IAEA

INTERLABORATORY COMPARISON FOR DEUTERIUM AND OXYGEN-18 ANALYSIS OF PRECIPITATION SAMPLES

REPORT

Prepared by

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INTRODUCTION

As part of the programme aimed at the strengthening of the Global Network “Isotopes in Precipitation” (GNIP), the IAEA Section of Isotope Hydrology organized an interlaboratory comparison test in which isotope laboratories contributing to the GNIP database were invited to participate. These laboratories routinely measure stable isotopes (oxygen-18 and deuterium) in precipitation samples from one or several meteorological stations in a given country and provide isotope data to the IAEA for publication and inclusion into the GNIP database. The list of laboratories which participated in the exercise is given in Annex I.

The main objective of this exercise was to help the laboratories engaged in routine analysis of isotope composition of precipitation to assess their precision and accuracy within the range of $^{18}$O and $^2$H contents normally observed in precipitation.

Invitations were sent to 28 laboratories, of which 26 sent oxygen-18 results and 23 deuterium. A reporting sheet (Annex II), requesting details on the sample preparation technique for both isotopes, as well as a normalization data procedure to obtain the isotope results in the normalized VSMOW-SLAP scale was sent to each laboratory.

Four water samples (A, B, C, D) plus a set of calibration materials (VSMOW, SLAP and GISP) were sent to the laboratories in May 1994. The laboratories were requested to perform the calibration of their internal and working standards prior to the actual measurements of the submitted water samples, and to report the delta values in the normalized VSMOW-SLAP scale, together with the overall one-sigma measurement error. The four samples were prepared by mixing precipitation samples from several bottles originating from stations included in GNIP. The prepared samples cover a range in $\delta^{18}$O of about 20 per mil (from around 0‰ to -20‰).

The samples were sent in 50 ml double capped polyethylene bottles. Laboratories received one single bottle of each sample plus 30 ml of the two standards and the GISP intercomparison sample.

PRESENTATION OF RESULTS

Each laboratory was assigned a sequential number to identify the results in the tables and graphs presented in this report. Tables 1a, 1b and 1c present the values reported by the participating laboratories with the quoted one-sigma error. All values are expressed in delta notation, normalized to the VSMOW-SLAP scale (Coplen, 1988).

All oxygen-18 measurements were carried out using the CO$_2$ equilibration method. The preparation methods of hydrogen gas for deuterium measurements were as follows: (i) Zn - reduction of water at around 450 °C using granulate zinc, (ii) U - reduction of water at 760-800°C over uranium, (iii) Cr - reduction of water at 800°C over chromium, and (iv) Eq - equilibration with H$_2$ using Pt as catalyst.
Table 1a. Results of the oxygen-18 analysis of samples A, B, C and D reported as per mil deviations vs. VSMOW. The quoted error is one-sigma error of individual analysis as reported by the laboratories.

<table>
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<th>Lab No</th>
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<th>SAMPLE-B (‰) ± σ</th>
<th>SAMPLE-C (‰) ± σ</th>
<th>SAMPLE-D (‰) ± σ</th>
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Table 1b. Results of the deuterium analysis of samples A, B, C and D reported as per mil deviations vs. VSMOW. Sample preparation methods are briefly explained in the text. The quoted error is one-sigma error of individual analysis as reported by the laboratories.

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Sample preparation methods for deuterium analysis:
- Zn - Zinc method
- U - Uranium method
- Cr - Chromium method
- Eq - Equilibration method
Table 1.c Results of the oxygen-18 and deuterium analysis of the intercomparison sample GISP reported as per mil deviations vs. V-SMOW. The adopted value for GISP is -189.73 ± 0.87‰ for δ²H and -24.784 ± 0.075‰ for δ¹⁸O (Gonfiantini et al., 1995). The quoted error is one-sigma error of individual analysis as reported by the laboratories.

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Sample preparation methods for deuterium analysis:
Zn - Zinc method
U - Uranium method
Cr - Chromium method
Eq - Equilibration method
STATISTICAL ANALYSIS OF THE RESULTS

The main objective of the data treatment was the determination of the best estimate or consensus value for the $^{18}$O and $^2$H content of the four samples and to quantify the scatter of data around the consensus value.

Estimation of the consensus values for samples A, B, C, D and GISP

To obtain the best estimates for the actual $^{18}$O and $^2$H content of the distributed water samples, the procedure adopted by Rozanski et al. (1992) in a similar interlaboratory comparison exercise was followed.

Stage I

In stage I of the statistical treatment, obvious outliers were discarded based on the frequency distribution of values: after the determination of the upper ($H_u$) and lower ($H_l$) quartiles, as well as the interquartile range, the values exceeding $H_u + 3\cdot (H_u - H_l)$ and $H_l - 3\cdot (H_u - H_l)$ were discarded. Five analyses failed to pass this first test, were discarded, and were not considered in stage II. All discarded values were oxygen-18 measurements; one measurement from samples B, C and D, respectively, and two from GISP. Summary statistics of the data after this initial stage are presented in Table II. For oxygen-18, the standard deviation for four out of five samples is below 0.10/$^\circ_\text{o}$ after the removal of five outliers. For deuterium, however, the standard deviation for four samples is still well above 1.0/$^\circ_\text{o}$, as shown in Table II.

Box and whisker plots for oxygen-18 and deuterium measurements in samples A to D after rejection of outliers using the procedure outlined above, are presented in Figs 1.1. and 1.2., respectively. In all plots, the same absolute range as $\delta$-values was used, allowing a direct comparison of the spread of data. In the case of oxygen-18, the interquartile range is almost constant (around 0.15/$^\circ_\text{o}$) and the total range of accepted values in all samples is around 0.4/$^\circ_\text{o}$.

For deuterium a distinct increase in the scatter of data is observed when moving towards more isotopically depleted samples. The interquartile range increases from sample A (1.0/$^\circ_\text{o}$) to sample D (2.1/$^\circ_\text{o}$) . The total range of accepted values also increases from 2.7/$^\circ_\text{o}$ in sample A to 9.7/$^\circ_\text{o}$ in sample D. The increasing spread of values in deuterium is also reflected in the standard deviation presented in the third column of Table II. No systematic effect with respect to the preparation method used for the measurement of deuterium was found.

Fig. 2 shows the distribution for oxygen-18 and deuterium results for the intercomparison sample GISP, after applying the same rejection procedure as used for samples A to D. Although GISP is an intercomparison material and, therefore, the accepted value was, in principle, known to the participating laboratories, the calculated standard deviation for deuterium analysis is significantly higher than the reported uncertainty of the analyzed $^3$H value for this material ($\pm 0.87\,^\circ_\text{o}$, Goffantini et al., 1995). The interquartile range and calculated standard deviation are 5.3/$^\circ_\text{o}$ and 1.24/$^\circ_\text{o}$, respectively. For oxygen-18, the standard deviation (see Table II) and the interquartile range is similar to those reported for other samples.
Table II. Summary statistics (average value and standard deviation of the population) of the original data and a preliminary estimate of the consensus isotopic values of the samples A to D and GISP, after removal of outliers in stage I of the data treatment described in the text. The number in brackets indicates the number of deuterium or oxygen-18 values submitted (column 2) and accepted after stage I of statistical treatment (column 3).

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<th>After removal of outliers Mean ± standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen-18 [%/oo] VSMOW</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SAMPLE A</td>
<td>+0.61 ± 0.11 (26)</td>
<td>+0.61 ± 0.11 (26)</td>
</tr>
<tr>
<td>SAMPLE B</td>
<td>-5.00 ± 0.12 (26)</td>
<td>-5.02 ± 0.09 (25)</td>
</tr>
<tr>
<td>SAMPLE C</td>
<td>-12.97 ± 0.28 (26)</td>
<td>-13.02 ± 0.09 (25)</td>
</tr>
<tr>
<td>SAMPLE D</td>
<td>-20.16 ± 0.24 (26)</td>
<td>-20.11 ± 0.08 (25)</td>
</tr>
<tr>
<td>GISP</td>
<td>-24.74 ± 0.24 (23)</td>
<td>-24.76 ± 0.08 (21)</td>
</tr>
<tr>
<td>Deuterium [%/oo] VSMOW</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SAMPLE A</td>
<td>+12.5 ± 0.68 (23)</td>
<td>+12.5 ± 0.68 (23)</td>
</tr>
<tr>
<td>SAMPLE B</td>
<td>-28.5 ± 1.24 (23)</td>
<td>-28.5 ± 1.24 (23)</td>
</tr>
<tr>
<td>SAMPLE C</td>
<td>-93.5 ± 1.34 (23)</td>
<td>-93.5 ± 1.34 (23)</td>
</tr>
<tr>
<td>SAMPLE D</td>
<td>-154.7 ± 2.15 (23)</td>
<td>-154.7 ± 2.15 (23)</td>
</tr>
<tr>
<td>GISP D</td>
<td>-189.1 ± 1.24 (22)</td>
<td>-189.1 ± 1.24 (22)</td>
</tr>
</tbody>
</table>

Stage II

In stage II of the statistical treatment, a selection of the remaining results was made based on the ratio of the difference between each reported isotopic content and the preliminary consensus value, and the quoted one-sigma error. The results with the ratio \(|(x-m)/s|\) larger than 2 were discarded, \(x\) being the reported delta value, \(s\) the quoted one-sigma error and \(m\) the preliminary consensus value. This procedure identifies those samples whose absolute delta value and quoted error are not homogeneous with respect to the rest of the group. This step led in some cases to the removal of up to 6 measurements. In the next step, the consensus values (weighted averages) were calculated by weighting the individual results by the reciprocal of the quoted variance:

\[
\bar{x}_w = \frac{\sum x_i / w_i^2}{\sum 1.0 / w_i^2}
\]

The estimated standard error of the mean was calculated according to the following formula:

\[
esd(\bar{x}_w) = \frac{\hat{\sigma}_w}{\sqrt{\sum 1.0 / w_i^2}}
\]

where

\[
\hat{\sigma}_w^2 = \frac{\sum ((x_i - \bar{x}_w)^2 / w_i^2)}{n}
\]

6
The results of the calculations performed in this stage are presented in the third column of Table III. The number in brackets indicates the number of values accepted for the calculation of the consensus value.

Table III. Calculated weighted mean values and estimated standard errors of the mean (ese) for samples A to D and GISP, following the procedure described in the text (column 3). Interlaboratory precision estimated on the basis of the accepted results, after applying iteratively the 2σ criterion (see text) is presented in column 4. The number in brackets indicates the number of analyses accepted for the calculations.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Original data</th>
<th>Consensus value</th>
<th>Interlaboratory precision</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \pm \text{es} )</td>
<td>( \pm \text{ese} )</td>
<td>(*)</td>
</tr>
<tr>
<td>Oxygen-18 ( [%o/o]_{SMOW} )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SAMPLE A</td>
<td>+0.61 ± 0.11 (26)</td>
<td>+0.609 ± 0.015 (20)</td>
<td>0.102 (25)</td>
</tr>
<tr>
<td>SAMPLE B</td>
<td>-5.00 ± 0.12 (26)</td>
<td>-4.992 ± 0.005 (20)</td>
<td>0.070 (23)</td>
</tr>
<tr>
<td>SAMPLE C</td>
<td>-12.97 ± 0.28 (26)</td>
<td>-13.017 ± 0.006 (18)</td>
<td>0.075 (23)</td>
</tr>
<tr>
<td>SAMPLE D</td>
<td>-20.16 ± 0.24 (26)</td>
<td>-20.106 ± 0.010 (21)</td>
<td>0.083 (25)</td>
</tr>
<tr>
<td>GISP</td>
<td>-24.74 ± 0.24 (23)</td>
<td>-24.762 ± 0.008 (20)</td>
<td>0.084 (21)</td>
</tr>
<tr>
<td>Deuterium ( [%o/o]_{SMOW} )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SAMPLE A</td>
<td>+12.5 ± 0.68 (23)</td>
<td>+12.28 ± 0.05 (20)</td>
<td>0.62 (22)</td>
</tr>
<tr>
<td>SAMPLE B</td>
<td>-28.5 ± 1.24 (23)</td>
<td>-28.24 ± 0.11 (19)</td>
<td>0.75 (19)</td>
</tr>
<tr>
<td>SAMPLE C</td>
<td>-93.5 ± 1.34 (23)</td>
<td>-93.49 ± 0.11 (19)</td>
<td>0.97 (20)</td>
</tr>
<tr>
<td>SAMPLE D</td>
<td>-154.7 ± 2.15 (23)</td>
<td>-155.00 ± 0.25 (17)</td>
<td>1.23 (20)</td>
</tr>
<tr>
<td>GISP - δD</td>
<td>-189.1 ± 1.24 (22)</td>
<td>-189.17 ± 0.13 (19)</td>
<td>0.70 (19)</td>
</tr>
</tbody>
</table>

(*) Calculated as \( \sigma = \sqrt{\frac{\sum_{i=1}^{n} (\delta_m - \delta_i)^2}{(n-1)}} \), after excluding outliers using the 2σ criterion.

Scatter of isotope results.

The scatter of the reported values (interlaboratory precision) is expressed by the standard deviation of the accepted values, after rejection of outliers according to the 2σ criterion (Table III). The rejection process was applied iteratively until all accepted values lie within \( \delta_m \pm 2\sigma \) band. In the worst case, four results were rejected by this method. The reported \( \sigma \)-values in the fourth column of Table III range between 0.07 and 0.10\%\text{o/o} for oxygen-18, and from 0.6 to 1.2\%\text{o/o} for deuterium.

Figs 3.1 to 3.10 show the oxygen-18 and deuterium results and quoted errors as provided by each laboratory for samples A to D and GISP. The laboratory codes were sorted according to the reported δ-values: from more negative to more positive. In order to keep a constant range of δ-values in all plots (0.8 per mil for \(^{18}\)O and 8 per mil for \(^{2}H\)) some outliers were not or only partially plotted. The consensus value (Table III, column 3) and the interlaboratory precision (Table III, column 4) were drawn in the plot as solid and dotted lines, respectively. The numerical values of the estimated consensus value of each isotope and the standard deviations (interlaboratory precision) were also included in the upper part of each plot.
Figures 3.1 to 3.10 highlight some additional features characterizing the performance of the laboratories which participated in the exercise: (i) some laboratories demonstrate very good precision but poor accuracy, i.e. small analytical error but disagreement with the consensus value; (ii) some other laboratories generally overestimate their analytical error.

The departure of reported values with respect to the corresponding consensus value for oxygen-18 and deuterium are presented for all measured samples in Tables IV and V, respectively. The last column in both tables contains the sum of the departures (absolute values) for a given isotope and for each participating laboratory. Figures 4.1 and 4.2 show the distribution of departures of the measured values to the consensus values for every laboratory. Laboratory codes have been sorted according to increasing cumulative departures. Figures 5.1 and 5.2 present the absolute cumulative departures in $^{18}$O and $^{2}$H, for every laboratory. Laboratories codes have been sorted as indicated for Figs. 4.1 and 4.2.
Table IV. Departures between the $\delta^{18}O$ values reported by the participating laboratories and the consensus values for analyzed samples (A, B, C, D and GISP). The last column contains the sum of all departures (absolute values) for each laboratory.

<table>
<thead>
<tr>
<th>Lab No.</th>
<th>Preparation method</th>
<th>Departure with respect to the consensus value ($%$) vs. VSMOW</th>
<th>Sum of departures ($%$) vs. VSMOW</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Sample A</td>
<td>Sample B</td>
</tr>
<tr>
<td>1</td>
<td>CO$_2$ ex</td>
<td>-0.009</td>
<td>-0.008</td>
</tr>
<tr>
<td>2</td>
<td>CO$_2$ ex</td>
<td>0.081</td>
<td>0.022</td>
</tr>
<tr>
<td>3</td>
<td>CO$_2$ ex</td>
<td>0.001</td>
<td>-0.018</td>
</tr>
<tr>
<td>4</td>
<td>CO$_2$ ex</td>
<td>0.151</td>
<td>0.042</td>
</tr>
<tr>
<td>5</td>
<td>CO$_2$ ex</td>
<td>-0.099</td>
<td>0.032</td>
</tr>
<tr>
<td>6</td>
<td>CO$_2$ ex</td>
<td>-0.029</td>
<td>0.082</td>
</tr>
<tr>
<td>7</td>
<td>CO$_2$ ex</td>
<td>-0.059</td>
<td>-0.108</td>
</tr>
<tr>
<td>8</td>
<td>CO$_2$ ex</td>
<td>0.191</td>
<td>0.392</td>
</tr>
<tr>
<td>9</td>
<td>CO$_2$ ex</td>
<td>0.181</td>
<td>-0.008</td>
</tr>
<tr>
<td>10</td>
<td>CO$_2$ ex</td>
<td>0.021</td>
<td>-0.098</td>
</tr>
<tr>
<td>11</td>
<td>CO$_2$ ex</td>
<td>-0.059</td>
<td>-0.018</td>
</tr>
<tr>
<td>12</td>
<td>CO$_2$ ex</td>
<td>-0.109</td>
<td>0.132</td>
</tr>
<tr>
<td>13</td>
<td>CO$_2$ ex</td>
<td>0.031</td>
<td>0.012</td>
</tr>
<tr>
<td>14</td>
<td>CO$_2$ ex</td>
<td>-0.239</td>
<td>-0.198</td>
</tr>
<tr>
<td>15</td>
<td>CO$_2$ ex</td>
<td>-0.139</td>
<td>-0.078</td>
</tr>
<tr>
<td>16</td>
<td>CO$_2$ ex</td>
<td>0.058</td>
<td>0.046</td>
</tr>
<tr>
<td>17</td>
<td>CO$_2$ ex</td>
<td>0.081</td>
<td>-0.138</td>
</tr>
<tr>
<td>18</td>
<td>CO$_2$ ex</td>
<td>0.000</td>
<td>-0.029</td>
</tr>
<tr>
<td>19</td>
<td>CO$_2$ ex</td>
<td>-0.179</td>
<td>-0.288</td>
</tr>
<tr>
<td>20</td>
<td>CO$_2$ ex</td>
<td>0.101</td>
<td>0.132</td>
</tr>
<tr>
<td>21</td>
<td>CO$_2$ ex</td>
<td>0.071</td>
<td>-0.058</td>
</tr>
<tr>
<td>22</td>
<td>CO$_2$ ex</td>
<td>-0.029</td>
<td>0.022</td>
</tr>
<tr>
<td>23</td>
<td>CO$_2$ ex</td>
<td>0.091</td>
<td>0.032</td>
</tr>
<tr>
<td>24</td>
<td>CO$_2$ ex</td>
<td>0.031</td>
<td>-0.008</td>
</tr>
<tr>
<td>25</td>
<td>CO$_2$ ex</td>
<td>-0.009</td>
<td>-0.078</td>
</tr>
<tr>
<td>26</td>
<td>CO$_2$ ex</td>
<td>-0.182</td>
<td>-0.058</td>
</tr>
</tbody>
</table>
Table V. Departures between the $\delta^2$H values reported by the participating laboratories and the consensus values for analyzed samples (A, B, C, D and GISP). The last column contains the sum of all departures (absolute values) for each laboratory.

<table>
<thead>
<tr>
<th>Lab No</th>
<th>Preparation method</th>
<th>Departure with respect to the consensus value ($^\circ$/o vs. VSMOW)</th>
<th>Sum of departures ($^\circ$/o vs. VSMOW)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Sample A</td>
<td>Sample B</td>
</tr>
<tr>
<td>1</td>
<td>Zn</td>
<td>-0.3</td>
<td>-1.8</td>
</tr>
<tr>
<td>2</td>
<td>U</td>
<td>0.2</td>
<td>1.3</td>
</tr>
<tr>
<td>3</td>
<td>Eq</td>
<td>-0.2</td>
<td>-0.6</td>
</tr>
<tr>
<td>4</td>
<td>Zn</td>
<td>0.2</td>
<td>0.9</td>
</tr>
<tr>
<td>5</td>
<td>Zn</td>
<td>0.7</td>
<td>0.5</td>
</tr>
<tr>
<td>6</td>
<td>U</td>
<td>0.0</td>
<td>-2.1</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>U</td>
<td>0.4</td>
<td>-1.2</td>
</tr>
<tr>
<td>9</td>
<td>Cr</td>
<td>-0.1</td>
<td>-0.3</td>
</tr>
<tr>
<td>10</td>
<td>U</td>
<td>0.1</td>
<td>-0.3</td>
</tr>
<tr>
<td>11</td>
<td>Zn</td>
<td>0.2</td>
<td>-0.4</td>
</tr>
<tr>
<td>12</td>
<td>Zn</td>
<td>1.4</td>
<td>1.2</td>
</tr>
<tr>
<td>13</td>
<td>Zn</td>
<td>-0.4</td>
<td>-0.9</td>
</tr>
<tr>
<td>14</td>
<td>Zn</td>
<td>-1.2</td>
<td>-0.5</td>
</tr>
<tr>
<td>15</td>
<td>Zn</td>
<td>1.1</td>
<td>0.5</td>
</tr>
<tr>
<td>16</td>
<td>U</td>
<td>-0.5</td>
<td>-2.2</td>
</tr>
<tr>
<td>17</td>
<td>Zn</td>
<td>0.4</td>
<td>0.0</td>
</tr>
<tr>
<td>18</td>
<td>Zn</td>
<td>1.5</td>
<td>0.5</td>
</tr>
<tr>
<td>19</td>
<td>Zn</td>
<td>1.3</td>
<td>1.0</td>
</tr>
<tr>
<td>20</td>
<td>Zn</td>
<td>0.1</td>
<td>0.4</td>
</tr>
<tr>
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<td>Zn</td>
<td>-0.4</td>
<td>-0.4</td>
</tr>
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<td>22</td>
<td>Zn</td>
<td>-0.3</td>
<td>-3.5</td>
</tr>
<tr>
<td>23</td>
<td>Zn</td>
<td>0.8</td>
<td>0.1</td>
</tr>
<tr>
<td>24</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>Zn</td>
<td>-0.4</td>
<td>1.3</td>
</tr>
</tbody>
</table>
Conclusions

The intercomparison test revealed significant differences in the interlaboratory precision of oxygen-18 and deuterium analyses of precipitation samples:

- for oxygen-18, the apparent scatter of the results, characterized by a mean standard deviation of about 0.08 ‰, is invariant with respect to actual \( \delta^{18}O \) content in the water sample being analyzed;

- for deuterium, the standard deviation increases from 0.6 to 1.2 ‰, with the actual \( ^2H \) content decreasing +12 ‰ to -190 ‰.

The different behaviour of the interlaboratory precision for both isotopes is at present not well understood and its clarification would require a more detailed investigation. The obtained values are, however, not far from the typical errors reported by the majority of laboratories engaged in routine analysis of water samples (0.1 ‰ for \( \delta^{18}O \) and 1 ‰ for \( \delta^2H \)). These values set up practical limits for comparing the results originating from different laboratories.

The obtained interlaboratory precision for \( \delta^{18}O \) and \( \delta^2H \) analyses also sets the limit for the precision of a secondary parameter, deuterium excess (\( d = \delta^2H - 8 \cdot \delta^{18}O \)) when derived from data sets produced by different laboratories. The limit is about ±2.5 ‰.

It is envisaged that similar interlaboratory comparison will be carried out in 1998.

References:


Fig. 1.1. Box and whisker plots of the results of oxygen-18 measurements for samples A to D after rejection of outliers as indicated in stage I of the data treatment. The central line in the box indicates the median, the box defines the interquartile range. Horizontal lines represent the values above or below the quartiles which can extend up to 1.5 times the interquartile range. Values outside this range are represented as single squares.
Fig. 1.2. Box and whisker plots of the results of deuterium measurements for samples A to D after rejection of outliers as indicated in stage I of the data treatment. The central line in the box indicates the median, the box defines the interquartile range. Horizontal lines represent the values above or below the quartiles which can extend up to 1.5 times the interquartile range. Values outside this range are represented as single squares.
Fig. 2 Box and whisker plots of the results of oxygen-18 and deuterium measurements for the intercomparison sample GISP after rejection of outliers as indicated in stage I of the data treatment. The central line in the box indicates the median, the box defines the interquartile range. Horizontal lines represent the values above or below the quartiles which can extend up to 1.5 times the interquartile range. Values outside this range are represented as single squares.
Fig. 3.1. Oxygen-18 content for sample A as reported by the participating laboratories. Vertical lines represent the analytical error quoted by each laboratory. The solid line represents the consensus value for the sample (Table III, column 3), and the dashed lines the one-sigma interlaboratory precision (Table III, column 4).
Fig. 3.2. Deuterium content for sample A as reported by the participating laboratories. Vertical lines represent the analytical error quoted by each laboratory. The solid line represents the consensus value for the sample (Table III, column 3), and the dashed lines the one-sigma interlaboratory precision (Table III, column 4).
Fig. 3.3. Oxygen-18 content for sample B as reported by the participating laboratories. Vertical lines represent the analytical error quoted by each laboratory. The solid line represents the consensus value for the sample (Table III, column 3), and the dashed lines the one-sigma interlaboratory precision (Table III, column 4).
Fig. 3.4. Deuterium content and one sigma error for sample B as reported by the participating laboratories. Vertical lines represent the analytical error quoted by each laboratory. The solid line represents the consensus value for the sample (Table III, column 3), and the dashed lines the one-sigma interlaboratory precision (Table III, column 4).
Fig. 3.5. Oxygen-18 content and one sigma error for sample C as reported by the participating laboratories. Vertical lines represent the analytical error quoted by each laboratory. The solid line represents the consensus value for the sample (Table III, column 3), and the dashed lines the one-sigma interlaboratory precision (Table III, column 4).
Fig. 3.6. Deuterium content and one sigma error for sample C as reported by the participating laboratories. Vertical lines represent the analytical error quoted by each laboratory. The solid line represents the consensus value for the sample (Table III, column 3), and the dashed lines the one-sigma interlaboratory precision (Table III, column 4).
Fig. 3.7. Oxygen-18 content and one sigma error for sample D as reported by the participating laboratories. Vertical lines represent the analytical error quoted by each laboratory. The solid line represents the consensus value for the sample (Table III, column 3), and the dashed lines the one-sigma interlaboratory precision (Table III, column 4).
Fig. 3.8. Deuterium content and one sigma error for sample D as reported by the participating laboratories. Vertical lines represent the analytical error quoted by each laboratory. The solid line represents the consensus value for the sample (Table III, column 3), and the dashed lines the one-sigma interlaboratory precision (Table III, column 4).
Fig. 3.9. Oxygen-18 content and one sigma error for GISP as reported by the participating laboratories. Vertical lines represent the analytical error quoted by each laboratory. The solid line represents the consensus value for the sample (Table III, column 3), and the dashed lines the one-sigma interlaboratory precision (Table III, column 4).
Fig. 3.10. Deuterium content and one sigma error for GISP as reported by the participating laboratories. Vertical lines represent the analytical error quoted by each laboratory. The solid line represents the consensus value for the sample (Table III, column 3), and the dashed lines the one-sigma interlaboratory precision (Table III, column 4).
Fig. 4.1. Differences between reported and accepted δ¹⁸O values for each sample. Laboratories are sorted according to increasing cumulative departure from the consensus values.
Fig. 4.2. Differences between reported and accepted $\delta^2$H values for each sample. Laboratories are sorted according to increasing cumulative departure from the consensus values.
Fig 5.1. Cumulative departures from the consensus values for the oxygen-18 measurements in each sample. Laboratories are sorted according to increasing cumulative departure from the consensus values.
Fig 5.2. Cumulative departures from the consensus values for the deuterium measurements in each sample. Laboratories are sorted according to increasing cumulative departure from the consensus values.
Annex I

List of laboratories engaged in deuterium and oxygen-18 analysis of precipitation which participated in the interlaboratory comparison
Mr. H.O. Panarello  
Instituto de Geocronología y Geología Isotópica  
Pabellón INGEIS, Ciudad Universitaria  
1428 Buenos Aires  
ARGENTINA

Mr. J. Dighton  
CSIRO Division of Water Resources  
Private Bag 2  
Glen Osmond SA 5064  
AUSTRALIA

Mr. Dieter Rank/Mr. W. Papesch  
Bundesversuchs- und Forschungsanstalt  
Arsenal, Geotechnisches Institut  
Faradaygasse 33 - Postfach 8  
A-1030 Vienna  
AUSTRIA

Isotope Hydrology Laboratory  
International Atomic Energy Agency  
Wagramerstrasse, 5  
A-1400 Vienna  
AUSTRIA

Mr. R. Victoria  
Universidade de Sao Paulo  
Campus de Piracicaba  
Centro de Energia Nuclear na Agricultura - CENA  
Av. Centenário 303, Caixa Postal 96  
Piracicaba, Sao Paulo  
BRAZIL

Mr. E. Drimmel/Mr. R. Heenskeer  
Department of Earth Sciences  
University of Waterloo  
Waterloo  
Ontario N2L 3G1  
CANADA

Mr. A. Pollastrt  
Laboratorio de Isótopos Ambientales  
Comisión Chilena de Energía Nuclear  
Amanategui 95, Casilla 188D  
Santiago  
CHILE

Mr. M. Dray  
Université Pierre et Marie Curie  
Centre de Recherches Géodynamiques  
47 Avenue de Corzent  
74203 Thonon Cedex  
FRANCE

Mr. H. Friedrichsen  
Freie Universität Berlin  
Institut für Mineralogie. Abt. Geochemie  
Boltzmannstrasse 18-20  
14195 Berlin 33  
GERMANY

Mr. P. Fritz/Mr. M. Gehre  
Umweltforschungszentrum  
Leipzig-Halle Ltd.  
Labor für Isotopenanalytik  
Permoserstraße 15, Leipzig  
GERMANY

Mr. P. Trimborn  
GSF-Institut für Hydrologie  
Ingolstädter Landstraße 1  
85764 Oberschleißheim  
GERMANY

Mr. M. Rao/Mr. S.N. Navada  
Isotope Group  
Bhabha Atomic Research Centre  
Trombay  
Bombay 400 085  
INDIA

Mr. A. Longinelli  
Istituto di Mineralogia e Petrografia  
Piazzale Europa, 1  
34100 Trieste  
ITALY

Mr. P. Squarci  
Istituto Internazionale per le Ricerche Geotermiche  
Piazza Solferino 2,  
56126 Pisa  
ITALY
Mr. R. Gedeon/ M. H. Amro
WAJ Laboratories
Ministry of Water and Irrigation
P.O. Box. 2412 Amman
JORDAN

H. A. J. Meijer
Centrum voor Isotopen Onderzoek
Nijenborgh 4
9747 RG Groningen
NETHERLANDS

Mr. M. K. Steward
Institute of Geological & Nuclear Sciences
P.O. Box 31312
Lower Hut
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ANNEX II

Data reporting sheet sent to the laboratories which participated in the intercomparison exercise
Sample preparation technique ($^{18}$O):

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Sample preparation technique ($^{2}$H):

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**NORMALIZATION DATA**

| Δ$^{18}$O of CO$_2$ equilibrated with VSMOW relative to your working standard in ‰$_{oo}$ (before normalization to the VSMOW-SLAP scale); corrections for dilution of water oxygen by CO$_2$ oxygen, valve mixing, background, and abundance of ions containing $^{13}$C and $^{17}$O should be incorporated in this value. |
| Δ$^{18}$O of CO$_2$ equilibrated with SLAP relative to your working standard in ‰$_{oo}$ (before normalization to the VSMOW-SLAP scale); corrections for dilution of water oxygen by CO$_2$ oxygen, valve mixing, background, and abundance of ions containing $^{13}$C and $^{17}$O should be incorporated in this value. |
| Δ$^{2}$H of H$_2$ evolved from VSMOW relative to your working standard in ‰$_{oo}$ (before normalization to the VSMOW-SLAP scale); corrections for contribution of H$_3^+$ ions, valve mixing and background should be incorporated in this value. |
| Δ$^{2}$H of H$_2$ evolved from SLAP relative to your working standard in ‰$_{oo}$ (before normalization to the VSMOW-SLAP scale); corrections for contribution of H$_3^+$ ions, valve mixing and background should be incorporated in this value. |

Normalization factor:
(VSMOW: Δ$^{18}$O = 0.0, Δ$^{2}$H = 0.0; SLAP: Δ$^{18}$O = -55.5, Δ$^{2}$H = -428)

| $^{18}$O: |
| $^{2}$H: |

**RESULTS**

$\delta^{18}$O and $\delta^{2}$H of the sample (normalized to the VSMOW-SLAP scale), with the overall measurement error (one sigma).

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\delta^{18}$O [‰$_{oo}$]</th>
<th>$\delta^{2}$H [‰$_{oo}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample &quot; A &quot;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample &quot; B &quot;</td>
<td></td>
<td></td>
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<tr>
<td>Sample &quot; C &quot;</td>
<td></td>
<td></td>
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<tr>
<td>Sample &quot; D &quot;</td>
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<td>GISP</td>
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</tbody>
</table>

Laboratory Manager........................................ Date.................................