottled glass ampoules and from the residual bias of evaluated mean values. Weighted means for all individual results for a given instrument were calculated (Table 3) using the combined uncertainties of all individual measurements including their calibration (data summary provided in two Excel files on the GRESP webpage [18]).

TABLE 3: SUMMARY DATA ON PERFORMED CALIBRATED MEASUREMENTS ON GRESP, AND ON STD13 RESPECTIVELY, IN VARIOUS ANALYTICAL SYSTEMS.

(Weighted means for each instrument are given as used to calculate the assigned value of GRESP. **In bold:** Weighted Averages with weighted standard uncertainties shown in brackets).

System	$\delta^2\text{H}$ (‰)				$\delta^{18}\text{O}$ (‰)		
	Weighted mean	Standard deviation	Number of analyses		Weighted mean	Standard deviation	Number of analyses
Data for GRESP							
Finnigan Delta+	-259.2	0.9	12		-33.38	0.04	24
LGR	-257.9	0.9	120		-	-	-
Picarro (T)	-257.9	0.3	20		-	-	-
Picarro (1)	-258.3	0.7	942		-33.45	0.10	944
Picarro (So)	-257.8	0.9	262		-33.41	0.08	198
Picarro (S)	-257.7	1.1	3619		-33.36	0.13	3213
Data from Cr and TCEA and	-258.0	0.8	50		n.a.	n.a.	n.a.
Cr/TCEA (UFZ Leipzig)	-257.5	1.0	50		-33.40	0.4	40
Weighted Average (GRES P)	-258.0	(0.01)*	5075		-33.39	(0.002)*	4419
Data for std13							
Finnigan Delta+	-259.6	0.8	3		-33.37	0.03	3
LGR	-257.8	0.8	108		-33.44	0.17	108
Picarro (1)	-257.8	1.1	221		-33.37	0.17	221
Picarro (So)	-259.0	0.5	20		-33.45	0.04	20
Weighted Average (std13)	-258.2	(0.02)*	352		-33.42	(0.006)*	352

\*Uncertainties for weighted means are similar to estimated standard errors for normal means (shown in brackets).

**Note:** The provided standard deviations for all data from each instrument only indicate the approximate performance of that analytical system. Additional GRESP data from UFZ Leipzig using two high temperature EA online techniques are presented as well.

Standard deviations in Table 3 for each instrument are provided only as an indication of the general spread of the respective data. The weighted average for GRESP from means of all instrument data constitutes the recommended value (in Table 7 further below).

The weighted average for std13 measured completely independent (Table 3) is in very good agreement with that for GRESP, therefore confirming independently the GRESP measurements.

It is interesting to note that the very few  $\delta^2\text{H}$  measurements by the dual inlet mass spectrometer showed a difference of more than 1 ‰ versus the other laser based measurements (no such difference is visible for corresponding  $\delta^{18}\text{O}$  values).

The resulting probability density function for the ten different instruments based on the individual standard deviations is shown in Fig. 4 for  $\delta^2\text{H}$ . The probability density function of any distribution is defined such that the whole area below the curve has the probability value of one, e.g. it shows the value probability along the x-space. Therefore, the area between any two x-values and the curve compared to the whole area provides the probability of the mean value being in this range. However, while Fig. 4 shows a distinct high probability around the peak area, this plot can easily be misinterpreted. In reality, averages for the individual instruments are distinctly different (Fig. 5), and are based on hugely different sized data sets.

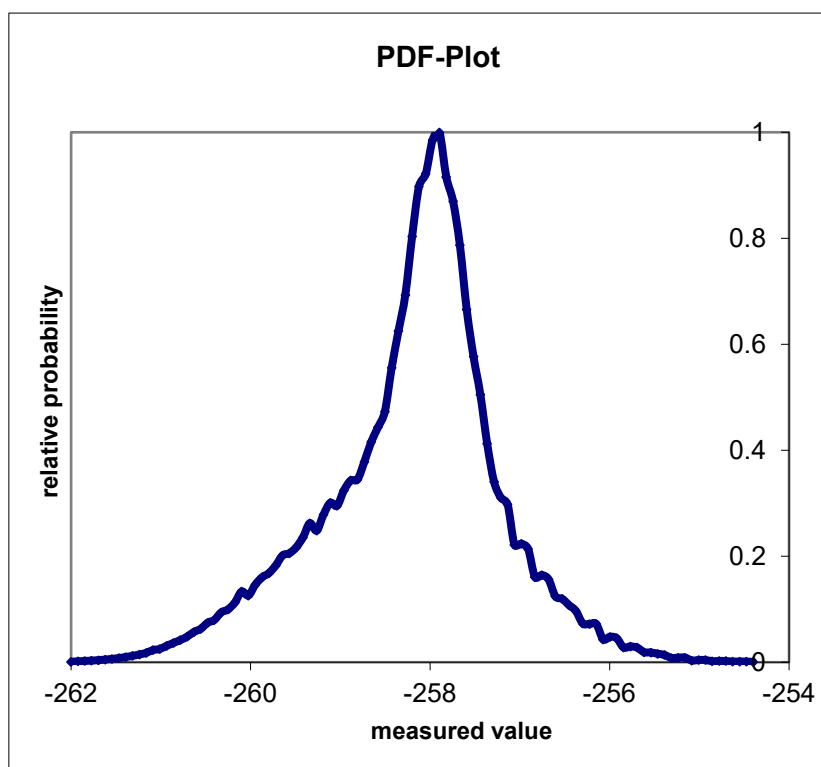


FIG. 4. Probability density function (PDF) plot for the 10  $\delta^2\text{H}$  mean values of Table 2, based on their standard deviations. Note that the area below the curve has the value 1 (100% probability), the y-scale is just artificially normalized to indicate distribution of the relative probability.

However, the data from Table 3 can be displayed in a different mode using a “pseudo” probability density function (PDF) [19], based on the calculation of estimated standard errors of the mean (standard deviation divided by square root of number of analyses) (Fig. 5).

It should be noted that this approach is only a rough approximation and not a mathematically sound process, as the standard deviations here are calculated with an equal weight per measurement in contrary to the weighted means approach. However, the main argument stays valid.

It is visible in Fig. 5 that the two instruments used for the majority of measurements – main peaks in the plot – do not provide consistent estimates for the mean value for both  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  (Picarro (1) type L1102-I; and Picarro (S) type L2130-i).

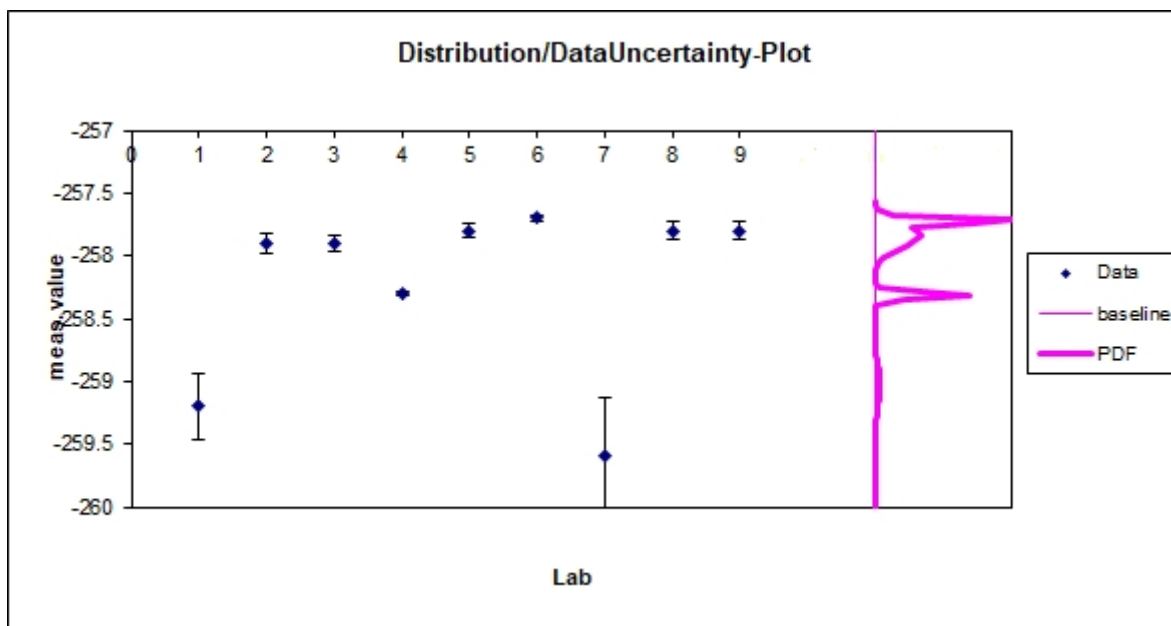


FIG. 5. “Pseudo” probability density function (PDF) plot (purple graph data at right side), providing a relative probability for the overall mean value, based on mean values of Table 3, and on related approximate estimated standard errors, as displayed on the plot. Obviously, the individual ranges of values (given as estimated standard error at 1-sigma level) do not overlap at all (shown in Fig.6a)

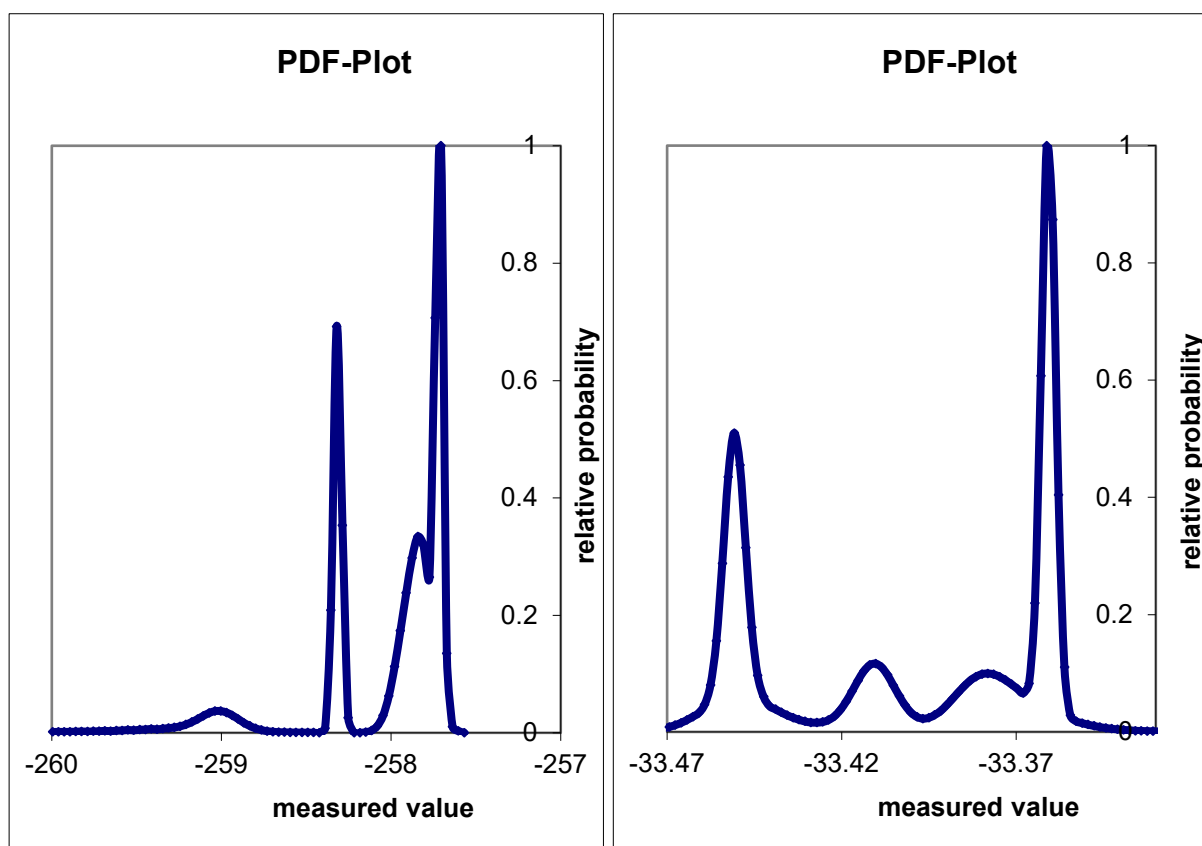


FIG. 6. Plot of the probability density function based on estimated standard errors for  $\delta^2\text{H}$  mean values (FIG.6a, left side) and for  $\delta^{18}\text{O}$  mean values (FIG.6b, right side), using data of Table 3.

This “pseudo” probability density function based on estimated standard errors from Fig. 5 and calculated according data of Table 3 is shown enlarged for  $\delta^2\text{H}$  (Fig. 6a) and for  $\delta^{18}\text{O}$  (Fig. 6b).

The two graphs of Fig. 6 show a low relative probability level at the position of the calculated gross GRESP average values from Table 3 for both  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$ . It reflects the fact that different instruments are obviously providing distinctly different mean values with remaining biases. This has consequences for the achievable accuracy and assignment of the final uncertainty of the GRESP reference values later (see Table 5 in Section 3.4 below), and using a conservative approach results in an increased final reported uncertainty.

Another independent method to assess the GRESP isotopic composition was performed in the year 2009, using two internal laboratory standards (“std9” and “std10”) of the Isotope Hydrology Laboratory, which had been subject to numerous careful calibrations over a period of 10 years (Table 5). With initial provisional measurements of GRESP at hand, these two internal laboratory standards were used to mix gravimetrically three sub-standards (ILS-25/-26/-27) in quantities of a quarter litre each (Table 4). Their mixing proportions were chosen to once exactly approximate the provisional  $\delta^2\text{H}$  value of GRESP (“ILS-26”), and to bracket it by the two other mixtures with  $\delta^2\text{H}$  values being 10 ‰ more positive (“ILS-25”), and being 10 ‰ more negative (“ILS-27”) (Table 5).

TABLE 4 GRAVIMETRIC MIXING OF LAB STANDARDS ILS-25, ILS-26 and ILS-27.  
(Uncertainties for balance drift and accuracy are  $\pm 0.01\text{g}$  each.)

	Weight std9 [g]	Weight std10 [g]	total weight [g]
for ILS-25	200.02	77.01	277.03
for ILS-26	180.00	88.23	268.23
for ILS-27	180.05	108.00	288.05

TABLE 5: ISOTOPIC COMPOSITION OF GRESP AS EVALUATED BY ASSESSMENT RELATIVE TO THREE ISOTOPICALLY SIMILAR STANDARDS ILS-25, ILS-26 AND ILS-27.  
(Average values in last row are weighted means with weighted standard uncertainties shown in brackets.)

Material	$\delta^2\text{H}$ (‰)				$\delta^{18}\text{O}$ (‰)		
	Weighted mean	Standard deviation	Number of analyses		Weighted mean	Standard deviation	Number of analyses
Std9	-189.6	0.4	Ref. value		-24.78	0.03	Ref. value
Std10	-397.7	0.3	Ref. value		-50.90	0.04	Ref. value
ILS-25	-247.4	0.3	101		-32.04	0.03	101
ILS-26	-258.1	0.3	149		-33.37	0.03	137
ILS-27	-267.6	0.3	149		-34.57	0.03	137
Evaluation of GRESP values based on respective isotopic values of the three ILS standards							
GRESP by ILS-25	-258.4	0.3			-33.42	0.03	
GRESP by ILS-26	-258.1	0.7			-33.41	0.04	
GRESP by ILS-27	-257.9	0.5			-33.40	0.07	
<b>Average GRESP by ILS approach</b>	<b>-258.2</b>	<b>(0.02)</b>			<b>-33.42</b>	<b>(0.002)</b>	



Therefore, this approach could allow a semi-independent assessment of the GRESP isotopic composition versus conventional calibration measurements. Measurements of GRESP together with the three gravimetrically mixed samples in the same analytical run would provide results being practically free of any isotopic bias normally caused by memory effects due to large isotopic differences. The isotopic values of std9 and std10 and for the three ILS-standards are derived from calibration values as obtained solely by dual inlet mass spectrometry with water/gas equilibration method and were directly calibrated versus VSMOW and SLAP standards.

The isotopic values for GRESP obtained by this approach to measure relative differences between GRISP and the three slab standards are displayed in the lower part of Table 5, being in very good agreement with calibrated measurements of Table 3.

Within stated standard uncertainties, all data for  $\delta^{18}\text{O}$  and for  $\delta^2\text{H}$  for GRESP and std13 in Tables 3 and 5 using two different evaluation approaches are consistent and not significantly different and allow to calculate firm weighted average values of -258.0 ‰ for  $\delta^2\text{H}$  and of -33.40 ‰ for  $\delta^{18}\text{O}$ .

Due to the large number of measurements for the GRESP characterization performed by different instrumentation, their respective statistical estimated standard errors of the mean (ESE) become very small. The largest effect is the deviation between the different mean values. Calculating the estimated standard error from the twelve GRESP values from Table 3 and from the three values from Table 5, the resulting ESE is 0.17 ‰ for  $\delta^2\text{H}$  and  $\pm 0.01$  ‰ for  $\delta^{18}\text{O}$  as purely statistical error component (Table 6).

Therefore the additional uncertainty component stemming from the assigned uncertainty of the used calibration materials VSMOW2 and SLAP2 become very relevant, as this component does not decrease with any number of measurements (for each one  $\pm 0.3$  ‰ for  $\delta^2\text{H}$  and  $\pm 0.02$  ‰ for  $\delta^{18}\text{O}$  respectively). In fact they form the dominating term for all uncertainty sources. This corresponds to a resulting uncertainty type B for GRESP of  $\pm 0.2$  ‰ for  $\delta^2\text{H}$  and  $\pm 0.014$  ‰ (rounded to 0.02 ‰) for  $\delta^{18}\text{O}$ . This uncertainty component for GRESP is even lower than each single uncertainty for the two primary calibrants, due to the shape of the uncertainty function, and GRESP being isotopically close to the midpoint between the isotopic composition of the two calibration standards.

However, it is concluded that the possible bias between different measurement methods and instruments is not fully taken into account by an estimated standard error calculation for GRESP, as obviously one or more instruments provided biased results. It seems not possible at this stage to find a solution or to apply a correction for the data from different instruments, as it is not clear and remains speculation which instrument may have had analytical problems e.g. in terms of non-linearities of spectral analysis for isotope intensities. As the old instruments used in the years 2009/2010 and 2013 no longer exist, this problem cannot be resolved by further tests.

It was therefore decided to apply a conservative approach and to increase the combined standard uncertainty of the final reference value to such level, that the majority of measured data would be covered within its 1-sigma uncertainty interval, now called combined uncertainty (Table 6, last line).

Individual measurement data are available in the supplementary Excel-Datasheets on the GRESP webpage [18].

TABLE 6: MAJOR UNCERTAINTY COMPONENTS FOR EVALUATION OF GRESP DATA.

GRESP	uncertainty component for $u(\delta^2\text{H})$ [‰]	uncertainty component for $u(\delta^{18}\text{O})$ [‰]
Weighted uncertainty for all weighted mean values	0.01	0.001
maximal measurement uncertainty as ese for individual methods (at $n \geq 20$ ) (to be applied both for sample and standards)	$\leq 0.12$	$\leq 0.016$
bias between 13 instrument / method means as ese	0.17	0.009
assigned uncertainty of used standards	0.20	0.02
<b>combined (4 terms above):</b>	<b>0.31</b>	<b>0.031</b>
<b>Combined uncertainty (‰) (at 1-sigma level), expanded conservatively for method offsets</b>	<b>0.4</b>	<b>0.04</b>

### 3.4. ASSIGNED REFERENCE VALUES AND UNCERTAINTIES

The assigned reference values and associated uncertainties for  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  of GRESP are the result of the data discussion in Section 3.3 and from data as provided both in Table 3 and Table 5 and uncertainties compiled in Table 6 (for details refer to Excel file ‘GRESP-Evaluation.xls’). The combined uncertainty of the reference value is assigned by slightly enlarging the original combined standard uncertainty on basis of expert judgment (compare rows 5 and 6 in Table 6), to allow for additional method offsets from data of individual instruments.

TABLE 7: REFERENCE VALUES AND ASSOCIATED COMBINED UNCERTAINTIES FOR THE CERTIFIED REFERENCE MATERIAL GRESP.

GRESP	Reference value (‰)	Combined uncertainty (‰) (at 1-sigma level)
$\delta^2\text{H}$	-258.0	0.4
$\delta^{18}\text{O}$	-33.40	0.04

On the GRESP webpage [18], in addition to the available individual data, a Reference Sheet for GRESP is available [20]. The details concerning all reported results as well as the criteria for certification may be found in the references as cited.

#### 4. METROLOGICAL TRACEABILITY

The  $\delta$ -values of the certified reference material GRESP have been calibrated on the  $\delta^2\text{H}_{\text{VSMOW-SLAP}}$  and  $\delta^{18}\text{O}_{\text{VSMOW-SLAP}}$  scales by directly using VSMOW2 and SLAP2 as calibration standards.

The traceability chain for  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  measurement results performed in testing laboratories, using VSMOW2 and SLAP2 as calibration standards, ends with the assigned  $\delta$ -values of these two materials calibrated in reference to their successor materials VSMOW and SLAP and therefore prolong the use of the VSMOW-SLAP scales established in 1976 ( $\delta^2\text{H}_{\text{VSMOW-SLAP}}$  and  $\delta^{18}\text{O}_{\text{VSMOW-SLAP}}$ ).

Only validated methods applied within stated scope were used by participating laboratories in this characterization study, using a common set of calibration values and a common scheme for data evaluation.

#### 5. CONCLUSIONS

This certification campaign allows the assignment of certified values for  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  with associated uncertainties following ISO guidelines. The certified values are derived from measurement results provided by the laboratories participating in the characterization study. Only validated methods were applied in the characterization of the certified reference material GRESP.

#### ACKNOWLEDGMENT

Several institutions contributed to the preparation of this reference material. The support of the Scientific Administration of the Greenland Summit Station (Ms. Sandy Starkweather) and the NSF is gratefully acknowledged for the collection of water at Summit Station and transport free of charge to the Thule airport in Greenland. Thanks to colleagues at the IAEA Isotope Hydrology Laboratory, to the IAEA Soil and Water Management and Crop Nutrition Laboratory for the use of their instrumentation, and to Mr. Matthias Gehre of the UFZ Stable Isotope Laboratory in Leipzig, Germany, as well as to Mr. Willi Brand, formerly at the MPI for Biogeochemistry, Jena, Germany, for performing stable isotope measurements for validation purposes.

All available IAEA reference materials may be found in the Reference Material Online Catalogue, <https://nucleus.iaea.org/sites/ReferenceMaterials/SitePages/Home.aspx>

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