CONSULTANTS' GROUP MEETING ON

STABLE ISOTOPE REFERENCE SAMPLES FOR GEOCHEMICAL

AND HYDROLOGICAL INVESTIGATIONS

IAEA, Vienna 16 - 18 September 1985

Report to the Director General

by

G. Hut

Scientific Secretary of the Meeting

April 1987
I. INTRODUCTION

A Consultants' meeting on Stable Isotope Reference Samples for Geochemical and Hydrological Investigations was convened in Vienna at the IAEA Headquarters from 16 to 18 September 1985. It was the fourth meeting on the same subject organized by the International Atomic Energy Agency. The other three meetings took place in November 1966, September 1976 and September 1983.

A follow up meeting was organized on 26 and 27 March 1987 in Vienna to settle the difference in opinions which arose about the draft of the report of the 1985 meeting. This is the final report on both meetings.

The meeting in 1983 was convened to review the results and the characteristics of the reference samples distributed after 1976 and to examine the need for the preparation of new reference materials.

The main conclusions of that meeting were (R. Gonfiantini, 1984):

- The same normalization method used so far for deuterium and oxygen-18 in water samples should also be applied for other isotopes and compounds;

- In order to have normalized, isotopically consistent systems, fractionation factors should be re-evaluated using the normalized scale. Until an agreement on new values has been reached, values from the literature should be used;

- New samples should be prepared in order to improve the intercomparison of isotopic results and possibly establish other normalized scales. Selected laboratories will receive sets of samples for intercomparison and calibration. Participation of other laboratories will be most welcome.
The IAEA should distribute the samples previously supplied only by the NBS:
NBS-14 (nitrogen)
NBS-21 (graphite)
NBS-22 (oil)
NBS-28 (quartz sand)

A new meeting should be convened in 1985 to evaluate the results obtained in the new intercomparison and to formulate recommendations on values to be adopted for some of the samples. Therefore results of the new intercomparison should be submitted by 31 January 1985.

This 1985 meeting was organized following the conclusions of the 1983 meeting.

The list of participants is given in Annex I and the list of participating laboratories in Annex II. The meeting was chaired by I. Friedman of the U.S. Geological Survey. Scientific Secretary was G. Hut from the IAEA Isotope Hydrology Section. The opening speech was given by B.R. Payne, Head of the Section of Isotope Hydrology.

The participants in the follow up meeting are denoted with an asterisk in Annex I.

The main recommendations of the meeting are:

- A distinction should be made between reference samples and intercomparison samples; three reference samples are proposed: VSMOW, SLAP and NBS19.

- Since PDB is virtually non-existent, a reference Vienna-PDB (VPDB) is introduced, defined by:

\[ \delta^{13}_C^{\text{NBS19/VPDB}} = +1.95 \, \text{‰} \]
\[ \delta^{18}_O^{\text{NBS19/VPDB}} = -2.20 \, \text{‰} \]

- PDB and VPDB are virtually identical, but the use of VPDB as a reference implies that the measurements have been calibrated through NBS19.

- Distribution of samples of reference and intercomparison materials be rationed to no more than one of each per laboratory every three years.
II. Presentation of isotopic data

II.1 The $\delta$ notation

Differences in isotopic composition are obtained by comparison of isotope ratios of a sample and a reference material. Since natural variations are small they are expressed as relative differences between isotope ratios:

$$\delta_{s/r} = \frac{R_{\text{sample}}}{R_{\text{reference}}} - 1$$  \hspace{1cm} (1)

where $R$ refers to the abundance ratio of the rare to the most abundant isotope of the element considered, and $s$ and $r$ to sample and reference material, respectively.

As an example for $^{18}O$:

$$\delta^{18}O_{s/r} = \frac{(^{18}O/^{16}O)_{\text{sample}}}{(^{18}O/^{16}O)_{\text{reference}}} - 1$$  \hspace{1cm} (2)

Since $\delta$-values are usually very small, it is customary to express these values in per mille ($^{\circ}/oo$). Note that $\delta$ has a dimensionless value.
II.2 Reference materials

The stable isotopes of hydrogen, carbon, nitrogen, oxygen and sulfur are included in the following considerations. Reference materials may be:

(a) existing materials, (b) previously existing materials, (c) defined, non-existing materials.

Details of many of these are described in Chapter III.

$\delta$ values for $^2$H in water and all other materials should be expressed relative to VSMOW (Vienna Standard Mean Ocean Water).

$\delta$ values for $^{13}$C of all substances should be expressed relative to the non-existing VPDB (Vienna Pee Dee Belemnite) which is defined in relation to the existing material NBS19 by:

$$\delta^{13}_C_{\text{NBS19/VPDB}} = +1.95 \, ^{\circ}/oo.$$  \hspace{1cm} (3)

$\delta$ values for $^{15}$N in all substances are generally expressed (see also IV.3) relative to nitrogen in air.

$\delta$ values for $^{18}$O in carbonates should be expressed relative to (non-existing) VPDB, which is defined in relation to the existing material NBS19 by:

$$\delta^{18}_O_{\text{NBS19/VPDB}} = -2.20 \, ^{\circ}/oo.$$  \hspace{1cm} (4)

$\delta$ for $^{18}$O in all other substances (e.g. water, silicates and sulfates) should generally be expressed relative to VSMOW.

$\delta$ values for $^{34}$S in all substances should be expressed relative to CDT (Canyon Diablo Troilite).
II.3. Reference scales for $^{18}O$

The mass spectrometric measurement for $^{18}O$ is usually performed on CO$_2$ where the $^{18}O/^{16}O$ ratio differs from that of the sample by a fractionation factor. Water is equilibrated with CO$_2$ at 25$^\circ$C, while carbonate is treated with 100 $^\text{O}$/oo phosphoric acid at 25$^\circ$C to produce CO$_2$. It is therefore convenient to express the results relative to reference materials which can be treated according to the same procedure. In those cases the fractionation factors need not (carbonates) or only approximately (water: this factor appears in correction term) be known.

The values of the fractionation factors for VSMOW-CO$_2$ (25$^\circ$C) and for VPDB-CO$_2$ (25$^\circ$C, 100 $^\text{O}$/oo H$_3$PO$_4$) have been subject to a long and sometimes controversial discussion [Gonfiantini (1984), Coplen et al (1984), Gonfiantini et al (1985)].

The fractionation factors recommended are given in Fig. 1 as the best known values yet.

II.4 Procedures to express $\delta$ values for $^2H$ and $^{18}O$ in waters

$\delta$ values for $^2H$ and $^{18}O$ in waters are obtained by comparing gases (H$_2$ or CO$_2$) prepared from samples and laboratory standard waters against the mass spectrometer standard working gas. Routine correction procedures have to be applied before the results can be converted to $\delta$ values on a scale where the zero point is the reference water VSMOW. Experience has shown that discrepancies exist between repeated or intercomparison results for samples showing large isotopic differences between sample gas and mass spectrometer standard working gas. These discrepancies reflect essentially multiplicative differences between mass spectrometers, periodic changes in individual spectrometers, or discrepancies in the chemical procedures which are not eliminated by the routine analytical corrections. Smoothing of these discrepancies is assisted by defining a scale based on two widely separated reference waters VSMOW and SLAP (see III.2).

As the supply of VSMOW and SLAP is limited, most laboratories employ their own widely separated pair of reference waters, which have been carefully calibrated on the VSMOW-SLAP scale. Measurements of these laboratory reference waters are made as a routine control with each batch of unknown samples.
Adjustments of the δ values for the samples are made by applying a correction factor derived after comparing the measured difference between the two laboratory reference waters with the once established calibration.

This procedure is commonly referred to as normalization. It is common practice to convert the measured δ values relative to the mass spectrometer working reference gas to δ values relative to the VSMOW using the measured difference between the working reference gas and the CO₂ equilibrated with VSMOW, δ₀/₀:

\[
\delta_x/₀ = \frac{\delta_x/₁ - \delta₀/₁}{1 + \delta₀/₀}
\]  

(4)

Similar equations apply for δ₁/₀ and δ₂/₀ by replacing x by 1 or 2.

Here 0, 1, 2, x and w refer to CO₂ equilibrated with VSMOW for ¹⁸O or hydrogen prepared from VSMOW, the laboratory reference samples 1 and 2 and the unknown water x, and the reference working gas, respectively.

The normalization procedure is applied if the difference between δ₁/₀ and δ₂/₀ differs from the proper value (obtained by comparison with VSMOW and SLAP):

\[
\begin{align*}
\delta^n_x/₀ - \delta^n₁/₀ & = \frac{\delta_x/₀ - \delta₁/₀}{\delta₂/₀ - \delta₁/₀} \\
\delta^n₂/₀ - \delta^n₁/₀ & = \frac{\delta₂/₀ - \delta₁/₀}{\delta₂/₀ - \delta₁/₀}
\end{align*}
\]  

(5)

For SLAP and VSMOW the normalized difference between δ₂/₀ and δ₁/₀ is:

\[
\begin{align*}
¹⁸O: & \quad \delta^n₂/₀ - \delta^n₁/₀ = -55.50 \degree/₀o \\
²H: & \quad \delta^n₂/₀ - \delta^n₁/₀ = -428.0 \degree/₀o
\end{align*}
\]

Combining equations (4) and (5) and results in:

\[
\delta^n_x/₀ = \delta^n_x/₁/₀ \cdot (\delta^n₂/₀ - \delta^n₁/₀) + \delta^n₁/₀
\]  

(6)
As can be seen from equation (6) it is irrelevant to carry out the scale conversion step (equation (4)). However, it is advisable to follow that procedure in order to check the proper functioning of the mass spectrometer and gas preparation procedures.

III. REFERENCE AND INTERCOMPARISON SAMPLES DISTRIBUTED FOR GEOCHEMICAL AND HYDROLOGICAL INVESTIGATIONS

III.1 VSMOW (Vienna Standard Mean Ocean Water): Water

This sample was prepared by H. Craig, University of California at San Diego by mixing distilled sea water (collected in the Pacific Ocean - lat. 0°, long 180° in July 1967) with small amounts of other waters in order to bring its isotopic composition as close as possible to that of the defined SMOW (Craig, 1961).

According to the control analyses made by Craig, VSMOW has the same $^{18}O / ^{16}O$ ratio as the defined SMOW but a slightly lower $^{2}H$ value of 0.2 $\delta^O/oo$. This difference, however, is much smaller than the experimental error of most laboratories. In the 1983 Advisory Group Meeting it has been adopted therefore, that VSMOW should be considered isotopically identical to the defined SMOW and adopted as zero point for $^{18}O$ and $^2H$ scale for natural compounds. To our knowledge, this decision, which is in accordance with Craig's recommendation, has been generally adopted.

The absolute isotopic composition of VSMOW is reported in Table I.

Until 1976 VSMOW was kept in a stainless steel container under nitrogen atmosphere. In 1977 it was transferred into sealed glass containers, part of which have been shipped to NBS in Washington D.C., USA. The amount stored is listed in Table II. The samples are considered to be reference materials.
III.2 SLAP (Standard Light Antarctic Precipitation): Water

SLAP was obtained from a firn sample collected by E. Picciotto, Université Libre de Bruxelles, at Plateau Station, Antarctica in 1967. Its absolute isotopic ratios are reported in Table I.

During the 1976 meeting, the $\delta$ values of SLAP with respect to VSMOW were conventionally fixed at: $\delta^{18}O = -55.50$ $^0/oo$ and $\delta^2H = -428.0$ $^0/oo$. It was recommended that the $\delta$ scales for $^{18}O$ and $^2H$ should be normalized using the above values in the isotopic analysis of natural water samples.

The amount of SLAP stored in sealed glass containers is shown in Table II. The samples are considered to be reference materials.

III.3 NBS1 and NBS1A: Water

NBS1 was derived from the Potomac River and NBS1A from snow collected at the Yellowstone National Park. The first sample was used by Craig to define SMOW (Craig, 1961): $\delta^{18}O_{NBS1/SMOW} = -7.94$ $^0/oo$ and $\delta^2H_{NBS1/SMOW} = -47.6$ $^0/oo$.

These samples, formerly kept at the NBS, were sent to the IAEA in the early sixties for distribution. There are doubts, however, concerning the way in which NBS1 and NBS1A were preserved during the years prior to 1977, when they were stored finally in sealed glass containers (see Table II). Therefore, use of these samples is not recommended for calibration purposes.

The isotopic composition of NBS1 and NBS1A was first determined by Craig (1961) and later reported by Halevy and Payne (1967) and Gonfiantini (1977, 1978) on the basis of analyses made by different laboratories:

$\delta^{18}O_{NBS1A/SMOW} = -24.33$ $^0/oo$

$\delta^2H_{NBS1A/SMOW} = -183.3$ $^0/oo$.

III.4 GISP (Greenland Ice Sheet Precipitation): Water

GISP was prepared by W. Dansgaard, University of Copenhagen from a sample of Greenland firn. It has been distributed together with VSMOW and SLAP for intercalibration purposes since 1977. GISP is considered to be an intercomparison material.
III.5 NBS16 and NBS17: Carbon dioxide

These materials have been prepared by T.B. Coplen and C. Kendall of the US Geological Survey at Reston, Virginia, USA and have quite different isotopic composition. NBS16 has low $\delta^{18}O$ and $\delta^{13}C$ values and is derived from CO$_2$ produced as an industrial by-product. NBS17 is CO$_2$ derived from a gas well in the southwestern United States. Its $\delta^{18}O$ and $\delta^{13}C$ values are less negative than those of NBS16. Details on the preparation of both gases are reported by Coplen and Kendall (1982).

The two samples have been split and stored in sealed glass tubes each containing approximately 300 μmoles of CO$_2$ (7 ml at STP). These samples were considered to be intercomparison materials. The supply of both materials is almost exhausted: the distribution is therefore terminated.

III.6 NBS18 and NBS19: Calcium carbonate

These two materials were prepared by I. Friedman, J.O'Neil and G. Cebula of the U.S. Geological Survey at Denver, Colorado and Menlo Park, California (1982). Their isotopic compositions are intermediate between VSMOW and SLAP. The amount stored is shown in Table II.

NBS18 is a carbonatite from Fen, Norway, collected by B. Taylor (University of California, Davis) and crushed by H. Friedrichsen (University of Tübingen, Federal Republic of Germany). The fraction between 40 and 170 mesh (1.7 kg) was sent to the NBS and stored and bottled as NBS18.

NBS19 (also called IS-Limestone) was obtained from a single slab of white marble of unknown origin. After crushing, the fraction between 48 and 80 mesh was selected. Of the 3 kg sent to NBS, half is kept in a sealed ampoule and the rest has been bottled for distribution. The bottles are stored over soda lime.
The detailed description of the preparation and preliminary isotopic analyses of NBS18 and NBS19 are reported in Friedman, O'Neil and Cebula (1982).

During the meeting it was recommended that NBS18 be used as an intercomparison material, whereas NBS19 be used as a reference sample for $^{13}$C. Since PDB is virtually non-existent, a reference Vienna-PDB (VPDB) approximately equal to PDB, is defined by:

$^{13}\text{C}_{\text{NBS19/VPDB}} = +1.95 \, ^0\text{o/oo}$ and $^{18}\text{O}_{\text{NBS19/VPDB}} = -2.20 \, ^0\text{o/oo}$.

The status of the availability of both samples is shown in Table II.

III.7 NBS20: Calcium carbonate

This material was prepared from Solenhofen limestone. It has been shown by a number of laboratories to be no longer satisfactory, especially for $^{18}\text{O}/^{16}\text{O}$ standardization, presumably because it was too finely ground and apparently exchanges with atmospheric $\text{H}_2\text{O}$. There is also a possibility that the original sample was contaminated with oil before it was crushed and ground. The original PDB scale was defined by

$^{13}\text{C}_{\text{NBS20/PDB}} = -1.06 \, ^0\text{o/oo}$ (Craig, 1957).

This material is available only from the NBS.

III.8 NBS21: Graphite

The supply of this material is almost exhausted, therefore the distribution by the IAEA is terminated.

III.9 NBS22: Oil

This material was prepared by S. Silverman of the University of California at San Diego, USA. Samples may be obtained from the IAEA or the NBS.

III.10 NBS23: SrCO$_3$

This material was prepared by I. Friedman of the USGS at Denver, Colorado, USA. Samples may be obtained from the IAEA or the NBS. There are doubts about the homogeneity. Therefore the distribution is discontinued.
III.11 NBS28: Quartz sand

This material is intended for δ¹⁸O intercomparison of silicates. The amount stored is shown in Table II.

III.12 NBS30: Biotite

The material was prepared by Friedman, O'Neil and Cebula from a sample of Lakeview tonalite (South California batholith) provided by L. Silver (California Institute of Technology, Pasadena). Granulometry 200 to 300 microns. The sample is intended for δ²H and δ¹⁸O measurement intercalibration in silicates. The δ²H value should be determined on the water fraction (3.5%). The amount stored is shown in Table II.

III.13 Sucrose ANU: Sucrose

This material was supplied by H. Polach, Australian National University, Canberra and was originally intended to replace NBS oxalic acid used for ¹⁴C standardization. The samples are to be used for intercomparison of ¹³C analyses. The amount stored is shown in Table II.

III.14 PEFl: Polyethylene foil

This material was prepared by H. Gerstenberger and M. Herrmann (1983), Zentralinstitut für Isotopen- und Strahlenforschung, Leipzig, GDR. The samples are to be used for intercomparison of δ²H and δ¹³C measurements. The amount stored is shown in Table II.

III.15 NGS1: Natural gas

This material was collected by G. Hut (University of Groningen, The Netherlands). The gas is coal related and consists of more than 80% CH₄ with a δ¹³C value of approximately -29‰/oo. The samples are stored in small pressurized cylinders. Laboratories in America may obtain samples through M. Schoell, Chevron Oil Field Research Co., La Habra, California, USA. All others should write to the IAEA. The amount stored is shown in Table II. The approximate chemical composition is shown in Table VIII.
III.16 NGS2: Natural gas

This material was collected by T. Ricchiuto (Agip S.p.A., Milano, Italy). The gas is oil related. Its CH₄ content is greater than 50 %, and the δ¹³C value of this methane is approximately −45 ‰. The samples are stored in small pressurized cylinders. Laboratories in America may obtain samples through M. Schoell, Chevron Oil Field Research Company, La Habra, California, USA. All others should write to the IAEA. The amount stored is shown in Table II. The approximated chemical composition is shown in Table VIII.

III.17 NGS3: Natural gas

This material was collected by T. Ricchiuto (Agip S.p.A., Milano, Italy). The gas is biogenic, and contains more than 95% CH₄ which has a δ¹³C value of approximately −72 ‰.

The samples are stored in small pressurized cylinders. Laboratories in America may obtain samples through M. Schoell, Chevron Oil Field Research Company, La Habra, California, USA. All others should write to the IAEA. The amount stored is shown in Table II. The approximate chemical composition is shown in Table VIII.

III.18 IAEA-N1: (NH₄)₂SO₄

This material was prepared by E. Salati (CENA, Piracicaba, Brazil). The samples should be used for intercomparison of δ¹⁵N results. The value of δ¹⁵N relative to atmospheric nitrogen is approximately +0.36 ‰. The amount stored is shown in Table II.

III.19 IAEA-N2: (NH₄)₂SO₄

This material was prepared by E. Salati (CENA, Piracicaba, Brazil). The samples should be used for intercomparison of δ¹⁵N results. The value of δ¹⁵N relative to atmospheric nitrogen is approximately +21 ‰. The amount stored is shown in Table II.
III.20  IAEA N3: KNO$_3$

This material was prepared by A. Mariotti (Université P. et M. Curie, Tour, Paris, France). The samples should be used for intercomparison of $\delta^{15}$N results. The amount stored is shown in Table II.

III.21  NSVEC: Nitrogen gas

This material was originally prepared by G. Junk and H.J. Svec, Iowa State College, USA, who determined the absolute ratio of $^{15}$N/$^{14}$N (Junk and Svec, 1958). The material was split into samples in glass containers by C. Kendall (USGS, Reston, VA, USA), similar to the method described by Coplen and Kendall (1982). The amount stored is shown in Table II.

III.22  NBS122: Sphalerite (ZnS)

This material is intended for intercomparison of sulfur isotope ratios. Its $\delta^{34}$S value relative to Canyon Diablo Troilite is approximately 0 $^\circ$/oo. There is some doubt about the homogeneity of the sample. The amount stored is shown in Table II.

III.23  NBS-123: Sphalerite (ZnS)

This material is intended for intercomparison of sulfur isotope ratios. $\delta^{34}$S of this sample vs CDT is approximately +17.00 $^\circ$/oo.

The amount stored is shown in Table II.

III.24  NBS127: BaSO$_4$

This material was prepared by J.R. O'Neil (USGS, Menlo Park, California, USA) and bottled by I. Friedman (USGS, Denver, Colorado, USA) for intercomparison of sulfur and oxygen isotope ratios from sulfates. The material was prepared by ion exchange of sulfate in seawater from Monterey Bay, California. The amount stored is shown in Table II. NBS127 should replace OGS.
III.25**  OGS: BaSO₄**

This material was prepared by J. Moribe (Japan Ocean Research Inst. Tokyo) directly precipitated from sea water sulfate. The material is in principle replaced by NBS127. The amount stored is shown in Table II.

III.26 **Sulfur (elemental)**

This material was prepared by E. Roth (CEN, Saclay, France) from Soufre de Lacq. The amount stored is shown in Table II.

IV. **RESULTS OF STABLE ISOTOPE MEASUREMENT INTERCOMPARISON**

IV.1 **Hydrogen**

The list of results normalized on the VSMOW-SLAP scale is reported in Table III.

Due to the limited number of results no averages are calculated. It should be noted that these results are in good agreement with those reported previously (Confiantini, 1984).

$\delta^2$H values of the three natural gases are new results.

IV.2 **Carbon**

The results reported relative to VPDB, using the defined value of $\delta^{13}\text{C}_{\text{NBS19/VPDB}} = +1.95^{\circ}/oo$, are reported in Table IV.

Most of the results are in good agreement with those reported earlier (Confiantini, 1984) except for the $\delta^{13}\text{C}$ value of NBS23 of $-35.32 + 0.16^{\circ}/oo$. It might be expected that normalization would give an improved standard deviation. However, this possibility can be ruled out because the mean $\delta^{13}\text{C}$ value of NBS16 is even more negative at $-41.59^{\circ}/oo$, and its standard deviation is excellent, $\pm 0.06^{\circ}/oo$. 
Repeated analyses by W.G. Mook, T. Coplen and J.R. O'Neil showed that the material is probably isotopically inhomogenous, so that NBS23 appears to be an unsatisfactory intercomparison or second reference material.

It was proposed at the meeting by T. Coplen that an NBS lithium carbonate may be a suitable replacement for NBS23 if that were necessary. The mean \( \delta^{13}C \) value reported at the meeting of 10 samples selected randomly from a 2 kg container is \(-46.65 \pm 0.06\) \(^{0}/oo\). The mean \( \delta^{18}O \) value relative to VPDB is \(-27.02 \pm 0.05\) \(^{0}/oo\). Thus, this material has the desirable characteristic that its \( \delta^{13}C \) value is significantly more negative than that of NBS23. Further analyses by several laboratories will be required to determine if this lithium carbonate is a satisfactory intercomparison material.

IV.3 Nitrogen

There were no samples distributed to determine \( \delta^{15}N \) values. However, the difficulty was discussed encountered in the use of air nitrogen as a standard. The influence of argon contents in nitrogen gas samples on \( \delta^{15}N \) values is described in Annex III by Gerstenberger et.al.

After the Consultants' Meeting a batch of NSVEC, nitrogen from a tank of pre-purified Matheson nitrogen gas prepared by Carol Kendall from the US Geological Survey, Reston, VA, USA was received. This gas has an absolute ratio of \(^{15}N / {^{14}N}_2 = 7326 \times 10^{-6} \) as reported by Junk and Svec (1958).

Kendall reported a \( \delta^{15}N \) value of \(-1.63 \pm 0.03\) \(^{0}/oo\) for NSVEC relative to NBS14 and a value of \(+1.65 \pm 0.10\) \(^{0}/oo\) for IAEA N1 relative to NBS14.

IV.4 Oxygen

The list of results is reported in Table V. The results are normalized as discussed in II.4: results of carbonates are expressed relatively to VPDB, respectively, defined by

\[
\delta^{18}O_{NBS19/VPDB} = -2.70\; ^{0}/oo \text{ and normalized such that} \\
\delta^{18}O_{SLAP/VSMOW} = -55.50\; ^{0}/oo. \text{ The results of waters and silicates}
\]
are reported relative to VSMOW and normalized on the VSMOW-SLAP scale. Where applicable, the fractionation factors from the scheme depicted in Figure 1 have been used.

Only very few results for $^{18}O$ of sulfates are available.

IV.5 Sulfur

The list of results is reported in Table VI. The current situation of intercomparison of sulfur isotope measurements is still far from ideal. It is felt that new intercomparison materials are needed. Among the available intercomparison materials NBS122 is thought to be inhomogeneous. Remeasurement after the meeting using different sample sizes for sample preparation, however, did not bring a clear answer to this problem as depicted in Table VII.

A new reference material, $Ag_2S$ has been prepared by B.W. Robinson, DSIR, Lower Hutt, New Zealand from a sphalerite provided by St. Halas, University Maria Curie-Sklodowska University, Lublin, Poland, with $\delta^{34}S$ vs CDT close to $O^{18}/oo$.

The group made the recommendation that the distribution of NBS122, NBS123 and NBS127 should be restricted until new samples become available.

V. PRESENT STATUS OF REFERENCE AND INTERCOMPARISON SAMPLES

V.1 Introduction

The Consultants' Group strongly emphasizes that reference and intercomparison samples are very valuable materials available in limited amounts which have required considerable efforts in their preparation and standardization by many laboratories worldwide. Therefore, the samples should be treated with care and only be used to calibrate laboratory working or secondary standards which each laboratory should prepare for its own routine use.

In summary, the recommendation of the Consultants' Group is to strictly ration these samples in such a way that no laboratory receives more than one
particular reference or intercomparison sample once in three years. Each laboratory is strongly advised to prepare its own internal working standards.

The Consultants' Group recommends that reference materials be properly stored. Solid samples should be kept in desiccators under vacuum.

Recommendations on individual reference materials are listed below.

V.2 Reference samples

- VSMOW and SLAP: if the schedule outlined above is followed, then the supply is sufficient for at least 10 years.
- NBS19: the same applies as for VSMOW and SLAP.

V.3 Intercomparison samples

- NBS1 and NBS1A: the use of these samples is not recommended.
- GISP: is available for at least 10 years.
- NBS16 and NBS17: due to the limited number of samples, the distribution is terminated.
- NBS18: with proper use, the supply will last for at least another 5 years.
- NBS20: use of it is not recommended. The material is only distributed by the NBS, the supply may last for 10 years or more.
- NBS21: the distribution by the IAEA and the NBS is terminated.
- NBS22: is available for at least 10 years.
- NBS23: the distribution is terminated.
- NBS28: is available for at least 10 years.
- NBS30: is available for at least 10 years.
- Sucrose ANU; is recommended for carbon-13 measurements only; the supply is enough for at least 10 years.
- PEFl: recommended for deuterium and carbon-13; the supply is enough for more than 10 years.
- NBS122: the homogeneity of the sample is still in question.
- NBS123: the supply is enough for at least 10 years.
- NBS127: the supply is enough for at least 10 years.
- OGS: in principle this sample is replaced by NBS127; the distribution is terminated.
- Soufre de Lac: is available for at least 10 years.
- IAEA N1: the supply is enough for at least 10 years.
- IAEA N2: the supply is enough for at least 10 years.
- IAEA N3: the supply is enough for at least 10 years.
- NGS1: the supply is enough for at least 10 years.
- NGS2: the supply is enough for at least 10 years.
- NGS3: the supply is enough for at least 10 years.

Distribution of the samples NGS1, NGS2 and NGS3 for North American laboratories is made through Dr. M. Schoell, Chevron Oil Field Research Company, P.O. Box 446, La Habra, CA 90631, USA. Others may obtain these materials from the IAEA.

VI. FUTURE REFERENCE AND INTERCOMPARISON SAMPLES

VI.1 Introduction

With regard to the preparation and distribution by the IAEA of new reference and intercomparison samples, it was felt by the Consultants' Group that this was only justified if a sufficient large number of laboratories were interested in a particular sample. It is recommended that in specific cases where only a few laboratories are interested, those laboratories should prepare their own intercomparison material.

In the following paragraphs the situation for the individual isotopes is discussed.

VI.2 Deuterium

The situation is satisfactory. The materials available are: water, biotite, polyethylene and natural gases.

It might be useful to have an additional organic material which is chemically stable. Therefore, a wax will be investigated and tested for homogeneity by I. Friedman and W. G. Mook.
VI.3 Carbon-13

Here the situation is satisfactory for carbonates, natural gases, polyethylene and mineral oil. For carbonates there is still need for a material depleted in $^{13}$C.

A replacement for NBS21 (graphite) is being prepared by the NBS.

VI.4 Nitrogen-15

The new material NSVEC is available now, it should replace NBS14 in the near future. For this purpose an intercomparison will be organised.

A standardized procedure to purify nitrogen from air is investigated (see Annex III).

IAEA N1 and IAEA N2 have not been analyzed extensively and need further testing for homogeneity. The situation for IAEA N3 is satisfactory.

VI.5 Oxygen-18

The situation is satisfactory for water, carbonates, silicates and sulfates.

The Consultants' group recommended to prepare a new organic material, a sulfate depleted in $^{18}$O and a silicate with either a depleted or an enriched oxygen-18 content.

VI.6 Sulfur-34

The situation is satisfactory for BaSO$_4$ and elemental sulfur. A new Ag$_2$S material has been prepared with $\delta^{34}$S relative CDT close to 0$^\circ$/oo. If this material is satisfactory, then other Ag$_2$S materials will be prepared with $\delta^{34}$S relative to CDT approximately +20$^\circ$/oo and approx. -20$^\circ$/oo.
VII. RECOMMENDATIONS

1. The Consultants' Group recommends that due to the limited availability of the reference and intercomparison samples, each laboratory receives no more than one particular sample once in three years. Each laboratory is strongly advised to prepare and use its own internal working standards.

2. Hydrogen and oxygen isotope data reporting of water should be done on the normalized VSMOW-SLAP scale.

3. Since PeeDeeBelemnite (PDB) is virtually non-existent it is recommended that a new reference standard is introduced: Vienna-PDB (VPDB), defined by $\delta^{13}C_{\text{NBS19/VPDB}} = +1.95^\circ/oo$ and $\delta^{18}O_{\text{NBS19/VPDB}} = -2.20^\circ/oo$.

4. It is recommended that purified atmospheric nitrogen is taken as the zero-point on the $\delta^{15}N$-scale and that the purification procedure is standardized.

5. It is recommended that additional samples be prepared as stated in Chapter VI:
- for hydrogen: a stable organic sample e.g. a wax
- for oxygen: a stable organic sample, a sulfate depleted in $^{18}O$ and a silicate either depleted or enriched in $^{18}O$.
- for sulfur: three $\text{Ag}_2\text{S}$ materials with low, intermediate and high values for $^{34}S$ content.

6. It is recommended that the Agency approaches the editors of scientific journals and suggest that they adopt a standard method of reporting isotopic data, as mentioned in II and that authors are requested to mention equations used for converting $\delta$ values from one scale to another and the values of the fractionation factors involved.
REFERENCES


Figure 1

Relations between oxygen isotopic composition of various reference samples. VPDB-CO₂ and NBS19-CO₂ refer to the CO₂ prepared by treating carbonate with 100% H₃PO₄ at 25°C. VSMOW-CO₂ and SLAP-CO₂ refer to CO₂ equilibrated with the water at 25°C. $D_c$ and $D_w$ denote defined differences in $\delta^{18}O$. $\alpha_1$ and $\alpha_2$ denote measured fractionation factors. The $\Delta$ values result from the foregoing definitions and measurements. The arrows point from reference to sample.
ANNEX 1

List of participants

<table>
<thead>
<tr>
<th>Country</th>
<th>Name</th>
<th>Laboratory Code</th>
</tr>
</thead>
<tbody>
<tr>
<td>Austria</td>
<td>E. Pak</td>
<td>A-1</td>
</tr>
<tr>
<td>China</td>
<td>Shen-jin Jin</td>
<td>CHI-2</td>
</tr>
<tr>
<td>Germany, Republic of</td>
<td>W. Stichler</td>
<td>D-6</td>
</tr>
<tr>
<td></td>
<td>H. Nielsen</td>
<td>D-2</td>
</tr>
<tr>
<td>German Democratic Republic</td>
<td>H. Gerstenberger*</td>
<td>DDR-1</td>
</tr>
<tr>
<td>Italy</td>
<td>A. Longinelli</td>
<td></td>
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<td>T. Ricchiuto</td>
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<td>The Netherlands</td>
<td>W.G. Mook*</td>
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<td>New Zealand</td>
<td>P. Blattner**</td>
<td>NL-1</td>
</tr>
<tr>
<td>Sweden</td>
<td>J. Burgman*</td>
<td></td>
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<tr>
<td>United Kingdom</td>
<td>W.G. Darling</td>
<td></td>
</tr>
<tr>
<td></td>
<td>P. Greenwood*</td>
<td>GB-5</td>
</tr>
<tr>
<td>USA</td>
<td>T. Coplen*</td>
<td>USA-7</td>
</tr>
<tr>
<td></td>
<td>I. Friedman</td>
<td>USA-3</td>
</tr>
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</table>

IAEA

T. Akiti
J.F. Aranyossy
R. Gonfiantini*
B.R. Payne
A. Plata Bedmar
P. Schwarz
I. Vovk
Y. Yurtsever
G. Hut*

* Present at the follow up meeting on 26 and 27 March 1987 in Vienna.
** C.B. Taylor represented P. Blattner at the follow up meeting.
ANNEX II

Laboratories which took part in the intercalibration

A-1 Institut für Radiumforschung und Kernphysik
der Österreichischen Akademie der Wissenschaften,
Vienna, Austria

CDN-1 Department of Physics
University of Calgary
Calgary, Alberta
Canada

CHI-2 Institute of Mineral Deposits
Chinese Academy of Geological Sciences
Beijing, China

D-2 Geochemisches Institut
Universität Göttingen
Göttingen, FRG

D-6 Institut für Radiohydrometrie
Gesellschaft für Strahlen- und Umweltforschung
Neuherberg, FRG

DDR-1 Zentralinstitut für Isotopen- und
Strahlenforschung
Akademie der Wissenschaften der DDR
Leipzig, GDR

F-4 Laboratoire d'hydrologie et géochimie isotopique
Université de Paris-Sud
Orsay, France

F-6 Société Nationale Elf-Aquitaine
Pau, France
GB-5  British Geological Survey
      London, United Kingdom

GB-7  BP Research Centre
      Sunbury-on-Thames
      Middlesex, United Kingdom

I-4   Agip SpA
      S. Donato Milanese
      Italy

IND-6 Department of Atomic Energy
       Atomic Minerals Division
       Hyderabad, India

I-2   Geological Survey of Japan
       Yatabe, Ibaraki
       Japan

J-7   Institute for the Study of the Earth’s Interior
       Okayama University
       Misasa, Japan

NL-1  Isotope Physics Laboratory
       University of Groningen
       The Netherlands

NZ-2  Institute of Nuclear Sciences
       DSIR, Lower Hutt
       New Zealand

PL-2  Institute of Physics
       Marie Curie-Sklodowska University
       Lublin, Poland

USA-3 LS Geological Survey
       Denver, Colorado
       USA
USA-5  Institute of Geophysics and Planetary Physics
       UCLA, Los Angeles
       California, USA

USA-6  US Geological Survey
       Menlo Park, California
       USA

USA-7  US Geological Survey
       Reston, VA, USA

USA-15  Chevron Oil Field Research Company
        La Habra, California
        USA

USA-16  Global Geochemistry Corporation
        Canoga Park, California
        USA

USA-17  Phillips Petroleum Company
        Bartlesville, Oklahoma 74004
        USA

USA-18  US Geological Survey
        Mail Stop 954
        National Center, Reston, VA 22092
        USA
ANNEX III

The influence of Argon contents in nitrogen gas samples on $\delta^{15}N$-values measured

H. Gerstenberger, K. Mühle and D. Rohmer
Central Institute of Isotope and Radiation Research of the Academy of Sciences of GDR, Leipzig

On the last Advisory Group Meeting (Vienna 1983), we were pointed out that atmospheric argon in the samples influences isotope analysis of nitrogen (cf. p. 19 of the report to the Director General). For our MAT M86 mass spectrometer we have found that 1% V/V of argon causes an apparent increase of $0.15 \(^{\circ}/oo\) of the $^{15}N/^{14}N$ ratio.

In the meantime we have continued this investigation in cooperation with the Institute of Lithosphere (Acad. of Sci. of the USSR) Moscow, using a MAT 250 mass spectrometer. The figure shows the results of these measurements. From these values results an argon influence on $^{15}N$-values of $+0.10$ and $+0.07 \(^{\circ}/oo\) per % V/V argon admixed.

MARIOTTI (1984) found in his excellent work an influence of the same order of magnitude namely $0.09 \(^{\circ}/oo\), but in the opposite direction (i.e. a negative deviation) using a VG Sira 9 mass spectrometer.

From ours and Mariotti's results can be stated:

- There is an actual influence of argon contents in nitrogen gas samples on the $\delta^{15}N$-values measured mass-spectrometrically (but maybe not for all types of instruments).

- Direction and amount of the influence depends not only on the type of the instrument used but also on measuring parameters (e.g. capillary conductance, focusing conditions, pressure in the ionization chamber). This influence may be caused by three different processes at least:
  - charge exchange effects of $Ar^+$ in connection with a kinetic isotope effect, e.g. P. GAUCHEREL and B. ROWE (1977) measured the reaction rate for the $Ar^+ + N_2 \rightarrow N_2^+ + Ar$ charge exchange process at 150 eV electron energy;
- changed kinetic isotope effect for the \( N_2 \) ionization in dependence on Ar content;
- influence on the molecular flow of \(^{15}N\) and \(^{14}N\) inside the ion source in the presence of Ar.

Mariotti demonstrated a non linear dependence of the Ar content on \( \delta^{15}N \) values. This means that likely act two different processes at least.

Taken into account the uniformity of \( ^{15}N/^{14}N \) ratio of air nitrogen stated also recently by different investigations (Mariotti, 1983; Mühle et al., 1981) we proposed the following recommendation: "\( \delta^{15}N \) is set to be ZERO for air nitrogen taken from the lower atmosphere which is made for measuring fairly free of all other constituents of the air using a procedure which causes no nitrogen isotope effect".

Since it is complicated and time-consuming to produce pure air nitrogen without any shift of the actual isotope ratio, we propose to create as soon as possible a secondary reference material with \( \delta \)-value in the vicinity of \( \delta^{15}N = 0 \).

The authors are very grateful to Dr. Medvedovskaja for carrying out the measurements on the MAT 250 and to Dr. M. Herrmann for stimulating discussions.

REFERENCES


A. MARIOTTI (1983): Atmospheric nitrogen is a reliable standard for natural \( ^{15}N \) abundance measurements; Nature 303, 685-7

A. MARIOTTI (1984): Natural \( ^{15}N \) abundance measurements and atmospheric nitrogen standard calibration; Nature 311, 251-2

FIGURE

**MS MAT 250**

Inst. dev. = 0.071 \%o

<table>
<thead>
<tr>
<th>standard</th>
<th>sample</th>
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<td>air N₂ (1.2 Vol % Ar)</td>
<td>air N₂ (1.2 Vol %) + Ar admix.</td>
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<tr>
<td>compr. N₂ (1.2 Vol % Ar)</td>
<td>compr. N₂ (1.2 Vol % Ar) + Ar admix.</td>
</tr>
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</table>

\[\Delta^{15}N \text{ o/cc} = 0.102 \text{ Vol. % Ar admix.} + 0.134\]

st. dev. of the slope = 0.017

\[\Delta^{15}N \text{ o/cc} = 0.070 \text{ Vol % Ar admix.} - 0.013\]

1) st. dev. was calculated from air N₂ data collection

2) samples were kindly measured by Medvedovskaja (Inst. of Lithosphere, Moscow)
### Absolute Isotopic Ratios of VSNOY and SIALAP

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<thead>
<tr>
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<th>SIALAP</th>
<th>VSNOY</th>
<th>Isotopic Ratio</th>
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<td>Girard and Mencach (1972)</td>
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<td></td>
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<table>
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<th>18/5.73</th>
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<td>1950.06</td>
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</table>

---

As determinations made by H.M. G. The value of VSNOY has been slightly revised with respect to that published (Mork, 1983; personal communication).


### Status of Stable Isotope Reference and Intercomparison Material stored by the IAEA as per 87-01-01

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<th>Unit on Stock</th>
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<td>NSVEC</td>
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**Table III**

Intercomparison of isotopic measurements: $\delta^2$H results in °/oo

normalized on the VSMOW/SLAP scale

<table>
<thead>
<tr>
<th>Institute Code</th>
<th>Person</th>
<th>NBS22</th>
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<tr>
<td>CHI-2</td>
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<td>W. Stichler</td>
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<td>-102.0</td>
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<td>DDR-1</td>
<td>H. Gerstenberger</td>
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<td>98.5</td>
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</tr>
<tr>
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<td>M. Coleman</td>
<td>-115.2</td>
<td></td>
<td>98.7</td>
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<td>NL-1</td>
<td>W.G. Mook</td>
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<td>I. Friedman</td>
<td></td>
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<tr>
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<table>
<thead>
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### Table IV

**Intercomparison of isotopic measurements: $\delta^{13}C$ results in $^\circ$/oo relative to VPDB and using $\delta^{13}C_{\text{NBS19/VPDB}} = +1.95 ^\circ$/oo**

<table>
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</table>

**Average**  
-41.59  -4.45  -5.04  -1.08  -28.16

**$\sigma$ of individual measurements**
0.06  0.05  0.06  0.06  0.11


**Table IV contd.**

δ$^{13}$C results

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<tr>
<th>Institute Code</th>
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<td>-35.48</td>
<td>-10.46</td>
<td>-31.76</td>
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<tr>
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<td>W.G. Mook</td>
<td>-29.76</td>
<td>-35.52</td>
<td>-10.41</td>
<td>-31.85</td>
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<tr>
<td>NZ-2</td>
<td>P. Blattner</td>
<td></td>
<td>-34.98</td>
<td></td>
<td></td>
</tr>
<tr>
<td>USA-3</td>
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<td>-35.28</td>
<td></td>
<td>-31.75</td>
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<tr>
<td>USA-6</td>
<td>J.R. O'Neil</td>
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<td>-31.89</td>
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<tr>
<td>USA-7</td>
<td>T. Coplen</td>
<td>-29.75</td>
<td>-35.40</td>
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<td></td>
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<tr>
<td>USA-15</td>
<td>M. Beeunas/M. Schoell</td>
<td>-29.75</td>
<td></td>
<td></td>
<td>-10.38</td>
</tr>
</tbody>
</table>

Average:  
-29.73  -35.32  -10.47  -31.77

σ of individual measurements:  
0.09  0.16  0.13  0.08

<table>
<thead>
<tr>
<th>Institute Code</th>
<th>Person responsible</th>
<th>NGS1 (CH₄)</th>
<th>NGS1 (C₂H₆)</th>
<th>NGS1 (C₃H₈)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F-6</td>
<td>J. Baradat</td>
<td>-28.9</td>
<td>-26.4</td>
<td>-19.9</td>
</tr>
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<td>I-4</td>
<td>T. Ricchiuto</td>
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<td>-26.02</td>
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</tr>
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<td>NL-1</td>
<td>W.G. Mook</td>
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<td>-25.42</td>
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</tr>
<tr>
<td>USA-15</td>
<td>M. Beeunas/M. Schoell</td>
<td>-28.91</td>
<td></td>
<td>-25.93</td>
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<tr>
<td>USA-17</td>
<td>D.C. Boatwright</td>
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<td>-26.3</td>
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</table>
Table IV contd.

$^{13}$C results

<table>
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<tr>
<th>Institute Code</th>
<th>Person responsible</th>
<th>NGS2 $({\text{CH}}_4)$</th>
<th>NGS2 $({\text{C}}_2{\text{H}}_6)$</th>
<th>NGS2 $({\text{C}}_3{\text{H}}_8)$</th>
<th>NGS2 $({\text{CO}}_2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>F-6</td>
<td>J. Baradat</td>
<td>-43.5</td>
<td>-31.1</td>
<td>-24.3</td>
<td>-7.5</td>
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<tr>
<td>I-4</td>
<td>T. Ricchiuto</td>
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<td>-32.1</td>
<td>-25.9</td>
<td>-8.08</td>
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<tr>
<td>NL-1</td>
<td>W.G. Mock</td>
<td>-44.76</td>
<td>-31.17</td>
<td>-25.70</td>
<td>-8.02</td>
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<tr>
<td>USA-15</td>
<td>M.Beeunas/M.Schoell</td>
<td>-44.57</td>
<td>-32.06</td>
<td>-25.70</td>
<td>-8.38</td>
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<tr>
<td>USA-16</td>
<td>P.D. Jenden</td>
<td>-44.58</td>
<td>-31.84</td>
<td>-25.01</td>
<td>-8.38</td>
</tr>
<tr>
<td>USA-17</td>
<td>D.C. Boatwright</td>
<td>-43.1</td>
<td>-31.7</td>
<td>-23.5</td>
<td>-8.9</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Institute Code</th>
<th>Person responsible</th>
<th>NGS3 $({\text{CH}}_4)$</th>
<th>NGS3 $({\text{C}}_2{\text{H}}_6)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>F-6</td>
<td>J. Baradat</td>
<td>-73.1</td>
<td>-59.8</td>
</tr>
<tr>
<td>I-4</td>
<td>T. Ricchiuto</td>
<td>-72.85</td>
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</tr>
<tr>
<td>NL-1</td>
<td>W.G. Mock</td>
<td>-72.67</td>
<td></td>
</tr>
<tr>
<td>USA-15</td>
<td>M.Beeunas/M.Schoell</td>
<td>-72.77</td>
<td></td>
</tr>
<tr>
<td>USA-16</td>
<td>P.D. Jenden</td>
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<td>USA-17</td>
<td>D.C. Boatwright</td>
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Table V

Intercomparison of isotopic measurements: $^{18}$O results in °/oo normalized as discussed in II. Values of NBS16 and NBS17 gas are relative VPDB-CO$_2$

<table>
<thead>
<tr>
<th>Institute Code</th>
<th>Person</th>
<th>NBS 16 vs VPDB-CO$_2$</th>
<th>NBS17 vs VPDB-CO$_2$</th>
<th>NBS18 vs VPDB</th>
<th>NBS20 vs VPDB</th>
<th>NBS23 vs VPDB</th>
</tr>
</thead>
<tbody>
<tr>
<td>D-6</td>
<td>W. Stichler</td>
<td>-36.31</td>
<td>-18.98</td>
<td>-22.98</td>
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<tr>
<td>DDR-1</td>
<td>H. Gerstenberger</td>
<td>-34.28*</td>
<td>-17.61*</td>
<td>-23.34</td>
<td></td>
<td></td>
</tr>
<tr>
<td>GB-7</td>
<td>M. Coleman</td>
<td>-36.25</td>
<td>-18.83</td>
<td>-23.06</td>
<td>-4.24</td>
<td>-30.54</td>
</tr>
<tr>
<td>I-4</td>
<td>T. Ricchiuto</td>
<td>-35.40</td>
<td>-18.45</td>
<td>-22.70</td>
<td>-4.24</td>
<td>-29.98</td>
</tr>
<tr>
<td>NL-1</td>
<td>W.G. Mook</td>
<td>-36.33</td>
<td>-18.77</td>
<td>-23.35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NZ-2</td>
<td>P. Blattner</td>
<td>-36.73</td>
<td>-18.81</td>
<td>-23.18</td>
<td></td>
<td>-30.45</td>
</tr>
<tr>
<td>USA-3</td>
<td>I. Friedman</td>
<td>-35.91</td>
<td>-18.71</td>
<td>-22.89</td>
<td></td>
<td></td>
</tr>
<tr>
<td>USA-6</td>
<td>J.R. O'Neil</td>
<td>-35.92</td>
<td>-18.58</td>
<td>-22.98</td>
<td></td>
<td></td>
</tr>
<tr>
<td>USA-7</td>
<td>T. Coplen</td>
<td>-36.09</td>
<td>-18.71</td>
<td>-23.00</td>
<td>-4.14</td>
<td></td>
</tr>
</tbody>
</table>

Average

|                | -35.94            | -18.65               | -23.05               |
| Average σ of individual measurements | 0.46        | 0.38                  | 0.19                  |

* outside 2 σ deleted

|                | -36.11            | -18.76               |
| Average σ of individual measurements | 0.35        | 0.15                  |

(n=11) (n=11) (n=11)
Table V contd.

$^18$D results

<table>
<thead>
<tr>
<th>Institute Code</th>
<th>Person responsible</th>
<th>NBS28 vs VSMOW</th>
<th>NBS30 vs VSMOW</th>
<th>NBS127 vs VSMOW</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH1-2</td>
<td>Sheng-jin Jin</td>
<td>+9.39</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F-7</td>
<td>J. Baradat</td>
<td></td>
<td></td>
<td>+9.7</td>
</tr>
<tr>
<td>GB-5</td>
<td>P. Greenwood</td>
<td>+9.55</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NZ-2</td>
<td>B.W. Robinson</td>
<td></td>
<td></td>
<td>+9.1</td>
</tr>
<tr>
<td>NZ-2</td>
<td>P. Blattner</td>
<td>+9.62</td>
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<td></td>
</tr>
<tr>
<td>PL-2</td>
<td>S. Halas</td>
<td></td>
<td></td>
<td>+9.21</td>
</tr>
<tr>
<td>USA-3</td>
<td>I. Friedman</td>
<td>+9.7</td>
<td>+5.6</td>
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<tr>
<td>USA-6</td>
<td>J.R. O'Neil</td>
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<tr>
<td>USA-7</td>
<td>T. Coplen</td>
<td>+9.64</td>
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</table>

Fractionation factors used for NBS28:
GB-5, USA-3, USA-6 and USA-7: 1.04120
others unknown.
Table VI

Intercomparison of isotopic measurements: $^{34}$S results in $\permil$ relative to CDT (Canyon Diablo Troilite)

<table>
<thead>
<tr>
<th>Institute Code</th>
<th>Person responsible</th>
<th>NBS122</th>
<th>NBS123</th>
<th>NBS127</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-1</td>
<td>E. Pak</td>
<td>+ 0.22</td>
<td>+ 17.12</td>
<td>+ 20.30</td>
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<tr>
<td>CDN-1</td>
<td>H.R. Krouse</td>
<td>- 0.3*</td>
<td>+ 16.7</td>
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</tr>
<tr>
<td>D-2</td>
<td>H. Nielsen</td>
<td>+ 0.39</td>
<td>+ 17.58</td>
<td>+ 20.03</td>
</tr>
<tr>
<td>F-4</td>
<td>J.C. Fontes/A. Filly</td>
<td>+ 0.36</td>
<td>+ 17.22</td>
<td></td>
</tr>
<tr>
<td>F-7</td>
<td>J. Baradat</td>
<td>+ 0.30</td>
<td>+ 17.1</td>
<td>+ 20.10</td>
</tr>
<tr>
<td>GB-5</td>
<td>P. Greenwood</td>
<td>+ 0.15</td>
<td>+ 17.06</td>
<td>+ 20.64</td>
</tr>
<tr>
<td>IND-6</td>
<td>A. Ahmed</td>
<td>- 0.02</td>
<td>+ 17.00</td>
<td>+ 19.90</td>
</tr>
<tr>
<td>J-2</td>
<td>A. Sasaki</td>
<td>+ 1.50*</td>
<td>+ 17.10</td>
<td>+ 20.24</td>
</tr>
<tr>
<td>J-7</td>
<td>M. Kusakabe</td>
<td>+ 0.83*</td>
<td>+ 17.60</td>
<td>+ 20.95</td>
</tr>
<tr>
<td>NZ-2</td>
<td>B.W. Robinson</td>
<td>+ 0.1</td>
<td>+ 16.5</td>
<td>+ 20.6</td>
</tr>
<tr>
<td>PL-2</td>
<td>S. Halas</td>
<td>+ 0.06</td>
<td>+ 16.90</td>
<td>+ 19.86</td>
</tr>
<tr>
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<td>D. Winter</td>
<td>+ 0.08</td>
<td>+ 16.95</td>
<td>+ 20.53</td>
</tr>
<tr>
<td>USA-18</td>
<td>W.C. Shanks III</td>
<td>- 0.44*</td>
<td>+ 17.32</td>
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</tr>
</tbody>
</table>

Average + 0.25 + 17.09 + 20.32

σ of individual 0.49 0.31 0.36

measurements (n = 13) (n = 13) (n = 10)

* outside 2 σ deleted + 0.18

σ of individual 0.14

measurements (n = 9)
Table VII

Homogeneity test for NBS122:
$\delta^{34}S$ in $\permil$ relative to CDT as a function of sample size prepared

<table>
<thead>
<tr>
<th>Institute</th>
<th>Person</th>
<th>~10 mg</th>
<th>~20 mg</th>
<th>~50 mg</th>
<th>~100 mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Code</td>
<td>responsible</td>
<td>Code</td>
<td>Code</td>
<td>Code</td>
<td>Code</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Institute</th>
<th>Code</th>
<th>Person</th>
<th>Code</th>
<th>~10 mg</th>
<th>~20 mg</th>
<th>~50 mg</th>
<th>~100 mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>F-4</td>
<td>J.C. Fontes/A. Filly</td>
<td>~0.59</td>
<td>-0.18</td>
<td>-0.63</td>
<td>-0.14</td>
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<tr>
<td>J-2</td>
<td>A. Sasaki</td>
<td>+1.13</td>
<td>+1.34</td>
<td>+0.20</td>
<td>-0.13</td>
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<td></td>
</tr>
<tr>
<td>J-7</td>
<td>M. Kusakabe</td>
<td>+1.1</td>
<td>+0.4</td>
<td>+0.6</td>
<td>-0.9</td>
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</tr>
<tr>
<td>NZ-2</td>
<td>B.W. Robinson</td>
<td>+0.8</td>
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<td>+0.6</td>
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<tr>
<td>NZ-2</td>
<td>B.W. Robinson*</td>
<td>+0.2</td>
<td>+0.6</td>
<td>+0.5</td>
<td>+0.6</td>
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<tr>
<td>PL-2</td>
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<td>+0.77</td>
<td>+0.68</td>
<td>+0.37</td>
<td>-0.02</td>
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</tbody>
</table>

* ZnS converted to Ag$_2$S
** Halas reports that his sampling method is not suitable for large amount of sample
Table VIII

Approximate composition of NGS1, NGS2 and NGS3 in volume %

<table>
<thead>
<tr>
<th></th>
<th>NGS1</th>
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<th>NGS3</th>
</tr>
</thead>
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<tr>
<td>CH₄</td>
<td>81.238</td>
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<tr>
<td>C₂H₆</td>
<td>2.832</td>
<td>2.650</td>
<td>0.042</td>
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<tr>
<td>C₃H₈</td>
<td>0.387</td>
<td>1.290</td>
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<td>tC₄H₁₀</td>
<td>0.09</td>
<td>0.26</td>
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<td>mC₄H₁₀</td>
<td>0.08</td>
<td>0.55</td>
<td>0.01</td>
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<td>iC₅H₁₂</td>
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<td>nC₅H₁₂</td>
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<td>0.08</td>
<td>0.00</td>
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<td>CO₂</td>
<td>0.999</td>
<td>25.143</td>
<td>0.009</td>
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</tbody>
</table>


* Measurements by J. Baradat, Société Nationale Elf Aquitaine, France.

Measurements by T. Ricchiuto, Agip S.p.A. Milano, Italy, G.F. van Rossum and J. Baradat on the same components show deviations from the quoted volume percentage of the components of less than 1%.