ADVISORY GROUP MEETING ON STABLE ISOTOPE
REFERENCE SAMPLES FOR GEOCHEMICAL AND HYDROLOGICAL INVESTIGATIONS

IAEA, Vienna, 19 - 21 September 1983

Report to the Director General

by

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Scientific Secretary of the Meeting

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1. INTRODUCTION

The Advisory Group Meeting on Stable Isotope Reference Samples for Geochemical and Hydrological Investigations, convened in Vienna at the IAEA Headquarters from 19 to 21 September 1983, is the third meeting on the same subject organised by the International Atomic Energy Agency. The other two meetings took place in November 1966 and in September 1976.

In November 1966, the preparation of two new water standards was recommended in order to facilitate the intercalibration of deuterium and oxygen-18 measurements in natural water samples and thus improve the intercomparison of results. These two standards were prepared by H. Craig, of the University of California at San Diego, USA. The first, called V-SMOW has an isotopic composition practically identical to the defined SMOW (1), and the second, called SLAP, has a heavy isotope content close to the lowest limit observed in natural waters.

V-SMOW and SLAP, together with NBS-1 and NBS-1A were distributed to various laboratories for intercalibration, the results of which were discussed at the meeting in 1976. In the same meeting, the preparation of other new samples was recommended - the list of which is given in ref. (2) and (3) - for intercalibration purposes of isotopic results also for compounds other than water and elements other than oxygen and hydrogen. Most of these samples were prepared soon after the meeting and distributed by the International Atomic Energy Agency and by the US National Bureau of Standards.

Seven years later, it was felt that it was the right time to examine and discuss the results obtained, to review in detail the characteristics of the reference samples distributed after 1976, and to examine the need for preparing new samples. These were the main objectives of the meeting recently convened. The list of participants is reported in Annex 1. The meeting was chaired by I. Friedman of the US Geological Survey. Scientific secretary was R. Gonfiantini, IAEA. The opening speech was given by V. Ferronsky, Director of the Division of Research and Laboratories, IAEA.
2. REFERENCE AND INTERCALIBRATION SAMPLES DISTRIBUTED BY IAEA FOR STABLE ISOTOPE MEASUREMENTS IN NATURAL COMPOUNDS

2.1 - V-SMOW (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 (1).

According to the control analyses made by H. Craig, V-SMOW has the same $^{18}\text{O}/^{16}\text{O}$ ratio as the defined SMOW, but a slightly lower D/H ratio (of 0.2 $^0$/oo). It should be pointed out, however, that this difference in deuterium content is much smaller than the experimental error of most laboratories. It has been decided, therefore, by the participants in the meeting, that V-SMOW should be considered isotopically identical to the defined SMOW and adopted as zero point for $\delta^{18}\text{O}$ and $\delta^D$ scale for natural compounds. This decision, which agrees with a recommendation expressed by Craig early after the preparation of V-SMOW, has been generally adopted, to our knowledge.

The absolute isotopic composition of V-SMOW is reported in Table I.

Until 1976 the V-SMOW 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 and distributed is listed in Table II.

2.2 - SLAP (Standard Light Antarctic Precipitation): water

It was obtained from a firn sample collected by E. Picciotto, Université Libre de Bruxelles, at the Plateau Station, Antarctica, in 1967. Its absolute isotopic ratios are reported in Table I.
During the 1976 meeting, the δ-values of SLAP with respect to V-SMOW were conventionally fixed at:

δ$^{18}$O = -55.5 ‰

δD = -428 ‰

and it was recommended that the δ-scales for $^{18}$O and D be normalized using the above values for the isotopic analysis of natural water samples.

The amount of SLAP stored in sealed glass containers and distributed is shown in Table II.

2.3 - GISP (Greenland Ice Sheet Precipitation): water

This sample has been prepared by W. Dansgaard, University of Copenhagen, by melting a sample of Greenland firn. It has been distributed together with V-SMOW and SLAP for intercalibration purposes since 1977. Its isotopic composition is intermediate between V-SMOW and SLAP. The amount stored and distributed is shown in Table II.

2.4 - NBS-1 and NBS-1A: water

The first is derived from the Potomac River and the second from snow collected at the Yellowstone National Park. The first sample was used by Craig to define SMOW (1).

These samples, formerly kept at NBS, were handled to IAEA in the early sixties for distribution. There are doubts, however, concerning the way in which NBS-1 and NBS-1A have been preserved during the years until 1977, when finally they were stored in sealed glass containers (see Table II). Therefore use of these samples is not recommended for calibraton purposes.

The isotopic composition of NBS-1 and NBS-1A was first determined by Craig (1), and later reported by Haley and Payne (4) and Gonfiuntini (2,3), on the basis of analyses made in different laboratories.
2.5 - NBS-19 and NBS-18: calcium carbonate

These two samples were prepared by I. Friedman, J. O'Neil and G. Cebula of the US Geological Survey at Denver, Colorado, and Menlo Park, California (5).

The sample NBS-19 (also called TS Limestone) derives from a single slab of white marble of unknown origin. After crushing, the fraction between 48 and 80 mesh (300 to 200 microns) 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 sample NBS-18 is a carbonatite from Fos, Norway, collected by R. Taylor (University of California, Davis) and crushed by H. Friedrichsen (Univ. of Tubingen, Fed. Rep. of Germany). The fraction between 40 and 170 mesh (1.7 kg) was sent to NBS and stored and bottled as NBS-19.

The detailed description of the preparation and preliminary isotopic analyses (to test homogeneity) of the samples NBS-19 and NBS-18 are reported in Ref. (5). For both of them, part of the bottles have been given to IAEA for distribution, the current status of which is given in Table II.

2.6 - NBS-17 and NBS-16: carbon dioxide

They have been prepared by T.B. Coplen and C. Kendall of the US Geological Survey at Reston, Virginia, and have a quite different isotopic composition. NBS-16, having low $\delta^{18}O$ and $\delta^{13}C$ values, derives from a CO$_2$ tank produced as industrial by-product. NBS-17 derives from a CO$_2$ tank obtained from a well in the southwestern United States. Details on preparation are reported by Coplen and Kendall (6).

The two samples have been split and stored in sealed glass tubes containing approximately 300 $\mu$ moles of CO$_2$ (7 ml at STP) each for distribution (Table II).
2.7 - NBS-30: biotite

Prepared by Friedman, O'Neil and Cebula from a sample of Lakeview tonalite (South California batholith) provided by L. Silver (California Inst. of Technology, Pasadena). Granulometry 200 to 300 microns. The sample is intended for $^{18}O$ and deuterium measurement intercalibration in silicates. The D/H ratio should be determined on the water fraction (3.5 $^0/o$), and the $^{18}O/^{16}O$ ratio on the whole sample. The sample is stored in glass bottles ready for distribution (Table II).

2.8 - OGS: (Ocean Research Institute - Geological Survey of Japan Standard): barium sulphate

Sample secured by Y. Horibe, University of Tokyo. It has been obtained from surface ocean water collected in March 1972 at 24°06' N and 179°28' W. Barium sulphate was precipitated with BaCl$_2$, it was filtered and washed first with 0.05 N HCl, then with distilled water until no chloride was detected in the filtrate, and finally with ethyl alcohol (letter from Y. Horibe of 21 November 1983). The sample is stored in sealed glass ampoules (Table II).

Homogeneity tests performed in two laboratories in Japan on the sulphur isotopic composition showed that the sample is homogeneous within $\pm 0.1^0/o$, that is within the experimental error. OGS is intended for $^{18}O$ and $^{34}S$ intercalibration.

2.9 - Soufre de Lacq: elemental sulphur

Sample provided by E. Roth, Centre d'Etudes Nucléaires de Saclay, France. It derives from native sulphur from Lacq in south-western France, and is stored in sealed glass ampoules (Table II).

Analyses performed by R. Hagemann, Centre d'Etudes Nucléaires de Saclay, showed that the sample is isotopically homogeneous within $\pm 0.1^0/o$. 
2.10 - IAEA-N-1 and IAEA-N-2: both ammonium sulphate

Samples prepared by E. Salati, Centro de Energia Nuclear na Agricultura, Piracicaba, Brazil. They differ by about 20 \(^{0}/oo\) in the \(^{15}\)N content. They are stored in sealed glass ampoules (Table II).

3. RESULTS OF THE STABLE ISOTOPE MEASUREMENT INTERCOMPARISON

Only some of the laboratories which have received the reference samples listed in section 2 have submitted their results for intercomparison. The mean \(\delta\)-values and their standard deviations are reported in Table III, for all the results and after elimination of outliers - defined as the results external to the interval \((\delta + 2\sigma_1, \delta - 2\sigma_1)\).

The detailed lists of the results submitted are reported in Tables IV-X.

3.1 - Water samples (V-SMOW, SLAP, GISP)

3.1.1 - Deuterium - The full list of results is reported in Table IV.

The adoption of the method of results normalisation based on a defined difference between V-SMOW and SLAP (-428 \(^{0}/oo\)) reduces considerably the spread of values for GISP (Fig. 1): With the normalisation, in fact, the standard deviation drops from 4.16 to 1.88 \(^{0}/oo\). There is the possibility that a significant part of the spread of the non-normalised results may be due to some spurious results which may not have been corrected for all the instrumental factors. If however the outliers are excluded (with the 2\(\sigma_1\) criterion) - which probably implies the exclusion of most of the non-corrected results - the difference in \(\sigma_1\) values between non-normalised and normalised values of GISP remains considerable: 2.71 and 1.20 \(^{0}/oo\) respectively. The last figure for normalised values is comparable with the experimental error of many laboratories.

3.1.2 - Oxygen-18 - The full list of results is reported in Table V.

Also in this case, the normalisation of the results assuming a defined difference of -55.5 \(^{0}/oo\) between the \(^{18}\)O content of V-SMOW and of SLAP,
determines a considerable decrease of the spread of GISP $\delta^{18}O$ values: $\sigma_1$ drops in fact from 0.349 to 0.147 $^{0/oo}$ (fig. 2). By excluding outliers, the $\sigma_1$ of the non-normalised values becomes 0.271 and that of the normalised ones 0.091 $^{0/oo}$: this last figure is comparable with the experimental error of many laboratories.

3.2 - Calcium carbonate samples (NBS-19, NBS-18)

The results submitted by 28 laboratories are reported in Table VI.

3.2.1 - Oxygen-18: The spread of the $\delta^{18}O$ values for NBS-19 is limited, especially if one outlier is excluded: the $\sigma_1$ is only 0.106, close to the usual experimental error. This indicates that the intercalibration of most laboratories in the range of $\delta^{18}O$ values close to PDB is rather good, in spite of the fact that PDB has not been available for many years. Therefore, the internal laboratory standards have been calibrated indirectly, by means of standards obtained from other laboratories or by using the NBS-20 (Solnhofen Limestone), calibrated by H. Craig already in 1957 (7).

The $\delta^{18}O$ values for NBS-18 show a spread similar to that of the non-normalised GISP, as would be expected, because of the similarity of the isotopic composition of the measuring gas. The spread does not decrease significantly by expressing the $^{18}O$ content of NBS-18 vs. NBS-19: this confirms that the spread is mainly due to the measurement technique rather than to difficulties in the calibration of laboratory standards vs. PDB. A similar intercalibration on carbonate samples previously organised by P. Blattner and J.R. Huston (8) seems to bring the same conclusion.

3.2.2 - Carbon-13: For NBS-19, the $\sigma_1$ of $\delta^{13}C$ vs. PDB is 0.114 $^{0/oo}$ for all the samples, and 0.089 $^{0/oo}$ if only one outlier is excluded. Only slightly higher (0.135 and 0.101 $^{0/oo}$) are the $\sigma_1$ values for NBS-18, the $^{13}C$ content of which, however, is only about 7 $^{0/oo}$ different from that of NBS-19.

The carbon isotopic composition of NBS-18 expressed vs NBS-19 shows a significantly lower $\sigma_1$: 0.084 for all the values, and 0.068 $^{0/oo}$ by excluding two outliers. In this case, the $^{13}C$ content of the two samples
being not too different, the part of the $\delta^{13}C$ spread due to the laboratory standard calibration vs. PDB is larger than that due to the measuring technique.

3.3 - Carbon dioxide samples (NBS-17 and NBS-16)

Only 11 laboratories have submitted their results, which are listed in Table VII.

3.3.1 - Oxygen-18: For both NBS-17 and NBS-16, the spread of $\delta^{18}O$ values is comparable with that of other samples having similar $^{18}O$ content in the measuring gas, namely NBS-18 and GISP, as can be seen by comparing the $\sigma_1$ values reported in Table III.

A normalisation of the NBS-17 $\delta^{18}O$ values can be attempted, by assuming $\delta^{18}O$ of NBS-16 vs. PDB-CO$_2$ a defined, arbitrary value, as for instance -36 $^0$/oo. We obtain then:

<table>
<thead>
<tr>
<th>Laboratory code</th>
<th>$\delta^{18}O$ of NBS-17 vs. PDB-CO$_2$ normalised assuming -36 $^0$/oo for $\delta^{18}O$ of NBS-16</th>
</tr>
</thead>
<tbody>
<tr>
<td>AUS-1</td>
<td>-18.65</td>
</tr>
<tr>
<td>RCH-1</td>
<td>-18.61</td>
</tr>
<tr>
<td>D-1</td>
<td>-18.91</td>
</tr>
<tr>
<td>IAEA</td>
<td>-18.43</td>
</tr>
<tr>
<td>NL-1</td>
<td>-18.66</td>
</tr>
<tr>
<td>NZ-2</td>
<td>-18.68</td>
</tr>
<tr>
<td>ZA-2</td>
<td>-18.66</td>
</tr>
<tr>
<td>CH-1</td>
<td>-18.72</td>
</tr>
<tr>
<td>USA-3</td>
<td>-18.67</td>
</tr>
<tr>
<td>USA-7</td>
<td>-18.62</td>
</tr>
<tr>
<td>USA-11</td>
<td>-18.80</td>
</tr>
</tbody>
</table>

Mean value: -18.67 $^0$/oo; $\sigma_1 = 0.119$ $^0$/oo; n = 11
Once more, data normalisation based on a defined difference between the reference and a second sample, improves the measurement intercomparison in a significant manner.

3.3.2 - Carbon-13: The agreement of the $^{13}$C data is surprisingly good. The spread of the values is low and comparable with the experimental error even for NBS-16, which is depleted by more than 40 $^0$/oo in $^{13}$C with respect to PDB. It seems that for the $^{13}$C measurements the instrumental errors are small (here no sample preparation is required) and that the calibration of the various laboratory standards vs. PDB is good, as also indicated by the measurements performed on NBS-19 and NBS-18.

3.4 - Biotite sample (NBS-30)

Only two laboratories have reported their results, which are listed in Table VIII.

3.5 - Barium sulphate (OGS) and elemental sulphur (Soufre de Lacq)

The results submitted are listed in Table IX.

3.5.1 - Oxygen-18: Only 6 measurements are available of the $^{18}$O content of OGS, which show a rather wide spread ($\sigma_1 = 0.671\,^0$/oo).

3.5.2 - Sulphur-34: Also for $^{34}$S the spread of values is wide: $\sigma_1 = 0.421\,^0$/oo for the 8 values submitted for OGS, and 1.001 $^0$/oo for the 7 values of Soufre de Lacq (which reduces to 0.643 if one value is omitted which is very different from the others - although within the 2$\sigma_1$ interval). The situation slightly improves for the OGS values vs. Soufre de Lacq: by eliminating one outlier the $\sigma_1$ drops to 0.213 $^0$/oo. This may simply be due to the smaller difference in the $^{34}$S content between OGS and Soufre de Lacq with respect to that between these two samples and the Cañon Diablo Troilit, but may also reflect an incorrect calibration of some laboratories versus CDT.
3.6 - Ammonium sulphate samples (IAEA-N-1 and IAEA-N-2)

Only 8 laboratories have submitted their results, which are listed in Table X.

The spread of the $\delta^{15}$N values is large, as indicated by the $\sigma_1$ values reported in Table III. Part of this spread may derive from differences in the isotopic composition of local atmospheric nitrogen, but most of it is probably introduced by the chemical preparation.

4. - DISCUSSION, CONCLUSIONS AND RECOMMENDATIONS

4.1 - General remarks on the normalisation of isotopic data

There is no doubt that the data normalisation using a defined difference between the isotopic composition of two samples significantly improves the intercomparison of results between laboratories. Ideally, the two samples should have isotopic ratios the first equal or close to that of the reference (as for instance V-SMOW for D/H and $^{18}$O/$^{16}$O), and as different as possible but still within the range of natural variations (as for instance SLAP). With this normalisation method the $\sigma_1$ values of the deuterium and oxygen-18 intercomparison measurements in water samples became practically equal to the experimental errors of most laboratories.

The normalisation in fact corrects for all the proportional errors due to the mass spectrometer and to the sample preparation, which seem to be the most frequent and important. In this respect it is worthwhile noticing that laboratories producing results for SLAP and GISP which deviate considerably from the average, very frequently produce normalised GISP values which very well compare with other results.

The usefulness of normalisation for intercomparison purposes was however already known and demonstrated by measurements on V-SMOW, SLAP, NBS-1 and NBS-1A reported at the 1976 meeting (2,3). Now data on GISP as well as data on NBS-17 and NBS-16 (as discussed in Section 3.3.1), confirm once more this finding.
There are however some problems connected with the data normalisation. The major ones are:

i) As already pointed out in 1976 (2,3), the data normalisation practically implies a change of the $\delta$-unit definition, which becomes:

$$\delta = \frac{R_{\text{sample}} - R_{V-SMOW}}{R_{V-SMOW}} x f$$

$$f = \frac{\delta^0_{\text{SLAP}}}{\frac{R_{V-SMOW}}{R_{SLAP}} - R_{V-SMOW}}$$

where $\delta^0_{\text{SLAP}}$ is -428 $^0/oo$ for deuterium and -55.5 $^0/oo$ for oxygen-18.

The $\delta$ definition of equation (1) coincides with the classical one only if $f = 1$, that is if the recommended value for $\delta^0_{\text{SLAP}}$ corresponds exactly to that foreseen by the classical definition of $\delta$. Otherwise, all the $\delta$-values normalised on the V-SMOW/SLAP scale will differ from those given by the classical definition by the factor $f$. This factor, with the values given above for $\delta^0_{\text{SLAP}}$ for D and $^{18}O$, is certainly very close to 1; nevertheless, in principle it cannot be excluded that future measurements may show deviations of $f$ from unity, especially if important refinements will be introduced in the analytical techniques.

ii) If the isotopic values of two samples are fixed, then the whole $\delta$ scale for that isotope is fixed, whatever the compound measured. For example, if we decide to normalise the $^{18}O$ scale by using a defined difference between V-SMOW and SLAP, this affects in principle not only the results of isotopic analysis of water samples, but also that of any oxygen compound. It is in fact desirable to have a unique scale for the same isotope, or scales which are exactly consistent - if more than one scale meets better the practical needs (as in the case of oxygen-18).

iii) Also the fractionation factors of the physico-chemical processes involving the isotopes normalised, should be in principle re-evaluated on the normalised scale.
Some of the problems connected with the isotopic data normalisation are discussed by P. Blattner in Annex II.

Let us now examine element by element the current situation of stable isotope results intercalibration.

4.2 - Hydrogen

Intercalibration of the D/H ratio measurements in natural waters is ensured by the adoption of two reference samples, namely V-SMOW and SLAP, assuming for the second a value of -428 ‰ with respect to V-SMOW. GISP can be used as auxiliary check sample. It should be stressed however that in principle it would be advantageous that deuterium measurements on all types of natural samples be normalised on the V-SMOW/SLAP scale, and not only those performed on water samples.

4.3 - Oxygen

As for deuterium, the intercalibration of $^{18}O/^{16}O$ data obtained on water samples is ensured by the two reference samples V-SMOW and SLAP, with an assumed $\delta^{18}O$ value of second versus the first of -55.5 ‰. Also in this case GISP can be used as auxiliary check sample.

More difficult, however, is the case of oxygen isotopes, the intercomparison of results being between samples of different nature. The current analytical technique is such that often the measurement is not performed on a CO$_2$ sample having the same isotopic composition as the mother compound, but rather on CO$_2$ with $^{18}O/^{16}O$ ratio related to that of the mother compound by a fractionation factor. This occurs for two of the natural compounds most frequently investigated, that is water and calcium carbonate.

Several measurements exist of the CO$_2$-water fractionation factor at 25°C, which are listed in Table XI. The difference between the extreme values, 1.0409 and 1.0424, may derive entirely from errors in sample treatment (as, for instance, memory effects, incomplete conversion, impure chemicals), but it cannot be excluded that the spread of values would reduce if data could be "normalised". As for the $\delta$ definition, attention should be paid to the fact
that a normalisation implies in principle a change of the fractionation factor
definition, which will coincide with the old one only if the defined value of
SLAP versus V-SMOW is exact. From the practical point of view, however, the
normalised value of the fractionation factor between CO₂ and water should
not differ significantly from that of 1.04115 proposed by Mook (fig. 3).

The best available value of the fractionation factor between the CO₂
obtained with 100 ₀/₀ H₃PO₄ and the mother calcium carbonate is 1.0125.
This value, reported by Friedman and O'Neil (9), derives from a careful
reevaluation of measurements previously performed by Sharma and Clayton (10),
but obviously is not normalised on the V-SMOW/SLAP scale.

The scheme of fig. 3, proposed by W. Mook and accepted by the other
participants in the meeting, is considered to give the best present estimates
of the various fractionation factors of the system V-SMOW, PDB, V-SMOW-CO₂
(25°C) and PDB-CO₂ (25°C, 100₀/₀ H₃PO₄), in expectation that some
time they will be redetermined on the V-SMOW/SLAP scale.

With the fractionation factors of fig. 3 the conversion equation of
oxygen-18 data of calcite samples vs. PDB to values referred to V-SMOW is:

\[ \delta^{18}C_{-SMOW} = 1.03086 \delta^{18}C_{-PDB} + 30.86 \text{ ₀/₀} \]

and for CO₂ samples:

\[ \delta^{18}G_{-SMOW} = 1.04143 \delta^{18}G_{-PDB(CO₂)} + 41.43 \text{ ₀/₀} \]

or

\[ \delta^{18}G_{-SMOW} = 1.04115 \delta^{18}G_{-SMOW(CO₂)} + 41.15 \text{ ₀/₀} \]

depending whether the isotopic composition of the CO₂ sample is expressed
versus CO₂ obtained from PDB or versus CO₂ equilibrated with V-SMOW.

On the whole, it appears that the two major scales to report ¹⁸O data,
namely the V-SMOW/SLAP scale and the PDB(CO₂) scale, need additional efforts
to be intercalibrated in a more precise way. On the other hand, it was the
general consensus in the meeting that both the scales should continue to be used, because they meet the practical requirements of essentially different categories of users.

In order to facilitate the intercalibration of $^{18}O$ measurements in calcium carbonate samples, the participants in the meeting proposed the adoption of the value of $-2.20^{\circ}/oo$ of NBS-19 versus PDB, which was also suggested by Friedman et al. (5). This value might be modified when more measurements in selected laboratories are available (see Table XII and Section 4.4).

A remark was made about the grain size of NBS-19, which seems too coarse: this could be a reason for poor reproducibility of isotopic results ($^{18}O$). However, the consensus was to keep the present grain size, which reduces the possibility of isotopic exchanges and assures a better preservation of the sample. The users can finely grind the sample just before the treatment with $H_3PO_4$ if they wish.

Concerning the carbonate sample NBS-28 calibrated by Craig vs. PDB (7), there are doubts on its present suitability for calibration of laboratory standards. This sample was prepared about 30 years ago from a piece of Solenhofen limestone containing some clay and which had been polished with linseed oil. The limestone was then very finely ground, and the powder preserved in bottles. Possible exchanges with atmospheric $CO_2$ and also contamination due to linseed oil traces cannot be excluded, which would explain doubtful results obtained in some laboratories.

Intercalibration of measurements of $^{18}O/^{16}O$ ratio in silicates may also present problems, but the results so far available on the biotite sample (NBS-30) are too scarce to allow any discussion. However, it may be worthwhile noticing that the agreement among the two results submitted is rather poor (they differ by 0.8 $^{\circ}/oo$). The members of the Advisory Group also expressed the recommendation that part of the quartz sample NBS-28, now distributed only by NBS, should be handled to IAEA for distribution for intercalibration purposes.
The agreement of results is also poor for the $^{18}O/^{16}O$ measurements in the barium sulphate sample (OGS). This may be due, at least in part, to the fact that OGS may contain traces of chloride, in spite of the precautions taken during its preparation. It is recommended therefore to prepare a new BaSO$_4$ sample from sea water, which should be treated with a specific ion-exchange resin to remove all impurities. J. O'Neil has accepted to undertake this task.

As a general conclusion on oxygen-18 measurements, which however would apply also to other isotopes, the Advisory Group expressed the recommendation that in future papers on isotope geochemistry should give some detail on how the measurements reported have been calibrated, indicating the samples used for this purpose among those distributed by IAEA and NBS, and the values and methods adopted.

4.4 - Carbon

The results obtained on samples NBS-19, NBS-18, NBS-17 and NBS-16 indicate that the intercalibration of laboratories seems on the whole acceptable. Also for very negative $\delta^{13}C$ values - as in the case of NBS-16 - the spread of results is rather limited. This conclusion can also be obtained from the $^{13}C$ measurement intercomparison organised by Schoell et al. (11).

In order to facilitate intercalibration of $^{13}C$ results, the members of the Advisory Group recommended:

i) to assign to the $^{13}C$ content of NBS-19 the value of +1.95‰ with respect to PDB;

ii) to establish a $^{13}C$ scale based on two carbonate samples with very different isotopic composition. The first of these samples will be NBS-19, having a $^{13}C$ (and $^{18}O$) content close to that of PDB. The second one, which should be depleted in $^{13}C$ - although within the range of the natural variations of this isotope - will be prepared by I. Friedman, and will probably consist of strontium carbonate. Possibly the new sample should also be depleted in $^{18}O$, so that it can be used, together with NBS-19, also to establish a $^{18}O$ scale for carbonates.
The second compound depleted in heavy isotopes cannot be the CO$_2$ sample NBS-16, because the amount available is limited. In addition, carbon dioxide is difficult to split into a large number of small, isotopically homogeneous samples, according to the experience of T. Copley and C. Kendall (6). In order to calibrate the future $^{13}$C scale, as well as the $^{18}$O content of carbonates on the V-SMOW/SLAP scale, a set of samples will be distributed by IAEA to selected laboratories. These will be asked to perform all the measurements within the shortest period of time, in order to have the maximum of steadiness in the preparation and in the measurement conditions. Oxygen-18 results should be reported normalised on the V-SMOW/SLAP scale as well as non normalised but corrected for all the instrumental and preparation factors.

The set of samples to be distributed and the list of laboratories selected to carry out this new calibration is reported in Table XIII.

4.5 - Carbon-13, deuterium and oxygen-18 in organic compounds

At the 1976 meeting preparation was recommended of a sample suitable for the intercomparison of isotopic analyses ([$^{13}$C/$^{12}$C, D/H, $^{18}$O/$^{16}$O] of organic substances. At that time the suggestion was made to use commercial tristearin. However, preliminary analyses performed at the Bundesanstalt fur Geowissenschaften und Rohstoffe, Hannover, Federal Republic of Germany, by C. Redding (letter to IAEA of 15 September 1978) showed: i) the isotopic inhomogeneity – especially in deuterium ($\sigma_1 = 6.1$ $^{0}/$oo) – of the Tristearin product manufactured by Fluka, ii) the rather low $\delta$D value of this tristearin (-230 $^{0}/$oo) with respect to most of the organic compounds of natural origin. The $\delta^{13}$C value was -27.8, and no measurements were performed of the $^{18}$O content.

Recently, Gerstenberg and Herrmann (12) have proposed the use of polyethylene foil for $^{13}$C and D intercomparison. There are doubts, however, on the isotopic homogeneity of this compound, which in addition will not be suitable for oxygen isotope analysis. An intercomparison test in which 16 laboratories participated, showed a rather large spread of results: $\delta^{13}$C = -31.62 $^{0}/$oo, $\sigma_1 = 0.64$, n = 14 (excluding 2 outliers); $\delta$D = -98.8 $^{0}/$oo,
\[ \sigma_1 = 3.4, \ n = 5 \] (excluding 1 outlier: only 6 laboratories submitted deuterium results). Repeated analyses at the Zentralinstitut fur Isotopen- und Strahlenforschung in Leipzig, German Democratic Republic, showed only slightly lower \( \sigma_1 \) values: 0.58 for \(^{13}\text{C} \) and 2.8 for deuterium. Gerstenberger has proposed that the IAEA distribute samples of the Leipzig polyethylene foil (PEF-1) to other laboratories, in order to make additional checks on the isotopic composition of this sample.

The possibility of having other samples which can be used for intercomparison purposes of isotopic analyses in organic compounds was discussed by the Advisory Group. The following proposals were formulated:

i) A sucrose sample: this can perhaps be obtained from H. Polach, of the Australian National University at Canberra. The Sucrose ANU used by Polach has a \( \delta^{13}\text{C} \) of -10.40 \(^{\circ}/\text{o} \) vs. PDB. The sucrose should be prepared in sealed glass containers, to protect it from exchanges.

ii) A natural gas sample, consisting of methane with only about 1 \(^{\circ}/\text{o} \) of heavier hydrocarbons. M. Coleman will look into the possibility of procuring and preparing it in containers (several hundreds) ready for distribution, possibly through co-operation with M. Schoell, of the Bundesanstalt fur Geowissenschaften und Rohstoffe, Hannover, Federal Republic of Germany. This sample, however, as the Leipzig polyethylene, will not be suitable for \(^{18}\text{O} \) measurement intercomparison.

It has also been recommended that part of the samples NBS-21 (graphite) and NBS-22 (oil), now only available at the US National Bureau of Standards, be given to IAEA for distribution.

Among the laboratories represented at the meeting, the following expressed their interest in participating in the calibration of the new organic samples which will become available:
Lab. Code  |  Person responsible
---------:|:---------------------
   D-7    |   H. Friedrichsen
   GB-5   |   J.E. Rouse
   GB-7   |   M.L. Coleman
    I-4   |   T. Ricchiuto
    NL-1  |   W.G. Mook
    PL-2  |   S. Halas
   USA-3  |   I. Friedman
   USA-6  |   J.R. O'Neil

Other laboratories which in future may express their interest in participating in this calibration are of course most welcome.

4.6 - Sulphur

The current situation of intercomparison of sulphur isotope measurements is discussed in Annex III by H. Nielsen, and it is rather serious. Therefore the members of the Advisory Group Meeting agreed on the preparation and distribution of new samples, which hopefully will lead to a better intercalibration of the $^{34}$S measurements.

The new samples proposed are:

i) A sample of sphalerite (ZnS) with an $^{34}$S/$^{35}$S ratio close to that of CDT. This sample will be procured possibly by S. Halas. Alternatively, it can perhaps be provided by J. Pilot, Bergakademie Freiberg, German Democratic Republic.

ii) Two samples of Ag$_2$S, with $\delta^{34}$S values of approximately +20 $^0$/oo and -20 $^0$/oo. These samples can possibly be provided by C.E. Rees, McMaster University, Hamilton, Ontario, Canada. I. Friedman will write to Rees for this purpose.

iii) A sample of BaSO$_4$ obtained by precipitation from sea water and treated with a specific ion-exchange resin to remove all the impurities. The sample will also be used for $^{18}$O measurement intercomparison in sulphates. It will be prepared by J. O'Neil.
These samples will be distributed to a number of selected laboratories (to be defined) for calibration versus CDT. The group also recommended to discontinue the distribution of OGS and Soufre de Lacq.

4.7 - Nitrogen

The current situation of nitrogen isotope measurement intercomparison has been summarised by A. Mariotti: according to this author, atmospheric nitrogen should be a reliable reference for nitrogen isotope measurements in natural compounds (13). In fact, atmospheric nitrogen seems to have a fairly uniform - practically within the experimental errors - isotopic composition throughout the world. However, dishomogeneities can be introduced during the chemical preparation of the samples. For instance, in the adsorption on silica gel, the nitrogen adsorbed is enriched in $^{15}\text{N}$ by $0.28\pm0.09\ %$ with respect to the gas, and this small fractionation can be disregarded only if more than $80\ %$ of the nitrogen is adsorbed.

Another possible source of errors was indicated by H. Gerstenberger, who pointed out that atmospheric argon may influence the isotopic analyses of nitrogen if not removed. He reported that $1\ %$ of argon determines an apparent increase of $0.15\ %$ of the $^{15}\text{N}/^{14}\text{N}$ ratio on his mass spectrometer.

Concerning new samples for the intercomparison of nitrogen isotope determinations, the group suggested that a sample of thiourea would be probably well suited. C. Kendall, of the US Geological Service at Reston, Virginia should be approached by IAEA in order to provide such a sample. A. Mariotti also offered to secure a sample of potassium nitrate with $^{15}\text{N} = 2\ %$.

The group recommended also that part of the NBS-14 sample (atmospheric nitrogen) be given to the Agency for distribution.
5. SUMMARY OF THE MAIN CONCLUSIONS AND RECOMMENDATIONS

5.1 - Isotopic scales based on two samples with defined values

It has been demonstrated that an isotopic scale based on two samples with defined \( \delta \)-values considerably improves the intercomparison of results among different laboratories. It is therefore desirable to use the same normalisation method - which is now limited to deuterium and oxygen-18 measurements in water samples - also for other isotopes and compounds.

5.2 - Re-evaluation of fractionation factors

In order to have normalised isotopic systems which are fully consistent, fractionation factors should in principle also be redetermined or re-evaluated using the normalised scale. It is however agreed that this cannot be done easily and rapidly, and therefore we shall continue to use the fractionation factors available in the literature. For the oxygen-18 measurements in the water-calcite system, the fractionation factors recommended are those of fig. 3.

It is also generally felt that the normalised fractionation factors for oxygen-18 and deuterium would be very close to the present best evaluation, most probably within the experimental errors.

5.3 - New intercomparison samples

New samples need to be prepared in order to improve the intercomparison of isotopic results and, possibly, try to have other normalised scales. The list of these samples is given in Table XIII. The new samples will be ready for distribution by February 1984. Selected laboratories will receive sets of samples for intercomparison and calibration. However, participation of other laboratories will be most welcome.

The results of the new intercomparison should be submitted within the shortest possible time.
5.4 - NBS-samples to be sent to IAEA

The new stable isotope intercomparison will be carried out also on some samples now distributed by NBS only. It is therefore recommended that these samples are given to IAEA for distribution. The list of these samples includes:

- NBS-14 (nitrogen)
- NBS-21 (graphite)
- NBS-22 (oil)
- NBS-28 (quartz sand)

5.5 - Next meeting

It is proposed to have another expert meeting to evaluate the results obtained in the new intercomparison and formulate recommendations on values to be adopted for some of the samples. The meeting will in principle take place in Vienna at the IAEA Headquarters, possibly in April 1985. Results of the new intercomparison should therefore be submitted by 31 January 1985.

5.6 - Publication of a communication

It was decided to publish a short communication on the main results and recommendations of the Advisory Group Meeting. Therefore, the Scientific Secretary has prepared the following communication:

**Communication**

An Advisory Group Meeting on Stable Isotope Reference Samples for Geochemical and Hydrological Investigations was convened by the International Atomic Energy Agency in Vienna from 19 to 21 September 1983. The meeting, which was a follow-up of similar meeting held in 1976 (*), was chaired by I. Friedman of the US Geological Survey, and was attended by 34 specialists from 14 countries.

Intercomparison measurements of the $^{2}\text{H}/^{1}\text{H}$, $^{18}\text{O}/^{16}\text{O}$, $^{13}\text{C}/^{12}\text{C}$, $^{15}\text{N}/^{14}\text{N}$ and $^{34}\text{S}/^{32}\text{S}$ isotopic ratios were reported and discussed during the meeting. These measurements were carried out on samples of water, calcium carbonate, CO$_2$, barium sulphate, elemental sulphur and ammonium sulphate. All these samples are distributed by both IAEA, Vienna, and the National Bureau of Standards, Washington D.C., USA.

The results obtained for a water sample (GISP) confirm that the intercomparison of data among different laboratories improves considerably using a $\delta$-scale based on two water reference samples (V-SMOW and SLAP), as recommended in the 1976 meeting.

A new carbonate sample (NBS-19) to replace the no-longer available PDB is now being distributed. The following values are now recommended for its isotopic composition versus PDB: $\delta^{18}\text{O} = -2.20 \, ^{0}/_{oo}$, $\delta^{13}\text{C} = +1.95 \, ^{0}/_{oo}$.

The need for new intercomparisons and other additional stable isotope reference samples was thoroughly discussed, and recommendations on the preparation and distribution of these new samples were formulated.

The next meeting on the same subject has been tentatively scheduled for spring 1985 in Vienna.

A copy of the meeting report can be obtained from R. Gonfiantini, IAEA, P.O. Box 100, 1400 Vienna, Austria.
The above communication has been sent for publication to the following journals:

Geochimica et Cosmochimica Acta
Earth and Planetary Science Letters
Isotope Geoscience
Nature
Science
Geostandards Newsletter
Journal of Hydology
Int. Journal of Applied Radiation and Isotopes
Isotopenpraxis

5.7. - Correspondance

Enquiries, requests for intercomparison samples, results of measurements, requestes for information on future meetings, etc. should be addressed to
R. Gonfiatini, Division of Research and Laboratories, International Atomic
Energy Agency, P.O. Box 100, A-1400 Vienna, Austria.

It is also recommended that copies of all correspondance between members
of the Advisory Group Meeting on matters dealing with the stable isotope
reference samples and with measurement intercomparison, be sent to
R. Gonfiatini.
REFERENCES


<table>
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<th>Isotopic ratio</th>
<th>V-SMOW</th>
<th>SLAP</th>
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<td>$(89.02 \pm 0.05) \times 10^{-6}$</td>
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<td>$(155.60 \pm 0.12) \times 10^{-6}$</td>
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<td>$^{18}O/^{16}O$</td>
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<td>$(374 \pm 9) \times 10^{-18}$</td>
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<td>IAEA laboratory. Direct gas counting</td>
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<td>(16 Sept. 76)</td>
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| Density       | 999.975 kg/m$^3$ | Girard and Menache (1972) |

* The value of V-SMOW has been slightly revised with respect to that published (Mook, 1983, personal communication).

** Determinations made by NMR.


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IAEA N-2 ((NH₄)₂SO₄):

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N.B. Flasks and ampoules are in pyrex glass, have been filled in Argon atmosphere and flame sealed. Bottles are in glass and provided with a double, tight cap.
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* single inlet system using D₂O as spike  
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I-4  T. Ricchiuto     -412.5  -184.7  -191.6  MAT 250  U
J-1  O. Matsubaya     -430.6  -190.5  -189.3  MAT 250  Zn
J-6  M. Kusakabe, H. Satake, Y. Mizutani
     NL-1  C.A.M. Brenninkmeijer, W.G. Mook  -427.3  -188.6  -188.9  MAT GD 150  U
     NZ-2  M.K. Stewart  -425.4  -188.7  -189.9  VG 602 C  Zn
     PAK-1  M.I. Sajjad, M.A. Tasneem  -414.8  -184.5  -190.4  MAT GD 150  U
(modified)
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R-1  L. Blaga, L.M. Blaga  -428.4  -189.6  -189.4  Thomson THM  U
R-2  D. Steflea        -428.5  -191.7  -191.5  MAT 250  Zn
E-1  J.A. Jimenez S.     -436.5  -193.9  -190.1  VG 602 D  U
GB-3  J. Borthwick, M. Raynolds, A.G. Miller  -395.8  -178.5  -193.0  VG 602 B  U
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TABLE V - Intercomparison of isotopic measurements on water samples: results on oxygen-18

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* E (a, b) means that a ml of water is equilibrated with b ml of CO₂ gas (STP).
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*Values calculated at IAEA

**Samples prepared by reaction with HCl
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* Results are expressed vs CO₂ obtained from PDB with 100 %/o H₃PO₄.

** Laboratory carbonate standards prepared at 22°C.
TABLE VIII - Intercomparison of isotopic measurements on the biotite sample (NBS-30)

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* Vs. Local atmospheric $\text{N}_2$

** Values vs NBS-14 are +1.36 and +20.85 o/oo respectively
### TABLE XI - Fractionation factor between CO₂ and liquid water at 25°C

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<td>1.0409±0.0002</td>
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<tr>
<td>F. Matsuhisa, O. Matsubaya, H. Sakai, 1971</td>
<td>1.0412</td>
</tr>
<tr>
<td>P. Blattner, 1973</td>
<td>1.0417±0.0004</td>
</tr>
<tr>
<td>F. Horibe, K. Shigehara, Y. Takakuwa, 1973</td>
<td>1.0413±0.00013</td>
</tr>
<tr>
<td>J.R. O'Neil, L.H. Adami and S. Epstein, 1975</td>
<td>1.0412±0.0001</td>
</tr>
<tr>
<td>G. Baric, A. Fehri and R. Létolle, 1981</td>
<td>1.0416±0.0003</td>
</tr>
<tr>
<td>C.A.M. Brenninkmeijer, P. Kraft and W.G. Mook, 1983</td>
<td>1.0411±0.00007</td>
</tr>
</tbody>
</table>

### REFERENCES:

TABLE XII - Samples and laboratories selected for calibration of 
$^{13}\text{C}$ and $^{18}\text{O}$ (carbonates) isotopic scales

a) Samples:

Water: V-SMOW, SLAP, GISP

Carbonate: NBS-18, NBS-19 and a new sample ($\text{SrCO}_3$) to be prepared by J. Friedman

Carbon dioxide: NBS-16, NBS-17

Graphite: NBS-21

b) Laboratories:

<table>
<thead>
<tr>
<th>Code</th>
<th>Person responsible</th>
</tr>
</thead>
<tbody>
<tr>
<td>D-6</td>
<td>W. Stichler</td>
</tr>
<tr>
<td>DDR-1</td>
<td>H. Gerstenberger</td>
</tr>
<tr>
<td>GB-5</td>
<td>J.E. Rouse</td>
</tr>
<tr>
<td>GB-7</td>
<td>M.L. Coleman</td>
</tr>
<tr>
<td>I-4</td>
<td>T. Ricchiuto</td>
</tr>
<tr>
<td>J-2</td>
<td>Y. Matsuhisa</td>
</tr>
<tr>
<td>NL-1</td>
<td>W.G. Mook</td>
</tr>
<tr>
<td>NZ-2</td>
<td>P. Blattner</td>
</tr>
<tr>
<td>USA-3</td>
<td>I. Friedman</td>
</tr>
<tr>
<td>USA-6</td>
<td>J.R. O'Neil</td>
</tr>
<tr>
<td>USA-7</td>
<td>T. Coplen</td>
</tr>
<tr>
<td>USA-13</td>
<td>R.N. Clayton</td>
</tr>
<tr>
<td>USA-14</td>
<td>H. Craig</td>
</tr>
</tbody>
</table>

N.B. The last two laboratories were not represented at the meeting.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Characteristics</th>
<th>Person responsible or to be asked to procure it</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrCO₃</td>
<td>Very negative in $^{13}$C ( -40 $^\circ$/oo) and possibly also in $^{18}$O</td>
<td>I. Friedman</td>
</tr>
<tr>
<td>BaSO₄</td>
<td>From sea water, treated with ion-exchange resin to remove all impurities</td>
<td>J.R. O'Neil</td>
</tr>
<tr>
<td>Polyethylene foil (PEF-1)</td>
<td>-31.6 $^\circ$/oo in $^{13}$C and -99 $^\circ$/oo in D. Homogeneity (not sure)</td>
<td>H. Gerstenberger</td>
</tr>
<tr>
<td>Sucrose</td>
<td>-10.4 $^\circ$/oo in $^{13}$C</td>
<td>H. Polach</td>
</tr>
<tr>
<td>Methane</td>
<td>It may contain up to 10$^\circ$/o of heavier hydrocarbons</td>
<td>M. Coleman</td>
</tr>
<tr>
<td>Sphalerite (ZnS)</td>
<td>$^{34}$S content close to CDT</td>
<td>S. Halas (or J. Pilot)</td>
</tr>
<tr>
<td>Ag₂S-1</td>
<td>With $\delta^{34}$S  + 20$^\circ$/oo</td>
<td>C.E. Rees</td>
</tr>
<tr>
<td>Ag₂S-2</td>
<td>With $\delta^{34}$S  - 20$^\circ$/oo</td>
<td>C.E. Rees</td>
</tr>
<tr>
<td>Thiourea</td>
<td>Not specified, but with $^{15}$N content within the natural range of variations</td>
<td>C. Kendall</td>
</tr>
<tr>
<td>KNO₃</td>
<td>With $\delta^{15}$N  + 20$^\circ$/oo</td>
<td>A. Mariotti</td>
</tr>
</tbody>
</table>
### TABLE XIV

**LIST OF LABORATORIES WHICH TOOK PART IN THE INTERCALIBRATION**

<table>
<thead>
<tr>
<th>Code</th>
<th>Laboratory Name and Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-1</td>
<td>Institut fur Radiumforschung und Kernphysik der Oesterreichischen Akademie der Wissenschaften, Vienna, Austria</td>
</tr>
<tr>
<td>AUS-1</td>
<td>Commonwealth Scientific and Industrial Research Organization, Glen Osmond, Australia</td>
</tr>
<tr>
<td>AUS-2</td>
<td>Commonwealth Scientific and Industrial Research Organization, Fuel Geoscience Unit, North Ryde, N.S.W., Australia</td>
</tr>
<tr>
<td>AUS-3</td>
<td>Australian Atomic Energy Commission, Research Establishment, Sutherland, N.S.W., Australia</td>
</tr>
<tr>
<td>B-1</td>
<td>Department of Botany, Antwerp University Centre, Antwerp, Belgium</td>
</tr>
<tr>
<td>BR-1</td>
<td>Centro de Energia Nuclear na Agricultura, Piracicaba, Sao Paulo, Brazil</td>
</tr>
<tr>
<td>CDN-1</td>
<td>Department of Physics, University of Calgary, Calgary, Alberta, Canada</td>
</tr>
<tr>
<td>CDN-2</td>
<td>Atomic Energy of Canada Ltd., Chalk River Nuclear Laboratory, Chalk River, Ontario, Canada</td>
</tr>
<tr>
<td>CDN-3</td>
<td>Atlantic Oceanographic Laboratory, Bedford Institute of Oceanography, Dartmouth, Nova Scotia, Canada</td>
</tr>
<tr>
<td>CDN-4</td>
<td>Department of Earth Sciences, University of Waterloo, Waterloo, Ontario, Canada</td>
</tr>
<tr>
<td>CH-1</td>
<td>Physics Institute, University of Bern, Switzerland</td>
</tr>
</tbody>
</table>
CH-2  Geology Institute
       Swiss Federal Institute of Technology
       Zurich
       Switzerland

CHI-1  Department of Geology
       Beijing University
       Beijing
       China

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

CS-1   Geological Survey
       Prague
       Czechoslovakia

D-1    Finnigan MAT
       Bremen
       FRG

D-2    Geochemisches Institut
       Universität of Göttingen
       Göttingen
       FRG

D-3    Bundesanstalt für Geowissenschaften
       und Rohstoffe
       Hannover
       FRG

D-4    Institut für Umweltphysik
       Universität Heidelberg
       Heidelberg
       FRG

D-5    Institut für Chemie
       Kernforschungsanlage Julich
       Jülich
       FRG

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

D-7    Abteilung Geochemie
       Universität Tübingen
       7400 Tübingen
       FRG

DDR-1  Zentralinstitut für Isotopen- und Strahlenforschung
       Akademie der Wissenschaften der DDR
       Leipzig
       DDR
DK-1  Geophysical Isotope Laboratory
       University of Copenhagen
       Denmark

E-1   Servicio de Aplicaciones Nucleares a las Obras Públicas
       Madrid
       Spain

F-1   Institut de Recherches Appliquées aux Boisson
       Créteil
       France

F-2   Centre d'Etudes Nucléaires de Saclay
       Gif-sur-Yvette
       France

F-3   Laboratoire de Chimie Organique Physique
       Université de Nantes
       Nantes
       France

F-4   Laboratoire hydrologie et géochimie isotopique
       Université Paris-Sud
       Orsay
       France

F-5   Departement de Géologie dynamique
       Université Pierre et Marie Curie
       Paris
       France

F-6   Société Nationale ELF-Aquitaine
       Centre Micoulan
       6400 Pau
       France

GB-1  Godwin Laboratory for Quaternary Research
       University of Cambridge
       Cambridge
       United Kingdom

GB-2  Department of Earth Sciences
       Cambridge University
       Cambridge
       United Kingdom

GB-3  Scottish Universities
       Research and Reactor Centre
       East Kilbride
       Scotland
       United Kingdom
GB-4  Clinical Research Centre  
      Harrow  
      Middlesex  
      United Kingdom  

GB-5  Institute of Geological Science  
      London  
      United Kingdom  

GB-6  Institute of Geological Sciences  
      Wallingford  
      United Kingdom  

GB-7  BP Research Centre  
      Chertsey Road  
      Sunbury-on-Thames  
      Middlesex TW1 67LN  
      United Kingdom  

GR-1  Nuclear Research Centre Democritos  
      Aghia Paraskevi  
      Attikis  
      Greece  

HK-1  Department of Chemistry  
      University of Hong Kong  
      Hong Kong  

I-1  Istituto di Mineralogia, Petrografia  
    e Geochimica dell'Università di Palermo  
    Palermo  
    Italy  

I-2  Istituto Internazionale per le Ricerche Geotermiche  
    Pisa  
    Italy  

I-3  Istituto di Geochimica dell'Università di Roma  
    Roma  
    Italy  

I-4  AGIP SpA  
    S. Donato Milanese  
    Italy  

IAEA  International Atomic Energy Agency  
      Vienna  
      Austria  

IND-1  Technical Physical Division  
      Bhabha Atomic Research Centre  
      Bombay  
      India
IND-2 Chemistry Division
Bhabha Atomic Research Centre
Bombay
India

IND-3 Hydrology and Tracer Section
Isotope Division
Bhabha Atomic Research Centre
Bombay
India

IND-4 Chemistry Division
Institute of Petroleum Exploration
Oil and Natural Gas Commission
Dherra-Dun
India

IND-5 National Geophysical Research Institute
Hyderabad
India

IND-6 Department of Atomic Energy
College House
Hyderabad
India

J-1 Research Institute of Underground Resources
University of Akita
Akita
Japan

J-2 Geological Survey of Japan
1-1-3 Yatabe-Higashi
Ibaraki
Japan

J-3 Water Resources Institute
Nagoya University
Nagoya
Japan

J-4 Ocean Research Institute
University of Tokyo
Tokyo
Japan

J-5 Mitsubishi-Kasii Institute of Life Science
Tokyo
Japan

J-6 Department of Earth Sciences
Toyama University
Toyama
Japan
NL-1 Isotope Physics Laboratory
University of Groningen
Netherlands

NZ-1 Ruakura Soil Plant Research Station
Hamilton
New Zealand

NZ-2 Institute of Nuclear Sciences
Department of Scientific and Industrial Research
Lower Hutt
New Zealand

PAK-1 Pakistan Institute of Nuclear Science and Technology
Rawalpindi
Pakistan

PL-1 Institute of Nuclear Physics and Techniques
University of Mining and Metallurgy
Krakow
Poland

PL-2 Institute of Physics
Maria Curie-Sklodowska University
Lublin
Poland

R-1 Institute of Isotopic and Molecular Technology
Cluj-Napoca
Romania

R-2 Comitetul de Stat pentru Energia Nuclear
Rimnicu Vilcea
Romania

RCH-1 Comisión Chilena de Energía Nuclear
Santiago
Chile

S-1 Laboratory for Isotope Geology
Swedish Museum of Natural History
Stockholm
Sweden

S-2 Hydrology Division
University of Uppsala
Uppsala
Sweden

SU-1 Estonian Institute of Geology
Tallin
USSR
<table>
<thead>
<tr>
<th>Code</th>
<th>Organization and Address</th>
</tr>
</thead>
</table>
| SU-2 | Institute of Seismology  
Uzbek Academy of Science  
Tashkent  
USSR |
| USA-1 | Krueger Enterprise Inc.  
Geochron Lab. Division  
Cambridge, Massachusetts  
USA |
| USA-2 | Geology Department  
Northern Illinois University  
De Kalb  
Illinois, USA |
| USA-3 | US Geological Survey  
Denver  
Colorado, USA |
| USA-4 | Department of Geological Sciences  
University of Southern California  
Los Angeles  
California, USA |
| USA-5 | Institute of Geophysics and Planetary Physics  
University of California  
Los Angeles  
California, USA |
| USA-6 | US Geological Survey  
Menlo Park,  
California, USA |
| USA-7 | US Geological Survey  
Reston,  
Virginia, USA |
| USA-8 | Institute of Geophysics and Planetary Physics  
University of California  
Riverside  
California, USA |
| USA-9 | University of Washington  
Seattle,  
Washington, USA |
| USA-10 | Washington University  
St. Louis,  
Missouri, USA |
| USA-11 | Cities Service Co.  
Energy Resources Group  
Tulsa,  
Oklahoma, USA |
USA-12
Department of Geology
University of Illinois at
Urbana-Champaign
Urbana,
Illinois, USA

USA-13
The University of Chicago
The Enrico Fermi Institute
Chicago
Illinois, USA

USA-14
Scripps Institution of Oceanography
University of California
La Jolla
California, USA

YU-1
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Skopje
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ZA-1
Nuclear Physics Research Unit
University of the Witwatersrand
Johannesburg
South Africa

ZA-2
National Physics Research Laboratory
Pretoria
South Africa
Fig. 1 - Intercomparison of GISP deuterium results. Upper part: non-normalised results; lower part: normalised results. Outliers (2σ1 interval) are shaded.
Fig. 2 - Intercomparison of GISP oxygen-18 results. Upper part: non normalised results; lower part: normalised results. Outliers (2σ1 interval) are shaded.
Figure 3 - $\delta^{18}O$ CONVERSION EQUATIONS

$\alpha_1$: $\alpha$ for PDB-CO$_2$ vs old SMOW-CO$_2 = 1.00022$ (Craig, 1965), confirmed by Mook (1968). Problem remains whether we define SMOW and V-SMOW to be equal or accept a difference of 0.05 %o which according to Mook is realistic.

$\alpha_2$: Taken from Friedman and O'Neil (1977), see Table XII.

$\alpha_4$: According to Brenninkmeijer et al. (1983), is the average of 3 independent determinations by 4 different laboratories.

$\alpha_5$: 1.03086 is exactly the figure quoted by Friedman and O'Neil (1977).

$\alpha_6$: 1.04143, almost equal to figure by Friedman and O'Neil (+0.01 %o).

The conversion equations are in general:

$$\delta^{18}O_{\text{lower}} = \alpha_1 \delta^{18}O_{\text{upper}} + (\alpha_4 - 1)10^3 \text{%o}$$

where $\alpha_4 = \alpha_1, \alpha_2,...,\alpha_6$, and "lower" and "upper" refer to the standard levels in the scheme.
For instance:

$$\delta^{18}_{O\text{-SMOW}} = 1.03086\delta^{18}_{O_{\text{PDB}}} + 30.86 \%$$

or

$$\delta^{18}_{O\text{-SMOW}} = 1.041436\delta^{18}_{O_{\text{PDB-CO}_2}} + 41.43 \%$$

References


ANNEX I

LIST OF PARTICIPANTS

AUSTRIA

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Nottinghamshire NG12 5G

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Geochemistry and Petrology Div.  
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Denver Federal Center  
Denver, Colorado 80225  

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B.R. Payne  
I. Vovk
ANNEX II

PROPORTIONAL ERRORS AND RE-DEFINITION
OF $\delta^{18}O$ REFERENCE SCALES

Based on data available at IAEA Advisory Group Meeting
on Stable Isotope Reference Standards, Vienna, 1983

P. Blattner, DSIR, Wellington, New Zealand
1. Zero point of scale, as opposed to size of units

The Nier-McKinney ("geochemical") mass spectrometer is designed to, and does measure very accurately, small differences of isotopic composition. Its strength is the comparison of very similar samples. If dissimilar samples are compared, two error sources exist and must be separated: (A) The position of the zero point of reference (Type I errors), (B) The variability in size of the permille units (for a given zero point), if measurements are made in different laboratories or under different conditions (Type II or proportional errors) (Fig. 1). For a sample far from zero, any combination of the two error contributions is possible. In this case the type II errors must be brought under control, before anything can be known about possible errors I, in the zero point position. Since no two materials are identical, type II errors should be considered first.

2. Proportional (type II) errors

Isotopic differences between materials may be expressed as relative isotopic enrichments

\[ \varepsilon_{1-2} = \alpha - 1 = \frac{\delta_{1-ref} + 1}{\delta_{2-ref} + 1} - 1 = \delta_{1-2} \]

where \( \alpha = \frac{R_1}{R_2} \) and \( R = \frac{^{18}O}{^{16}O} \), and we use the simplified definition \( \delta = (\frac{R}{R_{ref}}) - 1 \).

It is a well known fact that after the elimination of errors of internal reproducibility, different laboratories report different isotopic enrichment for paired samples. That is, the difference in isotope ratio between given samples, such as SMOW and SLAP, is scaled differently by each laboratory, if conditions remain unchanged, or in other words each set of conditions (or laboratory) "stretches" the \( \delta \)-scale for the given isotope ratio differently (Genfiantini 1978, Blattner and Hulston 1978).

*Although \( \delta_{1-2} \) is exactly equal to \( \varepsilon_{1-2} \), \( \delta_{1-2} \) might easily be confused with a \( \delta \) vs reference, and it seems preferable to use \( \varepsilon \) when dealing with type II problems.
The scale for a given type of isotopes (D/H, C, O etc.) should therefore be normalized to a uniform length for a specific sample pair. From then on the scale is determined for any pair of samples.

Type II errors have been widely held to be due to mass spectrometry, but could also contain a component contributed by sample preparation. In the first case they are usually believed to be strictly proportional within a laboratory, i.e. for one instrument, to the difference between two materials, whereas preparation errors could contribute proportional as well as random elements.

If type II errors were entirely proportional within laboratories, then given laboratories should produce consistently high, medium, or low nominal differences for given pairs of material, and the spread of the differences for a given sample pair as measured in different laboratories should be a constant proportion of their interlaboratory mean. **

If this working hypothesis holds, a plot of the original, machine corrected but not normalized, enrichment values for different sample pairs against their interlaboratory mean, should lead to an arrangement where each laboratory is represented by a linear ray, representing its particular scaling (or stretch) of the permille scale.

How do the actually available data on paired samples conform with this expectation?

Based on published data and new data available at the IAEA Advisory Group Meeting 1983, Fig. 2 has been drawn up strictly from a statistical point of view, with no regard for the "normalized" value even for SLAP vs SMOW.

** or any other statistically consistent point of the interlaboratory spread of values! It is impossible (and inadmissible) to arbitrarily fix or "define" such a point for more than one pair of materials in the case of a given type of isotopes.
The fan shaped plot indicates that this overall approach leads to remarkably good agreement between the centres of the $\varepsilon$ distributions for four paired materials in bottles, as well as for $\alpha_{\text{CO}_2-\text{H}_2\text{O}}$, which (in case of perfect sample preparation provides a universal natural standard for $\varepsilon$.

A measure of the spread of $\varepsilon$ values that is independent of the number $n$ of participating laboratories, is given by the interlaboratory standard deviation $s$, whereas the reliability of the mean, $\bar{\varepsilon}$, is indicated by its standard error (s.e.). Fig. 3 shows a good correspondence of $s$ with $\bar{\varepsilon}$, which means that to this approximation the above working hypothesis holds.

The Advisory Group Conference 1983 recommended to invite a small number of laboratories to re-analyse three of the bottled $^{18}$O sample pairs of Fig. 2 (as well as some other materials), of course without any attempt at "normalization". This effort would provide tie-lines for those laboratories and fixed conditions, between the distributions in a plot such as Fig. 2. Such tie lines would underpin the mere statistical approach in precise detail. In anticipation, some such tie lines can already be drawn from data presently available, although we cannot usually be certain that conditions in a given laboratory remained fixed, especially when reference pairs were analyzed in different years. Thus Fig. 2 contains tie lines from five laboratories, which seem to support the thesis of proportionality. One experimentally consistent set of data is reported admirably by Coplen et al. (1983).

3. Zero of scale (carbonates): Type I errors

PDB still exists, but on the other hand, it never existed.

A) It never existed because all materials have inhomogeneities, and no ideal standard is possible. (Inhomogeneities and contamination become more serious as analysts tend to reduce sample size). The average PDB never existed; in addition PDB-CO$_2$, even if obtained from an ideal average PDB-solid, might vary because of slightly varying extraction procedures.
B) PDB still exists, because a comparison of different materials, such as PDB, TKL, Ticino etc. from Craig (1957) is just as valid as a comparison of different aliquots of PDB, as long as a correction for the (small!) type II errors is made.

To avoid confusion, the PDB scale should remain the same, as much as possible. The value of $-2.20 \%_0 \delta^{18}O$ recommended for NBS-19 by the 1983 Advisory Group seems very close (0.01 to 0.02 \%?) to any "true" PDB value based on available data, but could be improved with data already existing. However, NBS-20 should be treated with caution (Friedman et al. 1982).

4. Value of $\alpha_{CO_2-H_2O}$ at 25°C

The Advisory Group briefly discussed the possible adoption of a value for this constant. Nine values are listed by Brenninkmeijer et al. (1983); of these, two are from the same laboratory, and none is accompanied by data on reference pairs that would allow normalisation. It emerges after the 1983 meeting that adoption of a value for SLAP vs SMOW (e.g. $-55.5\%_0$) will prejudice all other differences for paired materials, including equilibrated CO$_2$ and H$_2$O at 25°C. This constant requires reconsideration and probably re-measurement with normalisation, before a value can be recommended!
REFERENCES

Craig, Geochim. Cosmochim. Acta, 12, 133-149,
Friedman, O'Neil and Cebula, Geostandards Newsletter, 6, 11-12, (1982).
Figure 2
Fig. 1

Fig. 3
ANNEX III

The Standard Situation for Sulfur Isotopes

Heimo Nielsen
Geochemisches Institut der Universität Göttingen
Stable Isotope Laboratory

The primary standard which defines the Zero point of the $\delta^{34}S$ scale is troilite (FeS) from iron meteorites. The choice was made by the pioneers of sulfur isotope work and at a first glance this appears quite fortunate: troilite sulfur agrees so well with the mean isotopic composition of terrestrial sulfur that the measured $\delta^{34}S$ value gives a direct idea of the "overall fractionation" of an individual sample. Unfortunately, however, troilite is isotopically not as uniform as was expected in earlier days and should therefore be disqualified as a standard material for high precision measurements. Furthermore, troilite is not stoichiometrically pure FeS but contains some Co and Ni sulfides and carbides which render it difficult to recover pure sulfur at a 100% yield. Finally there are at least two different troilite standards in use: western researchers apply material from the Cañon Diablo Meteorite while Russian colleagues refer to Shikote Alin.

Another substance with relatively uniform S isotopic composition is the sulfate dissolved in the world oceans. Because there exist numerous published seawater sulfate values from all the principal S isotope laboratories these values might give a base to "normalize" the literature data. The "true" seawater $\delta^{34}S$ value, however, is still a matter of debate. REES, JENKINS and MONSTER (Geochim. Cosmochim. Acta 42, 377, 1978) have listed the disagreement between the results reported by different laboratories. Roughly the same spread occurs between the results of an inter-laboratory comparison measurement on the OGS seawater sulfate standard of the IAEA.

Fig. 1 compiles these values graphically.

Figure 1

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X
XX X X G X G
+++++++-----+++---
20 21
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The "X" are the values from the list distributed to the Advisory Group Members in mid 1983 and the "G's" represent the results obtained at the Göttingen Laboratory. The latter came out too late to be inserted into the list. The value of 20.8 had been determined with SO₂ as a sample gas while the value of 21.1 % was measured with SF₆ gas.

The reasons for this large difference are:

i) uncertainty on the Zero point;

ii) instrumental imperfections (non-linearities in the mass spectrometers);

iii) the badly known intensities superimposed on the mass 66 ion beam;

iv) uncertainty of the "memory" correction.

The "wrong" ion at mass number 66 is mainly $^{32}\text{S}^{16}\text{O}^{18}\text{O}^+$ which contributes almost 9 per cent to the whole signal amplitude. The proper correction for this superposition needs the absolute abundances of the $^{34}\text{S}$ and $^{18}\text{O}$ isotopes which are known only at a limited level of accuracy. Another ionic species at mass number 66 is the $^{32}\text{S}^{34}\text{S}^+$. Due to the low ion optical resolution of stable isotope mass spectrometers its presence cannot directly be deduced from the spectrum and therefore it is neglected in the published evaluation equations for SO₂ measurements. Nevertheless it is a reality in all cases where the $S_2O^+$ peak at mass 80 occurs in the spectrum. Perhaps the $S_2$ explains why all the data previously published for the absolute abundances of the rarer S isotopes are systematically too high. This is shown in Table I where the result of a preliminary re-determination of these values by means of SF₆ is compared with the "old" values:

Table I

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Literature values</th>
<th>Raw signal</th>
<th>After Correction for SF₆⁺</th>
<th>Molecular flow</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{32}\text{S}$</td>
<td>94.941 : 95.02</td>
<td>94.95</td>
<td>95.09</td>
<td></td>
</tr>
<tr>
<td>$^{33}\text{S}$</td>
<td>0.769 : 0.75</td>
<td>0.751</td>
<td>0.741</td>
<td></td>
</tr>
<tr>
<td>$^{34}\text{S}$</td>
<td>4.273 : 4.21</td>
<td>4.28</td>
<td>4.16</td>
<td></td>
</tr>
<tr>
<td>$^{36}\text{S}$</td>
<td>0.017 : 0.02</td>
<td>0.0145</td>
<td>0.0137</td>
<td></td>
</tr>
<tr>
<td>$^{32}\text{S}/^{34}\text{S}$</td>
<td>22.22 : 22.57</td>
<td></td>
<td>22.89</td>
<td></td>
</tr>
</tbody>
</table>

a = NIELSEN, Handbook of Geochemistry, Springer 1978
b = HOEFS, Stable Isotope Geochemistry, II. Ed. Springer 1980

The "memory" means the retention of gas molecules on the walls of the
sample reservoir and within the ion source. \( \text{SO}_2 \) is one of the "stickiest" gases applied in stable isotope work. After the changeover from unknown to reference sample and vice versa these molecules from the "wrong" side are slowly liberated from the walls and dilute the newly inflowing gas. Thus the isotopic difference between both gases is measured systematically too low. The deficit depends on instrumental parameters (total surface area "wetted" by both gases and its geometrical layout, coatings by impurities, temperature, pumping efficiency) and on the operating schedule (gas inflow rate, "idle time" from switching the changeover valves until the start of data collection). At the Göttingen MAT 251 the memory correction for normal routine \( \text{SO}_2 \) measurements with idle time = 10 sec, collection time = 8 sec, and ion current \(-10^{-9}\) amps is about 1 per cent of the measured difference. For samples far from Zero and for extreme precision requirements an extension of the idle time to 60 sec brings down the memory correction to a few parts per thousand. Many mass spectrometers have much stronger memory effects; REES (Geochim. Cosmochim. Acta 42, 377 (1978)) gives an example where the deficit is still \(-1.5\) per cent after an idle time of 60 sec.

Considering all these corrections and their badly known parameters it is not surprising that the results of \( \text{SO}_2 \) measurements on the OGS standard by different laboratories differ so strongly from each other. The application of \( \text{SF}_6 \) avoids these problems and minimizes the possible errors and therefore REES has already proposed in his 1978 paper to re-define the \( \delta^{34}\text{S} \) scale by means of \( \text{SF}_6 \) measurements.

\( \text{SF}_6 \) is prepared by reacting sulfide with \( \text{BrF}_5 \) or other highly reactive fluorine compounds. This needs an expensive laboratory equipment and the handling of extremely poisonous fluorination agents. For these reasons the \( \text{SF}_6 \) technique at present is applied routinely exclusively at REES' laboratory at McMaster University, Hamilton/Ont. Unfortunately REES has not yet measured the OGS standard but his seawater sulfate value reported in the cited paper with JENKINS and MONSTER is \(-21.0\) %. Within the limits of error this agrees with the value 21.1 mentioned above for the \( \text{SF}_6 \) measurement of the OGS standard at the Göttingen laboratory. The \( \text{SF}_6 \) sample for the latter measurement was prepared at the silicate oxygen line at FRIEDRICHSEN's laboratory at Tübingen/FRG. Our \( \text{SF}_6 \) could not adequately be purified and therefore the 21.1 % value should be regarded merely as preliminary. The measurement will be repeated as soon as the Göttingen \( \text{SF}_6 \) line (a copy of the line at REES' laboratory) is completed in spring 1984. Therefore the discussion concerning the "true" \( \delta^{34}\text{S} \) value should be postponed to next year. Anyhow the arguments for a seawater value around 21 %o become more and more convincing - although the compilation in Fig. 1 seems to support the "old" value slightly above 20 %o.
Nielsen -- Sulfur Standards

The present situation of the sulfur isotope "standards" (or reference samples) is quite unsatisfactory and needs further activities of the IAEA. The two IAEA standards now available - i.e. the seawater sulfate standard and "Soufre de Lacq" - are insufficient and should be replaced by materials of better quality. The strongest need, however, concerns a new Zero standard to replace physically the troilite standard. At the second place stands a standard sufficiently far from Zero to enable the "normalization" of $^{34}S$ isotope data for future publications. Seawater sulfate remains a good choice for this purpose because many geochemical investigations are directly concerned with modern and fossil seawater, groundwater, evaporites and ore deposits in that $\delta$ range. The new material, however, should be extracted by ion exchange techniques and not by simple precipitaiton of BaSO$_4$. Furthermore it is recommended to extend the line of reference materials to higher positive and to negative $\delta^{34}S$ values in order to improve the control of non-linearities. Another subject concerns the distribution of chemically different substances for comparing the results obtained with different methods of sample preparation. These materials, however, should not be given the rank of reference marks on the $\delta^{34}S$ scale. The need for checks of the chemical procedures is illustrated by the data in Table II, compiling the results of different methods to prepare the "Soufre de Lacq".

Table II

<table>
<thead>
<tr>
<th></th>
<th>$SO_2$</th>
<th>$SF_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>direct reaction of $S^0$ with $V_2O_5$ or $BrF_5$</td>
<td>15.1</td>
<td>16.8</td>
</tr>
<tr>
<td>Ag$_2$S from S vapor + Ag wool at hi temp. in vac.</td>
<td>16.8</td>
<td></td>
</tr>
<tr>
<td>KIBA reduction of $S^0$ and wet Ag$_2$S precip.</td>
<td>17.2</td>
<td>14.0</td>
</tr>
</tbody>
</table>

The range 16.8 to 17.2 agrees with previous measurements of H$_2$S samples from Lacq on an ATLAS CH4 spectrometer. The two very low values can not be explained but are probably due to overlooked losses during the chemical treatment. On the other hand GRINENKO and VDOVYKIN (Geokhimiya 1966, 351) have reported a value of 14.6 for elemental sulfur from the deposit of Lacq. The graphic compilation of the Göttingen data ("G") together with the values in the IAEA list ("X") and GRINENKO's value ("0") is shown in Fig. 2.
With the exception of the unreasonably low values the grouping of these data is quite similar to that of the OGS values in Fig. 1.

It was reported at the Advisory Group Meeting in Sept. 83 that REES already had started an independent attempt to supply a complete line of 9 substandards covering the most important section of the scale from about -30 to +50 %. These samples were stored as Ag₂S and the expense of the reagent finally forced REES to stop his activity. A new approach in the same direction with the financial support of the IAEA is recommended. Several members of the Advisory Group have manifested their readiness to support this operation by supplying sulfur raw compounds of suitable isotopic composition.