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Reference and intercomparison materials for stable isotopes of light elements

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FOREWORD

The stable isotope composition of chemical elements varies in natural compounds as a consequence of the slightly different physico-chemical behaviour of isotopes. In particular, isotopes of light elements, which have the largest relative mass difference and therefore also the most different behaviour, show the widest variations. For instance, natural waters exhibit variations of the $^{2}H/^{1}H$ ratio up to 1:2, and of the $^{18}O/^{16}O$ ratio up to 1:1.1, due to the different evaporation-condensation rate of $^{1}H_2{}^{16}O$ with respect to $^{2}H^{1}H^{16}O$ and $^{1}H_2{}^{18}O$. These variation ranges become even wider if all natural compounds containing hydrogen and/or oxygen are considered.

The possibility of measuring the stable isotope relative variations with high precision, using mass spectrometry, promoted the rise of new fields of research in geochemistry and hydrology and, more recently, in environmental studies. The steady growth of these investigations and of their practical applications has emphasized the need for high quality isotopic standards and intercomparison samples, with well determined isotopic composition, for the intercalibration of analytical techniques and results among laboratories

Although stable isotope standards have existed for more than three decades, there was a need to re-examine the whole matter, in view of the expansion of isotope applications and the continuous improvements and refinements of the analytical techniques, which make it possible to detect smaller and smaller isotopic variations. Just to give an example, up to ten or twenty years ago, a precision of ±0.1‰ in the determination of $^{13}C/^{12}C$ ratio relative variations was generally considered acceptable and even good. But with the application of carbon stable isotopes to study the atmospheric carbon dioxide with the aim of improving the understanding of the global carbon cycle, the long-term analytical precision had to be increased by an order of magnitude to detect the long term trend of less than 0.02‰ per year, superimposed on the seasonal variations. The laboratories involved in this work had, and still have, to go through lengthy check runs and intercomparisons of the analytical and sampling techniques, in order to be sure that the data obtained in different places are fully consistent.

For the past thirty years, the International Atomic Energy Agency, through its Section of Isotope Hydrology, has been active in the field of preparation and distribution of stable isotope reference and intercomparison materials for the determination of the isotopic composition of natural compounds.

The organization of the Consultants Meeting on Stable Isotope Standards and Intercomparison Materials held in Vienna from 1 to 3 December 1993, the fifth of this type (the previous meetings took place in 1966, 1976, 1983 and 1985), called for a review and a discussion of the characteristics, quality and availability of the existing standards and intercalibration materials, and for an assessment of needs for new materials, in view of recent developments and applications.

A large part of the discussions was devoted to the new materials prepared for sulphur isotope analysis and the analytical requirements for highly precise isotopic analysis of CO_2. The papers presented at the meeting are assembled in this volume.

For the first time, two institutions were represented which are actively engaged in the field of standardization and intercalibration of isotopic measurements: the Institute for Reference Materials and Measurements of the Commission of the European Communities, Geel, Belgium, and the National Institute for Standards and Technology of the US Department of Commerce, Gaithersburg, Maryland, USA. It is hoped that this marks the beginning of a new, fruitful collaboration between the IAEA and these institutions.

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CONTENTS

SUMMARY OF THE MEETING

In this summary of the fifth IAEA Meeting on Stable Isotope Standards and Intercomparison Materials, the major conclusions reached and the recommendations formulated at the meeting are presented. They are submitted to the community of those interested in the determination of stable isotope environmental variations for various scientific and technical purposes. Comments and proposals, related not only to the conclusions and recommendations of this specific meeting but also to stable isotope reference and intercomparison materials in general, will be most welcome and useful, and should be addressed to the IAEA, Section of Isotope Hydrology. They will be brought to the attention of the consultants who will participate in future IAEA meetings on the same subject, and will be of help to all national and international institutions involved in the preparation and distribution of stable isotope reference materials, in formulating working programmes and defining lines of co-operation and co-ordination.

1. Sulphur isotope reference and intercomparison samples

Early investigators adopted meteoritic sulphur, in particular that of troilite (FeS) from the Canyon Diablo meteorite, as a reference standard for sulphur isotope studies. The choice was based on the apparent isotopic homogeneity of meteoritic sulphur and the idea that it could have the same isotopic composition as the primordial sulphur, supported by the fact that its $^{34}S/^{32}S$ value is close to the average of terrestrial samples.

Later, however, it was recognized that the sulphur isotopic composition of Canyon Diablo Troilite (CDT) was not as homogeneous as desirable: differences of up to 0.25‰ were observed. This fact is not surprising in geological materials, which rarely have fully homogeneous isotopic and chemical compositions. Even so, CDT continued to be used as a primary reference for sulphur isotopes, and this unfortunate continuance has hampered progress and agreement among laboratories.

Intercomparison of results should now be improved by adopting for measurement calibration the sample of chemically pure Ag_2S, having a homogeneous isotopic composition calibrated vs. CDT, which was prepared by B.W. Robinson and C.A.M. Brenninkmeijer (Institute of Geological and Nuclear Sciences, Lower Hutt, New Zealand) in 1987. This sample has been tested by several laboratories, and is now distributed by IAEA with the code name IAEA-S-1 (see Appendix). CDT, for obvious reasons, is kept as a reference to express $\delta^{34}S$ results.

The following recommendations were formulated at the meeting:

(i) It has been recognized that it is practically impossible to define a very precise value of IAEA-S-1 versus the Canyon Diablo Troilite (CDT) reference standard, simply because CDT was not isotopically homogeneous and, in addition, has been exhausted for a long time. Thus, it is proposed to adopt for IAEA-S-1 the value of $\delta^{34}S$ = -0.30‰ vs. a defined, hypothetical V-CDT (where V stands for Vienna, in analogy with V-SMOW and V-PDB). It is recommended that laboratories re-calibrate their measurements versus IAEA-S-1 in order to remove ambiguities on the zero of the $\delta^{34}S$ scale and improve intercomparison of results. In reporting their results, laboratories should specify that the reference is V-CDT, and not CDT, indicating that the measurements calibration was made through IAEA-S-1.

(ii) A new Ag_2S sample shall be prepared with a $\delta^{34}S$ value close to -30‰ from 1 kg of sphalerite (ZnS) supplied by S. Halas, Maria Curie-Sklodowska University, Lublin, Poland. B.W. Robinson, New Zealand, is in principle ready to prepare the sample, with the support of IAEA. The new sample will be called IAEA-S-3.

(iii) A new $BaSO_4$ sample shall be prepared with a $\delta^{34}S$ value close to -30‰ from 1 kg of spahlerite supplied by S. Halas, Maria Curie-Sklodowska University, Lublin, Poland. This sample would complement NBS-127, also $BaSO_4$, with $\delta^{34}S = +20.32$‰ vs. CDT (average of 10 laboratories; Hut, 1987). H.R. Krouse, University of Calgary, Canada, is in principle ready to prepare the sample, with the support of IAEA. The new sample will be called IAEA-SO-4 (the code SO implies that the sample can be used for sulphur and oxygen isotopes).

(iv) The above new samples, together with IAEA-S-1 and IAEA-S-2, should be widely distributed to practising laboratories, which should report their results to IAEA with the objective of establishing recommended $\delta^{34}S$ values for IAEA-S-2, IAEA-S-3 and IAEA-SO-4 vs. IAEA-S-1.

(v) The determination of the absolute isotopic ratios and abundances of IAEA-S-1 is recommended.

(vi) The determination of $\delta^{33}S$ and $\delta^{36}S$, in addition to ^{34}S, by SF_6 technique and by thermal ionization mass spectrometry, for IAEA-S-2, IAEA-S-3 and IAEA-SO-4 vs. IAEA-S-1, should be encouraged.

(vii) Consideration should be given to the establishment of intercomparison samples for organic sulphur isotope analyses. In fact, the isotopic composition of organic sulphur is finding increased use in petroleum geochemistry, medical sciences, agriculture, forestry, and food studies. In view of the wide range of $\delta^{34}S$ values encountered in these studies and the variety of methods used (including recent on-line combustion techniques), it is appropriate to have relevant intercomparison materials. One difficulty in selecting the chemical compounds for the intercomparison samples is that different forms of organic sulphur exist in many natural materials, which may differ considerably in isotopic composition. For instance, in some oils these forms exhibit up to 20‰ difference in $\delta^{34}S$, attesting to their different geochemical histories. Cystine (melting point 260°C) and methionine (melting point 282°C) have been suggested as possible materials for the establishment of these intercomparison samples.

2. Other new intercomparison samples

New intercomparison samples for hydrogen, carbon, and oxygen stable isotope determinations in various categories of compounds are suggested for possible consideration at future IAEA meetings. They include:

(i) α-cellulose for hydrogen, carbon, and oxygen stable isotope variations in wood. A sample of α-cellulose is now available at IAEA with the code name IAEA-C-3, which is used for ^{14}C intercalibration: it is proposed to check its isotopic composition and homogeneity, in order to judge whether it is suitable as an intercomparison sample. The $\delta^{13}C$ of IAEA-C-3 was measured by a number of laboratories for a ^{14}C intercomparison exercise, and the great majority of results ranged from -24‰ to -26‰ (Rozanski, 1991).

(ii) A methane having δ^2H at about -300‰ vs V-SMOW and $\delta^{13}C$ at about -60‰ vs V-PDB. A sample with these characteristics may be available at NIST.

(iii) Two carbon dioxide samples to replace NBS-16 and NBS-17, which have been exhausted for several years. The new samples should have approximately the same isotopic composition as NBS-16 and NBS-17, the first of which had $\delta^{13}C$ = -41.59‰ and $\delta^{18}O$ = -36.11‰, and the second $\delta^{13}C$ = -4.45‰ and $\delta^{18}O$ = -18.76‰ vs. V-PDB (Hut, 1987). NIST will consider preparing these samples.

(iv) Two silver phosphate samples having respectively $\delta^{18}O$ of about 0‰ and +20‰ vs. V-SMOW, to be used for oxygen isotope measurements in phosphates.

Consideration was also given to other light elements, with the following provisional indications:

(i) No new intercomparison materials were suggested for lithium and nitrogen isotope determinations.

(ii) Two certified reference materials (both H_3BO_3), are available for boron isotopes, one from NIST (NIST-SRM-951, with $^{11}B/^{10}B = 4.04362 \pm 0.00137$), and the other from IRMM (IRMM-011, with $^{11}B/^{10}B = 4.0443 \pm 0.0052$). NIST-SRM-951 is currently used as a reference in boron isotope geochemistry. Sea water borate is enriched in ^{11}B by about 40‰ with respect to NIST-SRM-951.

(iii) IAEA-NO-3 (KNO_3), which is distributed for nitrogen isotope measurements intercomparison, can possibly also serve as intercomparison sample for oxygen in nitrates. Its oxygen isotopic composition and homogeneity needs to be checked.

3. Determination of the absolute isotopic ratios of reference samples

The materials used for isotopic measurement calibration vs. the reference standards, which so far include, for the most common light elements, V-SMOW, SLAP, NBS-19 and IAEA-S-1 need to be fully characterized, i.e. their absolute isotopic ratios must be determined. This in principle allows (i) to check whether the isotopic composition of the material will change with time, and (ii) to prepare new materials with identical (within the experimental errors) or very close isotopic ratios, when the present materials are exhausted or no longer suitable, or if the storage and handling conditions prove to be inadequate for their long-term conservation.

For these purposes, the absolute isotopic ratios of the samples indicated above must be determined with an overall error which is equal or better than the best current analytical precision for relative isotopic difference determinations. Thus, in principle, the error on the absolute isotopic ratios should not exceed 0.02‰ ($^{13}C/^{12}C$) for carbon, oxygen ($^{18}O/^{16}O$) and sulphur ($^{34}S/^{32}S$), and 0.2‰ for hydrogen ($^2H/^1H$). These limits have so far been approached only in the absolute $^2H/^1H$ ratio determination of V-SMOW and SLAP carried out by Hagemann *et al.* (1970), who quote errors of 0.32‰ and 0.56‰, respectively. The errors quoted by Baertschi (1976) and Li *et al.* (1988), for the $^{18}O/^{16}O$ and the $^{17}O/^{16}O$ determination of V-SMOW, 0.22‰ and 2.1‰ respectively, still appear large.

The absolute isotopic ratios are used for correction of results from interferences of isobaric ions in mass spectrometric analysis, and this is an additional reason for which their determination in materials used for measurement calibration is desirable. However, the accuracies required in this case are at least one order of magnitude less than those quoted above.

The Institute for Reference Materials and Measurements (IRMM) in Geel, Belgium, is currently involved in the Avogadro constant re-determination. With the same procedure and equipment, the overall precisions which can be attained on isotopic ratios are: 0.04‰ for $^{13}C/^{12}C$, 0.2‰ for $^{15}N/^{14}N$, $^{18}O/^{16}O$ and $^{34}S/^{32}S$, 1‰ for $^{17}O/^{16}O$. It is anticipated that these precisions will improve considerably in the near future; in particular, for $^{34}S/^{32}S$ the precision will soon reach 0.04‰. The IRMM is in principle ready to measure the absolute isotopic ratios of the calibration materials listed above. The determinations can be carried out in two phases: in the first phase the isotopic ratios will be determined by using the Avogadro procedure and equipment, and in the second by using synthetic isotopic mixtures.

Calibration materials of other light elements, including Li, B, Si, Cl, whose natural isotopic variations are used in geochemistry, should also be considered for accurate (re)determination of absolute isotopic ratios. For silicon, it is suggested to determine the $^{30}Si/^{28}Si$ and $^{29}Si/^{28}Si$ ratios of NBS-28 (SiO_2): this material can be used in principle for calibration of silicon isotope measurements.

4. Data reduction procedures

For high precision measurements of stable isotope variations, such as those carried out for atmospheric trace gases, and for the intercomparison of results between laboratories, there is a need to adopt common procedures of data reduction. The following is therefore recommended:

(i) The data reduction procedure used by modern automated mass spectrometers should be clearly documented and accessible to the user, in case he wants to change it. At present the software for data reduction incorporated in computers driving the mass spectrometers is often not accessible, and the computation procedure is not sufficiently documented.

(ii) The data reduction procedure should be based on a single consistent set of assumptions for:

(a) the $^{13}C/^{12}C$, $^{18}O/^{16}O$ and $^{17}O/^{16}O$ absolute isotopic ratios in the V-PDB CO_2, i.e. the CO_2 obtained from V-PDB by treatment with H_3PO_4 100% at 25°C, and

(b) the relationship between ^{17}O and ^{18}O in terrestrial materials.

It is desirable to agree on a common set of values for these parameters which appear in the correction algorithms. For the $^{18}O/^{16}O$ ratio, the value of 0.0020883, based on Baertschi's value for V-SMOW, enriched by 30.9‰ (recommended value of V-PDB vs. SMOW) and by another 10.25‰ (recommended value for the isotopic fractionation in CO_2 extraction from $CaCO_3$), seems to be the best assumption. Values for the other parameters are reported in papers included in these proceedings (Allison *et al.*, Gonfiantini *et al.*). For high precision isotopic measurements, the computation procedure for data reduction and the values adopted for the above parameters should be clearly documented by the authors.

In future, data reduction procedures for gases other than CO_2, such as N_2O, will need to be developed.

Note: The summary was prepared by W. Stichler, R. Gonfiantini and K. Rozanski. We would like to acknowledge with thanks the contribution of all the participants in the fifth IAEA Meeting on Stable Isotope Reference and Intercomparison Materials, and in particular of the Chairmen of the four working groups which elaborated the recommendations, i.e. Messrs. C.E. Allison, T. Coplen, P. De Bièvre and H.R. Krouse.

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Appendix

Starting 1994 the description of the intercomparison materials distributed by the IAEA, was changed as indicated in the following list. The new sample code indicates the directly affected isotope.

Old Sample Code	New Sample Code	Substance
IAEA-C1	IAEA-CO-1	calcite
IAEA-KST	IAEA-CO-8	calcite
IAEA-NZCH	IAEA-CO-9	carbonate
Sucr.Anu	IAEA-CH-6	sucrose
PEF-1	IAEA-CH-7	polyethelene
IAEA-N1	IAEA-N-1	ammonium sulfate
IAEA-N2	IAEA-N-2	ammonium sulfate
IAEA-N3	IAEA-NO-3	potassium nitrate
IAEA-NZ1	IAEA-S-1	silver sulfide
IAEA-NZ2	IAEA-S-2	silver sulfide
Sulfur	IAEA-S-4	sulfur

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STANDARDS AND INTERCOMPARISON MATERIALS DISTRIBUTED BY THE INTERNATIONAL ATOMIC ENERGY AGENCY FOR STABLE ISOTOPE MEASUREMENTS

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Abstract - *The Agency's current programme for the preparation and distribution of standards and intercomparison materials for the calibration of the measurements of stable isotope natural variations is reviewed. The need to carry out determinations of the absolute isotopic ratios in standards is discussed. This would facilitate the long-term quality control of existing standards as well as the establishment of new standards when the present ones are exhausted.*

1 - Introduction

For many years the International Atomic Energy Agency in Vienna has been distributing calibration and intercomparison materials for the interlaboratory calibration of measurements of stable isotope ratio variations in natural compounds. These materials were prepared and initially tested by laboratories having the reputation of performing high precision isotopic measurements, the collaboration of which is here gratefully acknowledged. The calibration and intercomparison materials were initially intended for use in isotope geochemistry and hydrology - fields in which the IAEA is actively engaged - but soon they were adopted also by scientists working in other fields, such as environmental studies, biology, food-stuff adulteration, etc.

The calibration and intercomparison materials typically consist of natural minerals and compounds commonly studied in isotope geochemistry, having the desired characteristics of isotopic composition, homogeneity, chemical purity and stability. Sometimes, however, it is not possible to find suitable natural materials, and it becomes necessary to prepare synthetic compounds with the required characteristics.

Standards, calibration and intercomparison materials can be grouped under the following categories and definitions:

(i) *Primary reference standards*: natural or virtual materials versus which, by general agreement, the relative variations of stable isotope ratios in natural compounds are expressed, using the well known $\delta\ ^0/_{00}$ notation:

$$\delta\ ^0/_{00} = \left(\frac{R_S}{R_R} - 1\right) \times 1000 \tag{1}$$

where R_S and R_R are the isotopic ratios ($^2H/^1H$, $^{13}C/^{12}C$, $^{15}N/^{14}N$, $^{18}O/^{16}O$, $^{34}S/^{32}S$) respectively in the sample and in the primary reference standard.

(ii) *Calibration materials*: natural and synthetic compounds which have been carefully calibrated versus the primary reference standards, and the calibration values have been internationally agreed and adopted. They are used to fix the δ-scale "zero" and hence express the results of isotopic composition determinations versus the common primary reference standards, to check the mass spectrometer linearity over a wide range of isotopic ratio variations, and to calibrate laboratory standards for a continuous internal check of the results.

(iii) *Intercomparison materials*: natural and synthetic compounds which provide the means for laboratories to periodically check the overall quality of the measurements performed, including the long-term reproducibility of sample preparation from a variety of materials, in comparison with those obtained by other laboratories. Intercomparison materials cover a broad spectrum of chemical compositions and a wide range of isotopic ratios. Their isotopic composition is computed by averaging the results of several laboratories obtained in intercomparison runs and in individual assays, after elimination of outliers using the 2σ interval criterion. Updated lists of these results are available at IAEA and are provided on request.

In this article, we review the status of the programme on standards and intercomparison materials distributed by IAEA for hydrogen, carbon, nitrogen, oxygen and sulphur stable isotope analyses.

2 - Primary reference standards

The primary reference standards used to express natural variations of isotopic composition of the five elements listed above are SMOW, PDB, CDT and atmospheric nitrogen.

2.1 - SMOW (Standard Mean Ocean Water)

SMOW was used since it was defined by Craig in 1961 as reference to express the relative variations of $^2H/^1H$ and $^{18}O/^{16}O$ ratios in natural waters. Shortly afterwards it was adopted as reference to express the variations of the same isotopic ratios in all natural materials, and then also those of the $^{17}O/^{16}O$ ratio. The latter isotopic ratio is of particular interest for extraterrestrial materials.

Before 1961, the reference standard mostly used for oxygen isotope determinations was the CO_2 obtained from PDB by treatment with phosphoric acid 100 %. This CO_2 has an oxygen isotopic composition very close to that of the CO_2 equilibrated with SMOW at 25°C (see section 2.2), and therefore to switch from it to SMOW as reference was relatively easy. The situation, however, was rather confusing, with reference standards and notations different for almost each laboratory (Gonfiantini, 1981).

The Craig's definition of SMOW was based on the water standard known as NBS-1, a water sample from the Potomac River, Washington D.C., originally deposited, as all samples with the same letter code, at the National Bureau of Standards, today the National Institute for Standards and Technology (NIST) of the U.S. Department of Commerce in Gaithersburg, Maryland. Craig gave the following relationships between SMOW and NBS-1:

$$(^2H/^1H)_{SMOW} = 1.050\ (^2H/^1H)_{NBS\text{-}1}$$

$$(^{18}O/^{16}O)_{SMOW} = 1.008\ (^{18}O/^{16}O)_{NBS\text{-}1}$$

Craig also evaluated the absolute isotopic ratios of SMOW: $^2H/^1H = (158 \pm 2) \times 10^{-6}$, and $^{18}O/^{16}O = (1993.4 \pm 2.5) \times 10^{-6}$.

SMOW is in principle an excellent primary reference standard especially for water, because the ocean has a rather uniform isotopic composition, contains about 97 % of the water present on the Earth crust, and is by far the major source and sink of all waters taking part in the hydrological cycle. For hydrogen, the ocean is also the largest reservoir on the Earth crust.

However, a major disadvantage of the defined SMOW was that it did not exist as a real water sample versus which the measurements could be directly calibrated. In addition, the isotopic composition of NBS-1 was quite different from that of SMOW, and this could introduce a non-negligible error in fixing the "zero" of the δ^2H and $\delta^{18}O$ scales which would had been particularly prejudicial for the measurement intercomparison of ocean water samples. Last but not least, there were some doubts about the state of conservation of NBS-1.

All these problems were at last overcome with the preparation of *V-SMOW* (see section 3.1), which, having an isotopic composition practically identical to that of the defined SMOW, became *de facto* the primary reference standard to express hydrogen and oxygen stable isotope variations.

2.2 - PDB (Peedee Belemnite)

PDB consisted of calcium carbonate from the rostrum of a Cretaceous belemnite, *Belemnitella americana,* from the Peedee formation of South Carolina. The CO_2 obtained from PDB by treatment with 100 % phosphoric acid at 25°C was initially adopted as a reference standard in palaeotemperature investigations based on oxygen isotope variations in calcite and aragonite deposited by marine organisms: PDB had the same $^{18}O/^{16}O$ ratio as the calcium carbonate deposited in thermodynamic equilibrium in modern "average" marine water at 16.5°C (Epstein *et al.*, 1953; Craig, 1965). Shortly afterwards, PDB was also adopted to express carbon isotope variations (Craig, 1953).

PDB has isotopic ratios close to those of limestone of marine origin, and is considerably enriched in ^{13}C with respect to organic carbon compounds. In particular, PDB's $^{13}C/^{12}C$ isotopic ratio is very close to that of bicarbonate dissolved in the ocean. Ocean bicarbonate largely controls the carbon isotopic composition of atmospheric CO_2, which represents only 2 % of the first. Atmospheric CO_2 and ocean bicarbonate provide the starting material and the sink for most of the processes involved in the carbon biogeochemical cycle: thus, PDB is for carbon isotopes the equivalent of SMOW for hydrogen and oxygen isotopes.

Craig (1957) evaluated the isotopic ratios of the PDB-derived CO_2 in order to establish the correction equations for the interference of ions of the same mass in mass spectrometric determinations. From measurements previously performed by Nier (1950) he derived the following values: $^{13}C/^{12}C = 11237.2 \times 10^{-6}$, $^{18}O/^{16}O = 2079 \times 10^{-6}$, and $^{17}O/^{16}O = 380 \times 10^{-6}$. It should be noted that the carbon isotope ratio of the PDB-derived CO_2 corresponds to that of PDB, while the two oxygen isotope ratios are different due to the isotopic fractionation during the phosphoric acid treatment. These values were indirectly derived by Craig from measurements performed by Nier (1950). In section 7 of this paper other values are reported for the PDB's isotopic ratios based on indirect determinations.

Craig (1965) also evaluated that PDB was enriched of 30.6 $^0/_{00}$ in ^{18}O with respect to the defined SMOW, and, taking into account the isotopic fractionations occurring in the CO_2 preparation from the $CaCO_3$ and in CO_2-water equilibration, he computed that the PDB-derived CO_2 was enriched of 0.20 $^0/_{00}$ with respect to the CO_2 equilibrated with SMOW at 25°C. Recent evaluations have indicated slightly different values, i.e. 30.9 $^0/_{00}$ for PDB versus V-SMOW, and 0.27 $^0/_{00}$ for the PDB-derived CO_2 versus the SMOW-equilibrated CO_2 (Hut, 1987).

PDB is exhausted from long time, but it has been kept as primary reference standard to express the natural variations of carbon isotopes in natural compounds and those of oxygen isotopes in carbonates, because the great majority of the published results were referred to PDB.

2.3 - Atmospheric nitrogen

Atmospheric nitrogen, with a very homogeneous isotopic composition all around the world (Mariotti, 1983), is an excellent primary reference standard for nitrogen stable isotope variations. This is a characteristic common to all inert gases which have a very long residence time in the atmosphere and therefore are well mixed.

Atmosphere is the largest terrestrial reservoir of nitrogen, and it is also the main source and sink of this element taking part in natural and man-controlled processes (production of fertilizers).

2.4 - CDT (Canyon Diablo Troilite)

CDT consisted of FeS (troilite) present in the iron meteorite of Canyon Diablo, Arizona. Meteoritic sulphur was taken as reference standard because its $^{34}S/^{32}S$ isotopic ratio exhibits only small variations and corresponds quite well to the average isotopic ratio of terrestrial sulphur (Macnamara and Thode, 1950). From this primordial value, isotopic fractionations in geochemical processes started to build up the differences of sulphur isotopic composition observed in terrestrial compounds (Ault and Kulp, 1959; Thode *et al.*, 1962).

CDT has a $^{32}S/^{34}S$ ratio of 22.22 (Thode *et al.*, 1962), and is considerably depleted in ^{34}S (about 20 $^{0}/_{00}$) with respect to marine sulphate, which isotopically is the most homogeneous sulphur reservoir on the earth crust. Like PDB, also CDT is exhausted, but it has been kept as a reference standard because all the result published for a long time were expressed versus it.

3 - Calibration materials

Among the four primary reference standards listed above, SMOW was never physically available, while PDB and CDT were exhausted for long time. In order to make possible the measurement calibration versus these reference standards, IAEA distributes materials which in turn have been carefully calibrated versus the primary reference standards, and the calibration values have been internationally agreed and adopted. These calibration materials include two water and one calcite samples, which are currently available for distribution, and two silver sulphide samples which will be ready soon. They are reported in Table 1 and described below. For oxygen-18, the interrelations between calibration materials are also shown in Fig. 1.

3.1 - V-SMOW (Vienna Standard Mean Ocean Water) and SLAP (Standard Light Antarctic Precipitation)

These two water samples are distributed for the calibration of the $^{2}H/^{1}H$, $^{18}O/^{16}O$ and $^{17}O/^{16}O$ variation measurements. V-SMOW has an isotopic composition practically identical to the SMOW defined by Craig (1961), while SLAP is considerably depleted in heavy isotopes with respect to V-SMOW. The absolute $^{2}H/^{1}H$, $^{18}O/^{16}O$ and $^{17}O/^{16}O$ isotopic ratios of V-SMOW and SLAP are shown in Table 1. The maximum density of V-SMOW is 999.975 $kg \cdot m^{-3}$ (Girard and Menaché, 1972).

V-SMOW was prepared by R. Weiss and H. Craig (Scripps Institution of Oceanography, La Jolla, California) by mixing distilled ocean water (collected in the Pacific Ocean in July 1967 at latitude 0^{0} and longitude 180^{0}) with small amounts of other waters until reaching the desired isotopic composition. SLAP was prepared from South Pole firn collected by E. Picciotto (Université Libre de Bruxelles) at the Amundsen-Scott Station.

At present, V-SMOW is the main calibration material for determinations of hydrogen and oxygen isotopic variations on natural compounds, and *de facto* also the main primary reference standard to express these variations. In fact all laboratories use V-SMOW for calibration purposes and assume that V-SMOW and defined SMOW are identical - even if this may not be fully true. Also in papers where the reference standard is indicated only by SMOW, this should in reality be read V-SMOW.

TABLE 1

Calibration standards distributed by IAEA

Name	Nature	Isotopic ratio		$\delta\ ^0/_{00}$	Reference standard
V-SMOW	water	$^2H/^1H$	$(155.76 \pm 0.05) \times 10^{-6}$ (1) $(155.75 \pm 0.08) \times 10^{-6}$ (2) $(155.60 \pm 0.12) \times 10^{-6}$ (3)	0.00	V-SMOW
		$^{18}O/^{16}O$	$(2005.20 \pm 0.45) \times 10^{-6}$ (4)	0.00	V-SMOW
		$^{17}O/^{16}O$	$(379.9 \pm 0.8) \times 10^{-6}$(5)	0.00	V-SMOW
SLAP	water	$^2H/^1H$	$(89.02 \pm 0.05) \times 10^{-6}$ (1) $(89.12 \pm 0.07) \times 10^{-6}$ (2) $(88.88 \pm 0.18) \times 10^{-6}$ (3)	−428.0 (6)	V-SMOW
		$^{18}O/^{16}O$	*$(1893.91 \pm 0.45) \times 10^{-6}$*(7)	−55.50 (6)	V-SMOW
NBS-19	calcite	$^{13}C/^{12}C$		1.95 (8)	V-PDB
		$^{18}O/^{16}O$		−2.20 (8) 28.6 (9)	V-PDB V-SMOW
IAEA-S-1	Ag_2S	$^{34}S/^{32}S$		*−0.30* (10)	CDT
IAEA-S-2	Ag_2S	$^{34}S/^{32}S$		*21.7* (11)	CDT

(1) - Hagemann *et al.*, 1970.

(2) - De Wit *et al.*, 1980. The value originally reported for V-SMOW was later modified into 155.75×10^{-6} (Mook, personal communication, 1983).

(3) - Tse *et al.*, 1980.

(4) - Baertschi, 1976.

(5) - Li *et al.*, 1988.

(6) - By international agreement (Gonfiantini, 1978).

(7) - Computed from V-SMOW using $\delta^{18}O = -55.50\ ^0/_{00}$.

(8) - By international agreement (Hut, 1987).

(9) - Computed using for PDB $\delta^{18}O = 30.9\ ^0/_{00}$ vs. V-SMOW (Hut, 1987).

(10) - Proposed (see in the text and Stichler and Gonfiantini, 1994).

(11) - Provisional value by Robinson and Brenninkmeijer (1987, 1990). IAEA-S-2 is under calibration.

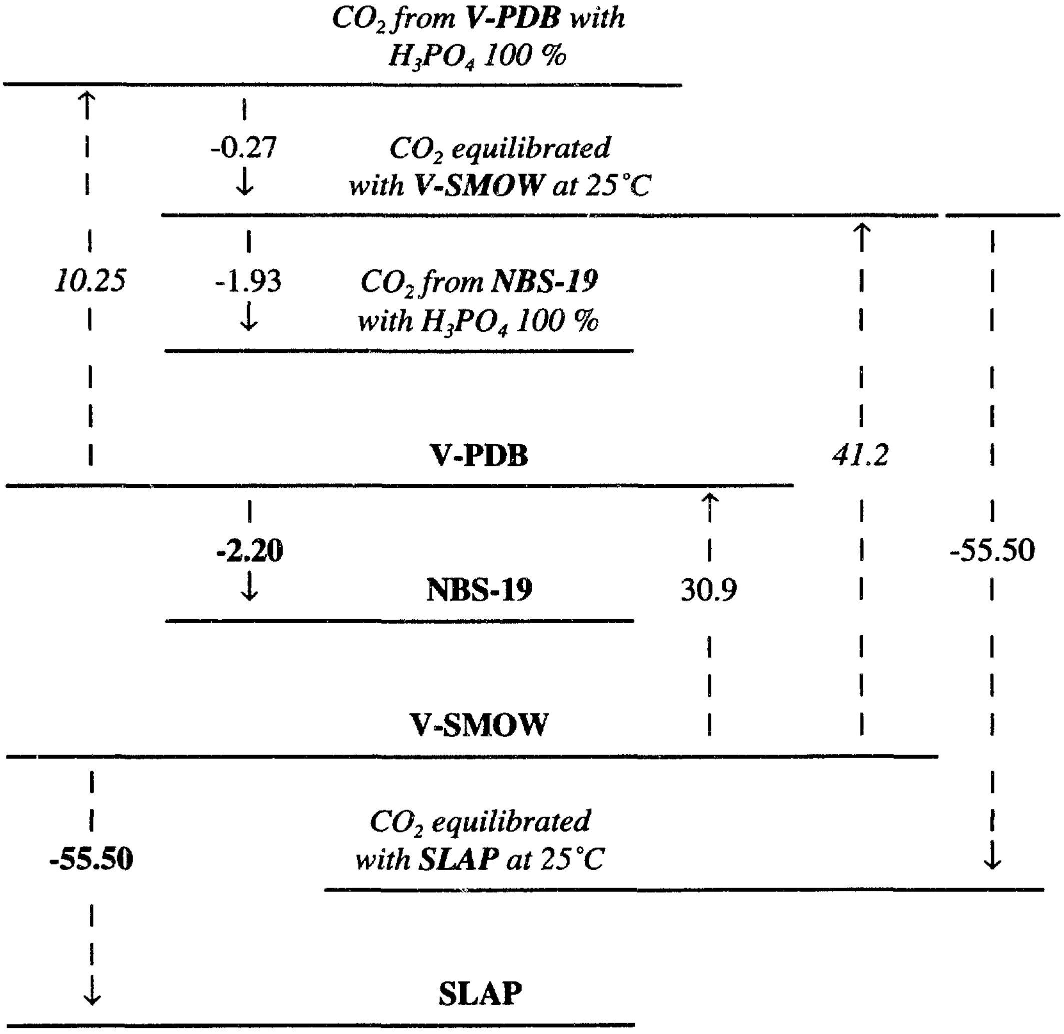

Fig. 1 - Internationally agreed values for oxygen-18 concentration differences between calibration materials, and for some related fractionation factors (in italics). Positive values give the relative ^{18}O enrichment of the upper compound, and negative values the relative ^{18}O depletion of the lower compound. All values are in $^0/_{00}$. Adapted from Hut, 1987.

The isotopic composition of SLAP versus V-SMOW is given by $\delta^2H = -428.0$ $^0/_{00}$ and $\delta^{18}O = -55.50$ $^0/_{00}$, values which have been internationally agreed on the basis of analyses performed by selected laboratories. These exactly defined isotopic differences between V-SMOW and SLAP, which encompass most of the isotopic variations of natural waters, are used to fix the δ^2H and $\delta^{18}O$ scales (Gonfiantini, 1978). In principle, all the δ^2H and $\delta^{18}O$ determinations - and in future also those of $\delta^{17}O$ when the ^{17}O concentration of SLAP will be calibrated versus that of V-SMOW - and the experimental fractionation factors of hydrogen and oxygen isotopes should be normalized on the V-SMOW/SLAP scale. This recommendation applies also to hydrogen and oxygen-bearing compounds other than water. Some of the normalized fractionation factors are indicated in Fig. 1.

3.2 - NBS-19 (calcite)

This $CaCO_3$ samples is distributed for the calibration of the $^{13}C/^{12}C$ and $^{18}O/^{16}O$ variation determinations. Being PDB exhausted for a long time, NBS-19 has been indirectly calibrated versus PDB. By international agreement, the isotopic composition of NBS-19 versus a hypothetical V-PDB (Vienna-PDB), supposed identical to PDB, has been fixed to $\delta^{13}C = 1.95\ ^0/_{00}$ and $\delta^{18}O = -2.20\ ^0/_{00}$. The absolute isotopic ratios of NBS-19 have not been determined. The $\delta^{18}O$ value of V-PDB versus V-SMOW is 30.9 $^0/_{00}$ (Hut, 1987).

NBS-19 was prepared by I. Friedman, J.R. O'Neil and G. Cebula, U.S. Geological Survey, Denver, Colorado, and Menlo Park, California, by crushing a white marble slab of unknown origin (Friedman *et al.*, 1982). The granulometry of NBS-19 ranges from 200 to 300 microns.

3.3 - IAEA-S-1 and IAEA-S-2 (Silver sulphide)

These two samples of synthetic silver sulphide, prepared by B.W. Robinson and C.A.M. Brenninkmeijer (Institute of Geological and Nuclear Sciences, Lower Hutt, New Zealand) and initially denominated NZ-1 and NZ-2 (where NZ stands for New Zealand; Robinson and Brenninkmeijer, 1987, 1990), are available for distribution although the calibration of IAEA-S2 versus IAEA-S1 has not been completed and their $\delta^{34}S$ value versus the primary reference standard CDT not yet fixed by international agreement. However, at the Consultants' Meeting held in December 1993 in Vienna, the value of $\delta^{34}S = -0.30\ ^0/_{00}$ versus a hypothetical V-CDT was proposed for IAEA-S-1 (Stichler and Gonfiantini, 1994). Although this value is based on a limited number of results, it appears practically impossible to obtain a more precise value because CDT was not isotopically homogeneous.

For IAEA-S-2, B.W. Robinson and C.A.M. Brenninkmeijer reported the provisional $\delta^{34}S$ value of 21.7 $^0/_{00}$ versus CDT. The absolute $^{34}S/^{32}S$ isotopic ratios of IAEA-S1 and IAEA-S2 have not yet been determined.

4 - Intercomparison materials

The intercomparison materials distributed by IAEA are listed in Table 2 and briefly described below. The isotopic composition values of Table 2 are based on the results reported by Gonfiantini (1984) and Hut (1987), and on additional results subsequently reported to IAEA by other laboratories. However, for some intercomparison materials the number of available results is still limited.

Probably the most used intercomparison material is GISP (Greenland Ice Sheet Precipitation), a water sample with an isotopic composition intermediate between those of V-SMOW and SLAP, which was provided by W. Dansgaard, University of Copenhagen.

Three calcium carbonate intercomparison materials are available: NBS-18, prepared by I. Friedman *et al.* (1982) from a carbonatite from Fen, Norway, collected by B. Taylor, University of California, Davis, and crushed by H. Friedrichsen, University of Berlin; IAEA-CO-1, prepared at IAEA from a slab of Carrara marble, Italy, provided by IMEG, Viareggio; and IAEA-CO-8, prepared at IAEA from a carbonatite from Kaiserstuhl, Germany, provided the Geologisches Landesamt, Freiburg. IAEA-CO-1 was originally prepared for ^{14}C measurement calibration (Rozanski, 1991; Rozanski *et al.*, 1992), but it appears to be a very good intercomparison sample also for stable isotope determinations. Its isotopic composition is close to that of NBS-19.

TABLE 2

Intercomparison samples distributed by IAEA

Name	Nature	Isotope	$\delta_m\ {}^0/_{00}$	$\sigma_1\ {}^0/_{00}$	n	Reference
GISP	water	^2H	−189.73	0.87	44	V-SMOW
		^{18}O	−24.784	0.075	46	V-SMOW
NBS-18	calcite	^{13}C	−5.029	0.049	16	V-PDB
		^{18}O	−23.035	0.172	17	V-PDB
IAEA-CO-1	calcite	^{13}C	2.480	0.025	10	V-PDB
		^{18}O	−2.437	0.073	11	V-PDB
IAEA-CO-8	calcite	^{13}C	−5.749	0.063	12	V-PDB
		^{18}O	−22.667	0.187	13	V-PDB
IAEA-CO-9	$BaCO_3$	^{13}C	−47.119	0.149	10	V-PDB
		^{18}O	−15.282	0.093	10	V-PDB
LSVEC	Li_2CO_3	^{13}C	−46.479	0.150	11	V-PDB
		^{18}O	−26.462	0.251	10	V-PDB
USGS-24	graphite	^{13}C	−15.994	0.105	8	V-PDB
NBS-22	oil	^{13}C	−29.739	0.124	17	V-PDB
IAEA-CH-7	poly-	^{13}C	−31.826	0.114	18	V-PDB
	ethylene	^2H	−100.33	2.05	6	V-SMOW
IAEA-C-6	sucrose	^{13}C	−10.431	0.126	16	V-PDB
NBS-28	quartz	^{18}O	9.579	0.092	8	V-SMOW
NBS-30	biotite	^{18}O	5.243	0.245	4	V-SMOW
		^2H	−65.70	0.27	3	V-SMOW
IAEA-N-1*	$(NH_4)_2SO_4$	^{15}N	0.538	0.186	11	air N_2
IAEA-N-2*	$(NH_4)_2SO_4$	^{15}N	20.343	0.473	11	air N_2
IAEA-NO-3*	KNO_3	^{15}N	4.613	0.191	3	air N_2
NBS-123	sphalerite	^{34}S	17.088	0.308	13	CDT
NBS-127	$BaSO_4$	^{34}S	20.315	0.357	10	CDT
		^{18}O	9.337	0.319	3	V-SMOW

N.B. - $\delta_m = \sum_{i=1}^{n} \delta_i/n$; $\sigma_1 = \sqrt{\sum_{i=1}^{n} (\delta_m - \delta_i)^2/(n-1)}$.

δ_m, σ_1 and n are the values obtained by excluding outliers (2σ criterion) after two iterations.

* Böhlke and Coplen (this volume) report slightly different average values, based on a larger set of measurements.

Two other carbonate materials with low ^{13}C and ^{18}O contents are distributed: IAEA-CO-9, synthetic barium carbonate prepared by C.A. Brenninkmeijer, Institute of Geological and Nuclear Sciences, Lower Hutt, New Zealand; and L-SVEC, lithium carbonate prepared by H. Svec, Iowa State University.

Intercomparicon materials with carbon isotopic composition in the range of natural organic compounds are: USGS-24, graphite, prepared by T.B. Coplen, U.S. Geological Survey, Reston, Virginia, from Baker® technical grade graphite; NBS-22, oil, provided by S. Silverman, University of California, San Diego; IAEA-CH-7, polyethylene foil (known before as PEF-1), provided by H. Gerstenberger and M. Herrmann (1983), of the formerly Zentralinstitut für Isotopen- and Strahlenforschung, Leipzig; and IAEA-C-6, sucrose, which was originally prepared by H. Polach, Australian National University, Canberra, for ^{14}C measurement calibration.

Materials of interest for the intercomparison of oxygen isotopic analyses of silicates are: NBS-28, quartz sand, and NBS-30, biotite, prepared by I. Friedman, J. O'Neil and G. Cebula. The latter derives from the Lakeview tonalite of the South California batholith.

For nitrogen isotope measurement intercomparison IAEA distributes: N-SVEC, nitrogen gas with $^{15}N/^{14}N$ absolute ratio of 3663×10^{-6}, prepared by Junk and Svec (1958), Iowa State College; two ammonium sulphate samples, IAEA-N1 and IAEA-N2, both prepared by E. Salati, Centro de Energía Nuclear na Agricultura, Piracicaba, Brazil; and IAEA-N3, potassium nitrate, prepared by A. Mariotti, Université Pierre et Marie Curie, Paris. IAEA-N3 may be considered in future intercomparison material also for oxygen isotopic analysis of nitrates, which is a promising tool for geochemical and water pollution studies (Amberger and Schmidt, 1987).

It should be mentioned that recently Böhlke *et al.* (1993) have proposed the use of three additional calibration standards with $\delta^{15}N$ spanning from −30 to 180 $^{0}/_{00}$ in order to normalize the $\delta^{15}N$ scale, in a similar way as it was done for the $\delta^{2}H$ and $\delta^{18}O$ scales with V-SMOW and SLAP.

Finally, for sulphur isotope ratio ($^{34}S/^{32}S$) measurement intercomparison IAEA distributes NBS-123, sphalerite (ZnS), and NBS-127, barium sulphate. The latter, prepared by J.R. O'Neil by precipitation of sulphate dissolved in sea water, is used also for intercomparison of the $^{18}O/^{16}O$ ratio determinations in natural sulphates.

5 - Distribution policy

All the above discussed calibration standards and intercomparison materials are kept at, and distributed by, the International Atomic Energy Agency. The amount stored for each materials will be sufficient for several decades if a prudent distribution policy is adopted. At present every laboratory can receive a portion of any IAEA calibration standard only once every three years. In fact, these standards are meant for calibration of laboratory standards to be used for routine work, an operation for which the amounts provided by IAEA are sufficient with the current analytical procedures.

For intercomparison samples it seems desirable that IAEA adopts in future a distribution policy more liberal than for calibration standards. In principle, intercomparison samples are easier to establish because they do not require an international agreement on the values of their isotopic composition.

6 - Need to determine the absolute isotopic ratios of calibration and intercomparison materials

In principle, in geochemical investigations as well as in most of other applications of environmental stable isotopes, it is not necessary to know the absolute isotopic ratios of standards and other materials used to calibrate the measurements. In fact, isotopic analyses are aiming to determine the relative variations of isotopic ratios in natural compounds with respect to primary reference standard, rather than the absolute isotopic ratios themselves. The relative variations of isotopic composition can be measured very precisely with well known analytical techniques based on the use of isotopic ratio mass spectrometers equipped with a double inlet system and a double or triple collector.

The main requirements to obtain results which are not only internally consistent but also directly comparable with those obtained by other laboratories, are that the measurements are well calibrated versus the primary reference standards through the internationally accepted calibration materials. The latter should have an isotopic composition which is homogeneous at the level of milligram sample size and remain constant in time. Finally, laboratories should adopt consistent methods to correct results for instrumental factors, i.e. the same correlation between $\delta^{17}O$ and $\delta^{18}O$ and the same absolute isotopic ratios for the reference standard.

Measuring the absolute isotope ratios with an accuracy at least equal, in relative terms, to the best accuracy achievable in determinations of relative isotopic ratio variations, is the only way to fix forever and unambiguously the isotopic composition of calibration and intercomparison materials, and to make it possible to periodically check whether changes have occurred since the preparation.

Below we discuss the circumstances in which the knowledge of absolute isotopic ratios of calibration materials would be helpful.

6.1 - Changes of isotopic composition during storage

It may happen that there are indications or doubts that a given calibration material does not have the expected isotopic composition. This may have changed slightly for reasons which were not foreseen, or not adequately considered, when the material was initially stored. The most direct way to check whether such a change occurred is redetermining the absolute isotopic ratios and compare the results with those of previous determinations. But if previous results are not available, it will be difficult to prove with any confidence and to quantify any eventual change of isotopic composition. As a consequence, the measurement re-calibration will become difficult and perhaps uncertain, and the isotopic results may be poorly comparable with the previous ones.

A change of the isotopic composition during storage is a real risk: it already happened in the past that some calibration materials had to be abandoned because there was the suspicion that their isotopic composition had changed. This was the case, for instance, of NBS-1 (water), with respect to which the isotopic composition of SMOW was originally defined by Craig (1961). Another case is that of the NBS-20 (Solenhofen limestone), which was used in the past to calibrate the $^{13}C/^{12}C$ and $^{18}O/^{16}O$ measurements versus PDB on the basis of the calibration made by Craig (1957). The reason for these changes of isotopic composition - which on the other hand were small and difficult to be definitely proved - is supposed to be poor storage conditions, allowing isotopic exchanges with atmospheric vapour and CO_2 and, for water, also evaporation from leaky containers.

6.2 - Imperfect homogeneity of the isotopic composition

It may occur that some calibration materials result or become isotopically not homogeneous, in spite of the tests made at the time of preparation. It may also be that isotopic inhomogeneities were introduced when these materials were split into portions for storage. This may have happened, for instance, to some intercomparison materials kept at IAEA, the distribution of which was discontinued due to suspected inhomogeneities in isotopic composition. Re-determining the absolute isotopic ratios in different portions of the suspected material would allow a check of the degree of homogeneity and the identification of those portions with isotopic values different from the expected ones.

6.3 - Establishment of new calibration materials

Although calibration materials are usually prepared in quantities which assure distribution for more than ten years at least, the time will come when they will be exhausted, and the preparation of new materials will become necessary. In order to assure a continuous consistency in measurement intercalibration, the isotopic composition of the new calibration materials with respect to the exhausted ones should be fixed with the best possible accuracy. Besides carrying out a calibration of the new materials versus the old ones when these approach exhaustion, the isotopic composition of new materials can be fixed unambiguously and independently through the measurement of their absolute isotopic ratios.

6.4 - Correction equations for interference of equal-mass ions

The $\delta^{13}C$ and $\delta^{18}O$ correction equations for interference of equal-mass ions for CO_2 mass spectrometric determinations have been reported by Craig (1957), Gonfiantini (1981) and Santrock *et al.* (1985). The correction terms are more important for the computation of $\delta^{13}C$ from δ_{45}, because the contribution of $^{12}C^{16}O^{17}O^+$ ions to the mass 45 ion peak is relatively large - almost 7 % of the $^{13}C^{16}O_2{}^+$ ion abundance.

The $^{17}O/^{16}O$ variations cannot be directly measured and are obtained from the $^{18}O/^{16}O$ variations, i.e. from the $\delta^{18}O$ determinations. The correction equation usually adopted is:

$$\delta^{13}C \;=\; \left(1+\frac{2R_{17}}{R_{13}}\right)\delta_{45}-\frac{2aR_{17}}{R_{13}}\delta^{18}O \qquad (2)$$

where $R_{13} = {}^{13}C/{}^{12}C$ and $R_{17} = {}^{17}O/{}^{16}O$ are the isotopic ratios in the machine standard, and $a = \delta^{17}O/\delta^{18}O$. This espression is a good approximation of the relation $R_{17(S)}/R_{17(R)} = (R_{18(S)}/R_{18(R)})^a$, where the subscripts indicate the sample and the reference as in equation (1), and $R_{18} = {}^{18}O/{}^{16}O$. δ_{45} is defined in the usual way as in equation (1), i.e. as the relative difference between the mass 45 to mass 44 ion ratios in the sample and in the standard, being $R_{45} = R_{13} + 2R_{17}$.

Let now examine the effects of errors on a, R_{13} and R_{17} factors in the $\delta^{13}C$ correction equation. a is usually taken as equal to 0.5, i.e. assuming that in natural processes the $^{17}O/^{16}O$ variations are the half of $^{18}O/^{16}O$ variations. In reality, a may range from 0.50 to 0.53 in physico-chemical processes, and an average value of 0.5164 ± 0.0033 has been observed for the ratio between $\delta^{17}O$ and $\delta^{18}O$ variations in natural compounds (Matsuhisa et al., 1978). Using for a this more appropriate value, an additional correction of -0.011 $^0/_{00}$ for a 10 $^0/_{00}$ increase of $\delta^{18}O$ is introduced by equation (2) in the $\delta^{13}C$ computation with respect of using $a = 0.5$. With $a = 0.53$, the correction becomes -0.020 $^0/_{00}$ for a 10 $^0/_{00}$ increase of $\delta^{18}O$.

TABLE 3

Isotopic ratios of CO_2 derived from V-PDB
with H_3PO_4 100 % at 25°C

$^{13}C/^{12}C$	11237.2×10^{-6} 11194.9×10^{-6}	(1) (2)
$^{18}O/^{16}O$	2079×10^{-6} 2088.3×10^{-6}	(1) (3)
$^{17}O/^{16}O$	379.95×10^{-6} 387.95×10^{-6}	(1) (4)

(1) From Craig (1953)

(2) Computed from the value measured by Zhang and Li (1987) for NBS-20 and assuming $\delta^{13}C_{(NBS\text{-}20/V\text{-}PDB)} = -1.06$ ‰ as reported by Craig (1957).

(3) Computed from the value measured by Baertschi for V-SMOW (1976) with an enrichment of 41.5 ‰, resulting from the from the enrichment of PDB vs. V-SMOW (30.9 ‰) and the fractionation factor for the CO_2 extraction (10.25 ‰) (see Fig. 1).

(4) Computed from the value reported by Li *et al.* (1988) for V-SMOW, with the same enrichment factor as for ^{18}O multiplied by 0.516.

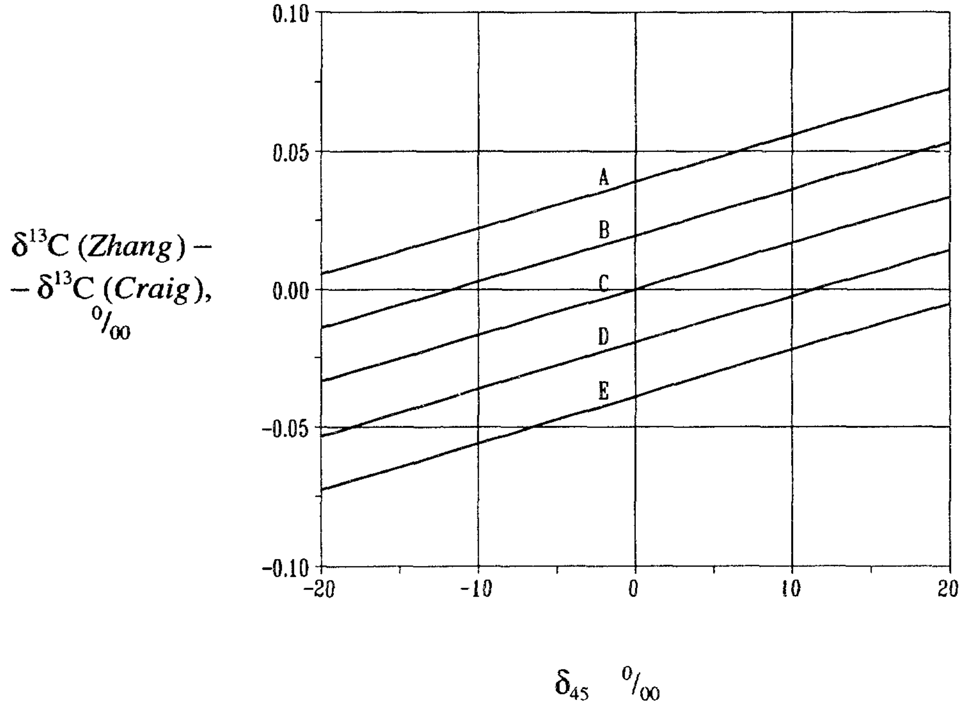

Fig. 2 - Difference ($\Delta\delta^{13}C$ ‰) between $\delta^{13}C$ obtained from δ_{45} with equation (2), using for R_{13} and R_{17} values computed from determinations by Zhang and coworkers on NBS-20 and V-SMOW and values reported by Craig (Table 3). $\delta^{18}O$s are as follows: A: -20 ‰; B: -10; C: 0; D: +10; E: +20.

The probable error on R_{13} is about 0.5 %, and its effects are negligible.

More important are the effects of errors on R_{17}. Assuming that the error on R_{17} is ±2-3 %, this entails an additional correction of up to 0.022 $^0/_{00}$ for each 10 $^0/_{00}$ variation of the term $(\delta_{45} - a\delta^{18}O)$, i.e., approximately, of the term $(\delta^{13}C - \delta^{18}O/2)$. Although this correction may appear small, for certain analytical requirements it may be not negligible. Thus, in order to reduce it, a more accurate determination of the absolute isotopic ratios of calibration materials, and especially of the $^{17}O/^{16}O$ ratio, is needed.

For instance, by adopting for the CO_2 obtained from PDB the isotopic ratios values proposed by Craig (1957), or those which can be computed from measurements on NBS-20 and V-SMOW performed by Zhang and coworkers (Table 3), we obtain $\delta^{13}C$ which may differ significantly (Fig. 2). This difference is almost entirely due to the R_{17} values, as indicated above.

The equation to transform δ_{46} into $\delta^{18}O$ is, for a triple collector mass spectrometer:

$$\delta^{18}O = \left(1 + \frac{R_{13}R_{17}(1-a)}{R_{18} + aR_{13}R_{17}}\right)\delta_{46} - \frac{R_{13}R_{17}}{R_{18} + aR_{13}R_{17}}\delta^{13}C \tag{3}$$

being $R_{46} = 2R_{18} + 2R_{13}R_{17}$. The correction terms are small, and the influence of current errors on the coefficients a, R_{13}, R_{17} and R_{18} is generally negligible.

Differences between $\delta^{13}C$ values corrected with different algoritms and different R_{13} and R_{17} values used by the softwares installed in two mass spectrometers, have been discussed by Francey and Allison (in Rozanski, 1992).

Interference of equal mass ions occurs also in mass spectrometric analysis of SO_2. The $^{32}S^{16}O^{18}O^+$ ions represent 8.3 % of the mass 66 ion peak, the rest being constituted by the $^{34}S^{16}O_2^+$ ions (the contribution of other mass 66 ions is less that 0.02 %). For a triple collector mass spectrometer the correction equation is:

$$\delta^{34}S = \left(1 + \frac{2R_{18}}{R_{34}}\right)\delta_{66} - \frac{2R_{18}}{R_{34}}\delta^{18}O \tag{4}$$

The influence of errors on $R_{34} = {}^{34}S/{}^{32}S$ on the correction terms to transform δ_{66} into $\delta^{34}S$, with $R_{66} = R_{34} + 2R_{18}$, is negligible. A 1 % variation of the R_{18} ratio of the SO_2 analyzed - which may be produced during the sample preparation - results in an error of 0.01 $^0/_{00}$ for each 10 $^0/_{00}$ variation of the term $(\delta_{66} - \delta^{18}O)$, i.e., approximately, of the term $(\delta^{34}S - \delta^{18}O)$.

In conclusion, there is a recognized need of adopting a common algoritms for δ correction, and of determining with an accuracy better than the current one the isotopic ratios of the reference standards and calibration materials. If this is not possible in the near future, the alternate solution could be to adopt a common set of values for the reference standard isotopic ratios, as recommended by the Consultants' Meeting on stable isotope standards and intercalibration (Stichler et al., these proceedings).

7 - Accuracy of absolute isotopic ratio determinations

The modern mass spectrometers are capable of measuring natural isotopic ratio variations in gaseous compounds of many light elements with an error in the range of 0.01-0.02 $^0/_{00}$. For hydrogen, the error is usually one order of magnitude greater because the natural $^2H/^1H$ isotopic ratio is one or two orders of magnitude smaller than the rare to most abundant isotope ratio of other elements. Additional, often larger, errors may be introduced by the sample treatment prior to mass spectrometric analysis.

In order to give an idea of the overall accuracy achievable in measuring absolute isotope ratios, we report here some results obtained on calibration and intercomparison materials. The errors quoted represent one standard deviation (1 σ).

High accuracy determinations of isotopic ratios are possible by calibrating the mass spectrometric measurements with mixtures prepared by gravimetric dosage from isotopically pure compounds, i.e. containing only one isotope. Hagemann *et al.* (1970) and De Wit *et al.* (1980) used mixtures of deuterium oxide and almost deuterium-free water to determine the $^2H/^1H$ ratio of V-SMOW and SLAP. For V-SMOW they found the values of $(155.76 \pm 0.05) \times 10^{-6}$ and $(155.75 \pm 0.08) \times 10^{-6}$ respectively[1]. The errors quoted correspond, in relative terms, to ±0.32 and ±0.51 $^0/_{00}$ respectively, which compare well with the current errors obtained by the best laboratories in δ^2H determinations in water samples. It should be noted that for several laboratories the typical error can go up to 1 $^0/_{00}$, which is acceptable in many geochemical and hydrological investigations.

The errors quoted by the same authors for SLAP are $\pm 0.05 \times 10^{-6}$ and $\pm 0.07 \times 10^{-6}$ respectively. In this case, the corresponding relative errors are greater, ±0.56 and ±0.79 $^0/_{00}$, because of the much lower $^2H/^1H$ ratio.

Baertschi (1976) used mixtures of almost pure $^2H_2{}^{18}O$ and $^1H_2{}^{16}O$ to determine the $^{18}O/^{16}O$ ratio of V-SMOW, for which he found the value of $(2005.20 \pm 0.45) \times 10^{-6}$. The relative error is ±0.23 $^0/_{00}$, i.e. considerably greater than the error in $\delta^{18}O$ determinations, which is usually better than ±0.10 $^0/_{00}$.

The $^{18}O/^{16}O$ ratio of V-SMOW determined by Baertschi allows a computation of the same ratio in PDB and NBS-19, and in the CO_2 extracted from PDB with H_3PO_4 100%. PDB is enriched 30.9 $^0/_{00}$ in ^{18}O with respect to V-SMOW, and therefore its $^{18}O/^{16}O$ ratio is 2067.2×10^{-6}; NBS-19 is depleted of 2.20 $^0/_{00}$ versus PDB and its $^{18}O/^{16}O$ ratio is 2062.6×10^{-6}. The CO_2 extracted from calcite is enriched in ^{18}O of 10.25 $^0/_{00}$ (Hut, 1987), and therefore its $^{18}O/^{16}O$ ratio is 2088.4×10^{-6}.

The $^{17}O/^{16}O$ ratio of V-SMOW was determined by Li *et al.* (1988). They compared in a double inlet, triple collector mass spectrometer first the O_2 obtained from V-SMOW with that obtained from a water sample depleted in oxygen heavy isotopes, and then the CO_2 formed by these oxygen samples with pure graphite with CO_2 obtained from a sample of NBS-20, the $^{13}C/^{12}C$ of which was previously determined (Zhang and Li, 1987; see below). This complex procedure allowed the determination of $^{17}O/^{16}O$ ratio of V-SMOW, which resulted equal to $(379.9 \pm 0.8) \times 10^{-6}$. The relative error is 2.1 $^0/_{00}$, i.e. an order of magnitude higher than that of $\delta^{17}O$ determinations.

The $^{13}C/^{12}C$ ratio of NBS-20 (Solenhofen limestone, distribution discontinued) was determined by Zhang and Li (1987) using mixtures of two barium carbonates, one enriched in ^{12}C and the other in ^{13}C, for the calibration of the mass spectrometric measurements. They found a value of $(11183 \pm 1.3) \times 10^{-6}$, i.e. with a relative error of ±0.11 $^0/_{00}$. Modern $\delta^{13}C$ determinations can have an error as low as ±0.02 $^0/_{00}$, as claimed by laboratories monitoring isotopic variations in atmospheric CO_2 (see for instance Rozanski, 1992).

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[1] - The $^2H/^1H$ value originally reported by De Wit et al. (1980) was later modified into 155.75×10^{-6} (Mook, 1983, personal communication).

It is worth noting that the value of the $^{13}C/^{12}C$ ratio of NBS-20 reported by Zhang and Li is considerably lower (−3.77 $^0/_{00}$) but much more precise than that computed by Craig (1957), $(11225.3 \pm 30) \times 10^{-6}$, on the basis of previous absolute isotopic ratio determinations made by Nier (1950). Besides, knowing that the $\delta^{13}C$ of NBS-20 versus PDB is -1.06 ± 0.04 $^0/_{00}$ (Craig, 1957), it is possible to re-compute the $^{13}C/^{12}C$ ratio of PDB from that reported by Zhang and Li for NBS-20, and we obtain the value of $(11194.9 \pm 1.4) \times 10^{-6}$: this value is probably more accurate than that computed by Craig.

The absolute isotopic ratios of NBS-123 (sphalerite, ZnS) have been determined by Zhang and Ding (1989) using SF_6 as gas for the mass spectrometric analysis. They obtained for the $^{34}S/^{32}S$ ratio the value of 45805×10^{-6} with a relative error of ±0.10 $^0/_{00}$, well comparable with the experimental error in $\delta^{34}S$ determinations. However, no indication is given on the method used for the mass spectrometer calibration, and if this has not been done, the $^{34}S/^{32}S$ value reported may be affected by an unknown systematic error.

Considerable improvements in absolute ratio determination of carbon isotopes were achieved recently by the Institute for Reference Materials and Measurements at the Joint Research Centre of the Commission of the European Communities in Geel, Belgium. Here, the Mass Spectrometry Group headed by P. De Bièvre has published (Valkiers *et al.*, 1993) the value of $(10753.3 \pm 0.4) \times 10^{-6}$ for the $^{13}C/^{12}C$ ratio in commercial CF_4 gas. The error quoted by Valkiers *et al.* corresponds to ±0.04 $^0/_{00}$ in relative terms, which well compares with the error obtained in $\delta^{13}C$ determinations in natural compounds.

The Institute for Reference Materials and Measurements in Geel is probably the place where the best determinations of absolute ratios of light element isotopes are carried out at present within the framework of the Avogadro project, which aims at a more precise determination of the Avogadro number. It appears, however, that for the determination of absolute ratios of nitrogen, oxygen and sulphur isotopes, the situation is not yet satisfactory, but it is believed that it can be easily improved in the near future.

For air nitrogen and oxygen the absolute isotopic ratios obtained by Valkiers and De Bièvre (1993) are: $^{15}N/^{14}N = (3612 \pm 7) \times 10^{-6}$ and $^{18}O/^{16}O = (2072 \pm 2) \times 10^{-6}$. This is probably the best result which can be obtained without calibrating the measurements with artificial isotopic mixtures. The errors associated with these measurements correspond to ±2 $^0/_{00}$ for nitrogen and ±1 $^0/_{00}$ for oxygen, which are at least one order of magnitude higher than errors quoted in routine determinations of $\delta^{15}N$ and $\delta^{18}O$.

Research is carried out at the Institute for Reference Materials and Measurements in Geel in order to achieve an accuracy in the order of 0.01 $^0/_{00}$ in relative terms in the determination of carbon, nitrogen, oxygen and sulphur absolute isotopic ratios. This would allow to fix the characteristics of the isotopic calibration and intercomparison materials distributed by IAEA.

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REPORTING OF STABLE CARBON, HYDROGEN, AND OXYGEN ISOTOPIC ABUNDANCES

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Abstract

To eliminate possible confusion in the reporting of isotopic abundances on non-corresponding scales, the Commission on Atomic Weights and Isotopic Abundances recommended at the 37th General Assembly at Lisbon, Portugal that (i) $^{2}H/^{1}H$ relative ratios in all substances be expressed relative to VSMOW (Vienna Standard Mean Ocean Water) on a scale such that $^{2}H/^{1}H$ of SLAP (Standard Light Antarctic Precipitation) is 0.572 times that of VSMOW, (ii) $^{13}C/^{12}C$ relative ratios in all substances be expressed relative to VPDB (Vienna Peedee belemnite) on a scale such that $^{13}C/^{12}C$ of NBS 19 carbonate is 1.00195 times that of VPDB, (iii) $^{18}O/^{16}O$ ratios in all substances be expressed relative to either VSMOW or VPDB on scales such that $^{18}O/^{16}O$ of SLAP is 0.9445 times that of VSMOW, and (iv) the use of SMOW and PDB be discontinued. Furthermore, if reported isotopic abundances of a mineral or compound depend upon isotopic fractionation factors, users should (i) indicate the value of all such isotopic fractionation factors, or (ii) indicate the isotopic abundance obtained for a reference material of the same mineral or compound.

1. COMMENT

Abundances of stable hydrogen, carbon, and oxygen isotopes in geochemical and environmental studies are generally expressed in parts per thousand (‰ or per mil) difference from a standard. Thus, for the oxygen isotopic composition of a sample x,

$$\delta^{18}O \text{ (in ‰)} = \left[\frac{\left(\frac{^{18}O}{^{16}O} \right)_{x}}{\left(\frac{^{18}O}{^{16}O} \right)_{Standard}} - 1 \right] 1000.$$

The standard may be an actual reference material or a hypothetical material whose isotopic abundance is set by assigning an isotopic composition to an existing reference material.

Irregularities concerning the choice of the standard have arisen for hydrogen, carbon, and oxygen isotopes [1, 2]. Friedman and O'Neil [1] point out that some laboratories are "tied" to each other by acceptance of the δ values of certain comparison materials. The situation for the SMOW (Standard Mean Ocean Water) standard has become increasingly aggravated. The SMOW standard was originally a hypothetical water sample with abundances of stable hydrogen and oxygen isotopes similar to those of average ocean water [3]. Its abundances of stable hydrogen and oxygen isotopes were defined in terms of NBS 1 water distributed by the U.S. National Bureau of Standards (now National Institute of Standards and Technology):

$$({}^{2}\mathrm{H}/{}^{1}\mathrm{H})_{\mathrm{SMOW}} = 1.050({}^{2}\mathrm{H}/{}^{1}\mathrm{H})_{\mathrm{NBS\ 1}}$$

and

$$({}^{18}\mathrm{O}/{}^{16}\mathrm{O})_{\mathrm{SMOW}} = 1.008({}^{18}\mathrm{O}/{}^{16}\mathrm{O})_{\mathrm{NBS\ 1}}.$$

Subsequently, H. Taylor and S. Epstein of the California Institute of Technology (Pasadena, California) used a hypothetical standard that they also called SMOW and defined it by assigning a δ^{18}O value of +15.5‰ to their laboratory reference material, a sample of Potsdam Sandstone [1]. Thus, their oxygen isotope scale is defined by

$$\delta^{18}\mathrm{O}_{\mathrm{Potsdam\ Sandstone/SMOW}} = +15.5‰.$$

Additionally, the International Atomic Energy Agency (IAEA) distributed a water sample they named SMOW. This sample was near (but not the same) in isotopic composition to the original SMOW defined in terms of NBS 1 water. Thus, three independent usages of SMOW are currently observed, leading to differing ^{2}H/^{1}H and ^{18}O/^{16}O abundances with the same name. The IAEA recognized the dilemma of naming a reference water as SMOW and subsequently changed the name to VSMOW (Vienna Standard Mean Ocean Water). Furthermore, they recommended that abundances of hydrogen and oxygen isotopes of all materials (except marine carbonates) be expressed using VSMOW rather than SMOW [2, 4, 5, 6]. However, these recommendations have not received wide distribution and may be unknown to numerous producers of data on abundances of oxygen and stable hydrogen isotopes, particularly in the rapidly expanding fields of environmental and climate studies.

A second standard is used for reporting abundances of oxygen isotopes of marine carbonates and is named PDB (Peedee belemnite). Because the supply of this material is exhausted, some laboratories have "tied" themselves to each other by adopting δ^{18}O values of various carbonate reference materials. The IAEA recognized the potentially serious problem that oxygen isotopic scales in different laboratories might not correspond. They recommended that abundances of oxygen isotopes of carbonates be expressed relative to VPDB (Vienna Peedee belemnite) by adopting a δ^{18}O consensus value of −2.2‰ for NBS 19 carbonate relative to VPDB at a meeting in 1983 in Vienna [2]. Thus,

$$\delta^{18}\mathrm{O}_{\mathrm{NBS\ 19/VPDB}} \equiv -2.2‰.$$

This satisfactory solution has had only limited distribution and is seldom used.

Because PDB is also the standard for carbon, a similar problem exists for reporting abundances of carbon isotopes. The IAEA provided a solution to reporting of carbon isotopic data on non-corresponding scales by recommending that carbon isotopic results of all materials be expressed relative to VPDB by adopting a $\delta^{13}C$ value of +1.95‰ for NBS 19 carbonate relative to VPDB:

$$\delta^{13}C_{\mathrm{NBS\,19/VPDB}} \equiv +1.95‰ .$$

This value was adopted by consensus [2]. Again, this viable solution has had little distribution and is seldom employed.

The δ^2H and $\delta^{18}O$ values of VSMOW lie closer to the upper end of the range of abundances of ^2H and ^{18}O of naturally occurring materials. By recommending δ^2H and $\delta^{18}O$ values of a reference material close to the lower end of the range of abundances of ^2H and ^{18}O of naturally occurring materials, the IAEA effectively normalized these scales. The IAEA selected a water sample from Antarctica and gave it the name SLAP (Standard Light Antarctic Precipitation). Three absolute isotope-ratio measurements of VSMOW and SLAP [7, 8, 9] suggested a δ^2H value of −428‰ for SLAP relative to VSMOW. The $^{18}O/^{16}O$ ratio of SLAP has not been determined and a consensus $\delta^{18}O$ value of −55.5‰ of SLAP relative to VSMOW was adopted in 1976 [4]. Also, the hydrogen isotopic composition of SLAP relative to VSMOW was defined by consensus to be −428‰; thus, $\delta^2H_{\mathrm{SLAP/VSMOW}} \equiv -428‰$. The result of normalization was that coherence between δ^2H and $\delta^{18}O$ results reported by different laboratories increased dramatically [4]. In 1983 the IAEA recommended that δ^2H and $\delta^{18}O$ results of all materials be reported on normalized scales [2]. Equations for normalization are given by Gonfiantini [2] and Coplen [6]. The process of normalizing should in theory increase the agreement between experimentally determined isotopic fractionation factors of physicochemical processes.

The Commission on Atomic Weights and Isotopic Abundances at the 37th General Assembly in Lisbon, Portugal, [10] discussed the reporting of isotopic abundances and recommended that:

(1) δ^2H values of all hydrogen-bearing substances be expressed relative to VSMOW on a scale such that $\delta^2H_{\mathrm{SLAP/VSMOW}} \equiv -428‰$;

(2) $\delta^{13}C$ values of all carbon-bearing substances be expressed relative to VPDB on a scale such that $\delta^{13}C_{\mathrm{NBS\,19/VPDB}} \equiv +1.95‰$;

(3) $\delta^{18}O$ values of all oxygen-bearing materials be expressed relative to VSMOW or relative to VPDB, defined by $\delta^{18}O_{\mathrm{NBS\,19/VPDB}} \equiv -2.2‰$, on a scale such that $\delta^{18}O_{\mathrm{SLAP/VSMOW}} \equiv -55.5‰$; and

(4) reporting of isotopic abundances relative to SMOW and PDB be discontinued.

Several values for an isotopic fractionation factor of a physicochemical process may have been measured. If reported isotopic abundances of a mineral or compound depend upon such isotopic fractionation factors, users should:

(1) indicate the value of all isotopic fractionation factors employed in calculating isotopic abundances, or

(2) indicate the isotopic abundance obtained for a reference material of the same mineral or compound.

The reader is reminded that δ values are not additive when converting from one scale to another, but are determined by the relation (*e.g.*, for oxygen)

$$\delta^{18}O_{a/VSMOW} = \delta^{18}O_{a/b} + \delta^{18}O_{b/VSMOW} + 10^{-3}\delta^{18}O_{a/b}\,\delta^{18}O_{b/VSMOW}.$$

This relation should be kept in mind especially in the case of hydrogen where δ values of several hundred occur; thus, the last term in the equation above may reach a value of several tens.

APPENDIX A; SOURCES OF REFERENCE MATERIALS

Reference materials VSMOW, SLAP, and NBS 19 may be obtained from:

International Atomic Energy Agency
Section of Isotope Hydrology
P.O. Box 100
1400 Vienna, Austria

or

Standard Reference Materials Program
Room 204, Building 202
National Institute of Standards and Technology
Gaithersburg, Maryland 20899
USA

Request RM8535 for VSMOW.
Request RM8537 for SLAP.
Request RM8544 for NBS 19.

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AUDIT OF VSMOW DISTRIBUTED BY THE UNITED STATES NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGY

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Abstract

Bright-orange floating matter (possibly algae) has been observed in the United States supply of some ampoules and in one of two 10-L primary glass storage flasks of the isotopic reference water VSMOW (Vienna Standard Mean Ocean Water). Within experimental error, ampoules with and without this orange matter are identical in stable hydrogen and oxygen isotopic composition. Thus, the North American supply of VSMOW has not been altered in isotopic abundance and remains fully functional as a primary isotopic reference material.

1. INTRODUCTION

The isotopic reference water VSMOW (Vienna Standard Mean Ocean Water) serves as a primary reference material for oxygen and hydrogen relative isotope-ratio measurements [1]. VSMOW is distributed in North America by the National Institute of Standards and Technology (NIST) of the United States Department of Commerce and distributed elsewhere by the International Atomic Energy Agency (IAEA), Vienna, Austria.

In 1993, it was noted that numerous ampoules of VSMOW, in the United States only, contained bright orange floating material that is possibly algae. Because this reference water is of critical importance to a large number of scientific fields, an investigation was undertaken to determine if the North American supply of VSMOW had degraded and been made worthless.

First, a visual audit of the North American supply of VSMOW and also of SLAP (Standard Light Antarctic Precipitation) and GISP (Greenland Ice Sheet Precipitation) was undertaken. Second, water from ampoules with and without orange "floaters" was analyzed for stable hydrogen and oxygen isotopic composition.

2. EXPERIMENTAL METHOD

Water was analyzed for stable hydrogen isotopic composition by equilibrating samples with gaseous H_2 using a Pt catalyst by the multiple sample method of Coplen, Wildman and Chen [2]. Water was prepared for oxygen isotopic composition by equilibrating samples with carbon dioxide using the method of Epstein and Mayeda [3], modified for multiple sample analysis by evacuating air through a capillary tube [4]. Carbon dioxide samples were analyzed on a double-focusing isotope-ratio mass spectrometer [5]. Oxygen and hydrogen isotopic results are reported in per mil relative to VSMOW and normalized on scales such that the oxygen and hydrogen isotopic values of SLAP are −55.5‰ and −428‰, respectively [1].

3. RESULTS

The visual audit of isotopic reference waters at NIST was undertaken by Robert Vocke, Jr. of NIST, Pedro Morales (visiting scientist at NIST) and one of the authors (Tyler Coplen) on November 10, 1993. This audit provided part of the information in Table 1. Ampoules

Table 1. Results of a visual audit of isotopic reference waters at NIST on November 10, 1993.

Label on glass vessel	Quantity	Comment
Vienna SMOW 77-02-21 P.S.	Unopened 10-L flask, sealed by glassblower.	Water looks clear. Under control of Robert Vocke, Jr. (NIST)
GISP 77-07-25 P.S.	Unopened 10-L flask, sealed by glassblower.	Water looks clear. Under control of Robert Vocke, Jr. (NIST)
SLAP 77-04-04 P.S.	Unopened 10-L flask, sealed by glassblower.	Water looks clear. Under control of Robert Vocke, Jr. (NIST)
Vienna SMOW 77-02-22 P.S.	10-L flask opened in 1985 and about one half of contents remains.	Orange material floating in water. Under control of Robert Vocke, Jr. (NIST)
GISP 77-07-25 P.S.	10-L flask opened in 1985 and about one half of contents remains.	Water looks clear. Under control of Robert Vocke, Jr. (NIST)
SLAP 77-04-04 P.S.	10-L flask opened in 1985 and about one half of contents remains.	Water looks clear. Under control of Robert Vocke, Jr. (NIST)
RM 8535 VSMOW	114 ampoules; about 20 ml each.	Water looks clear. Under control of Standard Reference Materials Program.
RM 8536 GISP	Did not count; probably more than 100.	Water looks clear. Under control of Standard Reference Materials Program.
RM 8537 SLAP	Did not count; probably more than 100.	Water looks clear. Under control of Standard Reference Materials Program.

of isotopic reference waters are distributed by the Standard Reference Materials Program at NIST. Ampoules of VSMOW are designated as RM 8535 and show no signs of bright-orange "floaters." The storage of the primary reservoirs of VSMOW, GISP, and SLAP in North America is under the control of Robert Vocke, Jr. Each of these three is stored in the dark in two 10-L sealed glass flasks. The following identical documentation was found with three of the six flasks (one VSMOW, one GISP, and one SLAP, all about one-half full):

> May 24, 1985
>
> NOTE:
>
> THIS BOTTLE WAS OPENED ON MAY 22, 1985 AND ABOUT 200 SAMPLES WERE REMOVED. THE END OF THE CONTAINER WAS BROKEN OFF, A CLEANED TEFLON TUBE INSURTED (sic) INTO THE BOTTLE AND BOTTLED IN 20 ML AMPULES ON THE OSRM AMPULE SEALING MACHINE. EACH AMPULE WAS FLUSHED WITH PURE ARGON IMMEDIATELY BEFORE FILLING. AFTER ABOUT 200 AMPULES WERE FILLED, THE BOTTLE WAS FLUSHED WITH ARGON AND SEALED OFF BY THE GLASSBLOWER (JEFF ANDERSON).
>
> EACH OF THE LARGE BOTTLES OF SMOW, SLAP AND GISP HAD INDICATIONS OF SOME TYPE OF CONTAMINATION BEFORE OPENING. I DO NOT KNOW WHAT THE CONTAMINATION WAS.
>
> AFTER RESEALING EACH BOTTLE HAD ABOUT ONE-HALF OF THE ORIGINAL CONTENTS.
>
> I.L. BARNES
> 5/24/85

Although the half-full flasks of GISP and SLAP were nearly colorless, that containing VSMOW contained bright orange-floating material (possibly algae). This is likely the source of the orange material in 20-mL ampoules that prompted this study. All three full 10-L flasks were nearly colorless. Note that none of the six 10-L flasks was opened and sampled for this study.

The stable hydrogen and oxygen isotopic composition of several ampoules of VSMOW and other reference waters is given in Table 2.

4. DISCUSSION

Within experimental error, the stable hydrogen and oxygen isotopic composition of three ampoules of VSMOW were identical. This suggests that the orange matter in one of the ampoules has not affected the isotopic composition of the water measurably. Furthermore, it is inferred that the half-full 10-L flask of VSMOW at NIST has probably not been altered in isotopic composition. Thus, no alteration of VSMOW distributed in the United States that affects its stable hydrogen and oxygen isotopic composition has been observed.

Table 2. Stable hydrogen and oxygen isotopic composition of several ampoules of VSMOW and other reference waters.

Description	δ^2H in ‰	no.	$\delta^{18}O$ in ‰	no.
Ampoule with "SMOW" and "502" written in blue (contains small amount of orange floating matter)	0.0±0.9	10	0.00±0.05	8
Ampoule of RM 8535, VSMOW obtained from SRMP at NIST on Nov. 10, 1993 (sample is clear)	0.0±0.6	12	0.00±0.05	4
Ampoule of VSMOW obtained from Robert Vocke, Jr. at NIST on Nov. 10, 1993 (sample is clear)	0.0±1.3	10	0.00±0.05	4
Puerto Rico laboratory reference, W-39500	−1.3±0.7	23	−1.52±0.07	37
Laboratory reference, W-28673	−53.5±0.7	6		
Laboratory reference, W-38888	−36.0±1.2	6	−6.21±0.05	30
Antarctic ice melt laboratory reference, W-35000	−394.5±0.8	29	−50.04±0.06	18
SLAP with "210" written in blue	−428.0±0.8	7	−55.5±0.03	6

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SULPHUR ISOTOPE STANDARDS

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Abstract

Although the early choice of meteorite standards for sulphur isotope investigations was good from the viewpoint of representing primordial sulphur and an average of terrestrial samples, it was soon recognised that chemical impurities and homogeneity were a problem. Although chemically pure Ag_2S standards were recommended as early as 1962, continued attempts to introduce geological materials as standards for almost 30 years considerably set back progress; agreement between laboratories has been typically poor. However, three chemically pure and homogeneous sulphur isotope standards are now available from the IAEA and NIST. They are NBS127 which is a $BaSO_4$ from 'ion exchanged' sea water sulphate; NZ1 and NZ2 which are Ag_2S calibration materials produced from a sphalerite close to 0 ‰ CDT and a gypsum close to +21 ‰ CDT respectively. NZ1 and NZ2 have been circulated by the IAEA for calibration. Fifteen, 2σ screened results for NZ1 give an average value of -0.26 ± 0.09 ‰ (1σ) and three analyses using SF_6 from this group gave an average of -0.30 ± 0.03 ‰ CDT. Although CDT is exhausted the value must be kept as a primary reference because most of the results published to date are expressed relative to CDT. Future results could now be expressed as δ values relative to V-CDT, with the calibration material NZ1 set at -0.30 ‰ V-CDT. The standard NZ2 has only been analysed by a few laboratories to date but agreement is good and this second sulphur isotope reference standard could be used for normalisation of the $\delta^{34}S$ scale. In addition, a third Ag_2S standard with $\delta^{34}S$ close to -30 ‰ is required as well as a $BaSO_4$ with similar 'light' sulphur and oxygen values.

1. INTRODUCTION

The early choice of meteorites as a primary standard for sulphur isotope studies is not surprising. Representing primordial sulphur, they lie at the mean for terrestrial samples. When problems were eventually recognised with the meteorite standards, a mineral sphalerite was introduced but also found to be inhomogeneous. This continuance of using geological and impure materials as primary standards hampered progress and agreement between laboratories has been typically poor. The need for pure chemical compounds as standards became increasingly urgent.

In 1986, an IAEA technical contract was awarded to the Institute of Nuclear Sciences in New Zealand to produce 1 kg of pure, homogeneous, Ag_2S near 0 ‰ to act as a calibration material and set the "zero part" of the $\delta^{34}S$ scale. This standard (NZ1) has been circulated to over 30 laboratories by the IAEA and the results obtained from 17 of these are reported here. In 1990, a similar technical contract to produce 1 kg of pure, homogeneous, Ag_2S near +21 ‰ was initiated. However, the calibration material produced (NZ2) has only been analysed by three laboratories to date. Reported here is a short summary of the history of sulphur isotope standards, the production of NZ1 and NZ2 and the results from laboratory intercomparisons.

2. HISTORY OF SULPHUR ISOTOPE STANDARDS

The first sulphur isotope measurements were made against available material such as Park City pyrite (USA) and Merck elemental sulphur (NZ). However, by 1950 meteorites had been adopted both in the USSR and the USA as primary standards. They were thought to be isotopically homogenous ($^{32}S/^{34}S = 22.22 \pm 0.01$); they represented primordial sulphur and were close to the average for terrestrial samples [1]. Sea water sulphate was also recognised as being homogeneous but being 21‰ enriched in ^{34}S with respect to meteorites was not initially adopted as a standard.

Sulphide materials were at first typically burnt with oxygen gas to produce SO_2 gas for isotopic measurement. $BaSO_4$ was reduced chemically or by graphite at high temperatures to give a sulphide phase. Gradually Ag_2S began to be favoured for analysis because it gives uniform burning characteristics.

By 1960, the Canyon Diablo Troilite (FeS phase from a large octahedrite iron meteorite collected around Meteor Crater, Arizona) had been adopted as the primary standard in the west but the Russians continued to use the Shikote Alin meteorite. Quite early in the history of sulphur isotope research [2] problems were, however, recognised with the Canyon Diablo Troilite standard. Different chemical treatment of meteorites yielded differences of up to 0.4‰. Since the early assignment of the $^{32}S/^{34}S$ ratio as 22.22 ‰ for CDT was somewhat arbitrary and, taking into account the homogeneity problems and the use of different meteorites, it was proposed in 1962 that three new standards be made [3]:

Ag_2S around	0 ‰
Ag_2S around	-35 ‰
$BaSO_4$ around	+20 ‰

No real progress with this recommendation was made and the 1966 IAEA Advisory Group Meeting on Stable Isotope Reference Samples for Geochemical and Hydrological Investigations concentrated on the water standards V-SMOW and SLAP. However, at the 1976 meeting, several new sulphur isotope standards were proposed: a $BaSO_4$ from sea water, galena or sphalerite at -20 to -30 ‰, elemental sulphur derived from natural gas and two different SO_2 samples for mass spectrometric calibration [4]. Two standards, OGS: a raw precipitated $BaSO_4$ from sea water, and Soufre de Lucq: an elemental sulphur, were prepared and circulated. At the 1983 IAEA Standards Meeting it was advised to abandon these standards because of very poor agreement between laboratories. In the IAEA report [5], H Nielsen documented the serious problems with sulphur isotope standards as follows:

- Troilite is not as isotopically uniform as expected.
- It is not stoichiometrically pure FeS.
- It contains some Co and Ni sulphides and carbides.

He suggested that:

- Ag_2S standards should be prepared.
- A sea water sulphate standard from 'ion exchanged' sea water should be made.

Meanwhile, C E Rees at McMaster University in Canada had prepared 10 Ag_2S standards from -30 to +50 ‰ and had analysed them by the superior SF_6 technique. He was approached to make standards at +20 and -20 ‰ for the IAEA but unfortunately died before completing this task. The meeting in 1983 also recommended that a sample of sphalerite close to 0 ‰ be introduced as a new standard. The latter was quickly supplied by S Halas of Poland and became NBS122.

At a 1985 IAEA meeting on Isotope Hydrology and Geochemistry of Sulphur, analytical techniques were discussed and it was recommended [6] that three $BaSO_4$ and three Ag_2S standards with $\delta^{34}S$ values of close to 0 ‰, about +20 ‰ and about -20 ‰ would ideally be made available. J O'Neil (USGS, Menlo Park) had already prepared an 'ion exchanged' sea water sulphate as $BaSO_4$ (NBS127) to replace OGS. B W Robinson agreed to produce the Ag_2S standards in New Zealand.

Also, later in 1985 a IAEA meeting on Reference Samples for Geochemical and Hydrological Investigations made the following recommendations [7] as published in 1987:

- NBS122 sphalerite is inhomogeneous and should no longer be distributed.
- NBS123, a spherite at about 17 ‰ was introduced for intercomparison.
- NBS127 $BaSO_4$ replaces OGS.
- Further circulation of standards be held until the Ag_2S standards are produced in New Zealand.

3. PREPARATION OF NZ1

The preparation of this standard was facilitated through the IAEA Technical Contract 4320/TC, March 1986-March 1987. The requirement was to produce 1 kg of pure, homogeneous Ag_2S with a $\delta^{34}S$ value close to 0 ‰. The starting material was 600 g of the same sphalerite which had been discontinued as NBS122, supplied by Dr S Halas. Initial analyses of this material indicated inclusions of chalcopyrite and a coarse darker sphalerite

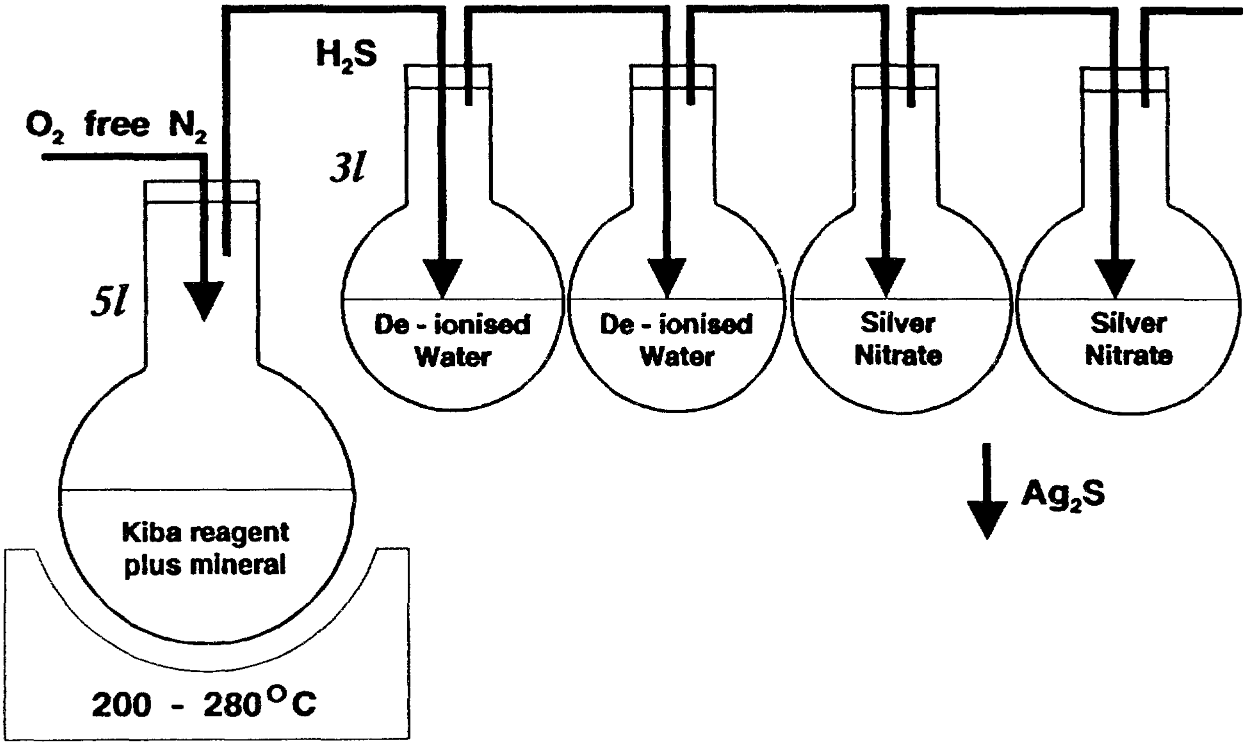

Fig 1: Large column reaction train used for the production of NZ1 and NZ2

which had probably contributed to the inhomogeneity problems. The sphalerite was reground, remixed and divided into batches for reaction with Kiba reagent (Sn^{2+} with strong phosphoric acid) at 200°C in a large volume reaction train (see Fig 1). This train consists of a 5 ℓ reaction vessel in a mantle heater, two 3 ℓ wash traps and two 3 ℓ $AgNO_3$ traps all connected to a supply of oxygen-free N_2 gas. Initially, two batches of 80 g sphalerite with 2 ℓ phosphoric acid and 200 g $SnCl_2$ were run at 200°C to produce about 140 g Ag_2S each. Then four batches of 100 g sphalerite each were run to produce about 200 g Ag_2S per run. Each batch was reacted for six hours. The large volume of the reaction train and the double wash traps help to mix and homogenise the H_2S gas which is transported by the carrier gas. All the Ag_2S batches were washed with distilled water until free of silver ions (as tested by addition of Cl^- to the washings). The weights of the batches were 133, 148, 178, 204, 196 and 188 g.

A preliminary check of the batches indicated that they were homogeneous and similar to each other within error of $\delta^{34}S$ measurements (±0.2 ‰). These batches were then ground and mixed together in a large mortar and pestle. The mixed sample was sieved through a nylon sieve: size 53 µm. Remaining material was reground to pass through the sieve using a sieve shaker. Eventually the grinding produced a residue to coarse 'metallic' balls which could not be sieved further and this residue (~50 g) was discarded. The bulk sample (<53 µm) was 'turned' in a plastic container held in a tilted lathe bed for one day to thoroughly mix the powder. The bulk sample was supplied to the IAEA where it was split into 500 mg portions for bottling and distribution.

4. PREPARATION OF NZ2

The IAEA Technical Contract (5654/TC, September 1989-September 1990) for this standard was to produce 1 kg of pure, homogeneous Ag_2S with $\delta^{34}S$ close to +21 ‰. As starting material, we acquired 6 kg of gypsum, naturally precipitated from present day sea water in evaporite ponds owned by Dominion Salt Ltd, New Zealand. The material was washed to remove halite, and dried at 200°C to convert the gypsum to anhydrite ($CaSO_4$). Several 1 g aliquots of the anhydrite were converted to Ag_2S using strong Kiba reagent (800 g $SnCl_2$ in 2.5 ℓ dehydrated phosphoric acid) at 280°C to test the conversion process. The efficiency of conversion is about 80% and the batches varied by less than 1 ‰ in $\delta^{34}S$.

A large volume reaction train similar to that used for the production of NZ1 (shown in Fig 1) was set up. Eleven batches of 90 g $CaSO_4$ with 3 ℓ strong Kiba solution were run at 280°C for two hours to produce about 90 g of Ag_2S each giving a total of 1024 g. All the Ag_2S batches were washed with distilled water until free of silver ions (as tested by addition of Cl^- to the washings).

A preliminary check of the batches indicated that they were homogeneous and similar to each other within error of measurement of $\delta^{34}S$. These batches were then mixed and ground in a large mortar and pestle. The mixed sample was sieved through a nylon sieve: size 53 µm, until only coarse metallic balls were left and about 70 g of this residue had to be discarded. The bulk sample (<53 µm) was 'turned' in a plastic container held in a tilted lathe bed for one day to thoroughly mix the powder. The 0.95 kg was split into 500 mg samples and bottled for distribution by the IAEA.

Table 1: INTER-LABORATORY COMPARISONS OF THE SULPHUR ISOTOPE STANDARD NZ1

		$\delta^{34}S_{CDT}$ [a] (‰)	$\delta^{34}S_{CDT}$ (‰)	$\delta^{34}S_{CDT}$ [c] (‰)
		-0.34	-0.34	-0.34
		-0.37	-0.37	-0.37
		-0.1	-0.1	-0.1
		-0.25	-0.25	-0.25
		-0.3	-0.3	-0.3
		-0.3	-0.3	-0.3
		-0.13	-0.13	-0.13
		-0.55	-0.55[b]	
		-0.25	-0.25	-0.25
		-0.35	-0.35	-0.35
		-0.14	-0.14	-0.14
		-0.39	-0.39	-0.39
		-0.21	-0.21	-0.21
		-0.33	-0.33	-0.33
		0.19[b]		
		-0.15	-0.15	-0.15
		-0.27	-0.27	-0.275
Mean	m	-0.249	-0.277	-0.259
	σl	0.155	-0.113	-0.091
	σl(n-1)	0.160	0.114	0.094
	n	17	16	15
	m+2σ	0.066	-0.054	-0.076
	m-2σ	-0.574	-0.510	-0.447
	σm	0.039	0.029	0.024

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[a] The first column contains the results reported from 17 laboratories

[b] Outliers excluded on the 2σ criterion

[c] The final column gives the accepted analyses together with δ_m, σ_1, n and σ_m ($= \sigma_1/\sqrt{n}$).

4. RESULTS FOR NZ1 AND NZ2

4.1 Analyses in New Zealand

Eight 15 mg and 2.5 mg portions were taken from the bulk sample of NZ1 and analysed for their sulphur isotopic composition on a VG Micromass 1202E mass spectrometer. The individual analyses did not vary outside the overall error of ±0.2 ‰ which is the estimated maximum combined error for our chemical and mass spectrometric processes. Therefore for the sample sizes taken the standard is homogeneous. For a sample size of 10 mg, Ag_2S will contain more than 2500 grains, which is sufficient to ensure isotopic homogeneity, and we suggest that for the purposes of laboratory intercomparison a reasonably large and constant amount of 10 mg is taken for analysis. Our best analytical results were produced on the 15 mg samples (because of the greater difficulty in handling smaller samples in our inlet system) to give an average value of -0.34 ± 0.07 ‰ CDT (n=8) using a value of +3.3 ‰ CDT for our laboratory standard R2268 [8].

Portions of NZ2 (10 mg) were taken from the bulk sample and analysed on a Micromass 1202E mass spectrometer. The results for NZ2 gave an average value of +21.7 ± 0.1 ‰ CDT (n=8). The individual analyses do not vary outside the overall error of ±0.2 ‰, indicating the sample is homogeneous at least to this level. Again we recommend that for the purposes of inter-laboratory comparison a reasonably large and constant sample amount, say 10 mg, is taken for isotopic analysis.

4.2 Inter-laboratory comparisons of NZ1 and NZ2

NZ1 was circulated by the IAEA to over 30 laboratories and to date 17 have supplied the results shown in Table 1. Fifteen of these passed the 2σ screening to give a mean $\delta^{34}S$ of –0.26 ‰. Of particular note are three SF_6 analyses of NZ1 from different laboratories. They gave $\delta^{34}S$ values of -0.27, -0.30 and -0.33, again indicating that the material is homogeneous, with a $\delta^{34}S$ value of -0.30 ‰ CDT.

To date only four other $\delta^{34}S$ analyses of NZ2 have been reported to the IAEA. They are: +21.42, +21.48, +21.52 and +21.58 ‰; none are by SF_6. Three of these laboratories and our New Zealand results show NZ2-NZ1 values of 21.38, 21.66, 21.78 and 22.04 ‰.

5. CONCLUSIONS

After a very protracted period during which geological and impure mineral samples were unsuccessfully used as sulphur isotope standards, a few chemically pure and homogeneous compounds have now been prepared and are readily available from the IAEA and NIST with reserves for well over 100 years. They are the $BaSO_4$ from sea water (NBS127) and the two silver sulphide calibration materials (NZ1 and NZ2).

NZ1 fulfils all the criteria for a calibration material. Although CDT is essentially exhausted, the value must be kept as a primary reference because most of the results published to date are expressed relative to CDT. However, now that NZ1 has been successfully analysed in many laboratories it could act as the calibration material for the primary reference standard (CDT). Future results would then be expressed as δ values relative to V-CDT with NZ1 set at -0.30 ‰. Coherence between δ values reported from different laboratories can be improved by adopting a second sulphur reference standard to which the $\delta^{34}S$ scale is then normalised. NZ2 partly fills this requirement, but in addition, there is a need for a third standard at about -30 ‰ to be produced and widen the span to a more useful 50 ‰. Furthermore, a $BaSO_4$ with 'light' sulphur and oxygen isotopic compositions is also required.

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VARIATIONS IN THE SULFUR ISOTOPE COMPOSITION OF CDT

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Abstract. *The sulfur isotope composition of Cañon Diablo troilite is variable as shown by high-precision analyses of three different samples and by an interlaboratory comparison. The present range in* $\delta^{34}S$ *values is* $0.4\ ^{o}/_{oo}$. *Because Cañon Diablo troilite is not a Standard Reference Material it should not be used for calibration of the sulfur isotope scale.*

Cañon Diablo troilite (CDT), although accepted as the reference for the sulfur isotope scale, is not a Standard Reference Material manufactured for international distribution, and its sulfur isotope composition is not well characterized. The troilite forms blebs in massive octahedrite and must be separated from fragments of Cañon Diablo iron meteorite obtained either from museum collections or commercial rock dealers. Interlaboratory comparison of a reference SF_6 gas (Beaudoin et al., 1994) indicate a range in $\delta^{34}S_{CDT}$ values of 0.41 ‰, one order of magnitude larger than analytical uncertainty (<0.03 ‰, Table 1). A small standard deviation of $\delta^{34}S$ values (± 0.005 ‰, n=8) is also obtained at the Geological Survey of Canada for this reference SF_6 gas. Aliquots of the reference SF_6 gas are isotopically identical and the difference in mean $\delta^{34}S_{CDT}$ value must therefore be a result of different calibrations relative to CDT, and thus imply that isotopically different aliquots of CDT were used to calibrate the sulfur isotope scales used in each laboratory.

Table 1. Summary of $\delta^{34}S_{CDT}$ (‰) values for the reference SF_6 gas

	x	±	1σ	n
Geophysical Laboratory	- 6.54	±	0.03	12
University of California San Diego	- 6.95	±	0.02	12

(From Beaudoin et al., 1994)

The average $\delta^{34}S$ value for three different samples of CDT relative to a common reference SF_6 ranges from 6.54 to 6.91 ‰ (Table 2; Beaudoin et al., 1994). The range in $\delta^{34}S$ values (0.37 ‰) for different samples of Cañon Diablo troilite is almost one order of magnitude larger than typical analytical uncertainty (0.05 ‰), indicating measurable differences in sulfur isotope composition of the primary reference for the sulfur isotope scale. Interlaboratory comparison of sample CDT3 yields similar $\delta^{34}S$ values in two laboratories (Table 2). Large ranges of averaged $\delta^{34}S_{CDT}$ values (1.1 to 1.9 ‰) are also reported for sulfur isotope intercomparison samples by several laboratories (HUT, 1987). A significant part of these variations could result from sulfur isotope variations in the samples of Cañon Diablo troilite used to calibrate the sulfur isotope scale in each of these laboratories. It is noteworthy, however, that recent high-precision sulfur isotope analyses of intercomparison materials from the I.A.E.A and China has yielded identical $\delta^{34}S_{CDT}$ values, within analytical uncertainty, to those accepted for these materials (GAO and THIEMENS, 1993).

Table 2. Summary of $\delta^{34}S$ (‰) values for samples of Canon Diablo troilite

Sample	Geological Survey of Canada				Geophysical Laboratory			
	x	±	1σ	n	x	±	1σ	n
CDT1	6.91	±	0.05	6		—		
CDT2	6.73	±	0.04	4		—		
CDT3	6.63	±	0.17	12	6.54	±	0.11	3

(From Beaudoin et al., 1994)

Conclusion: The sulfur isotope composition of Cañon Diablo troilite is variable as shown by high-precision analyses of three different samples and by an interlaboratory comparison. The present range in $\delta^{34}S$ values is 0.4 ‰, but more samples of different troilite inclusions from the Cañon Diablo meteorite should be analysed. Because Cañon Diablo troilite is not a Standard Reference Material it should not be used for calibration of the sulfur isotope scale.

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COMPARISON OF THE CONVENTIONAL-SO_2 AND THE LASER-SF_6 METHODS: IMPLICATIONS FOR THE SULFUR ISOTOPE SCALE

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Abstract. *Comparison of $\delta^{34}S_{CDT}$ values using conventional SO_2 and laser-SF_6 methods for powdered sulfide samples is presented. The laser-SF_6 method is recommended for the calibration of new reference and intercomparison materials for sulfur isotope analyses.*

Comparison of $\delta^{34}S$ values obtained using the conventional-SO_2 and the laser-SF_6 methods raises questions about the accuracy of the presently accepted sulfur isotope scale (Beaudoin and Taylor, 1994). Sulfur isotope intercomparison material has been dominantly analyzed by the conventional-SO_2 method but several corrections must be applied to these data to account for oxygen isotope composition and memory effects in the inlet system of the mass spectrometer (Rees, 1978). Rees (1978) showed that measurements using SF_6 yield correction-free isotope ratios which are linearly correlated with conventional-SO_2 data for a set of samples. Least-squares major axes regression of analyses of a set of samples by conventional-SO_2 and laser-SF_6 methods(Table 1, Beaudoin and Taylor, 1994) gives well-correlated $\delta^{34}S_{CDT}$ values with a slope different from unity (Fig. 1):

$$\delta^{34}S\ (SF_6) = (-0.18 \pm 0.04) + (1.035 \pm 0.002)\ \delta^{34}S\ (SO_2);\ r^2 = 0.99999 \qquad (1)$$

This linear regression is similar to that of Rees (1978):

$$\delta^{34}S\ (SF_6) = (-0.14 \pm 0.07) + (1.019 \pm 0.003)\ \delta^{34}S\ (SO_2);\ r^2 = 0.99996 \qquad (2)$$

These similar results are despite different sample suites, chemical extraction methods, and differences in mass spectrometers. The difference between conventional-SO_2 and laser-SF_6 data, therefore, is most likely due to a systematic error resulting from inaccurate corrections applied to SO_2 data for oxygen isobaric interference. SO_2-derived isotope ratios should be empirically corrected using intercomparison material analyzed with correction-free measurements using SF_6. Establishment of a new sulfur isotope reference and of a set of intercomparison materials is considered by the International Atomic Energy Agency to remove ambiguities on the origin of the sulfur isotope scale and to improve laboratory intercalibrations (Gonfiantini and Stichler, personnal communication 1994). The calibration of these new reference and intercomparison materials will be improved if measurements are made using SF_6.

TABLE 1. COMPARISON OF $\delta^{34}s_{CDT}$ VALUES USING CONVENTIONAL-SO_2 AND LASER-SF_6 METHODS FOR POWDERED SULFIDE SAMPLES

	SO_2			SF_6		
	x	± σ	n	x	± σ	n
PAF, pyrite	27.80	± 0.15	[a]	28.66	± 0.09	(5)
RICO, pyrite	0.19	± 0.21	(4)[a]	-0.11	± 0.05	(6)
ZNS, sphalerite	-3.12	± 0.15	(5)[a]	-3.43	± 0.03	(6)
SILVANA, galena	-7.84	± 0.15	(9)[a]	-8.25	± 0.06	(5)
KAZA, pyrite	-31.6		(2)[a]	-32.82	± 0.04	(4)
	-31.9		[b]			

[a] University of Ottawa. [b] University of Alberta (G.M. Ross, pers. com. 1992).

(From Beaudoin and Taylor, 1994)

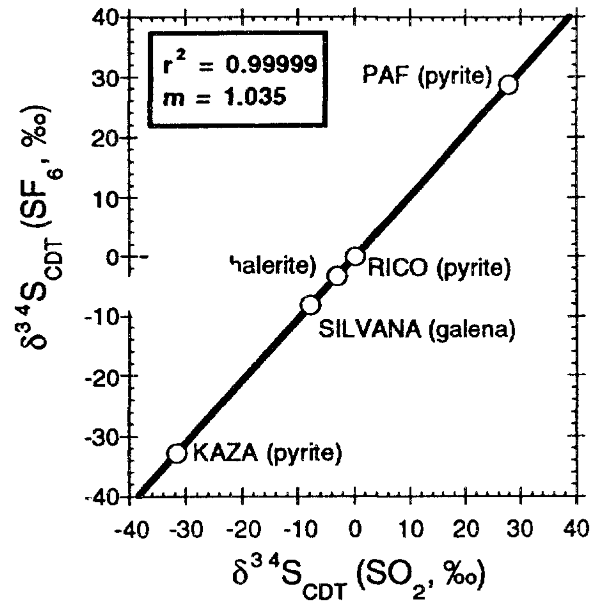

Figure 1. Diagram showing the correlation between $\delta^{34}S_{CDT}$ values for a set of samples analysed by conventional SO_2 and laser-SF_6 methods. The analyses correlated well over a range of 62 ‰ for several sulfide minerals (from Beaudoin and Taylor, 1994).

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INTERLABORATORY COMPARISON OF REFERENCE MATERIALS FOR NITROGEN-ISOTOPE-RATIO MEASUREMENTS

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Abstract

Aliquots of seven different reference materials were distributed for an interlaboratory comparison of stable nitrogen-isotope-ratio measurements. Results from 15 laboratories were compiled and evaluated selectively to yield provisional values of $\delta^{15}N$ for each material, *i*, with respect to atmospheric N_2 ($\delta^{15}N_{i/air}$). The $\delta^{15}N$ values reported by the different laboratories are correlated in such a way that some of the major discrepancies may be removed by normalization (*i.e.*, by altering the length of the $\delta^{15}N$ scale for each laboratory by an amount defined by local measurements of reference materials with extreme values). The results of the intercomparison test, after elimination of 2-σ outliers, before and after normalization, are as follows:

Identification	Substance	$\delta^{15}N_{i/air} \pm 1\sigma$ in ‰ (as reported)	$\delta^{15}N_{i/air} \pm 1\sigma$ in ‰ (normalized)
NSVEC	N_2 gas	−2.77 ± 0.05	−2.78 ± 0.04
IAEA-N1	$(NH_4)_2SO_4$	+0.43 ± 0.07	+0.43 ± 0.07
IAEA-N2	$(NH_4)_2SO_4$	+20.32 ± 0.09	+20.41 ± 0.12
IAEA-N3	KNO_3	+4.69 ± 0.09	+4.72 ± 0.13
USGS25	$(NH_4)_2SO_4$	−30.25 ± 0.38	−30.41 ± 0.27
USGS26	$(NH_4)_2SO_4$	+53.62 ± 0.25	+53.75 ± 0.24
USGS32	KNO_3	+179.2 ± 1.3	+180

1. INTRODUCTION

The primary standard for relative nitrogen (N)-isotope-ratio measurements is atmospheric nitrogen (N_2) gas, which is widespread and homogeneous and, by convention, has a $\delta^{15}N$ value of 0‰ ([1, 2, 3] and see Appendix A for notation). Despite the long history of N-isotope-ratio measurements in the natural sciences, there has never been a set of common-use secondary reference materials with widely accepted isotopic compositions. Secondary reference materials with a large range of isotopic compositions are essential for reporting or expressing isotopic compositions far from that of the primary standard on normalized scales.

The secondary reference materials most commonly analyzed for abundance of N isotopes in the last decade are IAEA-N1 and IAEA-N2, both $(NH_4)_2SO_4$, with $\delta^{15}N$ values near 0 and

+20‰, respectively [4, 5]. Other materials that have been widely distributed include IAEA-N3 (KNO_3; $\delta^{15}N$ unreported) and NSVEC (N_2 gas; $\delta^{15}N$ near −2.8‰ [6]). Recently, Böhlke *et al.* [7] described three new reference materials (USGS25, USGS26, and USGS32) intended to span the range of $\delta^{15}N$ values in all but a few of the many thousands of values reported in the literature for natural terrestrial substances.

Here we report the results of an interlaboratory comparison test (Appendix B) for those seven secondary reference materials (one gas and six salts), which cover approximately the range of $\delta^{15}N$ values known in natural terrestrial substances (Figure 1). The results of this study are complementary to those of Parr and Clements [8], who reported results of an interlaboratory comparison of five reference materials with high $\delta^{15}N$ values (IAEA-305A, 305B, 310A, 310B, and 311) intended for calibration of biological and medical materials involving substances artificially enriched in ^{15}N (Appendix C).

2. DESCRIPTION OF REFERENCE MATERIALS

Atmospheric Nitrogen [N_2 gas]: Atmospheric N_2 is the primary reference material for N-isotope-ratio analysis. By convention, it has a $\delta^{15}N$ value of 0‰. Mariotti [3] reports that it is isotopically homogeneous to within ±0.026‰. Junk and Svec [2] report several measurements of $(^{15}N^{14}N)^+/(^{14}N^{14}N)^+$ with an average value of 7.351×10^{-3} and conclude that atmospheric N_2 has a $^{14}N/^{15}N$ ratio of 272.0 ± 0.3 (atom ratio). The International Union of Pure and Applied Chemistry (IUPAC) recommends that conversions between the $\delta^{15}N$ scale and the $^{14}N/^{15}N$ ratio for nitrogen isotopes be based on values of exactly 0 and 272, respectively, for atmospheric N_2 (see Appendix A and [9]).

NSVEC [N_2 gas]: NSVEC is a pure tank gas held in a large high-pressure cylinder now residing in Reston, Virginia, USA, at the U.S. Geological Survey (USGS). It is believed to be the same tank gas as the one designated as "Matheson pre-purified N_2" by Junk and Svec [2], for which those authors report $(^{15}N^{14}N)^+/(^{14}N^{14}N)^+ = 7.326\times10^{-3}$. Kendall and Grim [6] report that it has a $\delta^{15}N$ value of −2.8‰ relative to atmospheric N_2, which by IUPAC convention would yield $^{14}N/^{15}N = 272.8$.

IAEA-N1 [$(NH_4)_2SO_4$]: IAEA-N1 is a relatively coarse-grained dried salt prepared by E. Salati (CENA, Piracicaba, Sao Paulo, Brazil) between 1978 and 1983 [4, 10]. Previous compilations of data reported by different laboratories indicated approximate values of $\delta^{15}N$:

+0.44 ± 0.39‰ (n=8)	[10]
+0.45 ± 0.32‰ (n=10)	[11]

IAEA-N2 [$(NH_4)_2SO_4$]: IAEA-N2 is a dried salt prepared by E. Salati (CENA, Piracicaba, Sao Paulo, Brazil) between 1978 and 1983 [4, 10]. Previous compilations of data reported by different laboratories indicated approximate values of $\delta^{15}N$:

+20.18 ± 0.70‰ (n=8)	[10]
+20.20 ± 0.59‰ (n=10)	[11]

IAEA-N3 [KNO_3]: IAEA-N3 is a dried salt prepared by A. Mariotti (Universite P. and M. Curie, Tour, Paris, France) between 1983 and 1985 [5, 10]. No previous compilation of analyses is available.

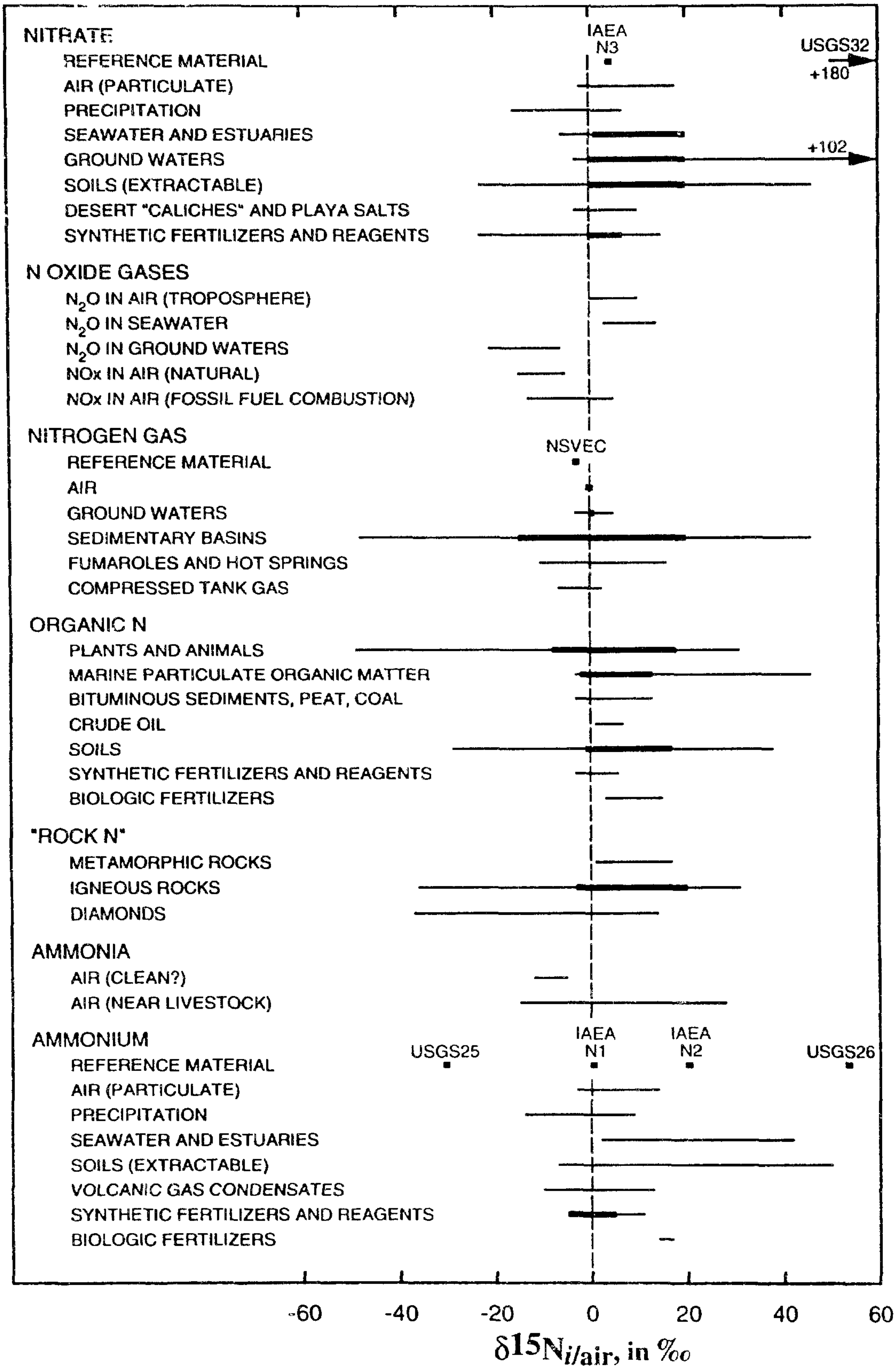

Figure 1. Partial compilation of $\delta^{15}N$ values for some categories of substances on Earth (modified from [7]). The value $\delta^{15}N_{i/air}$ is defined by Equation 1 of Appendix A. Thin lines indicate ranges of reported values; thick bars indicate typical values for some common substances. The secondary reference materials evaluated in this study ($\delta^{15}N_{i/air}$ = −30 to +180‰) allow normalization over almost the full range of reported values in natural substances on Earth, *i.e.*, those not enriched or depleted in ^{15}N by artificial processes.

USGS25 [$(NH_4)_2SO_4$]: USGS25 is a dried salt prepared by J.K. Böhlke (USGS, Reston, Virginia, USA) in 1992. It was prepared by dissolving and recrystallizing a mixture of normal reagent salt and ^{15}N-depleted salt and has a δ^{15}N value of approximately −30‰ [7].

USGS26 [$(NH_4)_2SO_4$]: USGS26 is a dried salt prepared by J.K. Böhlke (USGS, Reston, Virginia, USA) in 1992. It was prepared by dissolving and recrystallizing a mixture of normal reagent salt and ^{15}N-enriched salt and has a δ^{15}N value of approximately +54‰ [7].

USGS32 [KNO_3]: USGS32 is a dried salt prepared by J.K. Böhlke (USGS, Reston, Virginia, USA) in 1992. It was prepared by dissolving and recrystallizing a mixture of normal reagent salt and ^{15}N-enriched salt and has a δ^{15}N value of approximately +180‰ [7].

3. ORGANIZATION OF THE TEST

Each of 22 laboratories that agreed to participate received a package containing aliquots of seven reference materials (NSVEC, IAEA-N1, IAEA-N2, IAEA-N3, USGS25, USGS26, USGS32) in late 1992 or early 1993. The 15 laboratories and corresponding analysts from which results were received by March, 1994 are listed in alphabetical order in Appendix B. Analysts in the different laboratories prepared the materials by their own methods and used their own calibration schemes for isotopic abundance measurements.

4. ANALYTICAL METHODS

Methods for preparation of samples for N-isotope-ratio measurements differ widely among the participating laboratories. Some of the techniques are listed in Table 1 using abbreviations given below in square brackets. Most of the laboratories used some variation of a combustion procedure with Cu metal and Cu oxide (CuO or Cu_2O) to buffer oxygen fugacities at high temperature (designated as [CuO] in Table 1). In principle, the buffered combustion methods convert quantitatively all nitrogen species in a sample to N_2 gas, which is purified either by cooling the combusted sample slowly in contact with CaO [CaO] or by subsequent cryogenic separation [Cryo] or gas chromatography [GC]. In some laboratories, ammonium was oxidized to N_2 gas by reaction with a strong oxidant such as NaOBr [BrO], while nitrate was treated in aqueous solution with a metallic substance such as Devarda's alloy [Dev] to produce ammonium, which was then neutralized and distilled from the solution [Dist], collected, dried, and oxidized to N_2. Local calibrations of δ^{15}N values with respect to atmospheric N_2 were made using a variety of reference materials (air, salts, and tank gases) with δ^{15}N values between approximately −3‰ and +3‰.

Table 1. RESULTS OF INTERLABORATORY COMPARISON TEST OF NITROGEN ISOTOPIC REFERENCE MATERIALS*

ID, laboratory identification numbers assigned in order of increasing $\delta^{15}N$ values reported for IAEA-N1 (not in alphabetical order); BrO, oxidation using NaOBr or LiOBr; CaO, purification of N_2 using CaO; Cryo, cryogenic separation; CuO, combustion with CuO or Cu_2O; Dev, reaction with Devarda's alloy; and Dist, distillation.)

	NSVEC		IAEA-N1		IAEA-N2		IAEA-N3		USGS25		USGS26		USGS32		
ID	$\delta^{15}N$	n	$\delta^{15}N$	n	$\delta^{15}N$	n	$\delta^{15}N$	n	$\delta^{15}N$	n	$\delta^{15}N$	n	$\delta^{15}N$	n	Methods
1			0.19±0.19	3	20.68±0.13	3	4.64±0.02	3	−30.84±0.22	3	54.44±0.10	3	183.26±0.48	3	CuO, Cryo
2	−2.50±0.05	2	0.30±0.40	12	20.30±0.20	12	4.70±0.20	12	−30.80±0.30	10	53.80±0.50	12	180.50±1.00	12	CuO, GC
3	−2.87±0.14	3	0.37±0.10	3	20.42±0.07	8	4.83±0.03	2	−30.15±0.12	3	53.74±0.09	3	179.87±0.27	3	CuO, CaO
4	−2.70±0.06	4	0.38±0.14	4	20.14±0.06	6	4.14±0.12	4	−30.16±0.09	4	53.21±0.15	4	177.02±0.24	4	BrO, Dev, Dist
5	−2.79±0.03	6	0.38±0.02	5	20.37±0.02	5	4.68±0.02	4	−30.30±0.02	4	53.76±0.03	4	180.39±0.03	4	CuO, CaO
6	−2.74±0.05	3	0.40±0.18	9	20.38±0.13	10	4.57±0.09	9	−30.92±0.16	5	53.54±0.19	5	180.86±0.20	5	CuO, CaO
7	−2.72±0.17	4	0.42±0.24	6	20.34±0.26	6	4.95±0.56	6	−30.46±0.32	6	53.86±0.41	6	179.05±0.83	6	BrO, Dev, Dist
8	−2.79±0.01	2	0.42±0.01	3	20.45±0.09	3	4.88±0.16	5	−29.84±0.12	3	53.28±0.20	6	178.53±0.05	3	CuO, Cryo
9			0.44±0.05	9	20.28±0.10	11	4.70±0.16	10	−30.07±0.14	12	53.83±0.10	8	179.83±0.30	8	CuO
10	−2.81±0.01	2	0.45±0.03	4	20.39±0.05	5	4.68±0.02	3	−30.21±0.03	5	53.74±0.04	5	180.10±0.10	5	CuO, CaO
11			0.48±0.11	2	20.17±0.07	2	4.59±0.08	2	−29.94±0.32	2	52.94±0.15	2	177.77±0.11	2	CuO
12			0.53±0.14	3	19.75±0.04	3	3.97±0.14	3	−29.63±0.10	3	51.44±0.24	3	172.41±0.48	3	CuO, Cryo
13	−2.75±0.05	2	0.55±0.05	2	20.20±0.00	2	4.65±0.05	2	−29.80±0.00	2	53.20±0.00	2	177.10±0.10	2	BrO, Dev, Dist
14			0.62±0.08	2	20.31±0.21	2	5.60±0.27	4	−30.39±0.17	2	53.84±2.78	2	173.28±2.63	4	BrO, Dev, Dist
15	−2.95±0.05	2	1.00±0.40	4	20.40±0.10	5			−29.10±0.10	5	48.20±0.20	6			CuO, Cryo

* $\delta^{15}N$ values are given with respect to atmospheric nitrogen as reported by each laboratory (based on various local calibrations).

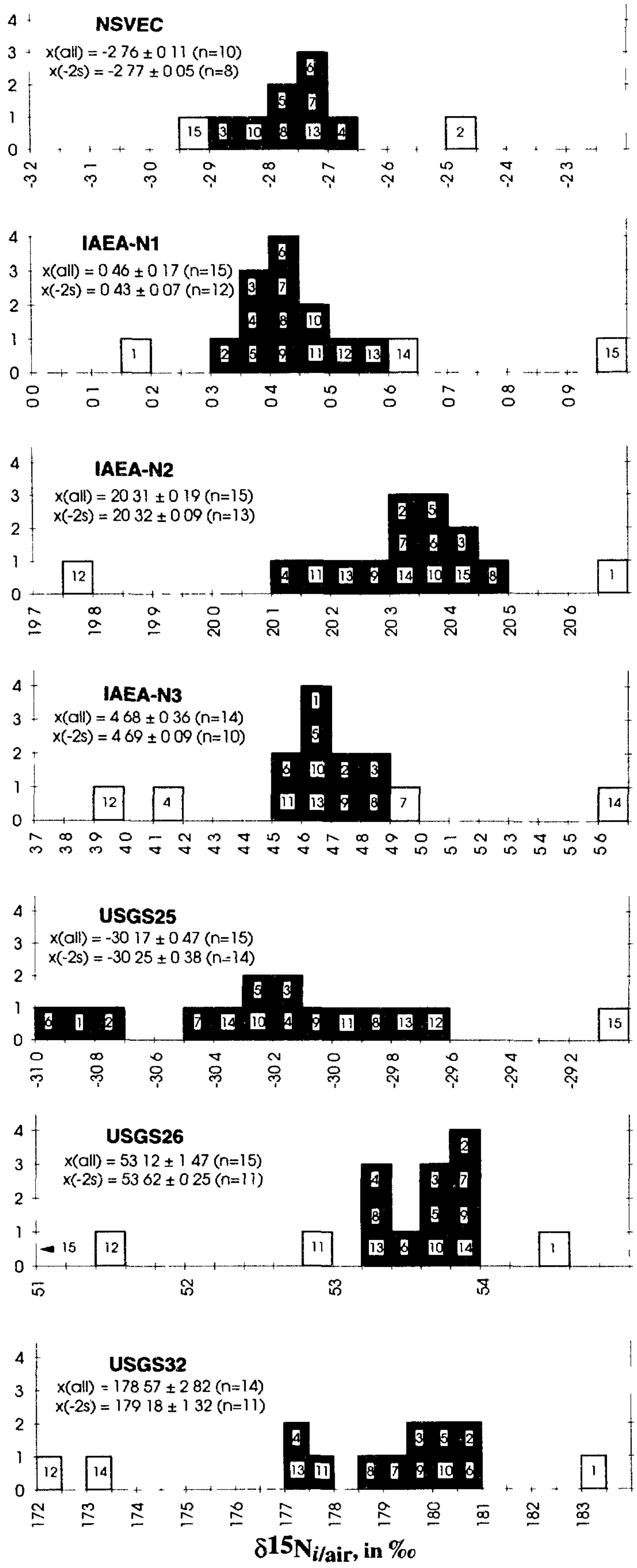

Figure 2. Histograms showing reported laboratory mean values of $\delta^{15}N_{i/air}$ for secondary reference materials. The numbers in the columns identify laboratories as listed in Table 1. Mean values (± 1σ) are given for all reported laboratory means (all) and those remaining after 2-σ outliers were rejected (-2σ).

5. TEST RESULTS

5.1. Summary and Selection of Data

Results of measurements by the 15 reporting laboratories are summarized in: (1) a table of reported values (Table 1); (2) a histogram for each reference material (Figure 2); and (3) selected correlation diagrams illustrating laboratory biases (Figure 3). Each laboratory was assigned an identification number which was arbitrarily chosen to reflect the relative magnitude of its $\delta^{15}N$ value for IAEA-N1 (Table 1). Those identification numbers appear in each of the summary figures. From the data in Table 1, arithmetic means and standard deviations (1σ) were calculated for: (1) all data with no selection; (2) all data after elimination of values that differ from the means by more than two standard deviations, followed by recalculation and elimination until all values were within 2 standard deviations (Table 2; Figure 2).

Table 2. OVERALL MEANS, SELECTED MEANS, AND NORMALIZED VALUES FOR $\delta^{15}N_{i/\mathrm{air}}$
[Data are given as $\bar{x} \pm 1\sigma$ (n), in ‰.]

	As Reported Not Normalized		Normalized to $\delta^{15}N_{\mathrm{USGS32/air}} = +180‰$	
ID	No Selection	Minus 2-σ Outliers	No Selection	Minus 2-σ Outliers
NSVEC	−2.76±0.11 (10)	−2.77±0.05 (8)	−2.75±0.10 (9)	−2.78±0.04 (8)
IAEA-N1	+0.46±0.17 (15)	+0.43±0.07 (12)	+0.43±0.11 (14)	+0.43±0.07 (12)
IAEA-N2	+20.31±0.19 (15)	+20.32±0.09 (13)	+20.46±0.21 (14)	+20.41±0.12 (13)
IAEA-N3	+4.68±0.36 (14)	+4.69±0.09 (10)	+4.72±0.38 (14)	+4.72±0.13 (11)
USGS25	−30.17±0.47 (15)	−30.25±0.38 (14)	−30.50±0.40 (14)	−30.41±0.27 (13)
USGS26	+53.12±1.47 (15)	+53.62±0.25 (11)	+53.91±0.61 (14)	+53.75±0.24 (13)
USGS32	+178.6±2.8 (14)	+179.2±1.3 (11)	+180	+180

From the data in Table 1 and Figure 2, it is evident that the range of reported $\delta^{15}N$ values for each reference material is larger than the precision reported for each value by most laboratories. Some possible reasons for this variability might include: (1) local calibrations with respect to atmospheric N_2 differ among the laboratories; (2) methods of analysis (including potential blanks and isotopic fractionations) differ widely among the laboratories; and (3) different mass spectrometers or data-reduction procedures may yield different $\delta^{15}N$ scales.

The reported data for some of the materials with $\delta^{15}N$ values far from 0‰ (*e.g.*, USGS26 and USGS32), after elimination of 2-σ outliers, are slightly skewed and bimodal, with the major modes farther from 0‰ (Figure 2). For those materials, it is possible that the larger modes farther from 0‰ may be closer to the correct values because: (1) experimental blanks are likely to cause deviations toward zero for those materials with $\delta^{15}N$ values far from zero; (2) one laboratory that reported relatively low $\delta^{15}N$ values for those

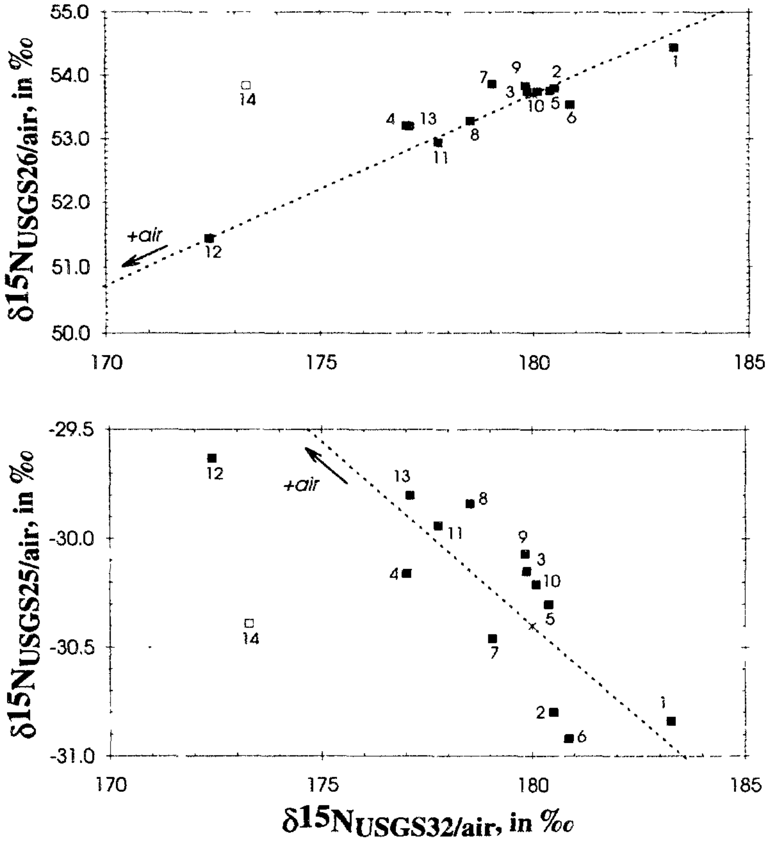

Figure 3. Correlation diagrams showing the effects of interlaboratory variations in $\delta^{15}N$ scales. Data labels identify laboratories as listed in Table 1. Dashed lines go through the origin ("air", representing the isotopic composition of atmospheric N_2) and through the recommended normalized values (Table 2, last column). Because most laboratory reference materials and most potential contaminants have $\delta^{15}N$ values relatively near zero, variations along the dashed lines could be caused by laboratory blanks, errors in values assigned to the laboratory reference materials, or mass spectrometric δ-scale variations.

materials (laboratory 8) reported possible incomplete recovery of N_2 from a molecular sieve trap; and (3) two other laboratories (laboratories 11 and 13) that reported relatively low $\delta^{15}N$ values for those materials reported only two trials each. Thus, for USGS32, it is possible that a value near +180‰ should be preferred to the mean (-2σ) of +179.2‰.

5.2 Effect of Normalization

From correlations such as the ones summarized in Figure 3, it appears that the different laboratories have consistently different (expanded or contracted) $\delta^{15}N$ scales. Therefore, some major discrepancies among the $\delta^{15}N$ values reported by different laboratories may be removed by adjusting the length of the $\delta^{15}N$ scale for each laboratory (*i.e.*, "normalization," as described by Gonfiantini [4] and Coplen [12]). To illustrate this effect, we calculated normalized $\delta^{15}N$ values for all of the analyses in Table 1 by assuming that the correct $\delta^{15}N$ value of USGS32 relative to N_2 in air is +180‰ exactly and that the corrections to the $\delta^{15}N_{i/\mathrm{air}}$ values for other materials are proportional to their $\delta^{15}N_{i/\mathrm{air}}$ values--see [4, 12] and Equation 8 in Appendix A. For example,

$$\delta^{15}N_{USGS32/air,norm} = \frac{\delta^{15}N_{USGS32/air,real}\,\delta^{15}N_{USGS26/air,meas}}{\delta^{15}N_{USGS32/air,meas}},$$

where $\delta^{15}N_{USGS26/air,norm}$ is the normalized value of USGS26 relative to N_2 in air, $\delta^{15}N_{USGS32/air,real}$ is +180‰, $\delta^{15}N_{USGS26/air,meas}$ is the measured value of USGS26 relative to N_2 in air, and $\delta^{15}N_{USGS32/air,meas}$ is the measured value of USGS32 relative to N_2 in air. Normalized values of $\delta^{15}N_{USGS26/air}$ and $\delta^{15}N_{USGS25/air}$ are summarized in Figure 4. The effect of the normalization in both cases is to reduce the range and standard deviation of $\delta^{15}N$ values and to shift the mean values slightly away from 0‰ (Table 2 and Figure 4). If the selection of data for USGS32 is justified, then the preferred $\delta^{15}N$ value for USGS26 with respect to atmospheric N_2 is approximately +53.8‰ and that for USGS25 is −30.4‰.

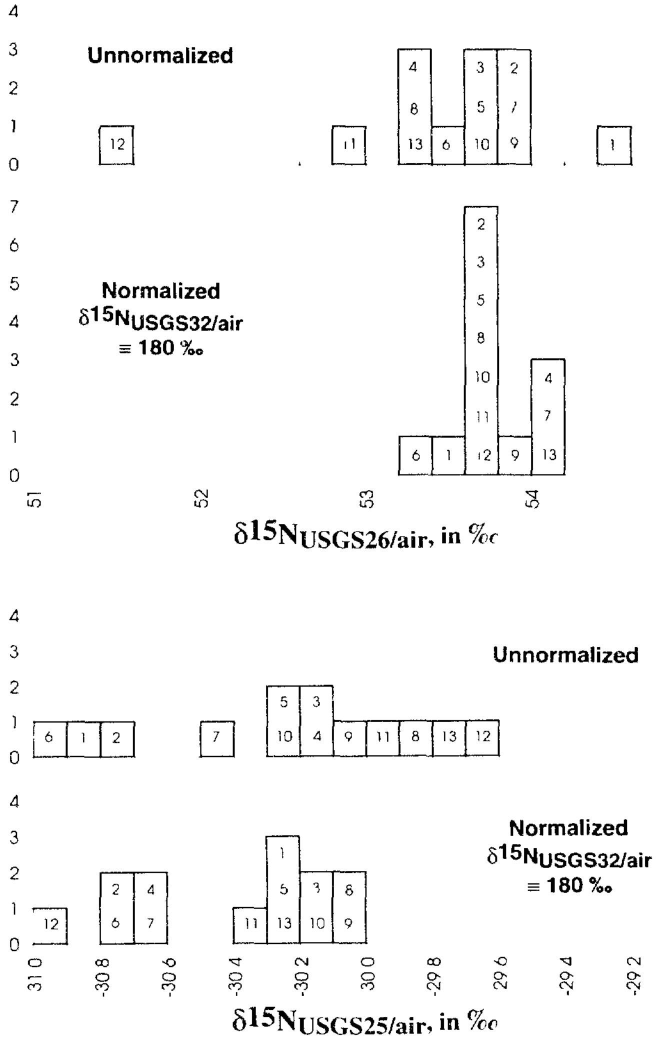

Figure 4. Histograms showing the differences between reported laboratory mean values of $\delta^{15}N_{USGS25/air}$ and $\delta^{15}N_{USGS26/air}$ before and after normalization (Appendix A, Equation 8). The numbers in the columns identify laboratories as listed in Table 1. Normalization reduces the variability of the data to levels that are not much greater than many of the individual laboratory uncertainties. The mean values of the normalized data are further from zero than the means of the reported data because the selected value of $\delta^{15}N_{USGS32/air}$ (+180‰) used for the normalization is slightly higher than the unbiased mean (-2σ) value (+179.2‰).

After normalization, the remaining variations in $\delta^{15}N_{USGS26/air}$ and $\delta^{15}N_{USGS25/air}$ from different laboratories (Figure 4) are smaller than those of the reported values (Figure 2), but still slightly larger than the reported uncertainties from individual laboratories (Table 1). From correlations like those in Figure 3, it is evident that similar results would be achieved by normalizing $\delta^{15}N$ values over the whole range from −30‰ to +180‰.

5.3 Calibration With Respect to Atmospheric Nitrogen

Precise calibration of N-isotope-ratio measurements with respect to atmospheric N_2 (the primary N-isotope-ratio standard) may be complicated by mass-spectrometer-specific measurement effects of argon in air, which can cause errors in $\delta^{15}N$ measurements of 0.1‰ to 0.2‰ [5, 13, 14]. None of the laboratories participating in this study reported testing the effect of argon on measurements of atmospheric N_2. Therefore, it is possible that

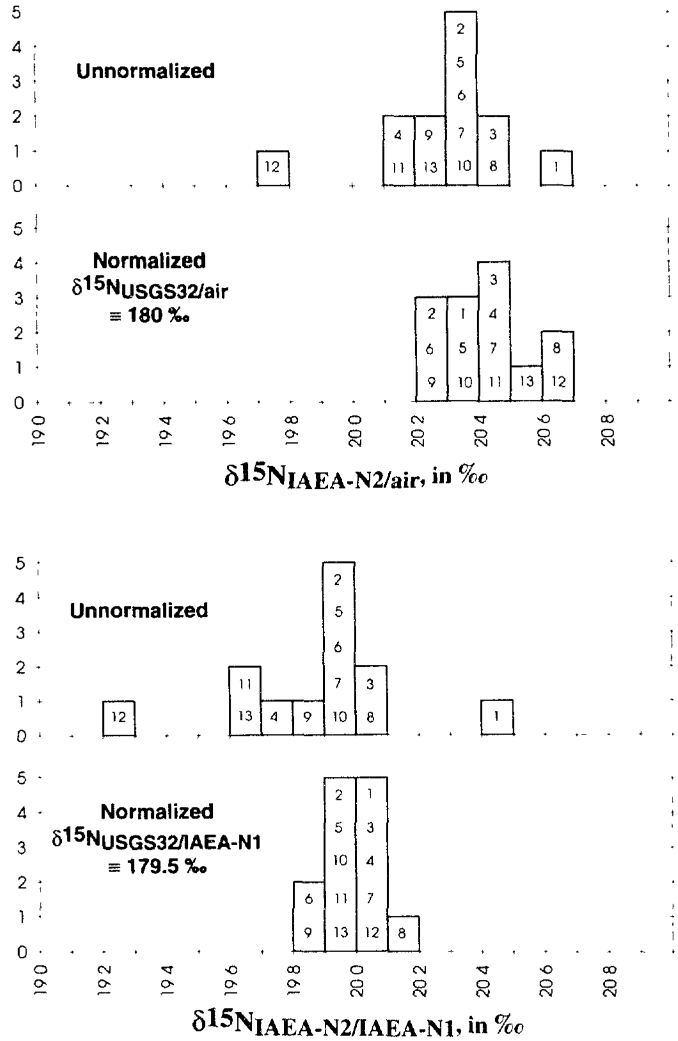

Figure 5. Histograms showing the differences between reported laboratory mean values of $\delta^{15}N_{IAEA\text{-}N2/air}$ and $\delta^{15}N_{IAEA\text{-}N2/IAEA\text{-}N1}$ before and after normalization (Appendix A, Equations 8 and 9). The numbers in the columns identify laboratories as listed in Table 1. After normalization, the interlaboratory differences are similar in magnitude to individual laboratory precisions. Slightly larger variability in normalized values of $\delta^{15}N_{IAEA\text{-}N2/air}$ compared to $\delta^{15}N_{IAEA\text{-}N2/IAEA\text{-}N1}$ may indicate a component of uncertainty associated with the calibration of laboratory standards near 0‰.

measurements against a secondary reference material like IAEA-N1 could yield simpler and more precise interlaboratory calibrations than measurements against atmospheric N_2. That possibility cannot be evaluated at present because only a few of the participating laboratories reported analyses of atmospheric N_2 samples. Instead, we compare the isotopic compositions reported for IAEA-N2 with respect to IAEA-N1 and for IAEA-N2 with respect to N_2 in air as determined by the various local calibrations (Figure 5). Normalized $\delta^{15}N$ values were calculated for IAEA-N2 with respect to IAEA-N1 with a version of Equation 8 in Appendix A:

$$\delta^{15}N_{\mathrm{IAEA\text{-}N2/IAEA\text{-}N1,norm}} = \frac{\delta^{15}N_{\mathrm{USGS32/IAEA\text{-}N1,real}}\,\delta^{15}N_{\mathrm{IAEA\text{-}N2/IAEA\text{-}N1,meas}}}{\delta^{15}N_{\mathrm{USGS32/IAEA\text{-}N1,meas}}},$$

where $\delta^{15}N_{\mathrm{USGS32/N1,real}}$ was assumed to be +179.49‰ based on values of +0.43‰ for IAEA-N1 and +180‰ for USGS32 (see Equations 6 and 7 in Appendix A). After normalization, the variation in $\delta^{15}N_{\mathrm{IAEA\text{-}N2/IAEA\text{-}N1,norm}}$ is slightly smaller than that for $\delta^{15}N_{\mathrm{IAEA\text{-}N2/air,norm}}$ (Figure 5). Thus, some of the overall uncertainties in the reported $\delta^{15}N_{i/\mathrm{air}}$ values may be attributable to errors in local calibrations; those errors are slightly larger than most laboratory precisions, but they are smaller than the effects of varying $\delta^{15}N$ scales when applied to materials with $\delta^{15}N$ values far from zero.

5.4 Evaluation of Isotopic Homogeneity

Only a few laboratories reported possible evidence of isotopic heterogeneity in isolated reference materials (IAEA-N1, IAEA-N3, USGS25, and USGS32 were each mentioned once). However, the data and the comments of the analysts do not indicate a consistent problem with any of the materials for sample sizes in the range of 10 to 100 μmol of N (see also [7] for homogeneity tests of USGS25, USGS26, and USGS32). Some laboratories reported regrinding and homogenizing the salts before analyzing them; that practice, if followed elsewhere, apparently removed measurable isotopic heterogeneity if it existed in the original materials.

6. DISTRIBUTION INFORMATION

Aliquots of the reference materials tested in this study are available from the U.S. National Institute of Standards and Technology (NIST), Standard Reference Materials Program, Room 204, Building 202, Gaithersburg, Maryland, 20899, USA, and from the International Atomic Energy Agency, Section of Isotope Hydrology, Wagramerstrasse 5, P.O. Box 100, A-1400 Vienna, Austria.

7. CONCLUSIONS

As a result of a new interlaboratory comparison among 15 laboratories, $\delta^{15}N$ values are known for 7 secondary reference materials for N-isotope-ratio measurements over almost the whole range of values encountered in natural substances on Earth. Patterns in the reported data indicate that discrepancies among $\delta^{15}N$ values measured in different laboratories are largely the result of (1) variations in the $\delta^{15}N$ scales of the different laboratories (either instrumental or procedural), and (2) errors of calibration with respect to atmospheric N_2. Discrepancies could be reduced significantly by adoption of universally-accepted $\delta^{15}N$ values for secondary reference materials for normalization purposes.

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Appendix A. Background Information

N Isotope Masses

$^{14}N = 14.003074008\ (23)$ u [15]
$^{15}N = 15.000108978\ (38)$ u [15]

N Isotopic Abundances in Atmospheric N_2

$^{14}N/^{15}N = 272.0 \pm 0.3$ [2]
$^{14}N/^{15}N \equiv 272$ [9]
$^{14}N = 99.6337$ fraction of, in % (or atom%) [16]
$^{15}N = 0.3663$ fraction of, in % (or atom%) [16]
Standard atomic weight = 14.00673 [17]

Delta Conversions

For an unknown, x, expressed relative to z or if $\delta^{15}N_{i/\mathrm{air}}$ is the $\delta^{15}N$ value of an unknown, i, expressed relative to atmospheric N_2, then we have the following equations.

$$\delta^{15}N_{x/z}\ (\text{in ‰}) = \left[\frac{\left(\dfrac{^{15}N}{^{14}N} \right)_x}{\left(\dfrac{^{15}N}{^{14}N} \right)_z} - 1 \right] 1000 \tag{1}$$

$$\delta^{15}N_{i/\mathrm{air}} = 1000 \left[272 \left(\frac{^{15}N}{^{14}N} \right)_i - 1 \right] \tag{2}$$

$$\left(\frac{^{15}N}{^{14}N} \right)_i = \frac{\delta^{15}N_{i/\mathrm{air}} + 1000}{272000} \tag{3}$$

$$\delta^{15}N_{i/\mathrm{air}} = 1000 \left[272 \left(\frac{\mathrm{atom\%}\,^{15}N_i}{100 - \mathrm{atom\%}\,^{15}N_i} \right) - 1 \right] \tag{4}$$

$$\mathrm{atom\%}\,^{15}N_i = \frac{100}{\dfrac{272}{\left(1 + \dfrac{\delta^{15}N_{i/\mathrm{air}}}{1000} \right)} + 1} \tag{5}$$

$$\delta^{15}\mathrm{N}_{i/z} = \delta^{15}\mathrm{N}_{i/x} + \delta^{15}\mathrm{N}_{x/z} + \frac{\delta^{15}\mathrm{N}_{i/x}\delta^{15}\mathrm{N}_{x/z}}{1000} \tag{6}$$

$$\delta^{15}\mathrm{N}_{x/z} = 1000\left[\frac{1000}{\delta^{15}\mathrm{N}_{z/x} + 1000} - 1\right] \tag{7}$$

Normalization Equations

For measurements calibrated directly by measurement of atmospheric N_2 (air) under the same conditions as USGS32 and the unknown (*i*) (equivalent to Equation 1 of [4]):

$$\delta^{15}\mathrm{N}_{i/\mathrm{air,norm}} = \frac{\delta^{15}\mathrm{N}_{\mathrm{USGS32/air,real}}\,\delta^{15}\mathrm{N}_{i/\mathrm{air,meas}}}{\delta^{15}\mathrm{N}_{\mathrm{USGS32/air,meas}}} \tag{8}$$

where $\delta^{15}\mathrm{N}_{\mathrm{USGS32/air,real}}$ is assumed provisionally to be +180‰. For measurements against a working reference gas (*rg*) and calibrated by measurement of a secondary reference material (*srm*) under the same conditions as USGS32 and the unknown (*i*) (numerically equivalent to Equations 14 and 15 in [12]; see also page 36 of [18]):

$$\delta^{15}\mathrm{N}_{i/\mathrm{air,norm}} = \left[\frac{\delta^{15}\mathrm{N}_{i/rg,\mathrm{meas}} - \delta^{15}\mathrm{N}_{srm/rg,\mathrm{meas}}}{\delta^{15}\mathrm{N}_{\mathrm{USGS32}/rg,\mathrm{meas}} - \delta^{15}\mathrm{N}_{srm/rg,\mathrm{meas}}}\right] \times \left[\delta^{15}\mathrm{N}_{\mathrm{USGS32/air,real}} - \delta^{15}\mathrm{N}_{srm/\mathrm{air,real}}\right] + \delta^{15}\mathrm{N}_{srm/\mathrm{air,real}} \tag{9}$$

where $\delta^{15}\mathrm{N}_{\mathrm{USGS32/air,real}}$ and $\delta^{15}\mathrm{N}_{srm/\mathrm{air,real}}$ are independently calibrated normalized values (e.g., 180‰ and 0.43‰ if *srm* is IAEA-N1).

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Appendix C. Other Reference Materials for Nitrogen-Isotope-Ratio Measurements

NBS-14 [N_2 gas]: NBS-14 has been loosely described as "atmospheric nitrogen" [10]. Kendall and Grim [6] report that it has $\delta^{15}N = -1.18‰$ relative to atmospheric N_2. Hut [5] suggests that NBS-14 should be replaced by NSVEC in common use.

IAEA-305A and IAEA-305B [$(NH_4)_2SO_4$]: IAEA-305A and IAEA-305B are dried salts provided by E. Fern (Nestle Research Centre, Vevey, Switzerland) before 1989 for use in medical and biological tracer studies [8]. Parr and Clements [8] report the results of an intercomparison test that yielded "provisional certified values" and 95% confidence intervals:

IAEA-305A	+39.8 ± 0.5‰ (n=23)
IAEA-305B	+375.3 ± 2.3‰ (n=25)

IAEA-310A and IAEA-310B [CO(NH2)2]: IAEA-310A and IAEA-310B are dried salts provided by H. Faust (Central Institute of Isotope and Radiation Research, Leipzig, Germany) before 1989 for use in medical and biological tracer studies [8]. Parr and Clements [8] report the results of an intercomparison test that yielded "provisional certified values" and 95% confidence intervals:

IAEA-310A	+47.2 ± 1.3‰ (n=24)
IAEA-310B	+244.6 ± 0.8‰ (n=23)

IAEA-311 [$(NH_4)_2SO_4$]: IAEA-311 is a dried salt provided by E. Fern (Nestle Research Centre, Vevey, Switzerland) before 1989 for use in medical and biological tracer studies [8]. Parr and Clements [8] report the results of an intercomparison test that yielded a "provisional certified value" and 95% confidence interval:

IAEA-311	+4693 ± 57‰ (n=28)

XA96 40896

INTERLABORATORY COMPARISON OF NEW MATERIALS FOR CARBON AND OXYGEN ISOTOPE RATIO MEASUREMENTS

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Abstract

Aliquots of five different intercomparison materials were distributed for an interlaboratory comparison test of stable carbon and oxygen isotope ratio measurements. The samples were sent to twenty-three laboratories, of which 13 reported their results. In addition, each laboratory received an aliquot of NBS19 and NBS18. All results were normalized with NBS19 and reported versus the V-PDB-scale. The results of the intercomparison, after elimination of 2-σ outliers, are listed below and represent provisional $\delta^{13}C$ and $\delta^{18}O$ values of these materials:

Identification	Substance	Carbon - 13			Oxygen - 18		
		δ C-13 (‰)	1-σ (‰)	n	δ 0-18 (‰)	1-σ (‰)	n
IAEA-CO-1	Calcite	2.480	0.025	(10)	-2.437	0.073	(11)
IAEA-CO-8	Calcite	-5.749	0.063	(12)	-22.667	0.187	(13)
IAEA-CO-9	Barium Carbonate	-47.119	0.149	(10)	-15.282	0.093	(10)
LSVEC	Lithium Carbonate	-46.479	0.150	(11)	-26.462	0.251	(10)
USGS 24	Graphite	-15.994	0.105	(8)			

Introduction

Since PDB is virtually non-existent, a reference Vienna-PDB (V-PDB) was introduced in 1985 defined by using NBS19 as a reference material with:

$$\delta^{13}C = + 1.95 \text{ ‰ and } \delta^{18}O = - 2.20 \text{ ‰ versus V-PDB}$$

In addition, only one carbonate intercomparison material NBS18 was available. The δ-values of this material represented mean values of measurements carried out by different laboratories.

Given the growing demand for $\delta^{13}C$- measurements at about -50 ‰ versus V-PDB, the Isotope Hydrology Section decided to produce a new intercomparison material (IAEA-CO-9). To avoid any problems with the diminishing supply of NBS18 and NBS19 two additional materials suitable to replace the above mentioned were produced (IAEA-CO-1 and IAEA-CO-8). Furthermore, the National Institute of Standards and Technology (NIST) put two additional materials at our disposal. One of them in a new graphite (UGS-24) and should replace the exhausted NBS21, the other is lithium carbonate (LSVEC) also depleted in ^{13}C.

These five new intercomparison materials were distributed in the interlaboratory comparison, test together with NBS18 and NBS19.

Description of the intercomparison materials:

IAEA-CO-1 Calcite (1g)

This material is marble used in the IAEA recent C1 Intercomparison Exercise. A slab of freshly cut Carrara marble was supplied by IMEG, Vareggio, Italy and milled down to powder by the IAEA. The consensus $\delta^{13}C$ value for this material calculated on the basis of 59 analyses reported by radiocarbon laboratories amounts to $\delta^{13}C = +2.42$ ‰ versus V-PDB. It is intended to be used as a complementary material to NBS19.

IAEA-CO-8 Calcite (1g)

This material is a natural carbonatite originating from Schelingen at the Kaiserstuhl, Germany. The material was ground from 0.09 to 0.5 mm grain size and put at our disposal by the Geologisches Landesamt, Freiburg, Germany. Preliminary measurements yielded values in the order of $\delta^{13}C \approx 6$ ‰ versus V-PDB and $\delta^{8}O \approx -23$ ‰ versus V-PDB. It is intended to use this material complementary to NBS18.

IAEA-CO-9 Barium carbonate (1g)

This barium carbonate powder was been prepared by C.A. Brenninkmeijer, Atmospheric Division, National Institute for the Atmosphere and Hydrosphere, Lower Hutt, New Zealand, with the following procedure. CO_2 was produced from burning natural gas and absorbed in a NaOH solution. Barium sulfide was used to precipitate the carbonate. The Barium carbonate was thoroughly purified over periods of weeks by washing it with distilled water. Homogenization was obtained with the solid still submerged in the liquid. The carbonate was dried under vacuum, after which further homogenization took place. The isotope measurements performed by the producer were reported as $\delta^{13}C = -47.23 \pm 0.03$‰ versus V-PDB and $\delta^{18}C = -15.95 \pm 0.05$‰ versus V-PDB.

LSVEC: Lithium carbonate (0.4g)

This lithium carbonate is intended to be used for $^{13}C/^{12}C$ and $^{18}O/^{16}O$ isotope ratio analysis. Furthermore, the lithium isotope abundance was determined and published by NIST to 7.525 atom percent ^{6}Li and 92.475 atom percent ^{7}Li (G.D. Flesch, A.R. Anderson and H.J. Svec, Int. J. Mass Spectrom. Ion Phys., vol 12, 265-272 (1973). It was prepared by H. Svec (Iowa State University). The preliminary values were given by NIST to $\delta^{13}C = -46.7 \pm 0.9$ ‰ versus VPDB and $\delta^{18}O = 26.8 \pm 0.1$ ‰ versus VPDB.

USGS24: graphite (0.4g)

This graphite was prepared by T.B. Coplen (U.S. Geological Survey) by using Baker technical grade graphite (96%, 325 mesh). Prior to splitting with a sample splitter, six spatially separated ~ 1 mg samples were analysed to ensure isotopic homogeneity of the material. Peak-to-peak variation was 0.11 ‰. It is intended to use this material in replacement of the exhausted NBS21. A preliminary value was given by NIST as $\delta^{13}C = -15.9 \pm 0.25$ ‰ VPDB.

Distribution of the intercomparison materials

The materials were sent to 15 laboratories which were selected on the basis of participating institutes in former interlaboratory tests organized by the IAEA. Eight laboratories reported their results. Furthermore, three laboratories wanted to participate in the ring test, two of them sent the results to the IAEA. To improve the statistics of the provisional values, a further eleven laboratories were informed and asked to participate. Five laboratories gave a positive answer but only three of them reported their results. Altogether, twenty three laboratories received the intercomparison materials and thirteen of them reported their results (about 55 %) to the IAEA. The different laboratories prepared the samples by their own methods and used NBS19 for calibration of the δ-values.

In Appendix A the participating laboratories are listed in alphabetical order.

Results

The results of the measurements reported by the 13 laboratories are summarized in table 1 and 2. These two tables contain the δ values and the one sigma error as reported by the participants. These data were used to calculate the arithmetic mean values (Mean), and standard deviation (Std. Dev) listed in Tables 3 and 4. Within one to three iteration steps values were eliminated which differ from the mean values by more than two standard deviations. The table in the Abstract summarizes the mean values where all measuring data were within two standard deviations. The number of values (n) used to calculate the mean values is indicated.

Conclusions

For carbon-13 it is clearly indicated that the uncertainty is small for the measurements of the different laboratories carried out on the materials: NBS18, IAEA-CO-1 and IAEA-CO-8. The absolute δ values are in the range of NBS19. Except IAEA-CO-8, the same can be seen in the oxygen-18 results. The standard deviations of the materials IAEA-CO-9, LSVEC and VGSG 24 are in the range of 0.09 to 0.25 ‰ (both isotopes), and are most of the time larger than the reported uncertainties from the individual laboratories (Tables 1 and 2).

Therefore, it is strongly recommended to introduce a second reference material (e.g. IAEA-CO-9 or LSVEC) with fixed δ-values to improve the present situation.

ACKNOWLEDGEMENTS

We sincerely thanks the participants in this intercomparison ring test. We are also grateful to NIST which supplied aliquots of two intercomparison materials (LSVEC and USGS24) distributed in the ring test.

Table 1 : δ – values reported by the participating laboratories.
(For laboratory No 6 the values were normalized with NBS 19, the results in line 6 and 6* were obtained by using different mass spectrometer and preparation device)

Intercomparison: Carbon-13 Results

LAB	NBS 18		IAEA-CO-1		IAEA-CO-8		IAEA-CO-9		LSVEC		USGS 24	
	δ C-13 (‰)	1-σ (‰)	δ C-13 (‰)	1-σ (‰)	δ C-13 (‰)	1-σ (‰)	δ C-13 (‰)	1-σ (‰)	δ C-13 (‰)	1-σ (‰)	δ C-13 (‰)	1-σ (‰)
1	-4.96	0.03	2.52	0.04	-5.72	0.02	-46.82	0.04	-45.99	0.03	-15.84	0.04
2	-5.038	0.024	2.488	0.020	-5.803	0.017	-47.03	0.05	-46.471	0.03	-15.970	0.023
3	-5.07	0.02	2.44	0.05	-5.78	0.02	-47.16	0.03	-46.56	0.04	-15.91	0.01
4	-5.10	0.008	2.45	0.028	-5.81	0.030	-47.23	0.034	-46.37	0.048	-16.08	0.007
5	-4.98	0.06	2.46	0.01	-5.77	0.01	-47.28	0.06	-46.56	0.03	-16.09	0.08
6	-4.89	0.01	2.28	0.24	-5.64	0.03	-47.42	0.01	-46.67	0.02		
6*	-5.02	0.04	2.49	0.01	-5.69	0.12	-47.56	0.19	-46.71	0.01		
7											-16.98	0.037
8	-4.99	0.05	2.51	0.05	-5.87	0.05	-47.04	0.04	-46.24	0.05	-16.09	0.05
9	-4.95	0.09	2.48	0.03	-5.68	0.08	-46.88	0.12	-46.58	0.12		
10	-5.06	0.070	2.46	0.046	-5.75	0.042	-47.11	0.055	-46.41	0.034	-16.11	0.036
11	-4.98	0.02	2.50	0.01	-5.70	0.02	-47.00	0.05	-46.47	0.05	-15.86	0.05
12					-6.68	0.14	-46.3	0.25	-45.58	0.26		
13	-5.06	0.014	2.34	0.012	-5.78	0.017	-47.04	0.006	-46.23	0.012		

Table 2 : δ – values reported by the participating laboratories.

(For laboratory No 6 the values were normalized with NBS 19, calculation from VSMOW scale in VPDB scale was performed, the results in line 6 and 6* were obtained by using different mass spectrometer and preparation device)

Intercomparison: Oxygen-18 Results

LAB	NBS 18		IAEA-CO-1		IAEA-CO-8		IAEA-CO-9		LSVEC	
	δ 0-18 (‰)	1-σ (‰)	δ 0-18 (‰)	1-σ (‰)	δ 0-18 (‰)	1-σ (‰)	δ 0-18 (‰)	1-σ (‰)	δ 0-18 (‰)	1-σ (‰)
1	-22.97	0.09	-2.36	0.03	-22.74	0.05	-16.02	0.03		
2	-23.033	0.06	-2.52	0.05	-22.795	0.03	-15.30	0.05	-26.920	0.027
3	-22.85	0.03	-2.47	0.17	-22.49	0.1	-15.70	0.03	-26.86	0.05
4	-23.19	0.019	-2.50	0.028	-22.87	0.023	-15.36	0.032	-26.74	0.036
5	-23.04	0.08	-2.44	0.03	-22.86	0.09	-15.27	0.03	-26.78	0.06
6	-23.01	0.02	-2.90	0.06	-22.69	0.18	-15.39	0.04	-26.61	0.08
6*	-22.98	0.01	-2.32	0.04	-22.53	0.36	-15.3	0.32	-26.35	0.06
8	-22.75	0.1	-2.40	0.05	-22.9	0.1	-15.25	0.19	-25.58	0.05
9	-22.90	0.09	-2.34	0.05	-22.67	0.17	-15.21	0.05	-26.27	0.11
10	-22.88	0.082	-2.42	0.029	-22.7	0.2	-15.08	0.072	-26.21	0.047
11	-22.99	0.02	-2.49	0.02	-22.78	0.02	-15.24	0.02	-26.81	0.06
12					-22.32	0.3	-14.85	0.26	-25.58	0.25
13	-23.05	0.014	-2.55	0.016	-22.33	0.012	-15.42	0.010	-26.83	0.011

Table 3: Evaluation of Carbon-13 Results

Intercomparison: Carbon-13 Results

LAB	NBS 18	IAEA-CO-1	IAEA-CO-8	IAEA-CO-9	LSVEC	USGS 24
	δ C-13 (‰)	δ C-13 (‰)	δ C-13 (‰)	δ C-13 (‰)	δ C-13 (‰)	δ C-13 (‰)
1	-4.96	2.52	-5.72	-46.82***	-45.99**	-15.84
2	-5.04	2.49	-5.80	-47.03	-46.47	-15.97
3	-5.07	2.44	-5.78	-47.16	-46.56	-15.91
4	-5.10	2.45	-5.81	-47.23	-46.37	-16.08
5	-4.98	2.46	-5.77	-47.28	-46.56	-16.09
6	-4.89	2.28*	-5.64	-47.42	-46.67	
6*	-5.02	2.49	-5.69	-47.56**	-46.71	
7						-16.98*
8	-4.99	2.51	-5.87	-47.04	-46.24	-16.09
9	-4.95	2.48	-5.68	-46.88	-46.58	
10	-5.06	2.46	-5.75	-47.11	-46.41	-16.11
11	-4.98	2.50	-5.70	-47.00	-46.47	-15.86
12			-6.68*	-46.30*	-45.58*	
13	-5.06	2.34**	-5.78	-47.04	-46.23	
Mean:	-5.008	2.452	-5.821	-47.067	-46.372	-16.103
Std Dev.:	0.058	0.068	0.255	0.296	0.297	0.325
(*)		2.467	-5.749	-47.131	-46.438	-15.994
		0.047	0.063	0.205	0.198	0.105
(**)		2.480		-47.092	-46.479	
		0.025		0.166	0.150	
(***)				-47.119		
				0.149		

(*), (**), (***) : Results outside of ± 2σ range rejected

Table 4: Evaluation of Oxygen-18 Results

Intercomparison: Oxygen-18 Results

LAB	NBS 18	IAEA-CO-1	IAEA-CO-8	IAEA-CO-9	LSVEC
	δ O-18 (‰)	δ O-18 (‰)	δ O-18 (‰)	δ O-18 (‰)	δ O-18 (‰)
1	-22.97	-2.36	-22.74	-16.02*	
2	-23.03	-2.52	-22.80	-15.30	-26.92
3	-22.85	-2.47	-22.49	-15.70**	-26.86
4	-23.19*	-2.50	-22.87	-15.36	-26.74
5	-23.04	-2.44	-22.86	-15.27	-26.78
6	-23.01	-2.90*	-22.69	-15.39	-26.61
6*	-22.98	-2.32	-22.53	-15.30	-26.35
8	-22.75*	-2.40	-22.90	-15.25	-25.58*
9	-22.90	-2.34	-22.67	-15.21	-26.27
10	-22.88	-2.42	-22.70	-15.08	-26.21
11	-22.99	-2.49	-22.78	-15.24	-26.81
12			-22.32	-14.85***	-25.58*
13	-23.05	-2.55	-22.33	-15.42	-26.83
Mean:	-22.970	-2.476	-22.667	-15.338	-26.462
Std Dev.:	0.109	0.146	0.187	0.271	0.456
(*)	-22.970	-2.437		-15.281	-26.638
	0.067	0.073		0.193	0.251
(**)				-15.243	
				0.153	
(***)				-15.282	
				0.093	

(*), (**), (***) : Results outside of ± 2σ range rejected

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CARBON, OXYGEN AND HYDROGEN ISOTOPIC INTERCOMPARISON OF FRUIT AND VEGETABLE JUICES

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Abstract. *Within the framework of the CEN (European Committee for Standardization) the Working Group 1 of the Technical Committee 174 "Fruit and Vegetable Juices" is in charge of developing and validating isotope analytical methods, capable to improve the athentication of fruit juices. Here we report the results of several round robins recently carried out.*

In 1991 the determination of the Carbon-13 content in fruit juice sugars was carried out. The 15 european laboratories, participating in this task are listed in Table 1.
They are mostly equipped with online combustion mass spectrometers. Sucrose from beet and cane as well as juice orange- and pineapple juice samples, all delivered by Pernod-Ricard, were analyzed along with the isotope standards NBS 22, sucrose ANU and PEF 1, granted by the IAEA.

The applied sample pretreatment of the juices according to Prof. H.L. Schmidt, TU-Munich, is shown in Fig. 1. The analyses were accomplished except in one case in triplicate and the results are given in the Tables 2 to 5.

The δ^{13}C-values were normalized against NBS-22, the mean value of which was determined by the participants as $\delta^{13}C_{PDB}$ = -29,8 ± 0,2 ‰.

From the statistical treatment of the data in compliance with ISO 5725 (Prof. G.J. Martin, University of Nantes) resulting in an average repeatability of 0,3 ‰ and an average reproducibility of 0,7 ‰, can be deduced, that sample preparation errors are of no great influence.

The ring test results can be summarized as acceptable and therefore the method was recommended as CEN standard procedure for C-13 content determinations in fruit sugars [1].

The second and third ring test concerning the determination of the Oxygen 18 and Deuterium content in fruit juice water respectively where accomplished in 1992.
The attending 17 laboratories are listed in Table 6. The orange juice- and apple juice samples were supplied by Pernod-Ricard.
The isotope standards SMOW and SLAP, obtained from the IAEA, were applied. Their GISP material was used for additional intercomparison.

Table 1:
Participants of the $\delta^{13}C$ inter-laboratory comparison and their instrumentation

No	Name *)	Organization	Location	Country	CO_2 preparation	Mass spectrometer
1	S. Brookes	Europa Scientific	Crewe	UK	On-line combustion, GC separation	Europa Tracer, direct inlet
2	H. Casabianca	Centre national de la Récherche Scientifique	Solaize	France	Microanalyser on-line	Finnigan Delta S
3	J. Fairchild/ A. Robertson	Atomic Energy Authority/Campden Food and Drink Research Association	Harwell Chipping Campden	UK	Manual combustion	VG 602, dual inlet
4	A. Filly	Laboratoire d'Hydrologie et de Geochimie Isotopique de l'Université Paris Sud	Orsay	France	Manual combustion	VG 602 C, dual inlet
5	P. Johnson	Bureau of Stable isotope Analysis	Brentford	UK	On-line combustion, trapping box system	VG SIRA II, dual inlet
6	J. Koziet	Pernod-Ricard Research Centre	Creteil	France	Manual combustion	Finnigan Delta S, dual inlet
7	B. McGaw	Rowett Res. Services	Aberdeen	UK	(11) Mc Gaw et al. Biomed MS 16(1988)269	G SIRA 12, dual inlet
8	N. Naulet	Université de Nantes	Nantes	France	a) Microanalyser, Carlo Erba (on-line) b) Manual combustion	
9	F. Pichlmayer	Österreichisches Forschungszentrum	Seibersdorf	Austria	On-line combustion GC separation	Finnigan MAT 251, dual inlet
10	J. Van der Plicht	State University	Groningen	Netherlands	Manual combustion	VG SIRA 9, dual inlet
11	F. Reniero	Istituto Agrario Provinciale	San Michele	Italy	On-line combustion, trapping box system	VG SIRA II, dual inlet
12	A. Rossmann	Technical University	Munich	Germany	Manual combustion	VG MM 903/602, dual inlet
13	A.L. Thelin	Nestlé	Lausanne	Switzerland	On-line combustion, trapping box system	Finnigan MAT 251, dual inlet
14	C. Tisse	Délégation Générale de la Concurrence, de la Consommation et de la Répression des Fraudes	Marseille	France	Microanalyser VG ISOPREP 13	VG 602 E, dual inlet
15	P. Trimborn	Neuherberg/Institut für Hydrologie	Neuherberg	Germany	On-line combustion, trapping box system	Finnigan Delta S, dual inlet

*) The laboratories are not referenced with the same numbers as in Tables 2 to 5.

Table 2: $\delta^{13}C_{PDB}$ ‰ results for orange juice sugar

Laboratory	Mean	S.D.	No. of replicates
1	-24.73	0.05	10
2	-24.17	0.15	3
3	-24.46	0.12	12
4	-24.91	0.15	9
5	-24.46	0.06	20
6	-24.64	0.11	3
7	-24.43	0.07	12
8	-24.67	0.04	8
9	-24.42	0.02	6
10	-24.56	0.03	4
11	-24.99	0.20	6
12	-24.51	0.01	3
13	-24.64	0.05	4
14	-24.57	0.07	5
15	-25.16	0.11	3

Table 3: $\delta^{13}C_{PDB}$ ‰ results for pineapple juice sugar

Laboratory	Mean	S.D.	No. of replicates
1	-12.34	0.04	10
2	-12.05	0.25	3
3	-11.89	0.07	12
4	-11.85	0.18	9
5	-12.23	0.27	17
6	-12.36	0.02	3
7	-12.15	0.08	12
8	-12.31	0.07	8
9	-12.05	0.03	6
10	-12.29	0.13	2
11	-12.37	0.10	6
12	-12.03	0.02	3
13	-11.71	0.07	4
14	-12.29	0.07	5
15	-12.56	0.19	3

Table 4: $\delta^{13}C_{PDB}$ ‰ results for beet sugar

Laboratory	Mean	S.D.	No. of replicates
1	-25.52	0.03	5
2	-24.56	0.11	3
3	-25.62	0.06	6
4	-26.05	0.13	3
5	-25.40	0.05	4
6	-25.73	0.06	3
7	-25.68	0.07	8
8	-25.52	0.03	3
9	-25.64	0.03	3
10	-25.72	--	1
11	-25.78	0.05	3
12	-25.70	0.02	3
13	-25.67	0.06	4
14	-25.66	0.06	5
15	-26.02	0.03	3

Table 5: $\delta^{13}C_{PDB}$ ‰ results for cane sugar

Laboratory	Mean	S.D.	No. of replicates
1	-11.26	0.05	5
2	-11.45	0.06	3
3	-11.07	0.10	6
4	-11.48	0.24	3
5	-11.02	0.06	3
6	-11.51	0.01	3
7	-11.27	0.09	8
8	-11.16	0.08	3
9	-11.19	0.03	3
10	-11.34	--	1
11	-11.10	0.09	3
12	-11.37	0.02	3
13	-10.76	0.22	4
14	-11.18	0.05	5
15	-11.30	0.06	3

Table 6: Participants of the inter-laboratory comparison for fruit juice water
- oxygen 18 determination (o)
- deuterium determination (d)

Name*)	Det.	Organisation	Location	Country
S. T. Brookes	o	Europe Scientific	Crewe	United Kingdom
H. Casabianca	o, d	Service Central d'Analyse CNRS	Vernison	France
J. Fairchild	o	Atomic Energy Authority	Didcot	United Kingdom
A. Filly	o, d	University Lab. Hydrogeologie	Orsay	France
H. Förstel	o	Institut für Radioagronomie	Jülich	Germany
J. F. Goiffon	o	Laboratoire Interregional	Montpellier	France
K. Habfast	d	Finnigan MAT	Bremen	Germany
P. Johnson	o, d	Bureau of Stable Isotopes Analysis	Brendford	United Kingdom
J. Koziet	o, d	Pernod-Ricard Research Centre	Creteil	France
G.J. Martin	o, d	Universite, RMN e Reactivite Chimique	Nantes	France
E. Milne	o, d	Rowett Research Institute, MS-Group	Aberdeen	United Kingdom
J. Morrison	d	VG Isotech	Middlewich	United Kingdom
F. Reniero	o	Istituto Agrario Provinciale	San Michele	Italy
A. Rossmann	o, d	Technical University Munich	Freising	Germany
A. Thelin	o, d	Nestle Ltd. Research Centre	Lusanne	Switzerland
P. Trimborn	o, d	GSF-Institut für Hydrologie	Neuherberg	Germany
J. Van der Plicht	o, d	University, Cent. for Isotop. Research	Groningen	Netherland

*) The partcipants are listed alphabetically in this Table, the numbers in Tables 7 and 8 represent a different sequence.

Table 7:
$\delta^{18}O_{SMOW}$ ‰ results for GISP water

Laboratory	Mean	S.D.	No. of replicates
1	-24.55	0.23	2
2	-24.73	0.08	3
3	-24.94	0.10	3
4	-24.62	0.00	2
5	-24.62	0.09	3
6	-24.72	0.06	3
7	-24.68	0.14	3
8	-24.75	0.13	3
9	-24.69	0.01	3
10	-24.72	0.01	2
11	-24.86	0.02	3
12	-24.61	0.01	3
13	-24.76	0.02	3
14	-24.77	0.05	3
15	-24.72	0.11	3

Table 8:
$\delta^{2}H_{SMOW}$ ‰ results for GISP water

Laboratory	Mean	S.D.	No. of replicates
1	-194.65	0.94	3
2	-190.30	0.70	3
3	-188.83	0.91	3
4	-188.17	0.42	3
5	-190.23	0.69	3
6			
7	-192.64	1.48	3
8			
9	-189.53	3.15	3
10	-189.10	0.92	3
11	-188.10	1.97	3
12	-187.30	0.36	3

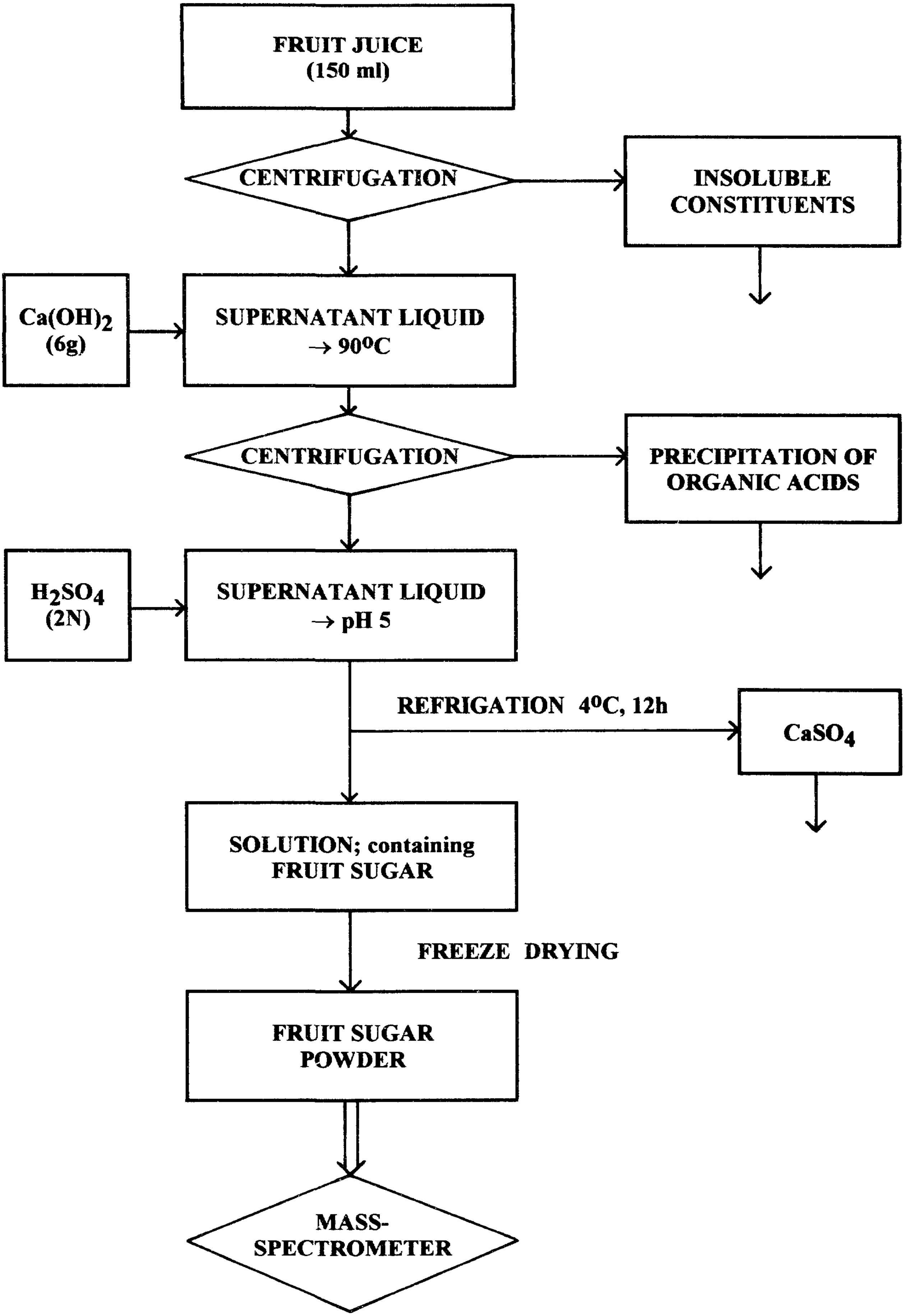

Figure 1: $\delta\ ^{13}C$ - analysis of fruit juice sugars - sample preparation

As sample preparation methods for the Oxygen and Hydrogen measurements CO_2-equilibration and water reduction, applying Uranium [2] or Zinc [3] respectively, were proposed.

Up to now, only the results of the IAEA-GISP material can be released and given in Tables 7 and 8. They agree with the mean value of $\delta^{18}O = -24,79 \pm 0,09$ ‰ obtained from a previous IAEA ring test [4].

At present two collaborative studies on the determination of D/H ratio in sugar of juices by MS or by NMR are performed.

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THE ISOTOPIC COMPOSITION OF THE GRONINGEN GS-19 AND GS-20 PURE CO_2 STANDARDS

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Abstract. *This brief note describes the production and the isotopic composition of two pure CO_2 isotopic standards, intended to be used primarily by the groups engaged in high-precision isotope monitoring of atmospheric carbon dioxide.*

Of all the application fields of isotope ratios, the measurements on atmospheric CO_2 demand the highest accuracy. This is caused by the fact that the expected trends in the isotope ratios caused by anthropogenic emissions are very small (typically ≈ -0.005‰ per year for ^{13}C), and should nevertheless be measured as accurately as possible and with a stable calibration basis over the years. Long-term observation records exist ([1],[2]), and at the present time more and more groups are setting up measurement sites of their own [3].

Since accuracy demands are so high, the intercomparison between the different groups should be of high quality too. Therefore the IAEA Hydrology Section has taken up the initiative to organise a world-wide, extensive intercomparison, dealing with all the steps from collecting the air up to the concentration and isotope ratio measurements [4]. Among the reference materials are also two pure CO_2 isotopic standards, prepared by our laboratory. This short contribution describes the production and the isotopic composition of these two CO_2 standards.

Logically, the isotope ratios of the CO_2 standards should match those of air CO_2 (being $\delta^{13}C$ around -8 ‰, $\delta^{18}O$ around 0 ‰ against VPDB-CO_2). Unfortunately, there is no CO_2 commercially available that meets these specifications. Therefore we decided to prepare a mixture of two "natural" CO_2's and one artificially enriched in ^{18}O. Table 1 shows the isotope compositions of these components, as well as their percentages in GS-19 and GS-20.

The enriched Rommenhöller has been prepared by letting 10 liters of natural Rommenhöller (component 1 in table 1) equilibrate with 100 ml of artificially (^{17}O, ^{18}O) enriched water. This water has been enriched by adding 0.4151 g water highly enriched by thermodiffusion [6],

<u>Table 1</u> *The isotope composition of the three CO_2 sources that GS-19 and GS-20 have been composed from. $^{13}\delta$ and $^{18}\delta$ are against VPDB-CO_2, using the method described by Gonfiantini [5], (see recommendation elsewhere in this volume).*

CO_2 source	$^{13}\delta$	$^{18}\delta$	% in GS-19	% in GS-20
1) Rommenhöller natural CO_2 from a well in Germany	-2.93‰	-10.76‰	81.65	77.77
2) Beer-fermentation natural CO_2 from a brewery	-28.90‰	-26.10‰	16.78	20.60
3) Rommenhöller artificially (^{18}O,^{17}O) enriched	-16.45‰	+831.7 ‰	1.56	1.63

with mass percentages : ^{16}O 47.8 %, ^{17}O 1.77% and ^{18}O 50.4%, to 99.61 g destilled tap water ($^{18}\delta \approx -7$ ‰). Obviously, the composition of this enriched water deviates very much from natural waters, also in the sense that the ^{18}O enrichment is much higher than the ^{17}O enrichment.

Theoretically, the equilibrium process would result in CO_2 having isotope ratios: $^{13}\delta = -2.93$ ‰, $^{18}\delta \approx 875$ ‰, $^{17}\delta \approx 150$‰. Enriched CO_2 in which ^{18}O and ^{17}O would be enriched equivalently, such that :

$$^{17}R_{sample} / {}^{17}R_{VPDB\text{-}CO_2} \approx \sqrt{(^{18}R_{sample} / {}^{18}R_{VPDB\text{-}CO_2})}$$

would give $^{18}\delta = 875$‰ , $^{17}\delta \approx 370$ ‰ , so the third component to GS-19 and GS-20 has a huge ^{17}O "anomaly". Since all algorithms for computing the $^{13}\delta$ and $^{18}\delta$ from the measured $^{45}\delta$ and $^{46}\delta$ assume some kind of relation between ^{17}O and ^{18}O, based on their terrestrial ratio, the $^{13}\delta$ values of this artificial CO_2 will be computed in an erroneous way. In the Gonfiantini algorithm this will lead to a deviation of ≈ -14.3 ‰ in the $^{13}\delta$ value (being ≈ 6.5% of the ^{17}O anomaly). The measurements in table 1 confirm this: although the ^{13}C / ^{12}C ratio itself is not influenced by the equilibrium process, we find $^{13}\delta = -16.45$ ‰ for the enriched Rommenhöller, or equivalently a mis-measurement of -13.52‰. This is indeed what we expect from the (necessarily not very accurate) computation above.

Of course the influences on GS-19 and GS-20 are much more limited, since only 1.56% and 1.63% of component 3 is used in GS-19 and GS-20, respectively. Still, the ^{17}O anomaly causes a $^{13}\delta$ deviation of -0.21 ‰ on GS-19, and -0.22 ‰ on GS-20.

The above does not implicate that GS-19 and GS-20 are not a good choice for intercomparison standards. On the contrary, although the isotopic composition as computed by the Gonfiantini algorithm from $^{45}\delta$ and $^{46}\delta$ measurements does not resemble the true isotopic composition of the gases, everyone measuring $^{45}\delta$ and $^{46}\delta$, **and using the Gonfiantini algorithm**, should get to the same results. Even more so, the above examples stress the fact that unification of the computation is essential, and that deviations between the results of different groups, both with high quality preparation techniques and accurately calibrated mass spectrometers can nevertheless be unacceptably high, due only to the use of different algorithms!

The paper by Alison et al (elsewhere in this Tecdoc) recommends the use of the Gonfiantini algorithm, and gives examples with which one can check the algorithm used (mostly an integral part of the mass spectrometer software).

Using the Gonfiantini algorithm, the CIO's best values for GS-19 and GS-20 are:

GS-19:	$^{13}\delta = -7.502$ ‰	$^{18}\delta = -0.193$ ‰
GS-20:	$^{13}\delta = -8.622$ ‰	$^{18}\delta = -0.991$ ‰

The absolute calibration error is estimated to be ± 0.025‰ for $^{13}\delta$ and ± 0.04‰ for $^{18}\delta$. Our calibration is based on the use of NBS19, NBS18 and two well-known local carbonate standards, as well as on 3 local pure CO_2's. The ratio of GS-20 relative to GS-19 is known much more accurately:

GS-20 rel. to GS-19: $^{13}\delta = (-1.128 \pm 0.011)$ ‰, $^{18}\delta = (-0.798 \pm 0\ 016)$ ‰.

These numbers are to a high extent calibration-insensitive.

There is about 200 liters in stock of each of the gases, in stainless steel containers with stainless steel Swagelock valves, at ≈ 45 Bar. Small (200 ml) stainless steel cylinders, at about 2 Bar, with stainless steel Swagelock valves[1], are available for distribution. There is no indication of spread between the different cylinders.

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[1] Several bottles have been distributed already. Those had brass Swagelock valves.

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A REPORT ON THE δ^{18}O MEASUREMENTS OF THE IAEA CELLULOSE INTERCOMPARISON MATERIAL IAEA-C3

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Abstract. *In this brief note we report the results of δ^{18}O analyses of the IAEA cellulose intercomparison material IAEA-C3, performed by five laboratories.*

The stable isotopic composition of organic material from terrestrial and lacustrine sources have provided valuable environmental information detailing various climatic and hydrologic changes that occurred during the past. Investigators from around the world employ different techniques to measure the oxygen, hydrogen and carbon isotopic compositions in organic material from which they infer environmental information. However, due to procedural intricacies in the techniques used, there is a potential for inherent variations in the isotopic measurements from different laboratories. The magnitude of these variations, and their subsequent effect on inferred environmental information, was the subject of a few casual discussions during an International Atomic Energy Agency (IAEA) meeting in Vienna, Austria, during April 1993[1]. These discussions resulted in an agreement, among some investigators, to test the extent to which isotopic results are bias to technique and procedure while in the process establishing a cellulose standard for isotopic studies using organic materials. Here we report the initial δ^{18}O cellulose results from investigators using various techniques.

The material used,cellulose intercomparison material IAEA-C3, was provided by Dr. W. Stichler at the IAEA in Vienna. Aliquots of the sample were sent from the University of Waterloo to other institutions equipped to measure the stable isotope composition of organic materials. They included: 1) GSF-Neuherberg, Germany; 2) Universität Bern, Switzerland; 3) The Weizmann Institute, Israel; 4) Cambridge University, UK and 5) The Oak Ridge National Laboratory, USA.

The measurement results are given in Table 1. At this time we reserve comment on the variability of the results pending further analysis and discussion at a future IAEA meeting dealing with isotopic techniques and environmental change (possibly in the spring of 1995). In the meantime it is hoped that these preliminary results will inspire additional δ^{18}O, as well as δ^{2}H and δ^{13}C, measurements from the Cellulose IAEA-C3. We welcome participation from other institutions not originally involved in this collaborative study.

Table 1.

Investigators	Affiliation	Technique	Measurements	ave. $\delta^{18}O$ ‰
W.M. Buhay, B.B. Wolfe, R.J. Elgood	University of Waterloo	Nickel Pyrolysis[2]	n = 6	31.8 ± 0.14
M. Saurer & S. Borella	Universität Bern	Nickel Pyrolysis[3]	n = 7	32.2 ± 0.11
P. Trimborn	GSF Neuherberg	Nickel Pyrolysis[3]	n = 5	31.3 ± 0.19
D. Yakir	The Weizmann Institute	Mercuric Chloride[4]	n = 3 n = 3	31.4 ± NA 31.7 ± NA
V.R. Switsur	Cambridge University	Mercuric Chloride[5]	n = 4	32.7 ± 0.13

Note: Results from the Oak Ridge National Laboratory are not available presently.

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USE OF PLATINIZED MAGNESIUM AS REAGENT REPLACING ZINC IN HYDROGEN ISOTOPE ANALYSIS

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Abstract

Platinized magnesium has recently been proposed as a new reducing agent for the conversion of small quantities of water to hydrogen in a flame-sealed borosilicate glass tube at 400°C for isotopic analysis. The reagent, Mg-Pt, in contrast to zinc can be prepared in every laboratory by coating of a magnesium granulate with a thin layer of platinum by reaction with $H_2PtCl_6*6H_2O$ dissolved in acetone-ether mixture. Excellent reproducibility of the isotope ratios in hydrogen gas prepared from water samples has been obtained at proportion 4 μL of water to 120mg of the reagent.

Introduction

Mass spectrometric analysis of hydrogen isotope ratio is recently performed in most laboratories on hydrogen gas produced by reduction of small quantities of water with zinc [1]. The reagent used in this method is AnalaR zinc shot supplied by Hopkin and Williams, or BDH Chemicals, so far. It is not clear why zinc from other suppliers, e.g. Merc, produces wrong results owing to apparent incompletness of the reaction [2,3]. Although the zinc method has become matured, Tanweer et al. [4] have found optimal conditions for water reaction by Zn (BDH Chemicals) to be 460°C for the conversion temperature, and 10 x the stoichiometric amount of zinc. These conditions slightly differ from those given in the original paper [1].

In the mean time two Chinese scientists Jin Deqiu and Wang Zhengxin [5] have published a new approach in hydrogen preparation for isotope analysis. They applied Mg powder activated by a very thin layer of Pt on its surface. In this paper we describe this method in detail. Our experience confirmed a tremendous reactivity of the platized magnesium and thereby excellent reproducibility of isotopic composotion of hydrogen obtained with this reducing agent.

It is the purpose of this report to inform the scientific community about use of platinized magnezium for hydrogen preparation, particularly because BDH Chemicals is no more able to supply zinc as suitable as it was previously [6]. Moreover, optimum conditions have been found which differ from those given in the Chinese paper [5].

Reagents

Two reagents are used: a comercial magnesium in form of granulate 0.5 to 2 mm and chloroplatinic acid, $H_2PtCl_6*6H_2O$, dissolved in waterless acetone-ether mixture which is used for magnesium coating with platinum black.

Magnesium is highly base metal. It reacts with water much below 100°C, but a thin layer of magnesium oxides once formed slows down this reaction. With boiling water it yields rapidly magnesium hydroxide, $Mg(OH)_2$. For this reason magnesium cannot be used for *total* decomposition of water at 100°C. Although $Mg(OH)_2$ could be decomposed at about 550°C [7], however such a high temperature exclude use of borosilicate glass (pyrex) for reaction ampoules. Jin Deqiu and Wang Zhengxin [5] have found that Mg coated with platinum black (Mg-Pt) yields *total* decomposition of water at 400°C. Probably the Mg-Pt is so reactive that no formation of the hydroxides proceeds.

Chloroplatinic acid is prepared by dissolving of platinum in *aqua regia* in a ceramic dish. For this purpose waste pieces of platinum (e.g. remainings of reaction vessels, pieces of thermocouple wire etc.) can be used after their purification and roasting in a furnace or flame. When platinum is dissolved completly, the solution in heated continuously while small portions of concentrated HCl and water are added alternately to the remaining syrup-like solution. The chloroplatinic acid being prepared is then cooled down to room temperature if a sample taken on a glass rod quickly solidifies during its cooling down. (The melting point of $H_2PtCl_6*6H_2O$ is 60°C, while at 110°C starts to decompose yielding Cl_2, H_2O, and $PtCl_2$). Then the reagent is transferred to a tightly closed bottle made of a dark glass. The remainings are rinsed off from the ceramic dish by acetone-ether being mixed in proportion 1:5. Both solvents should be distilled prior to use.

To prepare 60 mL of the acetone-ether solution one should take 10 mL of acetone, 50 mL of ether and 100mg $H_2PtCl_6*6H_2O$. This quantity of the solution one btains from 40mg of platinum. The bottle containing the solution of $H_2PtCl_6*6H_2O$ is n tightly closed against loss of solvents and a contact with air humid (the reagent is hygroscopic).

Preparation of Mg-Pt

The granulate is sieved to select a fraction of 0.5 to 1.0 mm. If magnesium ribbons are used, then they are cut into small pieces (e.g. 1mm x 5mm) before their roasting in order to have more convenient material to do in weighting and filling of the ampoules. Then the magnesium granulate is roasted under vacuum at 550°C during 2 hours in order to desorb water and hydrogen.

The vacuum roasted magnesium granulate is then coated by a thin layer of platinum in the following way: 28g of Mg granulate is dropped into a flask up to the end of the reaction (gas bubbles disappear). Then the solution is poured off into the original bottle for further use, whereas the Mg-Pt is dried gently with the stream of hot air until complete disappearance of any smell of the organic solvents. The reagent, Mg-Pt, prepared in this way is stored in a dark and hermetic vessel. Prior to its use, the Mg-Pt is outgased under vacuum (10^{-2} mbar) at 400°C during one hour.

Preparation of hydrogen

The further preparation steps of a small water sample (4 to 10 μL) to yield pure hydrogen gas for the isotopic analysis are identical as in the zinc method [1] with the exception of heating condition. The ampoule containing a water sample with the Mg-Pt reagent is heated to 400°C (instead 460°C in the case of zinc reagent) during one hour. Jin Deqiu and Wang Zhengxin used 200mg of Mg-Pt for the decomposition of 15 μL of water. We reduced these amounts about three times conserving the proportion of the reagent to water [8]. In this study the quantity of water was 4μL but the amount of the reagent varried from 20 to 200mg in order to find optimal mass ratio.

Results and discussion

The isotope ratios, D/H, were determined on cycloidal mass spectrometer with dual inlet and dual collector systems [9]. The results obtained for a distilled water sample are shown in Table 1 and plotted in Fig.1 as permil deviations from D/H of reference H_2 gas. The best accuracy and reproducibility of the new method is somewhat above the recent precision of the mass spectrometer ($1\sigma=0.2$ ‰) at mass of the reagent of 120 to 140mg.

Table 1. The results obtained for 4μL water sample at different mass of the reagent.

Mass (mg)	δD(‰)	Comments
20	not determined	lack of reaction
40	-183.0	extremaly little fraction reacted
60	-103.0	a major fraction reacted
80	-57.5	apparently complete reaction
100	-45.0	total decomposition of water
120	-42.2	total decomposition of water
140	-41.7	total decomposition of water
160	-32.3	total decomposition of water
200	-25.3	total decomposition of water

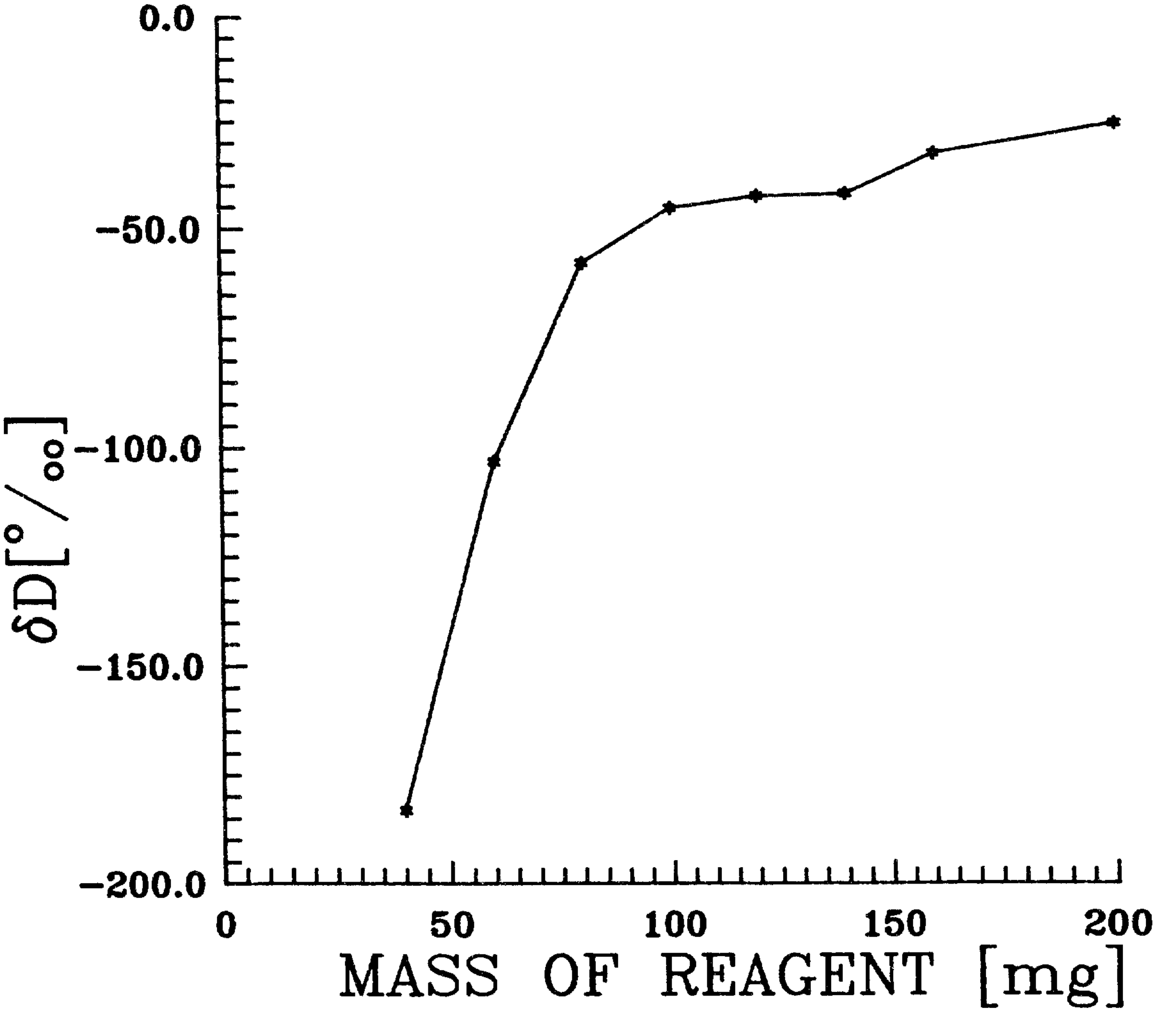

Fig. 1. A plot of δD values of H_2 prepared from 4µL of water versus mass of the reagent.

We do hope that due to better reactivity of platinized magnesium than that of zinc, Pt-Mg will be more effective in the case of analysis of brines and hydrous salts. Such materials are extremely cumbersome in isotope analysis and special methods have been developed recently: Horita described a new approach based on H_2-water equilibration with reusable Pt catalyst [10], while Horita and Gat [11] removed Ca^{2+} and Mg^{2+} from natural brines in form of unsoluble carbonates prior to azeotropic distillation of all residual waters which was then prepared by the standard method. Recently Tanweer [12] developed a procedure for brines and hipersaline aqueous solution without removal of alkaline earth metal cations, in which mached amounts of zinc have to be taken per analysis.

Acknowlegements

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CARBON ISOTOPE (^{14}C, ^{12}C) MEASUREMENTS TO QUANTIFY SOURCES OF ATMOSPHERIC CARBON MONOXIDE IN URBAN AIR*

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ABSTRACT. Atmospheric air samples were collected during the Winter of 1989-90 in Albuquerque, NM USA, for carbon isotope (^{14}C, ^{12}C) analysis of carbon monoxide (CO). An experimental sample design was prepared to target periods when the concentration of CO exceeds the 9 μL/L (volume fraction), 8 hour National Ambient Air Quality Standard (NAAQS) and during periods of attainment. Sampling sites, time of day, sampling duration, and meteorology were carefully considered so that source impacts be optimal. A balanced sampling factorial design was used to yield maximum information from the constraints imposed; the number of samples was limited by the number of sample canisters available, time, and resources. Carbon isotope measurements of urban air, *"clean-air"* background from Niwot Ridge, Colorado, average (wood) logs and oxygenated-gasolines were used in a 3-source model to calculate the contribution of woodburning to the total atmospheric CO burden in Albuquerque. Results show that the estimated fractional contribution of residential wood combustion (Θ'_{RWC}) ranged from 0 to 0.30 of CO concentrations corrected for *"clean-air"* background. For these same samples, the respective CO concentrations attributed to woodburning range from 0 to 0.90 μmol/mol (mole fraction), well below the NAAQS. In all cases, fossil CO is the predominant source of ambient CO concentrations ranging from 0.96 to 6.34 μmol/mol. A final comment is made on the potential of fossil CO measurements as an indirect tracer of atmospheric benzene, relevant to exposure risk estimates of motor vehicle emissions and occupational health and safety standards.

1. INTRODUCTION

1.1. Carbon isotopes (^{14}C, ^{12}C) for tracing bio- and fossil-mass combustion sources

Radiocarbon, a cosmogenically produced radionuclide with a half-life of 5730 years, has the unique capability of quantifying the relative contribution of bio- and fossil-mass combustion sources. The degree to which these two pure sources can be resolved is nominally 2-orders of magnitude, constrained by the $^{14}C/^{12}C$ ratio of contemporary carbon at ~1.4 x 10^{-12} (modern carbon = 1.2 x 10^{-12}) and the ratio of fossil carbon at ~1 x 10^{-14}, including a chemical process blank of ~1% modern carbon. The power to discriminate, *e.g.*, carbon monoxide (CO) from woodburning *vs* CO from motor vehicle emissions, is further limited by the uncertainty of

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knowing the ^{14}C abundance (age) distribution of the sources. Estimates of the average age of logs burned are determined by integrating the historical record of atmospheric $^{14}CO_2$ over the mean calendar years of growth [1,2]; the ^{14}C record is obtained from direct ^{14}C measurements of individual tree-rings [*e.g.*, ref. 3] and of atmospheric CO_2 [*e.g.*, ref. 4]. For ^{14}C tracer studies where woodburning and motor vehicle emissions are the predominant sources of carbonaceous gases or aerosols, a simple 2-source model can be used to calculate the fractional contribution from each source given a measure of total ^{14}C of the chemical fraction of interest. For example, this approach has been applied to several studies designed to quantify sources of aerosols in urban airsheds during winter months [*e.g.*, ref. 2,5].

However, in the case of CO, aside from wood and motor vehicle emissions that contribute to wintertime concentrations, there is a natural *"clean-air"* background component of CO with a relatively low concentration (nominally 50 nmol/mol), but with a ^{14}C abundance several times greater than that of modern carbon. This "hot" CO is a result of primary ^{14}CO produced by cosmic ray interaction with ^{14}N that produces ^{14}C with rapid oxidization to CO [6]. Its $^{14}C/^{12}C$ ratio depends on the extent that this cosmogenic CO mixes with stratospheric and tropospheric CO. This background CO component, although small, can be significant in urban air since its ^{14}C activity is greater than that of modern carbon. Therefore, a model designed to estimate the impact of woodburning and motor vehicle emissions on total CO concentration must take into account the effect of a *"clean-air"* CO background.

1.2. Sources of wintertime carbon monoxide emissions - Albuquerque, NM USA

Over the past decade during the winter months, the City of Albuquerque, NM, (35.05 °N, 106.40 °W; elevation of 1.6 km) has failed to comply with the U.S. Environmental Protection Agency's (EPA) National Ambient Air Quality Standard (NAAQS) for CO of 9 μL/L over an 8-hour period. Results from emission inventories conducted in the past have suggested that the dominant sources of CO are residential wood combustion (RWC) and motor vehicle (MV) emissions [7]. These conclusions were further supported by a winter aerosol study (1984-85) of Albuquerque using fine-particle K and Pb concentrations as surrogate tracers to estimate CO contributions from RWC and MV emissions, respectively [8]. The results indicated that MV emissions were responsible for ~75% of the ambient CO concentration while RWC accounted for the remainder. Limitations to this indirect tracer technique are discussed by Currie *et al.* [9]. During this same period, ^{14}C measurements of CO fractions separated from six nighttime (1600-0200) whole air samples revealed a median RWC contribution of 30% having a range from 11% to 63% [10,11]. These results verified that RWC was a significant source of CO to the urban airshed and that further studies were necessary to consider source contributions during both day and night, as well as factors, *e.g.*, meteorology, that influence the accumulation of CO at ground level.

In an attempt to comply with the NAAQS, several local and federal controls have been instituted over the past 10 years. It was not until 1988 that the number of annual exceedances dropped significantly due in part to three likely factors: a cleaner vehicle fleet, the mandatory use of oxygenated fuels - ethanol and methyl tertiarybutyl ether (MTBE), and the implementation of enforced designated *no-burn* days, the latter based on a meteorological forecast 24-hours in advance. In light of the implementation of *no-burn* days, a second ^{14}CO study was funded by the City of Albuquerque, Environmental Health Department, to re-evaluate the impacts of RWC and MV emissions on ambient CO concentrations. Constrained by cost and resources, a factorial (sampling) design including a few replicates and controls was constructed to obtain the most information from 10 ambient samples. A three-factor two-level full factorial design included the following: 1) sampling location, residential *vs* traffic sites, 2) time-of-day, daytime *vs* nighttime, and 3) forecast meteorology, dynamic *vs* stagnant air mass, to cover effectively time-space. Two additional samples (replicates) were collected under conditions that were more likely to favor high woodburning CO emissions. For model validation and quality control purposes, ^{14}C ages were also determined on the following source samples: 1) an ambient underground parking garage (UPG) sample collected during the early morning (0600-0900) on a weekday, 2) log cross-sections of pinion pine and juniper wood, and 3) two composite samples each of ethanol- and MTBE-gasoline.

2. EXPERIMENTAL SECTION

2.1 Field sampling apparatus

Integrated air samples were collected in 32 L steel canisters. An in-line diaphragm (compressor) pump supplied filtered air to a flow controller set at ~200 mL-min^{-1} to obtain ~303 kPa (abs) in the canister over 8 hours. An MSA®[1] particulate filter, having an efficiency of 99% for particles 0.3 μm diameter and larger, was used to remove particles from the air stream. Outputs from a calibrated flow meter and a CO concentration monitor were recorded continuously on a strip chart recorder while sampling.

2.2 Carbon (^{12}C) composition

Carbon monoxide concentrations were determined by scrubbing the sample of CO_2 and H_2O with pre-columns of Ascarite® and Aquasorb®, respectively, followed by gas chromatography (GC) using a 5Å molecular sieve column, a methanation system for converting CO to CH_4, and a flame ionization detector. Concentrations are reported for dry conditions (H_2O and CO_2 removed) in μmol/mol along with the ***standard uncertainty***[2] for v = 2-5 degrees of freedom (Table I). The calibration curves were based on responses from NIST CO and CH_4 Standard Reference Materials (SRMs). Standards of CO and CH_4 at the 10 μmol/mol level (exact concentration listed below) were used to determine the efficiency of the Ni catalyst for converting CO to CH_4 for flame ionization detection; responses from CH_4 SRMs at the 1 and 4 μmol/mol levels were used to expand the calibration curve to include the entire sample concentration range. The following standards were used to obtain sample concentrations based on dry gas: SRM 2612a CO in air, 9.70 ± 0.15 μmol/mol, *"primary"* gravimetric CO standard X-138329 in air, 16.21 ± 0.02 μmol/mol, SRM 1658a CH_4 in air, 0.98 ± 0.01 μmol/mol, SRM 1659a CH_4 in air, 9.79 ± 0.08 μmol/mol, and SRM 1660a CH_4 in air, 3.88 ± 0.04 μmol/mol.[3]

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[1] Certain commercial equipment, instruments, or materials are identified in this paper to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

[2] *All uncertainty estimations in the text and Tables, unless otherwise noted, are* ***combined standard uncertainties*** ***(u_c, estimated standard deviation)*** *obtained by combining individual* ***standard uncertainties (u, standard errors)*** *using* ***law of propagation of standard deviations*** *according to Ku, H.H. [12] with nomenclature defined by Taylor and Kuyatt [13]. Where appropriate, degrees of freedom (ν) are reported.*

[3] *All uncertainties for gas Standard Reference Materials are reported as 95% confidence intervals.*

TABLE I. SAMPLE VOLUME, CO CONCENTRATION, RECOVERY, AND RADIOCARBON (f_M) RESULTS

Sample	Vol. Proc. [L,STP]	CO (u,ν) [μmol/mol]	Rec. Vol. (u_c) [μL,STP]	Chem. Rec. [%]	f_M	f_M cor.
3	87	5.31 (0.06,2)	490 (6)	107	0.39	0.34
6	84	2.42 (0.02,5)	223 (3)	110	0.42	0.33
7	79	1.96 (0.04,3)	170 (2)	110	0.45	0.38
8	82	6.31 (0.03,2)	554 (6)	107	0.20	0.14
9	81	1.91 (0.01,2)	176 (2)	115	0.60	0.52
UPG	71	12.9 (0.10,3)	913 (10)	100	0.16	0.16
10	83	3.60 (0.03,5)	326 (4)	109	0.38	0.30
11	85	3.82 (0.03,5)	343 (4)	107	0.36	0.32
12	77	1.37 (0.01,2)	120 (1)	115	0.67	0.59
13	74	1.34 (0.01,2)	113 (1)	115	0.74	0.67
14	76	1.40 (0.01,5)	122 (1)	115	0.59	0.50

Sample - sample identification, underground parking garage (UPG) sample
Vol. Proc. - volume of air (wet) processed in Liters at STP
CO - total carbon monoxide concentration (dry), standard uncertainty (u), number of degrees of freedom (ν)
Rec. Vol. - volume of CO_2 (μL) recovered and combined standard uncertainty (u_c) from the CO fraction
Chem. Rec. - recovery of the CO fraction in percent with u_c ranging from 2 to 5%. See text for discussion of a positive bias inferred from recoveries >100%.
f_M - uncorrected fraction of modern carbon defined by the $^{14}C/^{13}C$ ratio signal of the CO fraction (as Fe-C) relative to 0.95 times the $^{14}C/^{13}C$ ratio signal of the NIST Oxalic Acid Radiocarbon Dating Standard Reference Material (SRM) 4990B. The u_c of f_M is ±0.01 based on weighted 1σ-Poisson counting statistics and the AMS target blank of $f_M = 0.01$ for as little as 65 μg C.
f_M cor. - f_M of the CO fraction corrected for blank CO_2, *i.e.*, excess CO_2, due to an inefficiency of separating all the atmospheric (sample) CO_2 in the traps #1 and #2. The u_c of f_M cor. ranges from 0.02 to 0.04. See text for details regarding the correction of ^{14}C data for this excess CO_2.

Separate GC analyses were performed using the same system to obtain CO_2 concentrations for quality assurance of the separation process. Similarly, H_2O was removed prior to CO_2 separation on a 3.6 m length x 3.2 mm diameter Poropak Q® column. Carbon dioxide SRMs and *"primary"* standards at ambient levels were used to determine sample concentrations. Samples had been stored at ~20 °C for ~10 months before GC analysis.

2.3 Separation of CO from whole air

The approach for chemical separation of the CO from whole air is based on the work of Klouda and coworkers [10,14]. A gas separation (GS) system has been designed to separate simultaneously the following chemical fractions from 0.1 m^3 whole air: 1) low vapor pressure volatile organic compounds *(LVP-VOCs)* and H_2O, 2) high vapor pressure VOCs *(HVP-VOCs)*

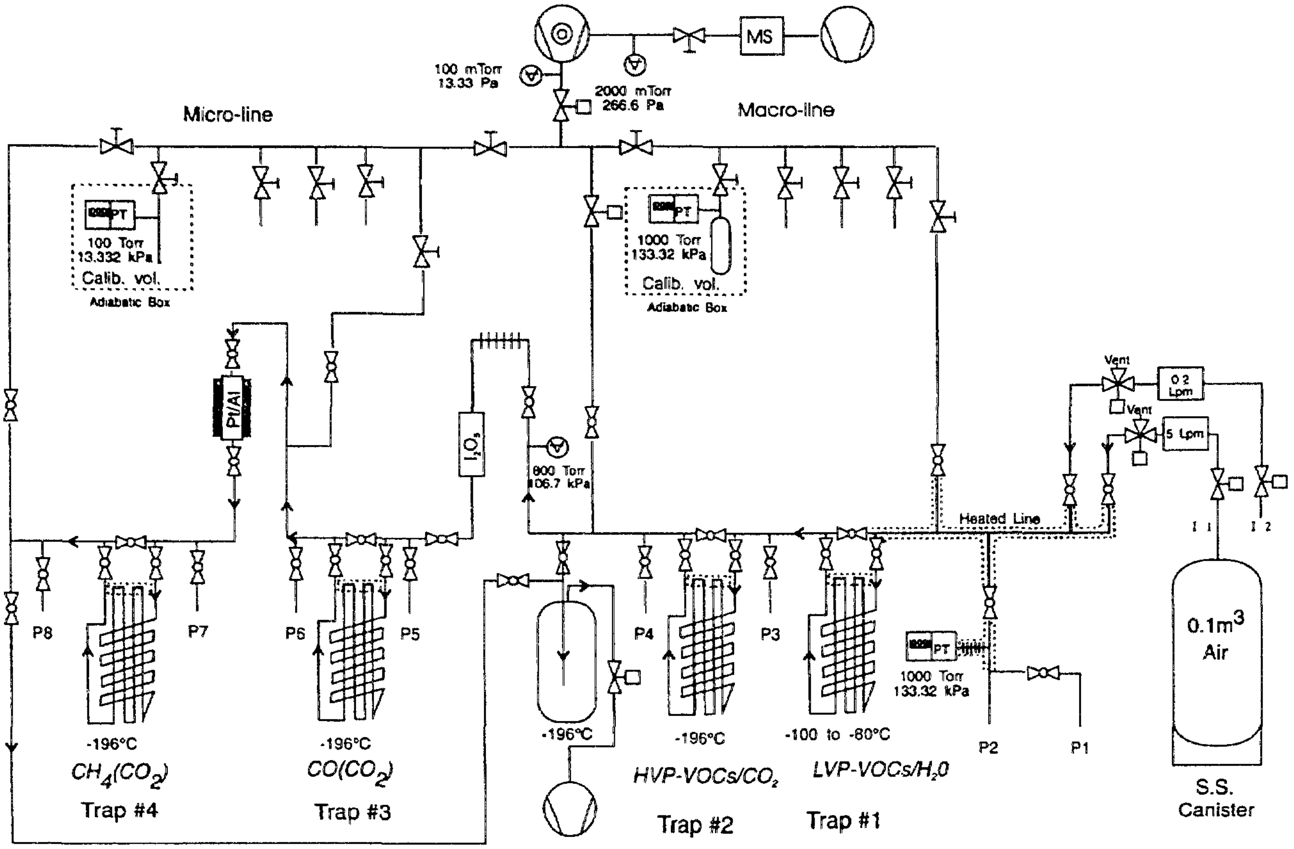

Figure 1: Schematic diagram of the NIST Gas Separation Facility. Lower half of diagram is the manifold for separating carbonaceous gases from whole air, from right to left: 1) Trap #1 was designed to collect low vapor pressure (LVP) volatile organic compounds (VOCs) and H_2O at nominally -78 °C. For this study, trap #1 was operated at -196 °C to remove the CO_2 fraction. 2) Trap #2 is operated at -196 °C to collect high vapor pressure (HVP) VOCs and traces of CO_2 that pass through trap #1 as aerosol. 3) Trap #3 is operated at -196 °C to collect CO_2 from the oxidation of CO over Schütze Reagent. 4) Trap #4 is operated at -196 °C to collect the CH_4 fraction as CO_2 following its oxidation over the high temperature catalyst, Pt on alumina at ~830 °C. The upper half of the system, stainless steel vacuum lines, is designed for manometric determination of the recovered gases in calibrated volumes.

and CO_2, 3) CO oxidized to CO_2, and 4) CH_4 oxidized to CO_2. A schematic diagram of this system is illustrated in Figure 1 and described in detail elsewhere [14]. The following description of the system emphasizes the separation of the CO fraction from 0.1 m^3 of air.

The lower half of the GS system is the sample processing section made of glass tubing with primarily glass valves. This section contains flow controllers, traps for collecting condensible gases at cryogenic temperatures, a packed column of Schütze Reagent (I_2O_5 on silica gel) to oxidize CO to CO_2 at room temperature, and a packed column of Pt on alumina pellets to oxidize CH_4 to CO_2 at ~830 °C. A reference gas mixture or ambient air sample, previously analyzed for gas composition, is adapted to one of the two inlet ports (I1 or I2) of the system. For most experiments, inlet I1, with a 0-5 L-min^{-1} flow controller, is used at a flow of 0.5 L-min^{-1}. The 0-0.2 L-min^{-1} flow controller is for processing He when evaluating the blank or for on-line dilution of NIST high concentration (µmol/mol) SRMs. For experiments reported here, trap #1, normally maintained at *ca.* -78 °C for isolating *LVP-VOCs* and H_2O, is operated at -196 °C to condense the bulk of the CO_2. Trap #2 is operated at -196 °C to collect *HVP-VOCs* and traces of CO_2 that pass through trap #1 as aerosols. Trap #3 is operated at -196 °C to recover CO_2 after the selective oxidation of CO to CO_2 over Schütze Reagent at room temperature. Finally, although not relevant to this study, trap #4 is maintained at -196°C to collect CO_2 and H_2O from the high temperature catalytic oxidation of CH_4 to CO_2 and H_2O for isotope measurements of CH_4. Sample fractions as CO_2 are individually cryo-transferred to the appropriate section of the upper manifold for manometry. The combined standard uncertainty of the recovered volume is 1.2% based on the volume determination assuming Ideal Gas behavior. This uncertainty considers the calibration of the pressure transducer, the containment volume, and the temperature probe. Samples are stored in break-seals to await the preparation of AMS targets for ^{14}C analysis.

The GS system is evaluated by processing NIST SRMs, gravimetrically prepared mixtures, and reagent He under dry conditions with and without CO_2 present, to estimate the recovery of the CO fraction and blank. As a measure of recovery, the volume measurement of each fraction is compared to the expected volume determined from the concentration of CO in the sample or standard and the volume of gas processed. For samples, the mass of air processed, obtained from the canister weight before and after processing, and the ambient air density are used to calculate the volume of air processed and is expressed in liters of moist air at standard conditions (STP), 101.3 kPa (abs) and 273.15 K (Table I). The moist-air density of each sample is determined from density tables given the average ambient temperature, barometric pressure, and dew point during sampling with subsequent conversion to STP. The combined standard uncertainty for the processed volume is 1%. Any loss of H_2O to the walls of the canister while at laboratory temperature (~23 °C) should be insignificant.

The combined efficiency for oxidation of CO to CO_2 and cryogenic trapping of CO_2 is 101.1 ± 0.4 % *(u, ν=5)* based on the above mentioned controls. The equivalent ***blank*** (excess CO_2) of the CO fraction is 2.3 ± 0.8 µL *(u, ν=13)* at STP. The yield estimates, for the samples after 2.5 years of storage prior to processing, are reported in Table I with individual combined standard uncertainties ranging from 2-5% based on the uncertainties of the total volume of CO_2 recovered, the CO concentration, and the volume of air processed. The excess CO_2 is relatively small for the control experiments, but is significant for the samples processed, average of 20 ± 3 µL *(u, ν=10)* at STP. This average bias from CO_2 cross-contamination amounts to 10 ± 1% *(u, ν=10)* of the recovered volume for samples with concentrations ranging from 1.3 to 12.9 µmol/mol. The total carbon recovered in the CO fraction for these samples ranged from 61 to 491 µg C with an average blank (bias) of 11 ± 2 µg C *(u, ν=10)*. The ^{14}C results are corrected for this bias; details are described in Section 2.4. *The sample recoveries reported in Table I are greater than 100% possibly because of frequent major swings in temperature, e.g., 90 °C to 200 °C, at the heated zone of trap #2; designed to optimize CO_2 collection by preventing the loss of CO_2 as aerosol, but in fact contributed to the inefficiency in separating the CO_2 fraction completely.* By replacing trap #2 with a Russian Doll trap collection efficiencies for CO_2 are expected to be consistently 100% [15].

2.4 Radiocarbon measurements

Once the CO fraction is selectively oxidized to CO_2 and quantified by manometry, it is catalytically reduced to graphite with hot Zn and Fe wool and fused to an Fe-C solid solution for measurement of the $^{14}C/^{13}C$ ratio [16]. Accelerator mass spectrometry $^{14}C/^{13}C$ ratio measurements were performed at the NSF Facility for Radioisotope Analysis, University of Arizona, Tucson. Details of the measurement process have been reported by Linick *et al.* [17].

The sample $^{14}C/^{13}C$ ratios were referenced to the measured $^{14}C/^{13}C$ ratio of the NIST Standard Reference Material (SRM) 4990B Oxalic Acid [HOx(I)] for radiocarbon dating with a $^{13}C/^{12}C$ abundance ($\delta^{13}C$) of -19 ‰ and are reported as the fraction of modern carbon (f_M) according to Equation 1 below (Table I):

$$f_M = \frac{^{14}C/^{13}C_{[\text{sample CO}]}}{0.95 \times {}^{14}C/^{13}C_{[\text{HOx(I)}]}} \qquad \text{Eq. 1}$$

Modern carbon activity is defined as 0.95 times the activity of HOx(I) referenced to $\delta^{13}C$=-19.0 ‰ which is approximately equivalent to the activity of 1890 wood. Normally, f_M is defined in terms of $^{14}C/^{12}C$ ratios corrected to reference $\delta^{13}C$ values. However, since $\delta^{13}C$ measurements were not obtained for these samples, $^{14}C/^{13}C$ ratios of sample and HOx(I) as stated above closely approximate f_M to within a few percent of values otherwise corrected for $\delta^{13}C$. Quality control of the isotope measurement process is best determined from f_M calculated from the measurement of SRMs 4990B and 4990C [HOx(II)]; the latter is also oxalic acid with an activity about 34% greater than SRM 4990B. The certified f_M (consensus) value for these two SRMs when calculating f_M, *i.e.*, $HO_x[II]/(0.95*HO_x[I])$, is 1.3588 ± 0.0005 (*u*) based on a series of observations from 13 independent laboratories [18]. The results of $HO_x[II]/(0.95*HO_x[I])$ measurements for this study were within 2% of the consensus value for sample sizes ranging in mass from 70 µgC to 320 µgC. The dead (^{14}C=0) control, used to represent the AMS target blank, is the NIST Reference Material (RM) 21 Graphite. Target blanks in terms of f_M, *i.e.*, $RM21/(0.95*HO_x[I])$, range from 0.014 ± 0.001 for 65 µgC to 0.008 ± 0.001 for 170 µgC. These measured standard and blank values have combined standard uncertainties based on weighted 1σ-Poisson counting statistics.

Since the f_M results of the CO fractions contain a significant contribution from cross-contamination of atmospheric sample CO_2, f_M measurements are corrected given the ^{14}C and ^{12}C abundances of this excess CO_2 according to the following equation:

$$f_M \text{ cor.} = \frac{f_M - [\Theta_{BLK} \cdot f_M(BLK)]}{(1 - \Theta_{BLK})} \qquad \text{Eq. 2}$$

where Θ_{BLK} is the fractional amount of CO_2 in excess of the amount expected for the CO fraction. The blank CO_2 is assumed to have a fraction of modern carbon [f_M(BLK)] resulting from two sources: 1) from background atmospheric CO_2 with a concentration of 355 µmol/mol and $f_M \approx 1.15$ [4] and 2) CO_2 from pollution sources making up the amount of CO_2 in excess of background concentration. The pollution CO_2 is assumed to be composed of 50% RWC and 50% MV emissions with bounds for uncertainty based on the extreme values; the excess being entirely from RWC (upper bound) *vs* the excess being entirely from MV (lower bound). (Estimated ages [f_M values] for these two sources are f_M=0.10 for MV emissions and f_M=1.06 for RWC emissions. Details for obtaining these f_M values are reported later in the text and in Table III.) Therefore, estimated f_M (BLK) values would range from 1.00 to 1.11 with lower and upper bounds equal to 0.87 and 1.14, respectively. The combined standard uncertainty for f_M corrected (cor.) ranges from 0.02 to 0.04 which takes into account the lower and upper bounds for f_M(BLK).

3. SAMPLING DESIGN

3.1 Sample conditions

The sampling conditions were designed to focus on wintertime woodburning contributions to CO concentrations in Albuquerque, NM. The design was an attempt to satisfy the need to collect samples during conditions favorable for non-attainment of the NAAQS for CO, *e.g.*, during the night (1630-0030) when the air is likely to be cold and stagnant at a residential site (Zuni Park [2ZE], intersection of Espanola, Mesilla and Prospect Sts.). In contrast, samples during attainment were important for comparison purposes, *e.g.*, during the day

TABLE II. FACTORIAL DESIGN SAMPLING STRATEGY:
TWO-LEVEL AND THREE FACTOR (2^3)

X_1: Sampling Period: AM (-) *vs* PM (+)
X_2: Forecast Meteorology: Dynamic (-) *vs* Stagnant (+)
X_3: Sampling Site: San Mateo (-), traffic site (2ZK), *vs* Zuni Park (+), residential site (2ZE)

Factors (Variables)/Sampling Conditions

Design #	Sample	FACTOR		
		X_1	X_2	X_3
1	6	-	-	-
2	13	+	-	-
3	14	-	+	-
4	3	+	+	-
5	9	-	-	+
6	7	+	-	+
7	11	-	+	+
8	8	+	+	+
9	10	+	+	+
10	12	+	+	+

* Design #9 and #10 are replicates of #8.

Yates Algorithm:

$$Y\ Predicted = \mu + 0.5[\beta_1X_1 + \beta_2X_2 + \beta_3X_3 + \beta_{12}X_{12} + \beta_{13}X_{13} + \beta_{23}X_{23} + \beta_{123}X_{123}]$$

where β*'s* are coefficients of variables (*X's*), μ is the mean response, and *Y* is the predicted response. Variables and coefficients are subscripted according to main effects, single numerical identities, and interactions representing some combination of main effects, two or three variables.

(0630-1430) when the air was likely to be more dynamic at a traffic site (San Mateo [2ZK], intersection of San Mateo and Menaul Blvds.). Each site is within ~1 km of a shopping mall, Winrock and Coronado, respectively. Given the three factors, *i.e.*, sampling period, forecasted meteorology, and sampling site, the design allowed us to investigate if any one factor or combination of factors was a dominant influence on the CO concentration. *The design conditions with reference to meteorology were influenced by the local "no-burn" control strategy for residential wood stoves and fireplaces when forecasted meteorology (24-h in advance) suggested cold stagnant conditions that were likely to affect CO concentrations to the extent of exceeding the NAAQS.*

An optimized sampling, full two level factorial design (2^3), was constructed to include complete coverage and balance of the above mentioned factors considered most important in affecting the ^{14}C response surface (see Table II, hypothetical design #1-8). Each possible combination of the three critical factors defined a unique sample to be collected. Since the prime objective of the study was to focus on nighttime non-attainment of NAAQS, replicates #9 and #10 were chosen to match the conditions of #8. An additional ambient sample was collected in an underground parking garage as a control that was expected to show that all the CO originated from motor vehicle exhaust.

The factorial design theory used to specify the optimal sampling conditions when constrained to n=8 observations has been summarized by Box *et al.* [19] reference textbook on experimental design. Unfortunately, natural variability dictated the order that samples were collected even though a randomized sampling is suggested to avoid any correlation with time. Using the generalized additive model based on the Yates algorithm (Table II) for the 2^3 factorial (balanced) experimental design and graphical means, results indicated that no significant main factor effect of those studied, *i.e.*, time of day, forecasted meteorology or site, was detected. This was partially expected due to the natural variability of CO concentration and Θ'_{RWC} that was evident from replicates (n=3) of the sampling condition most favorable for high Θ'_{RWC}., *i.e.*, nighttime-stagnant-residential. Although this sampling design was not able to detect any significant factor effects, it allows for comparison of extreme conditions that is essential for developing future experiments which may lead to new and possibly more effective control strategies.

3.2 Source materials for quality control and model calculations

A few representative samples of gasoline were collected from area gas stations for ^{14}C measurements. Albuquerque was then required to add ethanol or MTBE to the gasoline to meet a minimum 2% (by wt.) oxygen content for reducing CO emissions during the winter months. Data from a market survey and a spot audit revealed the distribution of these fuels, 36% MTBE- and 64% ethanol-gasoline [20], so that the average ^{14}C signature for gasoline could be calculated from direct measurements of gasoline samples. Two composite samples were prepared from each set of MTBE- and ethanol-gasolines for combustion to CO_2 and ^{14}C age determination. In addition, samples of two representative logs were collected to estimate the typical age of logs burned in Albuquerque. Cross-sections of these wood (log) samples were taken and the cellulose plus lignin was burned to CO_2 for ^{14}C age determination.

4. MODEL ESTIMATES - FRACTION OF RESIDENTIAL WOOD COMBUSTION (Θ'_{RWC})

Direct ^{14}C measurements on the source materials and ambient samples were used in a 3-source model (Equation 3) to calculate the fractional contribution of RWC emissions to the total CO concentration as follows:

$$f_M(MEAS) = [\Theta_{RWC} \cdot f_M(RWC)] + [\Theta_{MV} \cdot f_M(MV)] + [\Theta_{BKG} \cdot f_M(BKG)] \qquad \text{Eq. 3}$$

where Θ_i is the fractional contribution of source "i" given by

$$\Theta_i = [CO]_i/[CO]_{total} \qquad \text{Eq. 4}$$

If f_M(MEAS) is corrected for *"clean-air"* background using ^{14}CO measurements by Tyler and Klouda [21] and CO concentration measurements by Novelli *et al.* [22] from Niwot Ridge, Colorado, then f_M(MEAS) corrected for CO background [f_M'(MEAS)] can be expressed as:

$$f_M'(MEAS) \equiv \frac{f_M(MEAS) - \Theta_{BKG} \cdot f_M(BKG)}{(1 - \Theta_{BKG})} \qquad \text{Eq. 5}$$

A reduced 2-source model can then be expressed by the following equation

$$f_M'(MEAS) = [\Theta'_{RWC} \cdot f_M(RWC)] + [\Theta'_{MV} \cdot f_M(MV)] \qquad \text{Eq. 6}$$

where Θ'_{RWC} and Θ'_{MV} are now relative to *background corrected CO concentration.* Finally, substituting $\Theta'_{MV} = 1 - \Theta'_{RWC}$ into Equation 6 and solving for Θ'_{RWC} yields the following expression:

$$\Theta'_{RWC} = \frac{[f_M'(MEAS)/f_M(MV)] - 1}{[f_M(RWC)/f_M(MV)] - 1} \qquad \text{Eq. 7}$$

The controls used to evaluate accuracy and precision of ^{14}C measurements are NIST SRMs 4990B [HOx(I)] and 4990C [HOx(II)] for radiocarbon dating and Reference Material (RM) 21 Graphite for ^{14}C blank (contamination) determination.

5. RESULTS AND DISCUSSION

Table III summarizes measured f_M results of source materials and published background CO concentrations used in the above equations to calculate the fractional contribution of residential wood combustion. The best estimate of the average f_M value and the uncertainty for typical logs burned in Albuquerque is equivalent to $f_M = 1.06 \pm 0.02$ supported by the ^{14}C measurements of log samples and estimates derived from tree-ring models [1,2] assuming on average 200 year old logs. The average f_M value of gasoline used in Albuquerque during the Winter of 1989-1990 is equivalent to $f_M = 0.10 \pm 0.01$. This value for gasoline is estimated from direct ^{14}C measurements of MTBE- and ethanol-gasoline and the distribution of these fuels based on a market survey and spot audit during this period [20].

TABLE III. MEASURED ^{14}C SOURCE SIGNATURES (f_M): INPUT TO MODEL FOR ESTIMATES OF THE FRACTIONAL CONTRIBUTION OF RESIDENTIAL WOOD COMBUSTION TO CO CONCENTRATIONS

I. Residential Wood Combustion (RWC) CO: f_M (RWC) = 1.06 ± 0.02[†]

- Pinion Pine[*]: $f_M = 1.033 \pm 0.008$
- Juniper (200 year old)[*]: $f_M = 1.031 \pm 0.007$
- Equal Mass and Equal Width Tree-Ring Models (200 year old logs): $f_M = 1.08 \pm 0.04$ (median, $\nu=1$)

[†] Based on measured f_M values of logs and Tree-Ring Model [1,2] estimates mentioned above.

[*] The u_c is based on weighted 1σ-Poisson counting statistics.

II. Motor Vehicles (MV) CO: f_M (MV) = 0.10 ± 0.01[†]

- Underground Parking Garage CO Fraction[*]: $f_M = 0.16 \pm 0.02$ [$f_M = 0.13 \pm 0.02$ when corrected for *"clean-air"* CO background (see text)]
- MTBE-gasoline[*] (2.0% oxygen by wt.): $f_M = 0.026 \pm 0.001$
- Ethanol-gasoline[*] (2.3% oxygen by wt.): $f_M = 0.148 \pm 0.002$

[†] Based on the f_M values measured for additive-gasolines (above) and the distribution of fuels sold, 36% MTBE- and 64% ethanol-gasoline, from a market survey and spot audit [20].

[*] The u_c is based on weighted 1σ-Poisson counting statistics.

III. Average "Clean-Air" CO Background: f_M (BKG) = 3.1 ± 0.5 (u)[†]

[†] Based on an average Northern Hemispheric CO (^{14}C, ^{12}C) abundance of 12.7 ± 1.7 (u, $\nu=3$) ^{14}CO molecules-cm^{-3} (STP) determined from clean air at Niwot Ridge, Colorado. ^{14}C measurements were made on just one day of the following month/year: 18 December 1990/9 January 1991 (composite), 27 February 1991, 6 December 1991, and 3 January [21]. The median ^{12}C abundance from Niwot Ridge, corresponding in time with the urban samples, is estimated at 0.140 μmol/mol with a range from 0.115 to 0.160 μmol/mol [22]. The effect of this CO background on sample f_M ranges from 0.03 to 0.30.

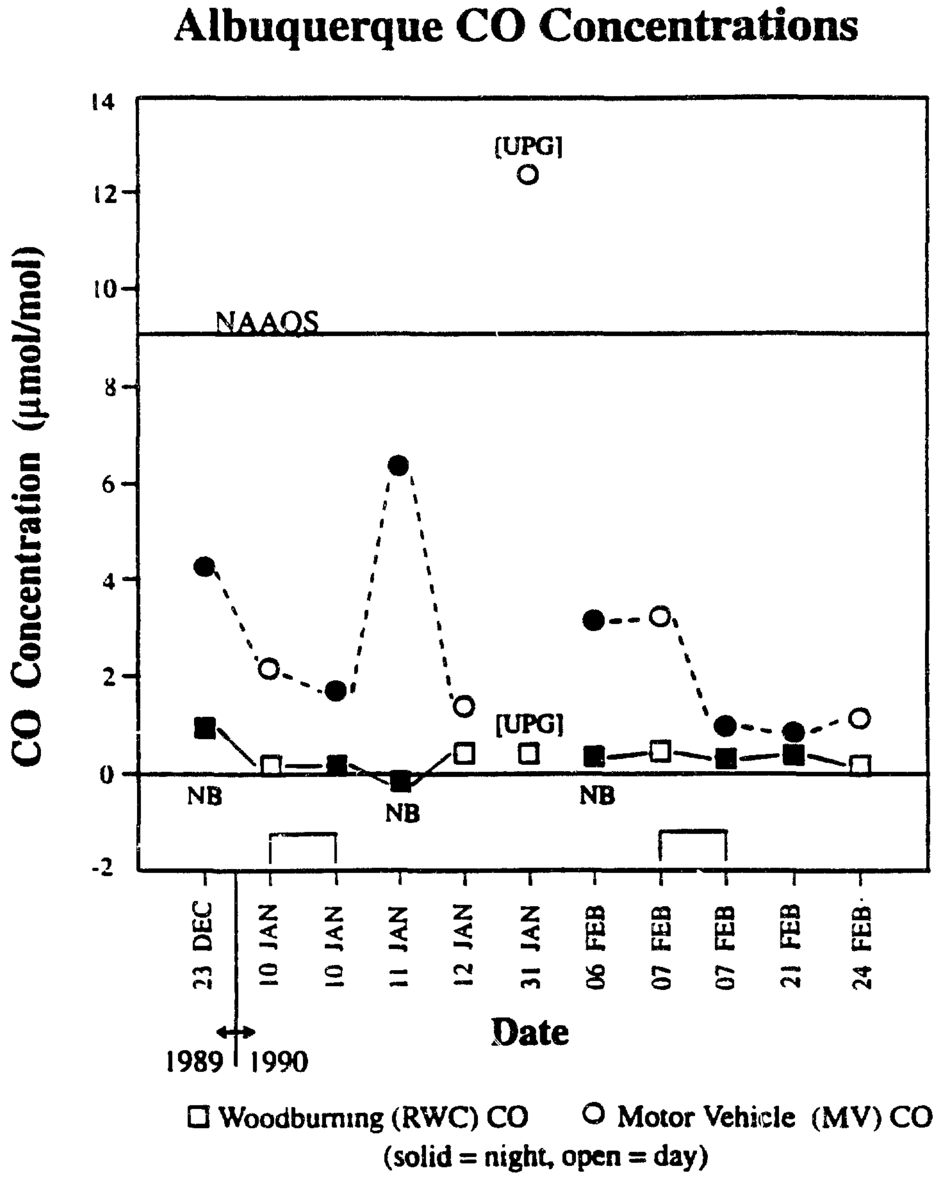

Figure 2: Ambient CO concentrations during day (0630-1430) and night (1630-0030) time periods attributed to residential wood combustion and motor vehicle emissions for 10 ambient samples. Early morning (0600-0900) CO concentrations from an underground parking garage are designated by UPG. Days identified by NB are periods designated as *"no-burn."* See Table IV for sampling conditions and estimates of the fractional contribution to residential wood combustion.

The ambient underground parking garage f_M result of 0.16 ± 0.02 is fairly consistent with the estimated average gasoline f_M value considering that *"clean-air"* background CO and potentially a small but significant contribution from wood combustion would increase the signal expected from motor vehicles alone.

The best estimate for background correction of *"clean air"* CO comes from CO (^{14}C,^{12}C) measurements at Niwot Ridge, Colorado [41.03 °N, 105.53 °W, elevation of 3.15 km]. An average ^{14}C abundance for December-February months [n(samples)=4] was measured to be 12.7 ± 1.7 (*u*) ^{14}CO molecules-cm^{-3} at STP [21] and a median CO concentration of 0.140 µmol/mol with a range from 0.115 to 0.160 µmol/mol [22]. The equivalent f_M value for this ^{14}C

background is 3.1 ± 0.5 (u) assuming the median CO concentration noted above. The effect of this background correction is proportional to the fractional amount of the background relative to the total CO concentration for each sample. Therefore, the effect of this correction when calculating Θ'_{RWC} ranges from 0.03 to 0.30. See Table III for additional information.

Figure 2 is a time-ordered plot of the CO concentration attributed to residential wood combustion and CO concentration attributed to motor vehicle emissions for each sample measured. The wood CO is determined from the product of Θ'_{RWC} and the background corrected CO concentration. The concentration of CO attributed to motor vehicles is simply the quantity $(1-\Theta'_{RWC})$ times the background corrected CO concentration. Without ^{14}C measurements of the CO fractions separated from these samples, quantitative source impacts as seen in Figure 2 would not be possible. The plot illustrates that the motor vehicle contribution is in all cases greater than the residential wood combustion contribution.

Table IV summarizes the sampling conditions for each ambient air sample, the designated mandatory control, burn (B) or no-burn (NB), the ambient temperature taken from

TABLE IV. SAMPLING CONDITIONS, CO CONCENTRATIONS AND ESTIMATED FRACTIONAL CONTRIBUTION OF RESIDENTIAL WOOD COMBUSTION (Θ'_{RWC})

Dsgn #	Smpl	Date	ToD	FMet	Site	Ctrl	Temp	CO (u,v)	Θ'_{RWC} (u_c)
4	3	23 DEC	N	Stg	Traf	NB	0.2	5.31 (0.06,2)	0.17 (0.04)
1	6	10 JAN	D	Dyn	Traf	B	9.8	2.42 (0.02,5)	0.07 (0.07)
6	7	10 JAN	N	Dyn	Res	B	6.4	1.96 (0.04,3)	0.08 (0.09)
8	8	11 JAN	N	Stg	Res	NB	7.2	6.31 (0.03,2)	-0.03 (0.03)
5	9	12 JAN	D	Dyn	Res	B	4.9	1.91 (0.01,2)	0.23 (0.08)
-	UPG	31 JAN	EM	-	Dwnt	B	3.2	12.9 (0.10,3)	0.03 (0.02)
9	10	06 FEB	N	Stg	Res	NB	2.9	3.60 (0.03,5)	0.09 (0.05)
7	11	07 FEB	D	Stg	Res	B	5.0	3.82 (0.03,5)	0.12 (0.05)
10	12	07 FEB	N	Stg	Res	B	7.2	1.37 (0.01,2)	0.22 (0.11)
2	13	21 FEB	N	Dyn	Traf	B	2.8	1.34 (0.01,2)	0.30 (0.11)
3	14	24 FEB	D	Stg	Traf	B	7.4	1.40 (0.01,5)	0.12 (0.11)

Dsgn # - experimental design identification number (Table II)
Smpl - sample identification, underground parking garage (UPG)
Date - calendar date: all sampled in 1990 except for #3 sampled in 1989
ToD - time of day: night (N) 1630-0030, day (D) 0630-1430, early morning (EM) 0600-0900
FMet - forecasted meteorology: stagnant (Stg) or dynamic (Dyn)
Site - residential (Zuni Park, 2ZE), traffic (San Mateo, 2ZK), downtown (Dwnt)
Ctrl - mandatory control: no burn (NB) or burn (B)
Temp - average ambient temperature in degrees Celsius
CO - total carbon monoxide concentration (dry) and standard uncertainty (u) in μmol/mol, number of degrees of freedom (v)
Θ'_{RWC} - estimated values for the fractional contribution of residential wood combustion corrected for an average *"clean-air"* CO background. See text for discussion of background correction. The u_c is based on error propagation [12] of variables specified in Equations 1-7 of text.

NOAA 3-hour averages and averaged over the sampling period, the total integrated CO concentration (dry) and the fractional contribution of residential wood combustion (Θ'_{RWC}) calculated from the corresponding measured sample f_M value and the other values to the model as described in Table III.

5.1 Relationship of fossil CO and benzene - inferences relevant to potential changes to the US Occupational Health and Safety Standard

Aside from obtaining quantitative CO source information from this study, it also gave us the opportunity to investigate the contention that ^{14}CO measurements may be useful information in apportioning sources of atmospheric benzene [23]. It is well known that benzene is an emission of engine exhaust and unburned gasoline. A study by the American Petroleum Institute on tail-pipe emissions has shown that the emission factor of benzene relative to CO for auto exhaust is ~0.0033 for late model (1980's) automobiles [24]. In addition, studies have shown that benzene is a product of wood burning having an emission factor for wood stoves of ~0.002 [25]. Estimates of benzene emissions for 1988 in the U.S. indicate that industrial sources may be responsible for only ~15% of the total benzene emitted annually while biomass combustion, ~50%, and auto emissions, ~35%, seem to account for the bulk of the benzene [24]. Given that the levels of benzene emissions from wood burning may be comparable to that of auto gasoline, total hydrocarbon speciation was carried out on the same canister samples prior to CO separation to determine the benzene concentrations.

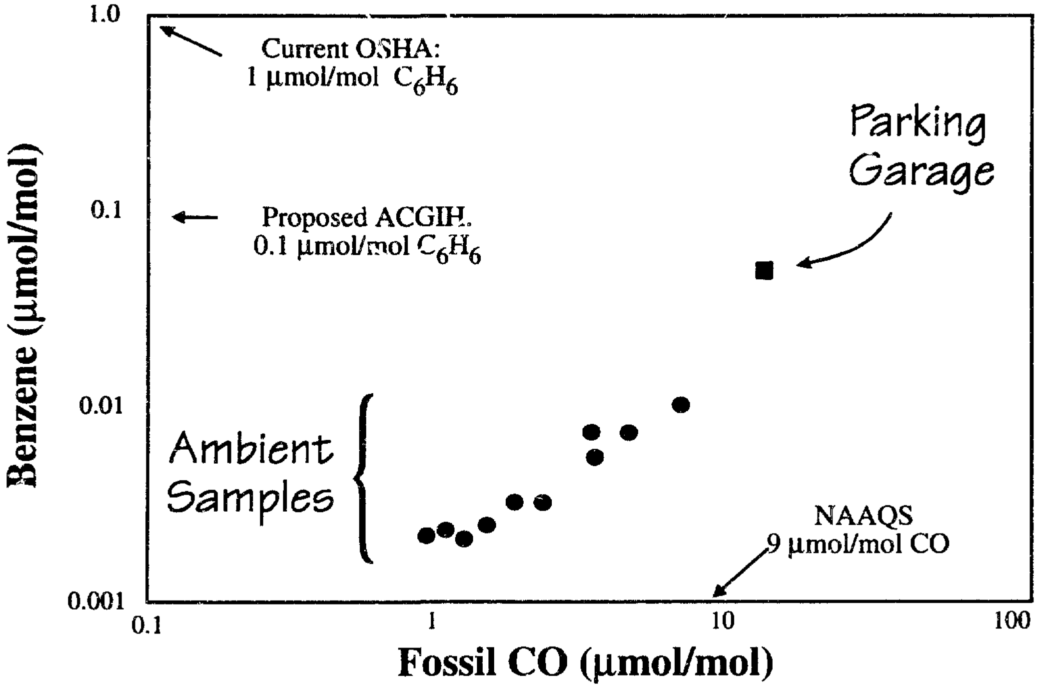

Figure 3: Scatter plot of wintertime benzene and fossil CO for Albuquerque, NM for the same samples plotted in Figure 2. Ambient results are shown with current and proposed CO standards: U.S. National Ambient Air Quality Standard, NAAQS (defined as volume fraction, here represented as mole fraction), benzene Occupational Safety and Health Administration, OSHA, and the American Conference of Governmental Industrial Hygiene, ACGIH. If a lower benzene standard is to be enforced, direct ^{14}C dating for benzene may be required to help discriminate between ambient and industrial contributions.

A scatter plot of the Albuquerque benzene *vs* fossil CO concentrations in log-log space is shown in Figure 3. The parking garage sample (■) is included to illustrate a point regarding the Occupational Safety and Health Administration (OSHA) Standard for benzene at 1 μmol/mol. If the OSHA standard is reduced to 0.1 μmol/mol, as suggested by some organizations, background benzene concentrations from sources other than industrial, *e.g.*, RWC and MV emissions as reported here, may also require controls for compliance with the standard. Ambient levels of benzene, as shown here, may be significant and variable enough to occasionally cause industrial levels to exceed a proposed 0.1 μmol/mol OSHA standard. Therefore, if the existing OSHA standard for *"benzene exposure"* is to be reduced, isotope measurements made directly on benzene separated from whole air samples may be the only way to identify source contributions from the ambient urban air *vs* industrial environments.

6. CONCLUSIONS

From ^{14}C results of 10 ambient samples, one ambient underground parking garage sample, and source signatures for logs, gasoline, and *"clean-air"* CO background (^{14}C, ^{12}C) used in the 3-source model, estimations of the fraction of the total CO concentration due to residential wood combustion (Θ'_{RWC}) ranged from 0 to 0.30. For these same samples, the respective CO concentrations attributed to woodburning range from 0 to 0.90 μmol/mol, well below the NAAQS. In all cases, fossil CO is the predominant source of ambient CO concentrations ranging from 0.96 to 6.34 μmol/mol. See Table IV for sample characteristics and Θ'_{RWC} results.

The model is evaluated by comparing the ambient underground parking garage control, where the fraction of residential wood combustion was estimated to be 0.03 ± 0.02, with an expected value of nearly zero. The assumption that this sample is dominated by motor vehicle exhaust is reasonable given the sampling site, the high CO concentration [12.9 ± 0.1 (*u*) μmol/mol)], the dominant motor vehicle source, and the CO concentration pattern consistent with time-space activities of motor vehicles in a downtown metropolitan area. The measured/modeled resultant for this sample is statistically no different than zero. This comparison also gives validity to the use of Niwot CO data for the background correction. *However, any future studies should include examples of regional background CO measurements (chemical and isotopic) and variability for more precise measures of the fraction of residential wood combustion.*

The *"clean-air"* CO background correction was the *single most significant correction* applied to the ^{14}C results with an effect on the fraction of residential wood combustion ranging from 0.03 for the sample with the highest CO concentration to 0.30 for the sample with the lowest CO concentration. Therefore, for the samples that approach the NAAQS for CO, these results will have the smallest correction applied.

For three of the 10 ambient samples that were collected during mandatory *no-burn* periods, which exhibited the higher CO concentrations, estimated values for the fraction of residential wood combustion ranged from 0.0 to 0.17. One particular sample was interesting for it was collected two nights before Christmas (23 Dec 1989) during a mandatory *no-burn* condition. This sample exhibited the coldest period (0.2 °C), showed one of the highest measured CO concentrations (5.31 μmol/mol), and had an estimated fraction of residential wood combustion equal to 0.17 ± 0.04. *The low fraction of woodburning for this sample indicates that the no-burn control strategy appears to be effective (see Figure 2).* Conversely, the fraction of CO from motor vehicles for this particular sample was 0.83 ± 0.04. A quasi-bimodal pattern of CO concentrations for this evening (sample #3) showed an early evening peak from *ca.* 1700-2000 followed by a valley centered at around 2030 that was followed by another increase from *ca.* 2100-0030; both peaks being broad with frequent spikes of relatively low magnitude riding on top. This pattern may represent the evening shopping pattern due to numerous cold starts that would be associated with shopping mall activities. This event seems to be atypical of the set studied.

Meteorological factors, 3-hour averages, combined with the ^{12}CO patterns for these samples may give valuable insight regarding what conditions may favor a potential exceedance in this particular area [26].

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THE CARBON DIOXIDE ISOTOPIC MEASUREMENT PROCESS: PROGRESS AT NIST ON MEASUREMENTS, REDUCTION ALGORITHMS AND STANDARDS

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ABSTRACT: We report progress on our evaluation and development of the carbon dioxide isotope measurement process, with special emphasis on highly reproducible measurements essential for global atmospheric programs addressing climate change and human health. Three specific aspects of the measurement process are treated: 1) The propagation of uncertainty through algorithms, and assumptions used to convert conventional measurements to δ^{13}C values; we apply Monte Carlo methods for the purpose of illustrating δ^{13}C distributions from several model algorithms. 2) Utilizing non-conventional $\delta^{47}CO_2$ measurements to remove reliance on certain limiting assumptions, we describe the data reduction algorithm for calculation of δ^{13}C. Monte Carlo methods are used to define measurement reproducibility requirements for this method, and special procedures are used to obtain highly repeatable measurements. 3) We describe a method for production of isotopic gas standards having reproducibility essential for global programs. Feedback is invited concerning the standards and reference materials needed for adequate modeling, calibration and quality assurance for specific applications.

1. Uncertainty[1] in δ^{13}C from Natural Variations in the Oxygen Isotope Relationship

Modern gas isotope ratio mass spectrometers have improved so that single-instrument measurement repeatability can easily be better than 0.01 ‰ for δ^{13}C, and can approach 0.002‰ under certain conditions.[2] Expert interlaboratory measurement reproducibility of pure CO_2 reference materials, however, has been observed as 0.05-0.06‰ [2], although preparation reproducibility for these reference materials was 0.02-0.03‰ [3]; the source of this discrepancy has been unclear. Inconsistencies from the effects of uncontrolled isotopic fractionation are suspected, but another effect may be present (natural variations in the oxygen isotope relationship), as described in following sections. This effect can account for the poor reproducibility observed in δ^{13}C measurements, and can also be largely avoided by following the procedures recommended in these proceedings (Annex 1) for the calibration and use of working standards.

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[1] Uncertainties in measurements are expressed in accordance with recommendations of the International Organization for Standardization [1].

[2] δ^{13}C is the "per mill" (‰) relative difference in $^{13}C/^{12}C$ ratios (defined here as ^{13}R) of a sample from that of a reference standard; δ^{17}O and δ^{18}O are defined analogously using $^{17}O/^{16}O$ (^{17}R) and $^{18}O/^{16}O$ (^{18}R) ratios, respectively.

1.1 Conventional Isotopic CO_2 Measurement

Isotopic compositions are typically determined by differential measurement of ion beam ratios between a sample and reference standard using an isotope ratio mass spectrometer with multiple ion collectors. For CO_2, molecular isotopic compositions are measured and expressed using the *delta* (δ) notation, e.g. Eq.1, where ^{m}R values are ratios of CO_2 ions of m/z m (m = 45 or 46) versus m/z 44 ions (the CO_2 base peak) for a sample and standard. The numerical methods used to convert measured $\delta^{45}CO_2$ and $\delta^{46}CO_2$ values to basic $\delta^{13}C$ and $\delta^{18}O$ compositions were developed by Craig [4] and enhanced subsequently [5,6,7,8]. In 1981,

$$\delta^{m}CO_2 = \left[\frac{^{m}R_{sam} - {}^{m}R_{std}}{^{m}R_{std}}\right] \cdot 1000 \qquad (1)$$

the International Atomic Energy Agency (IAEA) recommended the general use of an explicit reduction algorithm for precise intercomparability of measurements [9]. To solve for the three unknowns $\delta^{13}C$, $\delta^{18}O$ and (implicitly) $\delta^{17}O$ from only two measurements ($\delta^{45}CO_2$ and $\delta^{46}CO_2$), this algorithm assumes an exact relationship among oxygen isotopes between any sample and working standard, Eq.2, where the fractionation constant a = 0.5.

$$\frac{^{17}R_{sam}}{^{17}R_{std}} = \left[\frac{^{18}R_{sam}}{^{18}R_{std}}\right]^{a} \qquad (2)$$

Developments have prompted a reassessment of the validity and utility of the IAEA-1981 algorithm. The values for absolute ratios (^{13}R, ^{17}R, ^{18}R) in reference standards have been redetermined through new measurements [10,11,12] and recalculated using new assumptions [13]. These studies suggest that the conventionally accepted values for absolute ratios in reference standards may be biased as much as 8%, translating to biases up to 5‰ in $\delta^{13}C$. Santrock *et al.* [10] noted that the oxygen isotope fractionation assumption of a = 0.5 was probably inaccurate for two reasons: first, based on theoretical aspects [14] and empirical evidence [15,16], the fractionation coefficient a varies slightly among terrestrial chemical systems so that no *fixed* value of a could be generally applied in a reduction algorithm. Secondly, unless the true value of a was known for a particular differential measurement, a = 0.516 should be the assumed value since it represents the average fractionation observed among 35 terrestrial silicate minerals and natural waters [15]. Later, Robert *et al.* [17] measured a = 0.512-0.525 in terrestrial cherts, basalts, and industrial oxygen gas (vs Vienna Standard Mean Ocean Water - VSMOW), and Thiemens *et al.* [18] reported a = 0.517 in tropospheric CO_2 and *very* unusual values (a = 0.6-0.7) in stratospheric CO_2. Mass-independent isotopic fractionations may play an important role in many natural physicochemical subsystems [19].

To address concerns that the IAEA-1981 algorithm may be an invalid approach to data reduction, we have compiled several alternative approaches for the calculation of $\delta^{13}C$ and $\delta^{18}O$ values. An all-important perspective is the uncertainty of these calculated values, so we propagate the uncertainties from measurement repeatabilities *and* natural variation in a. The resulting distributions in $\delta^{13}C$ and $\delta^{18}O$ depict the true differences and limitations of conventional algorithms, and clarify several vital areas for development and implementation.

1.2 Monte Carlo Error Propagation

The Monte Carlo method for the propagation of uncertainty through complex mathematical expressions offers advantages of conceptual simplicity, choice of input error distributions, accurate response to covariance, and the facility to inspect visually (and statistically) the resulting distributions of output values [20].

The data reduction approach of Santrock *et al.* [10] was used to calculate, through the Monte Carlo method, distributions of values for $\delta^{13}C$ and $\delta^{18}O$ from random normal distributions of $\delta^{45}CO_2$, $\delta^{46}CO_2$, a_{sam} (sample vs working standard), a_{std} (working standard vs VSMOW), and three discrete values of $^{17}R_{VSMOW}$ (Eqs.7-9). This approach required that the ^{13}R, ^{17}R and ^{18}R values in the working standard be defined versus a reference standard.[3] The input parameters to five Monte Carlo simulations are given in Table I. The effects of isobaric interferences, isotopic fractionation, and instrumental effects, which may also influence actual $\delta^{13}C$ and $\delta^{18}O$ distributions in practice, have not been treated here. These effects are expected to be negligible under controlled conditions.

TABLE I
SIMULATION INPUT PARAMETERS

$\delta^{45}CO_2 \pm u$ (‰) vs working std	$\delta^{46}CO_2 \pm u$ (‰) vs working std	$a_{sam} \pm u$	$a_{std} \pm u$	Figure
-30.000 ± 0.000	-30.000 ± 0.000	0.516 ± 0.020	0.516 ± 0.020	1
-30.000 ± 0.010	-30.000 ± 0.030			2
			0.516 ± 0.000	3
		0.516 ± 0.000	0.516 ± 0.020	4
0.000 ± 0.010	0.000 ± 0.030			5

Standard uncertainties (u) of δ values are hypothetical analytical repeatabilities. Standard uncertainty (u) of a values is from [15], where uncertainty of mean is reported as 0.5164 ± 0.0033 (standard error, n=35).

Working Standard is defined as:

$$^{13}R = 0.0112591 \tag{3}$$

$$^{18}R = 0.0020838 \tag{4}$$

$$^{17}R = {}^{17}R_{VSMOW} \cdot [{}^{18}R/{}^{18}R_{VSMOW}]^{a} \tag{5}$$

$$^{18}R_{VSMOW} = 0.0020052 \text{ [21]} \tag{6}$$

$$^{17}R_{VSMOW} = 0.0003732 \textit{ via } [4] \tag{7}$$

$$= 0.0003799 \text{ [11]} \tag{8}$$

$$= 0.0004023 \text{ [10]} \tag{9}$$

1.3 Results of Simulations

Results of all simulations are summarized in Table II and presented in Figs.1-5. Each plot contains 900 points (300 for each value of $^{17}R_{VSMOW}$); for reference in all plots, the IAEA-1981 value is also presented. In discussions below, the term "unrelated" is used to describe CO_2 samples or working standards that have unmeasured a values and have separate oxygen pool lineages [15]. In contrast, isotopically "related" CO_2 must either be measured independently for $\delta^{17}O$ and $\delta^{18}O$ (vs. VSMOW) or measured absolutely for ^{17}R and ^{18}R [22];

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[3] This calibration method has been a standard laboratory practice. In these proceedings, Francey and Allison have recommended that working standards be calibrated for ^{45}R and ^{46}R only (Annex 1). This method of calibration avoids unnecessary propagation of uncertainty in a by relating measurements against the reference standard directly.

TABLE II
RESULTS OF SIMULATIONS

Figure	Symbol	$\delta^{13}C$ ± U (‰) vs working std	$\delta^{18}O$ ± U (‰) vs working std
1	□	-30.971 ± 0.104	-29.967 ± 0.004
	+	-30.989 ± 0.106	-29.966 ± 0.004
	×	-31.047 ± 0.112	-29.964 ± 0.004
	◆	-31.015	-29.967
2	□	-30.975 ± 0.104	-29.966 ± 0.056
	+	-30.993 ± 0.106	-29.966 ± 0.056
	×	-31.052 ± 0.112	-29.964 ± 0.058
	◆	-31.015	-29.967
3	□	-30.974 ± 0.030	-29.966 ± 0.056
	+	-30.992 ± 0.030	-29.965 ± 0.056
	×	-31.050 ± 0.032	-29.963 ± 0.056
	◆	-31.015	-29.967
4	□	-30.972 ± 0.106	-29.968 ± 0.062
	+	-30.989 ± 0.106	-29.968 ± 0.062
	×	-31.048 ± 0.112	-29.965 ± 0.062
	◆	-31.015	-29.967
5	□	0.001 ± 0.104	-0.002 ± 0.062
	+	0.001 ± 0.106	-0.002 ± 0.062
	×	0.001 ± 0.106	-0.002 ± 0.062
	◆	0.000	0.000

The $\delta^{13}C$ and $\delta^{18}O$ distributions are expressed by mean value ± expanded uncertainty (U) where $U = 2 \cdot u$. Here, u is the standard deviation of the population of simulated delta values.

"interrelated" CO_2 samples, where $a_{sam}(1) = a_{sam}(2)$, must originate from a common oxygen pool and be linked through mass-dependent isotopic fractionation exclusively.

Figure 1 shows the distributions of possible $\delta^{13}C$ (plot a) and $\delta^{18}O$ (plot b) values from (hypothetically) infinitely precise measurements. The $\delta^{18}O$ distributions exhibit only 0.004‰ expanded uncertainty ($U = 2 \cdot u$), demonstrating that $\delta^{18}O$ is not significantly influenced by variations in $\boldsymbol{a}$. However, $\delta^{13}C$ values are dispersed over a 0.3‰ range (U = 0.1‰).

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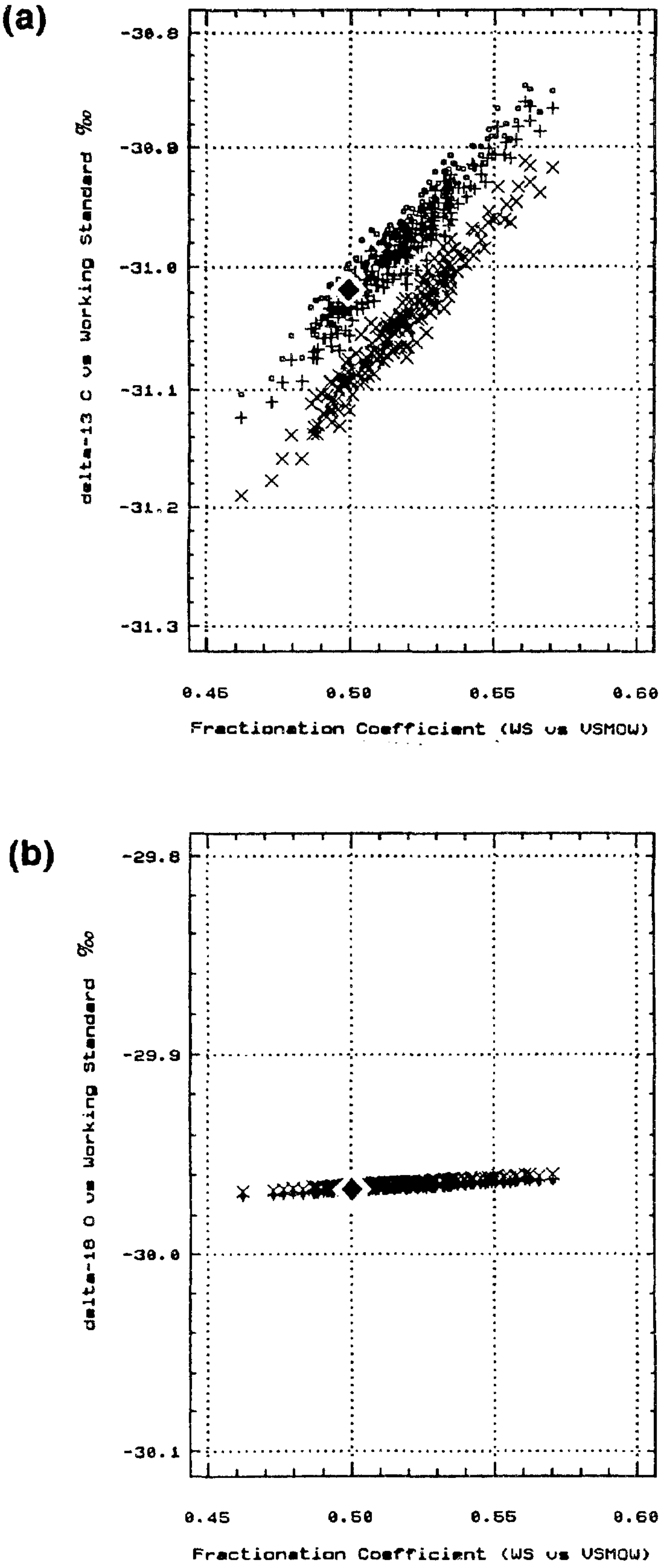

Figure 1: Scatterplot of results from Monte Carlo simulations for infinitely precise measurements (see Table I for input parameters and Table II for statistics); $\delta^{13}C$ (plot a) and $\delta^{18}O$ (plot b) distributions are plotted versus possible oxygen isotope fractionation values between working standard and VSMOW. Three distributions (300 points each) are presented in each plot, generated through different assumptions: □: Eq.7; +: Eq.8; ×: Eq.9; ◆: IAEA-1981 reference value. See section 1.3.

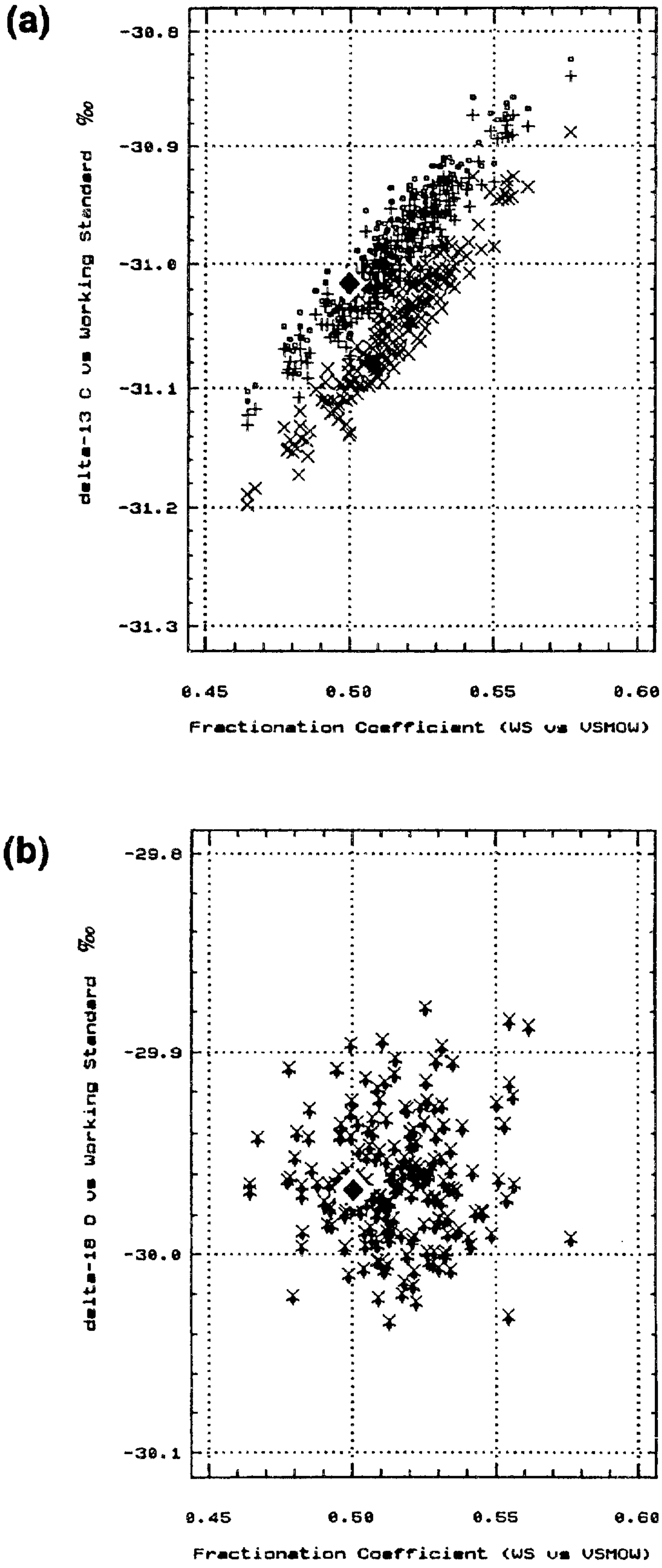

Figure 2: Scatterplot of results from Monte Carlo simulations for measurements with typical repeatabilities (see Table I for input parameters and Table II for statistics); $\delta^{13}C$ (plot a) and $\delta^{18}O$ (plot b) distributions are plotted versus possible oxygen isotope fractionation values between working standard and VSMOW. Three distributions (300 points each) are presented in each plot, generated through different assumptions: ▫: Eq.7; +: Eq.8; ×: Eq.9; ◆: IAEA-1981 reference value. See section 1.3.

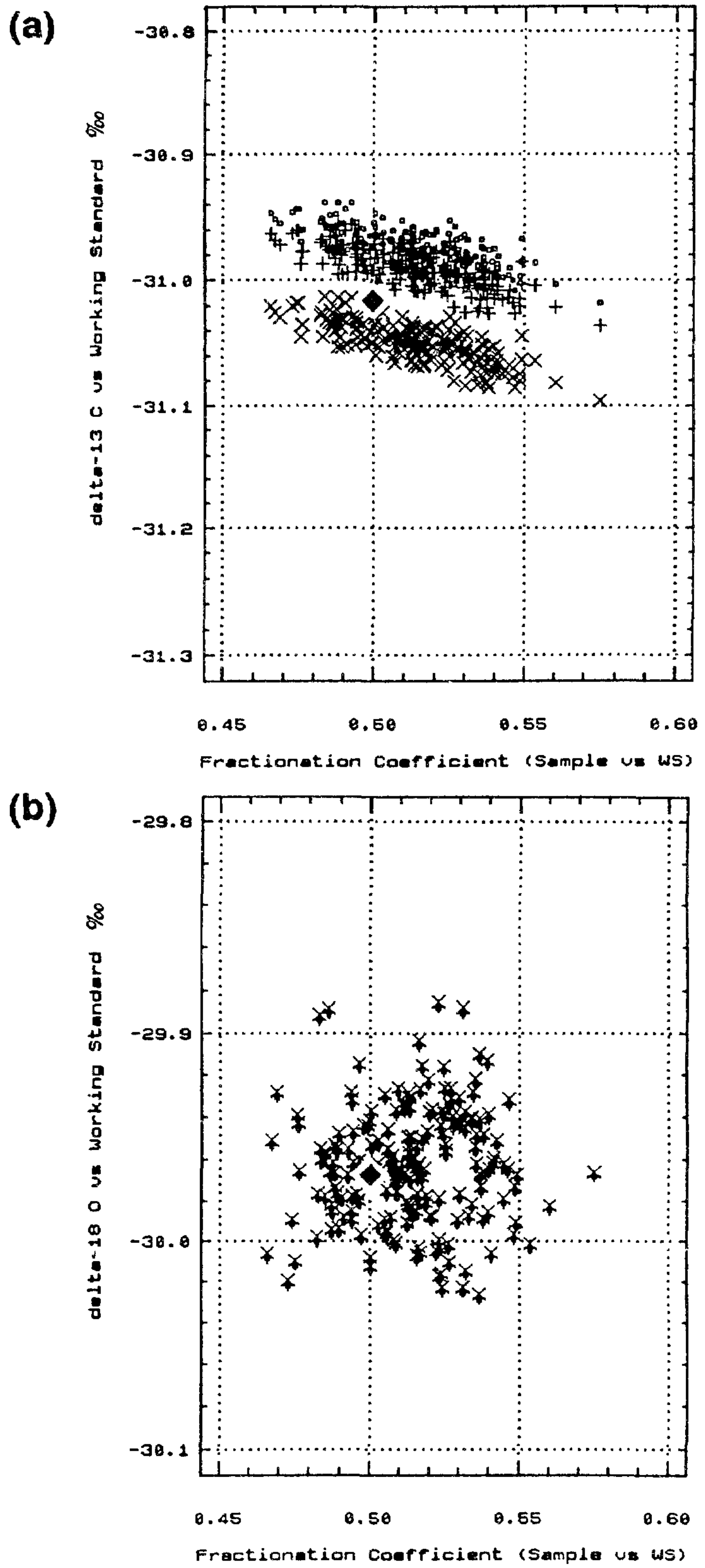

Figure 3: Scatterplot of results from Monte Carlo simulations (see Table I for input parameters and Table II for statistics); $\delta^{13}C$ (plot a) and $\delta^{18}O$ (plot b) distributions are plotted versus possible oxygen isotope fractionation values between sample and working standard. Three distributions (300 points each) are presented in each plot, generated through different assumptions: □: Eq.7; +: Eq.8; ×: Eq.9; ◆: IAEA-1981 reference value. These uncertainty distributions of delta values are expected among intralaboratory measurements using one working standard, or interlaboratory measurements using working standards calibrated as recommended in these proceedings. See section 1.3.

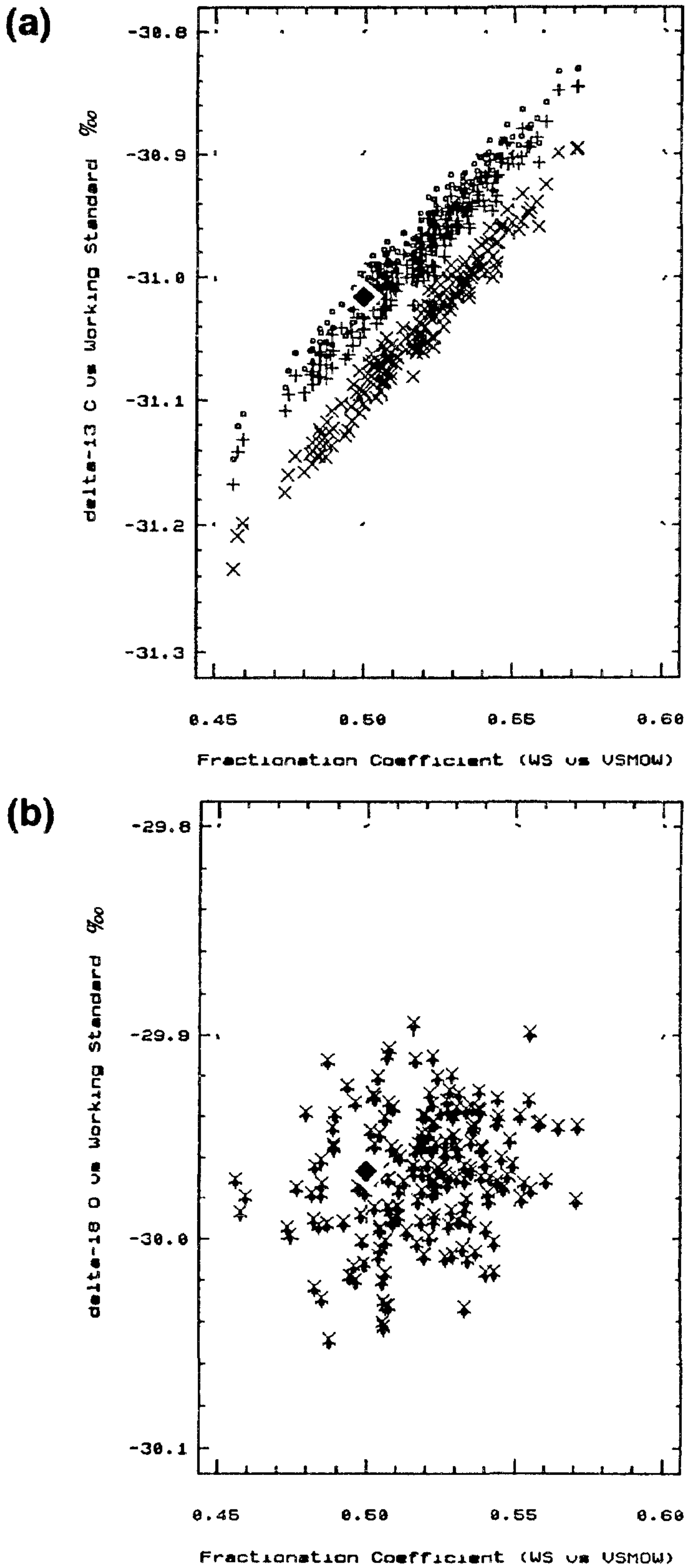

Figure 4. Scatterplot of results from Monte Carlo simulations (see Table I for input parameters and Table II for statistics), $\delta^{13}C$ (plot a) and $\delta^{18}O$ (plot b) distributions are plotted versus possible oxygen isotope fractionation values between working standard and VSMOW. Three distributions (300 points each) are presented in each plot, generated through different assumptions: □ Eq 7, + Eq 8, × Eq 9, ◆ IAEA-1981 reference value. These uncertainty distributions of delta values are expected among interlaboratory measurements using unrelated working standards calibrated for ^{13}R, ^{17}R and ^{18}R. See section 1.3.

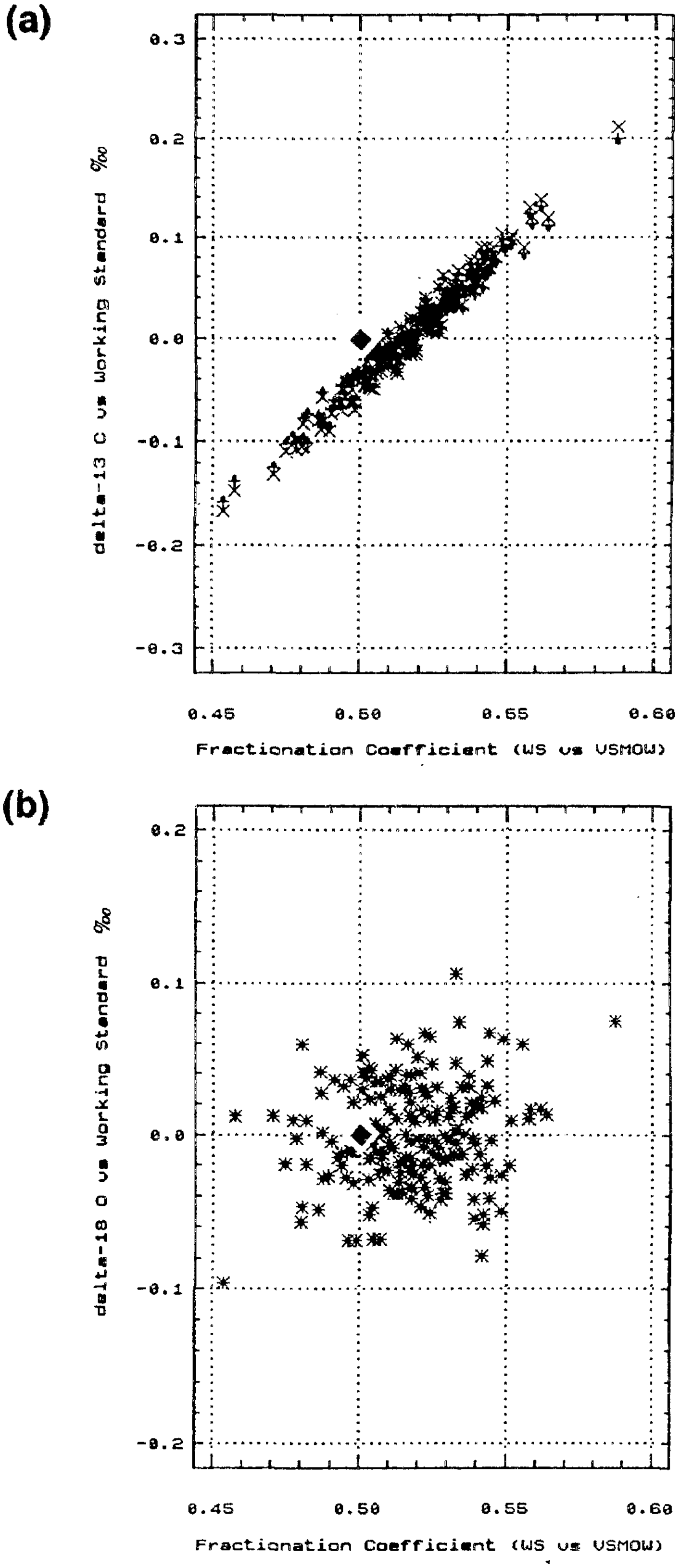

Figure 5: Scatterplot of results from Monte Carlo simulations (see Table I for input parameters and Table II for statistics); δ^{13}C (plot a) and δ^{18}O (plot b) distributions are plotted versus possible oxygen isotope fractionation values between working standard and VSMOW. Three distributions (300 points each) are presented in each plot, generated through different assumptions: □: Eq.7; +: Eq.8; ×: Eq.9; ◆: IAEA-1981 reference value. These uncertainty distributions of delta values are expected among interlaboratory measurements using unrelated working standards calibrated for ^{13}R, ^{17}R and ^{18}R. See section 1.3.

Comparison of these distributions with those generated when measurements possess typical precision values (Fig.2) demonstrates that measurement repeatability defines $\delta^{18}O$ uncertainty but adds insignificant uncertainty to $\delta^{13}C$. The means of the three $\delta^{13}C$ distributions arising from the use of the three $^{17}R_{VSMOW}$ values are offset by as much as 0.08‰. Distributions in Fig.2 represent the interlaboratory (global) uncertainties expected when unrelated samples and unrelated working standards are differentially measured by conventional methods. The IAEA-1981 value is well within all ranges expressed.

In contrast, Fig.3 illustrates the relatively good intralaboratory distributions of possible $\delta^{13}C$ values for unrelated samples, given that only one working standard is used. These distributions also represent expected interlaboratory error when working standards are calibrated as recommended in these proceedings. Reproducibility of $\delta^{13}C$ for unrelated samples (U = 0.030‰) is only slightly worse than for interrelated samples (U = 0.020‰, measurement repeatability). This indicates that variation in fractionation coefficient between samples and a common working standard is a minor source of uncertainty in $\delta^{13}C$. A significant effect arises from using different $^{17}R_{VSMOW}$ values to define the composition of the working standard; the maximum offset is again 0.08‰. The IAEA-1981 value for $\delta^{13}C$ is within the expanded uncertainty range of one distribution (+), and plots between the other two distributions.

Figures 4 & 5 illustrate the reproducibilities expected during intercomparisons, when a sample of CO_2 is split and measured against many unrelated working standards. Surprisingly, the range of $\delta^{13}C$ values is about 0.3‰ (U = 0.1‰) -- much greater than intralaboratory reproducibility (Fig.3), and (coincidentally?) equal to the dispersion of $\delta^{13}C$ measurements during the last IAEA intercomparison [2]. This dispersion is independent of the magnitude of measured $\delta^{45}CO_2$ and $\delta^{46}CO_2$ (cf. Figs.4-5). The effect on $\delta^{13}C$ from using different $^{17}R_{VSMOW}$ values *is* dependent on the magnitude of input deltas; the smaller the isotopic differences between sample and standard, the smaller the $^{17}R_{VSMOW}$ effect on $\delta^{13}C$. Therefore, unless the working standard is calibrated as outlined in these proceedings, *variation in fractionation coefficient between working standards and a common reference material can be a major source of uncertainty in consequential values of $\delta^{13}C$.*

1.4 Covariation Between $\delta^{13}C$ and $\delta^{18}O$

Because conventional reduction algorithms must assume a fixed oxygen isotope fractionation coefficient between sample and working standard, a functional relationship between calculated values of $\delta^{13}C$ and $\delta^{18}O$ can result when the true value of $\boldsymbol{a}$ differs from the value assumed. We have determined the magnitude of this effect by simulating compositions of ten hypothetical CO_2 samples, keeping ^{13}R constant and varying ^{18}R through the natural range. Three values for ^{17}R were calculated for each simulated gas, using Eq.5, for $\boldsymbol{a} = 0.5$, 0.52 and 0.54. Then, ^{45}R and ^{46}R values were constructed through Eqs.10-11; the working

$$^{45}R = {}^{45}CO_2/{}^{44}CO_2 = {}^{13}R + 2\cdot{}^{17}R \tag{10}$$

$$^{46}R = {}^{46}CO_2/{}^{44}CO_2 = 2\cdot{}^{18}R + 2\cdot{}^{13}R\cdot{}^{17}R + ({}^{17}R)^2 \tag{11}$$

standard was defined as NBS-19-CO_2 with $\boldsymbol{a} = 0.52$ vs VSMOW. Simulated $\delta^{45}CO_2$ and $\delta^{46}CO_2$ values (from Eq.1) were reduced to $\delta^{13}C$ and $\delta^{18}O$ (using the IAEA-1981 algorithm [9]); results are displayed in Fig.6. The magnitudes of the biases in $\delta^{13}C$ values ($\delta^{13}C_{true}$ - $\delta^{13}C_{calc}$) were independent of the value of ^{13}R within the natural range. Inspection of Fig.6 reveals that resulting values for $\delta^{13}C$ are *not* fixed, but are functionally related to $\delta^{18}O$ and $\boldsymbol{a}$. When $\boldsymbol{a} =$ 0.5, as is assumed in the algorithm, $\delta^{13}C$ values are well behaved and deviations are insignificant. The covariation effect increases, however, as $\boldsymbol{a}$ values depart from 0.5. Values of $\delta^{13}C$ from samples having $\boldsymbol{a} = 0.52$ (vs the working standard) will be biased > 0.01‰ when $|\delta^{18}O| > 10$‰. Since the true value for $\boldsymbol{a}$ is not usually known for a particular measurement,

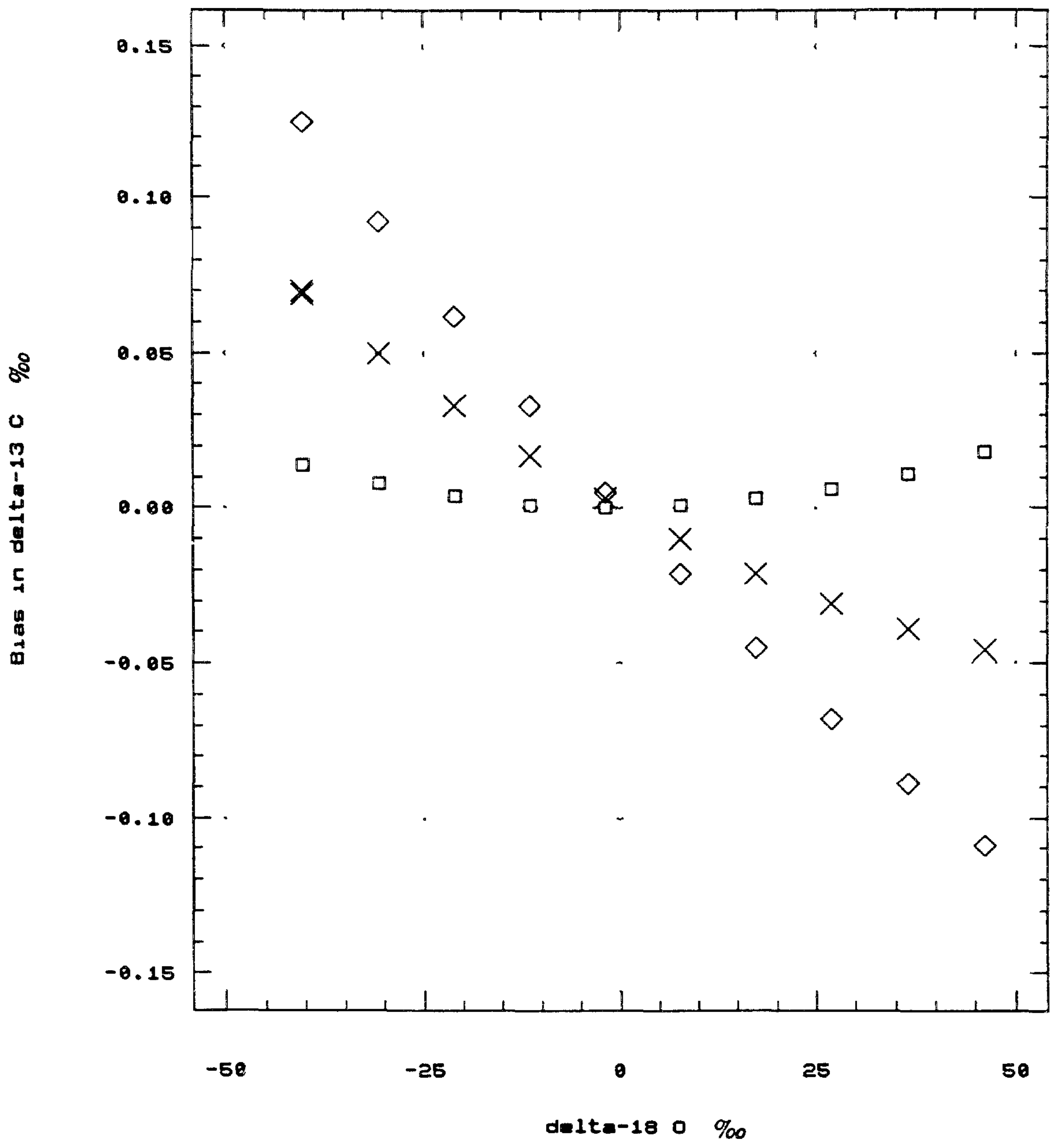

Figure 6: Covariation between $\delta^{13}C$ and $\delta^{18}O$ values (from the IAEA-1981 algorithm) as a function of the actual oxygen isotope fractionation relationship (*a*) between sample and working standard. All hypothetical CO_2 samples were constructed with one value for $\delta^{13}C_{true}$. Symbols designate true value of *a*: □: 0.5; ×: 0.52; ◇: 0.54. Bias ($\delta^{13}C_{true}$-$\delta^{13}C_{calc}$) is independent of the value of $\delta^{13}C_{true}$. See section 1.4.

the bias cannot be corrected; the total uncertainty of $\delta^{13}C$ is partially a function of the $\delta^{18}O$ value. The uncertainties from this effect have been covered in our Monte Carlo treatment described above.

1.5 Conclusions and Recommendations

For unrelated samples and working standards of CO_2, the IAEA-1981 algorithm generates $\delta^{13}C$ and $\delta^{18}O$ values within expanded uncertainty (U) distributions of alternative algorithms that use various values of *a* and $^{17}R_{VSMOW}$. As an historical and explicit data reduction standard the IAEA-1981 algorithm should continue to be employed. However, isotopic analyses of CO_2 should include the reporting of $\delta^{45}CO_2$ and $\delta^{46}CO_2$, the isotopic composition and source of the working standard, and algorithm/assumption identifiers, to provide a link with any future changes. Working standards should be calibrated for $\delta^{45}CO_2$ and $\delta^{46}CO_2$ vs. RM8544-CO_2 (NBS-19-CO_2) and linked directly to the VPDB scale before reducing measurements to $\delta^{13}C$ and $\delta^{18}O$, as detailed by Francey and Allison (Annex 1). Reports of measurements should include not only measurement repeatability but also uncertainty based on natural variations in α with respect to the calibration procedures utilized; these uncertainties may be as high as ±0.1‰ (U). The α-effect would also influence isotopic analyses of gases such as SO_2 and N_2O that rely on an oxygen isotope fractionation assumption.

Further independent measurements of $\delta^{17}O$ and $\delta^{18}O$, and absolute ratio determinations, are needed on terrestrial and atmospheric samples of interest, and on gases used as working standards, to place tighter constraints on the fractionation coefficient among and between samples and typical working standards. Further measurements of absolute ratios of carbon and oxygen isotopes in standard reference materials are also encouraged.

2. Calculation of $\delta^{13}C$ and $\delta^{18}O$ from $\delta^{45}CO_2$, $\delta^{46}CO_2$ and $\delta^{47}CO_2$ Measurements

Due to natural variations in the mass-dependent relationship between pools of terrestrial oxygen isotopes, conventional methods for determining $\delta^{13}C$ and $\delta^{18}O$ from $\delta^{45}CO_2$ and $\delta^{46}CO_2$ measurements are inherently limited in achievable reproducibility; Section 1 describes limitations that can translate into expanded uncertainties (U) of 0.1‰ for $\delta^{13}C$ *independent* of intralaboratory measurement repeatability. Here, a method is introduced for calculation of $\delta^{13}C$ and $\delta^{18}O$ from $\delta^{45}CO_2$, $\delta^{46}CO_2$ and $\delta^{47}CO_2$ measurements, independent of the relationship among oxygen isotopes. Measurements are reported that demonstrate the feasibility and current limitations of this technique.

2.1 "3-Measurement" Algorithm

From measured $\delta^{45}CO_2$, $\delta^{46}CO_2$ and $\delta^{47}CO_2$, values for ^{45}R, ^{46}R and ^{47}R are calculated using Eqs.1,10,11, and a third definition for isotopic CO_2:

$$^{47}R = {}^{47}CO_2/{}^{44}CO_2 = 2\cdot{}^{13}R\cdot{}^{18}R + 2\cdot{}^{17}R\cdot{}^{18}R + {}^{13}R\cdot({}^{17}R)^2 \qquad (12)$$

The value of ^{13}R is solved through an iterative quadratic expression, Eq.13,

$$^{13}R(i+1) = \frac{-B + \sqrt{B^2 - 4\cdot A(i)\cdot C}}{2\cdot A(i)} \qquad (13)$$

where:

$$A(i) = 5\cdot{}^{13}R(i) - 3\cdot{}^{45}R \qquad (14)$$

$$B = 4\cdot{}^{46}R - ({}^{45}R)^2 \qquad (15)$$

$$C = 4\cdot{}^{45}R\cdot{}^{46}R - 8\cdot{}^{47}R - ({}^{45}R)^3 \qquad (16)$$

No higher order terms have been neglected; the relationships are exact. Seeding ^{45}R into $^{13}R(1)$ and ten iterations gives a $^{13}R(11)$ value with the required precision; this value is used to solve for ^{17}R and ^{18}R using Eqs.10-12.

To determine the required level of $\delta^{47}CO_2$ measurement repeatability for the "3-measurement" (3-M) approach, Monte Carlo methods (section 1.2) were used to generate distributions of $\delta^{13}C$ and $\delta^{18}O$ values from various levels of measurement uncertainty. These simulations showed that the 3-M algorithm is limited by the repeatability of $\delta^{47}CO_2$ measurements -- these must approach 0.03‰ (equal to the repeatability of $\delta^{46}CO_2$ during conventional measurements) to rival the "2-measurement + a-assumption" (2-M) technique. In natural abundance CO_2, the m/z 47 ion beam is about two orders of magnitude less intense than the m/z 46 ion beam, so unconventional measurement methods were required to reach the repeatability requirements.

2.2 Measurements

Two CO_2 samples from our inventory, differing in $\delta^{13}C$ compositions by about 45‰, were measured on a Finnigan[4] MAT 252. The Faraday cup detector array was physically arranged so that m/z 44-47 CO_2 ion beams were collected individually and simultaneously. Due to software limitations only two ion beam ratios could be simultaneously acquired, so automated methods were used that repeatedly alternated acquisition configurations between m/z 44, 45, 46 and m/z 44, 45, 47. The resistor/capacitor pairs in the detector array were selected so that all output voltages were similar. To improve repeatability of $\delta^{47}CO_2$ measurements, pressures of CO_2 (40 kPa) about eight times larger than normal were used [23]. This required an increase in ion source pumping capacity that was achieved with differential pumping; gas pressures during acquisitions were 50 μPa (500 pbar) in the ion source and 3 μPa (30 pbar) in the analyzer tube. The ion source was operated with an emission current of 1 mA, electron energy of 80 eV, and accelerating voltage of 8 kV. The output signal of the mass 44 peak was automatically centered and adjusted to 4 V to start each set of measurement cycles; the idle time for each half-cycle was 3 minutes. Peak 44 overlap onto the mass 45 signal was measured and found to contribute less than 0.001‰ to the measured values for $\delta^{45}CO_2$. Each gas was measured repeatedly; the grand mean (‰) and standard uncertainty (u) were $\delta^{45}CO_2 = 41.560 \pm 0.006$, $\delta^{46}CO_2 = 10.645 \pm 0.007$, and $\delta^{47}CO_2 = 53.756 \pm 0.030$.

2.3 Results and Conclusions

Grand means and standard uncertainties were reduced using 2-M and 3-M algorithms, and uncertainty distributions were generated by Monte Carlo methods; $\delta^{13}C$ results are plotted as frequency histograms in Fig.7. The top three histograms arise from 2-M algorithms using three discrete values of $^{17}R_{VSMOW}$; the bottom histogram depicts results of the 3-M algorithm. The uncertainty of the 3-M result is slightly smaller than the 2-M distributions. All distributions overlap, although some barely. A sensitivity analysis of the two algorithms indicates that the 3-M method is more susceptible to isobaric interferences owing to its reliance on the low abundance (*ca.* 0.0048%) of the m/z 47 ion beam. Isobaric interferences of 2.5 ppbv (parts-per-10^9 by volume) at this m/z position can lead to biases in $\delta^{13}C$ of 0.10‰. The same effect for the 2-measurement method requires a 1200. ppbv perturbation at the m/z 45 position. Because we have not characterized these gases for isobaric interferences, a statistical comparison of these $\delta^{13}C$ distributions is unwarranted at this time. The 3-M method is best applicable to the differential measurement of well-characterized standard materials. We continue to develop this approach through improvement in measurement repeatability and identification of error sources.

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[4] Certain commercial equipment, instruments, or materials are identified in this paper to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

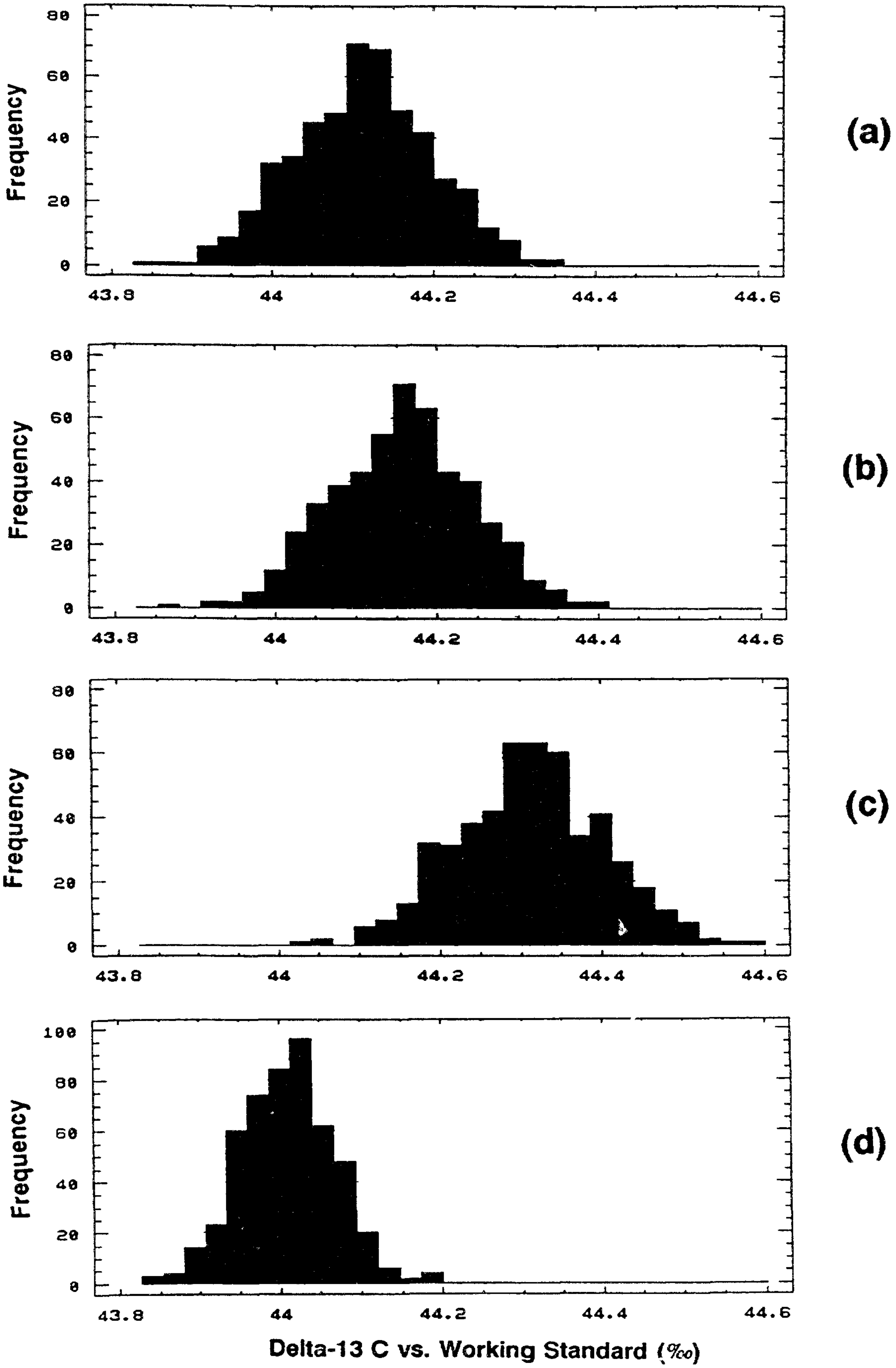

Figure 7: Frequency histograms of Monte Carlo $\delta^{13}C$ results through the 2-M (plots a c) and 3-M (plot d) algorithms using highly-repeatable $\delta^{45}CO_2$, $\delta^{46}CO_2$ and $\delta^{47}CO_2$ measurements Plots a-c use different assumptions: (a) Eq.7, (b) Eq 8, (c) Eq 9. See section 2 3.

3. Requirements, Production and Measurements of Isotopic Gas Standards

To detect small but significant temporal and spacial variations of $\delta^{13}C$ in carbonaceous trace gases, interlaboratory reproducibility of 0.01‰ (u) for CO_2 is a goal of the global atmospheric monitoring and modeling communities; the measurement reproducibility goals for $\delta^{13}C$ in other carbonaceous gases are somewhat more relaxed [24]. These goals require the general use of one reduction algorithm (Annex 1) and the global accessibility of intercomparison standards prepared with isotopic homogeneity among replicates better than 0.01‰ (u).

The isotopic measurement quality requirements for our group program are similar. We are integrating $\delta^{13}C$ measurements with our established ^{14}C measurement capability to characterize atmospheric aerosols and carbonaceous gas species [25]. Multi-isotopic signatures of these species, as conservative tracers, improve discrimination power for source apportionment, chemical transport/transformation, and receptor modeling [26]. Because chemical separation and purification of gases are accompanied by some degree of isotopic fractionation, we are producing isotopic gas standard mixtures to explore these effects and to achieve maximum measurement reproducibility. We are developing an approach to characterize pure gases for $\delta^{13}C$ and f_M then blend them with each other and with nitrogen or

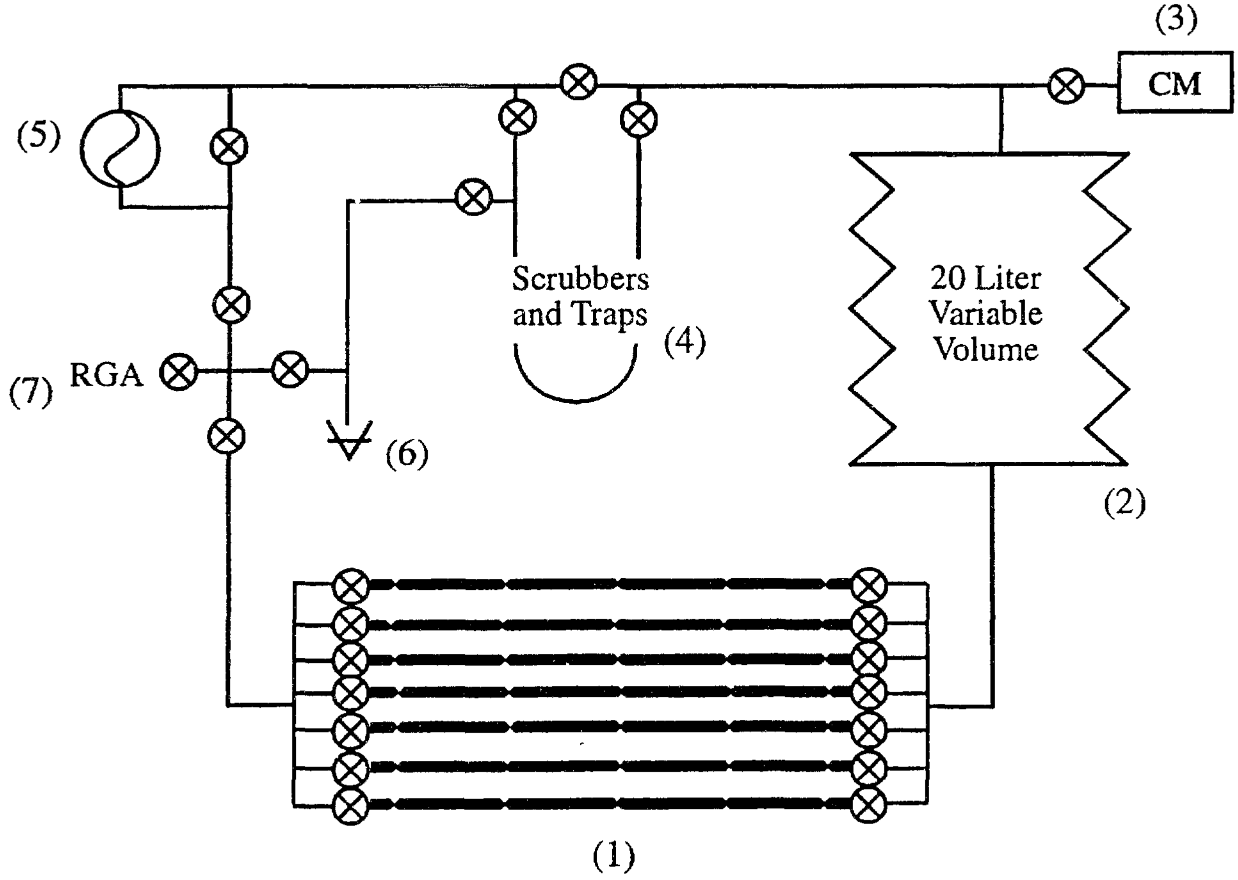

Figure 8: Gas isotope standard production system. (1) Set of seven parallel glass lines, prepinched into several open breakseals; valves are driven by pneumatic solenoids; (2) 20 liter stainless steel variable volume; (3) Capacitance manometer; (4) Scrubbers and traps for gas purification; (5) Metal bellows pump; (6) Vacuum system - molecular drag pump; (7) Gas inlet and residual gas analyzer. See section 3.1.

synthetic air.[5] In this section we describe the first stage: a production method for pure isotopic gas standards. Measurements on a prototype standard demonstrate that gas isotope standards and reference materials can be prepared with the reproducibility necessary for atmospheric programs.

3.1 Production of Isotopic Gas Standards

Using information gained from prior studies [2-3, 27], we have designed, built, and tested a parallel-process gas manifold (Fig.8) to allow the precise preparation of replicate units of pure gas and gas mixtures. Our system consists of a 20 L stainless steel variable volume, metal bellows pump, and circulation loop with a set of seven parallel glass tubes prepinched into several open breakseals. A quadrupole mass spectrometer is used to test for leaks and to identify impurities, and a high-throughput Russian doll cryotrap [28] is available to remove condensable impurities such as water vapor. To keep the internal pressure constant (about 70 kPa) during the breakseal filling procedure, the variable volume can be precisely adjusted. After each fill, a torch is used to quickly seal the prepinched areas of the tubes. Over one thousand 400 μmole replicates of an isotopic gas standard can be generated from one fill of the variable volume; the method is applicable to most gases.

The method was tested with pure CO_2 from a cylinder stored in our inventory. Seven prepinched borosilicate tubes (9 mm outer diameter) were annealed overnight at 600 °C; one tube was positioned and the system evacuated. The CO_2 was expanded to 70 kPa and recirculated through the dry ice/methanol cryotrap overnight. Then, the cryotrap was isolated and the gas allowed to recirculate for 30 minutes. Afterwards, the breakseals were torch-sealed, another prepinched tube installed, evacuated, and the gas expanded and recirculated for another 30 minutes through the new tube. The sequence was repeated several times and resulted in 28 replicates of the prototype standard. Ordinarily the seven tubes would be installed and filled together, but this method simulated the actual procedure without requiring an excessive number of tubes. The replicates produced were measured against a working standard prepared from the same gas to determine preparation reproducibility and possible isotopic differences among tubes.

3.2 Measurements

All delta values reported were measured on a Finnigan MAT 252. Automated methods were used that alternated acquisition configurations between m/z 44, 45, 46 and m/z 44, 45, 47. The ion source was operated with an emission current of 1 mA, electron energy of 80 eV, and accelerating voltage of 10 kV. Normal gas pressures (5 kPa) were used in the inlets. The output signal of the m/z 44 peak was automatically centered and adjusted to 5 V to start each set of measurement cycles; the idle time for each half-cycle was 5 minutes. Five replicates have been measured repeatedly; grand means (‰) and standard uncertainties (u) are: $\delta^{45}CO_2$: 0.047 ± 0.005; $\delta^{46}CO_2$: 0.230 ± 0.006; and $\delta^{47}CO_2$: 0.24 ± 0.08. No significant differences, within or between tubes, were observed among the replicates. The degree of reproducibility is quite sufficient for the needs of the atmospheric monitoring community. We continue to measure remaining replicates to monitor long-term stability of the isotopic compositions.

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5) f_M is the ^{14}C content expressed as the fraction of modern carbon, as related to the oxalic acid standard SRM 4990B.

3.3 Isotopic Gas Standards: Status at NIST

Facilities now exist at NIST to prepare a variety of isotopic gas standards. In conjunction with the IAEA, we are collecting feedback from the measurement and modeling communities on the most useful chemical and isotopic compositions and packaging options. Currently, our inventory contains several candidate natural and biogenic gases (Table III) and we are interested in identifying and locating other possibly important standard gases and mixtures.[6] At this time, however, only the IAEA-NGS gases [2] are available for informal distribution from our group.[6]

TABLE III
ISOTOPIC COMPOSITIONS[7] AND SOURCES OF
CANDIDATE STANDARD GASES

Gas	$\delta^{13}C_{VPDB}$ (‰)	$\delta^{18}O_{VPDB}$ (‰)	$f_M(^{14}C)$	Source
CO_2	-10.4	0.2	1.4	Grain Fermenter
CH_4	-43.6	-	1.3	Brazilian Sewer
Natural Gas (81% CH_4)	-29	-	0	IAEA: NGS-1
Natural Gas (53% CH_4)	-45	-	0	IAEA: NGS-2
Natural Gas (99% CH_4)	-73	-	1	IAEA: NGS-3

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HIGH PRECISION STABLE ISOTOPE MEASUREMENTS OF ATMOSPHERIC TRACE GASES [1]

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Abstract: *An overview of the CSIRO-DAR stable isotope program is presented. The broad scope of the program and application of the results to atmospheric science are illustrated. Some problems associated with the maintenance of a stable isotope program are described and the CSIRO-DAR data reduction procedure for stable isotope measurements is described.*

Part 1: An Overview

1.1. Introduction

The Commonwealth Scientific and Industrial Research Organisation Division of Atmospheric Research (CSIRO-DAR) has a significant interest in solving problems concerning the physics, dynamics and chemistry of the atmosphere. Four research programs address specific objectives in the areas of atmospheric pollution, atmospheric processes, climate modelling and global atmospheric change.

The global atmospheric change program focuses on the chemistry of the troposphere including observational and modelling studies. Specific objectives include:

- Determination of global distributions and trends of long-lived radiatively active (greenhouse) and ozone-depleting gases, their isotopic composition and precursors from atmospheric observations, ice cores and archived air samples.
- Modelling of atmospheric transport and exchange of these gases for interpretation of observations and prediction of future atmospheric concentrations.
- Quantification of rates and processes controlling emissions of climatically active trace gases from natural, agricultural and urban/industrial systems in Australia.
- Assistance in developing national inventories of gaseous emissions.
- Support and scientific collaboration in the Cape Grim Baseline Air Pollution Station.
- Development and enhancement of instrumentation and calibration techniques as required to achieve the scientific objectives.

As a key component of the study of the distributions and trends of long-lived radiatively active gases, CSIRO-DAR operates GASLAB (Global Atmospheric Sampling Laboratory) which is involved in addressing the reduction of uncertainties in the global carbon cycle, through coordination of measurements of trace gas concentrations and isotopic composition with transport modelling.

GASLAB maintains state-of-the-art instrumental facilities for the analysis of radiatively active trace gases and their isotopic composition. Whole air samples are collected from a number of land-based sites from the South Pole, Antarctica, to Alert, Ellesmere Island, Canada, through collaboration with international organisations. Figure 1 indicates some of the sampling locations. Samples are also collected on Antarctic supply voyages and on aircraft over-flights at various locations for specific projects.

One of the main interests of GASLAB is the high precision measurement of the stable isotopes of carbon dioxide, CO_2. This paper concentrates on this aspect of the CSIRO-DAR research interests.

1.2. *Isotopic ratio and composition*

Isotopic ratio is usually expressed as the ratio of the less common heavy isotope to the more common light isotope of an element, e.g. for carbon $r13 = {}^{13}C/{}^{12}C$ and for oxygen $r17 = {}^{17}O/{}^{16}O$ and $r18 = {}^{18}O/{}^{16}O$. Isotopic composition is usually expressed using the δ-notation as the difference in isotopic ratio between a sample material and a reference material (subscripts S and R respectively).

$$\delta^{13}C = \left[\frac{r13_S - r13_R}{r13_R}\right] \tag{1}$$

$$\delta^{18}O = \left[\frac{r18_S - r18_R}{r18_R}\right] \tag{2}$$

Isotopic composition is often expressed in units of parts-per-thousand or "per mil", ‰, obtained by multiplying the above expressions by 1000. Many processes of relevance to atmospheric studies, particularly biological processes, discriminate against the heavier isotopes, therefore, isotopic composition expressed in the δ-notation is usually negative.

1.3. *Cape Grim in situ record*

The CSIRO study of the stable isotopes of CO_2 was initiated in 1977 [2] with CO_2 being extracted cryogenically from whole air at the Cape Grim Baseline Air Pollution Monitoring Station, in north-west Tasmania, and returned to GASLAB for mass spectrometer analysis.

Although commenced in 1977, the Cape Grim in situ stable isotope program did not produce consistent high quality data until 1982 [3] and, to date, analyses of data have concentrated on the period from 1982. From 1982 until mid-1990 a VG602D mass spectrometer was used exclusively for the stable isotope analysis. In mid-1990 a new mass spectrometer, a Finnigan MAT252, was commissioned and both mass spectrometers were used to analyse the CO_2 samples extracted at Cape Grim [4]. At the end of 1991 the VG602D was de-commissioned.

The Cape Grim in situ CO_2 stable isotope record is presented in Figure 2. The solid lines represent data from the VG602D and the diamonds represent data from the MAT252.

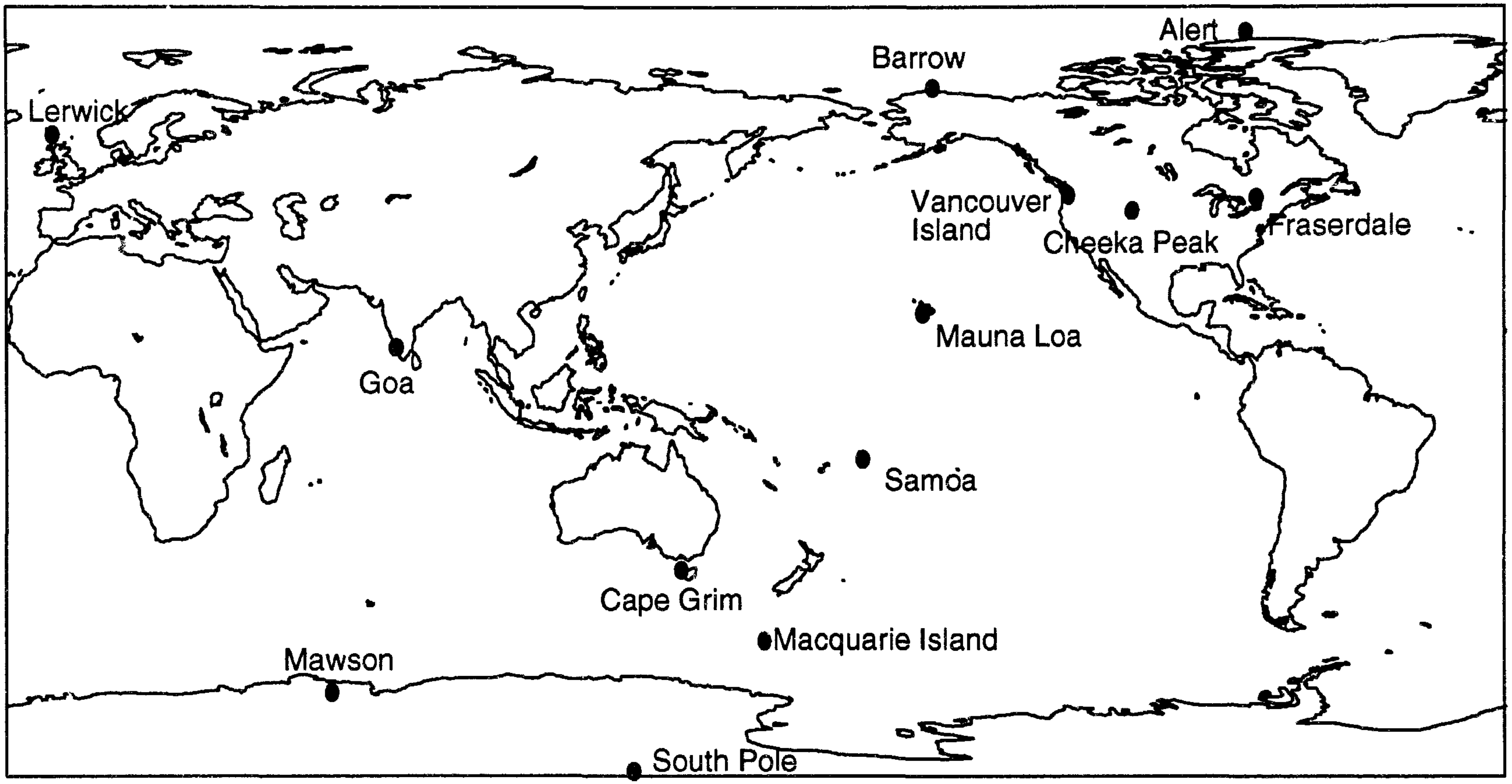

FIGURE 1. Locations of some of the global sampling sites at which air is collected for analysis by GASLAB.

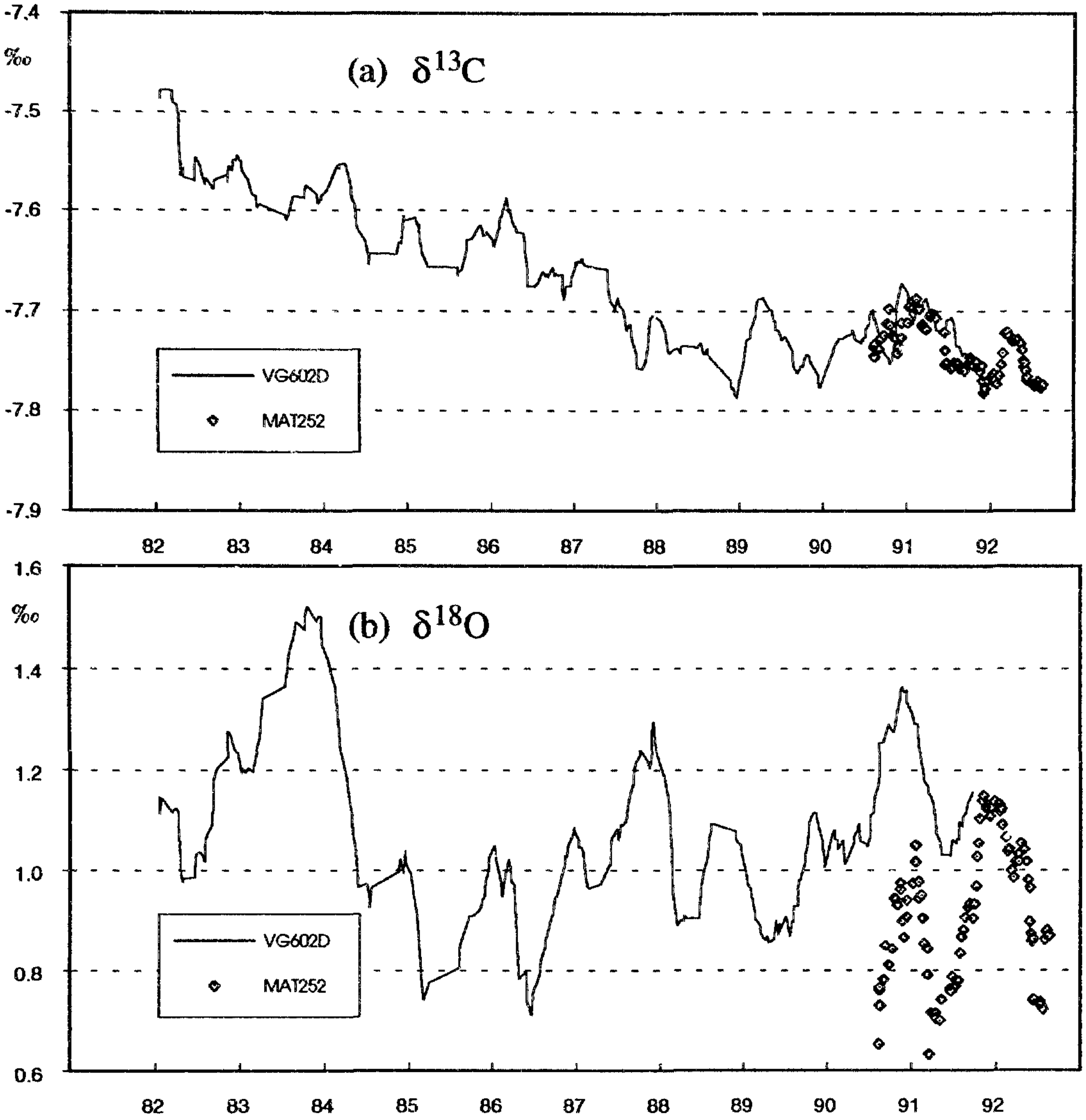

FIGURE 2. The **(a)** $\delta^{13}C$ and **(b)** $\delta^{18}O$ isotopic records for Cape Grim in situ CO_2 for the period 1982 through 1992 inclusive. The solid line represents a 5-point average, corresponding to an approximately 4-6 week average, of the VG602D data. The diamonds represent the same average for the MAT252 data. All δ measurements are in per mil, ‰, against VPDB. The slow convergence in $\delta^{18}O$ has been addressed elsewhere[4].

Each point is an average of 5 analyses and represents an approximately 4-6 week average. Comparison of data from the two mass spectrometers is the subject of a separate paper [4] and was the trigger for the work described in Part 2 of this paper. While both $\delta^{13}C$ and $\delta^{18}O$ records exist, discussion will be limited to the $\delta^{13}C$ record.

Three phenomena are clear in the $\delta^{13}C$ record. The first is the seasonal signal present in the data suggesting exchange with terrestrial biota, possibly a combination of exchange with southern hemisphere plants and a 4-6 month lagged signal from northern hemisphere plants. The second is a general decrease in the $\delta^{13}C$ of atmospheric CO_2 from 1982 until 1989, due to the release of isotopically depleted CO_2 into the atmosphere from

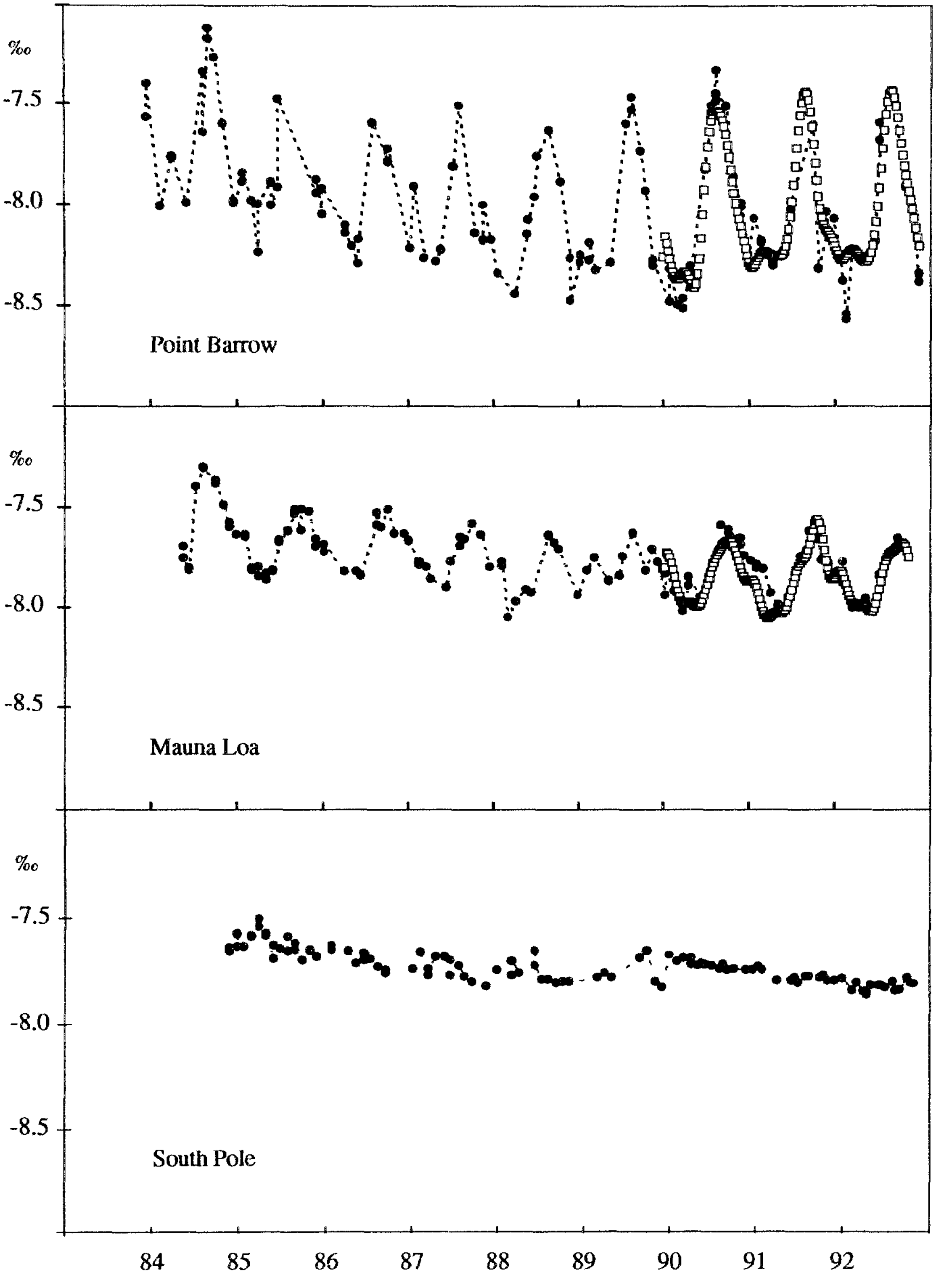

FIGURE 3. The $\delta^{13}C$ records for 3 global sampling sites. The solid circles (dashed lines) are the GASLAB measurements. The open squares are a spline fit to data obtained by NOAA-UC (Ref [5]). No NOAA-UC data are available for the South Pole.

fossil fuel. The third is the cessation of this decrease in 1989 with the ^{13}C isotopic composition of CO_2 remaining relatively constant. This "flattening" is the subject of a separate paper [5].

1.4. Global sampling sites

In 1984 a program was established to collect 10 L air samples, chemically dried, from a network of global sampling sites. The air samples were returned to GASLAB where the trace gas concentrations were measured and CO_2 (about 3 mL) was extracted cryogenically for gas isotope ratio mass spectrometer analysis. A recent upgrade of GASLAB has allowed the sampling program to reduce the air requirement from 10 L to 1 L, and modifications to the CO_2 extraction facility have reduced the amount of air required to perform a routine isotopic analysis to about 30 mL, ie about 10 µL of CO_2.

Figure 3 shows the $\delta^{13}C$ records obtained from the whole air sampling program from three sites (solid circles) [5]. Each of the three sites exhibits a change to less negative slope in $\delta^{13}C$ from about 1988. Superimposed over the GASLAB record are measurements made by a separate sampling program (open squares). The excellent agreement between the two independent programs at the end of the decade 1982-1992 lends support to the CSIRO record over the whole period, particularly in view of the consistency of calibration standards and procedures in the CSIRO program.

1.5. Analysis of the CO_2 stable isotope record

Total CO_2 in the atmosphere is a composite of CO_2 from various sources or reservoirs. Likewise, the isotopic composition of the atmospheric CO_2 is a composite of the isotopic signatures of the different reservoirs. Neglecting fractionations which may occur in transferring CO_2 between reservoirs, we can construct a relationship, from Dalton's law of partial pressures, which combines the concentration and isotopic composition of CO_2 from all reservoirs. Using $\delta^{13}C$ for the isotopic composition of the CO_2, and designating the various reservoirs of CO_2 with the subscripts x, y, ..., we determine the observed isotopic composition of the atmosphere.

$$\delta^{13}C_{x+y+...}[CO_2]_{x+y+...} = \delta^{13}C_x[CO_2]_x + \delta^{13}C_y[CO_2]_y + ... \qquad 3$$

The addition of isotopically distinct CO_2 to the atmosphere will affect the overall composition of the atmosphere as determined by this relationship.

To demonstrate this, consider the atmospheric concentration of CO_2 to be 350 ppmv and the isotopic composition of this CO_2 to be $\delta^{13}C = -8‰$. The addition of 1 ppmv CO_2 with $\delta^{13}C = -25‰$, typical of terrestrial plant carbon, will increase the atmospheric CO_2 concentration to 351 ppmv, and decrease the $\delta^{13}C$ by about -0.05‰. Likewise, the addition of 1 ppmv of CO_2 with $\delta^{13}C = -10‰$, such as from atmospheric CO_2 which is in equilibrium with ocean mixed-layer carbon, would increase the total CO_2 concentration to 351 ppmv, but would decrease the atmospheric $\delta^{13}C$ by about -0.006‰.

Using these results, it is possible to constrain the global carbon budget by considering separately the changing atmospheric carbon content and the changing atmospheric isotopic composition. We can separate the left hand side of Equation 3 into the sum of two components.

$$d(C_a\delta_a)/dt = \delta_a d(C_a)/dt + C_a d(\delta_a)/dt \qquad 4$$

Detailed analysis of this relationship [5,6,7] has grouped significant components of the isotopic constraint on the global carbon budget as a combination of net and gross biospheric fluxes, Nb and Gb, and net and gross ocean fluxes, Ns and Gs. This allows us to consider the release of carbon into the atmosphere from fossil fuel, and the biospheric and ocean sources and sinks for carbon. GASLAB has accumulated examples which demonstrate the major influences on atmospheric $\delta^{13}C$; two examples are given here.

1.5.1. Net biosphere term, Nb

The dominant influence on atmospheric $\delta^{13}C$ on time scales less than centuries is the photosynthetic kinetic fractionation by terrestrial plants. The influence over seasonal time scales is illustrated in Figure 4(a) , for the Canadian station at Alert, Canada (R.J. Francey, C.E. Allison and N.B.A. Trivett, private communication). The seasonal decrease in CO_2 (northern hemisphere summer) is accompanied by an increase in $\delta^{13}C$ due to the preferential uptake of the lighter CO_2 during photosynthesis.

Figure 4(b) shows $\delta^{13}C$ plotted against CO_2 concentration (open triangles) and against inverse CO_2 concentration (solid diamonds). The plot of $\delta^{13}C$ versus CO_2 indicates the change in $\delta^{13}C$ to be about -0.05‰ per ppmv. The plot of $\delta^{13}C$ versus $1/[CO_2]$ concentration shows the isotopic composition of the CO_2 being used in photosynthesis to be about -25.8‰.

1.5.2. Gross air-sea exchange, Gs

Figure 5 shows the $\delta^{13}C$ latitudinal gradient obtained on a ship cruise between Hobart, Tasmania, and the east coast of Antarctica in January, 1993 (R.J. Francey, C.E. Allison and H.M. Beggs, private communication). The observed $\delta^{13}C$ gradient is the reverse of that expected from the southward drift of northern hemisphere air, which is depleted in $\delta^{13}C$ due to fossil fuel release. We expect, and have confirmed elsewhere, that no significant influence is expected on $\delta^{13}C$ as a result of net exchange with the oceans. The observed change is however, consistent with the change in air-sea fractionation factor due to the 14°C change in sea surface temperature [8]. The gross exchange of CO_2 with the oceans transmits this signal to the atmosphere even in the absence of net exchange. Rapid atmospheric mixing reduces the signal in $\delta^{13}C$ in the atmosphere due to air-sea fractionation by around an order of magnitude, however, as seen in Figure 5, the signal is still detected.

1.6. Other isotopic measurements

Atmospheric CO_2 isotopes can be measured for past atmospheres by sampling air held in two types of air archives. Measurement of a number of isotopic ratios, other than $\delta^{13}C$ and $\delta^{18}O$ of CO_2, are possible in GASLAB. The isotopes of N_2 and O_2 can be measured as can the $\delta^{13}C$ of methane, CH_4.

1.6.1. Air archives - archive tanks

Since the establishment of the Cape Grim baseline station, air has been stored for future analysis of atmospheric constituents in high-pressure stainless steel tanks. The $\delta^{13}C$ of atmospheric CO_2 since 1978 can be accessed through this resource, as can atmospheric trace gas compositions and isotopic measurements on other species.

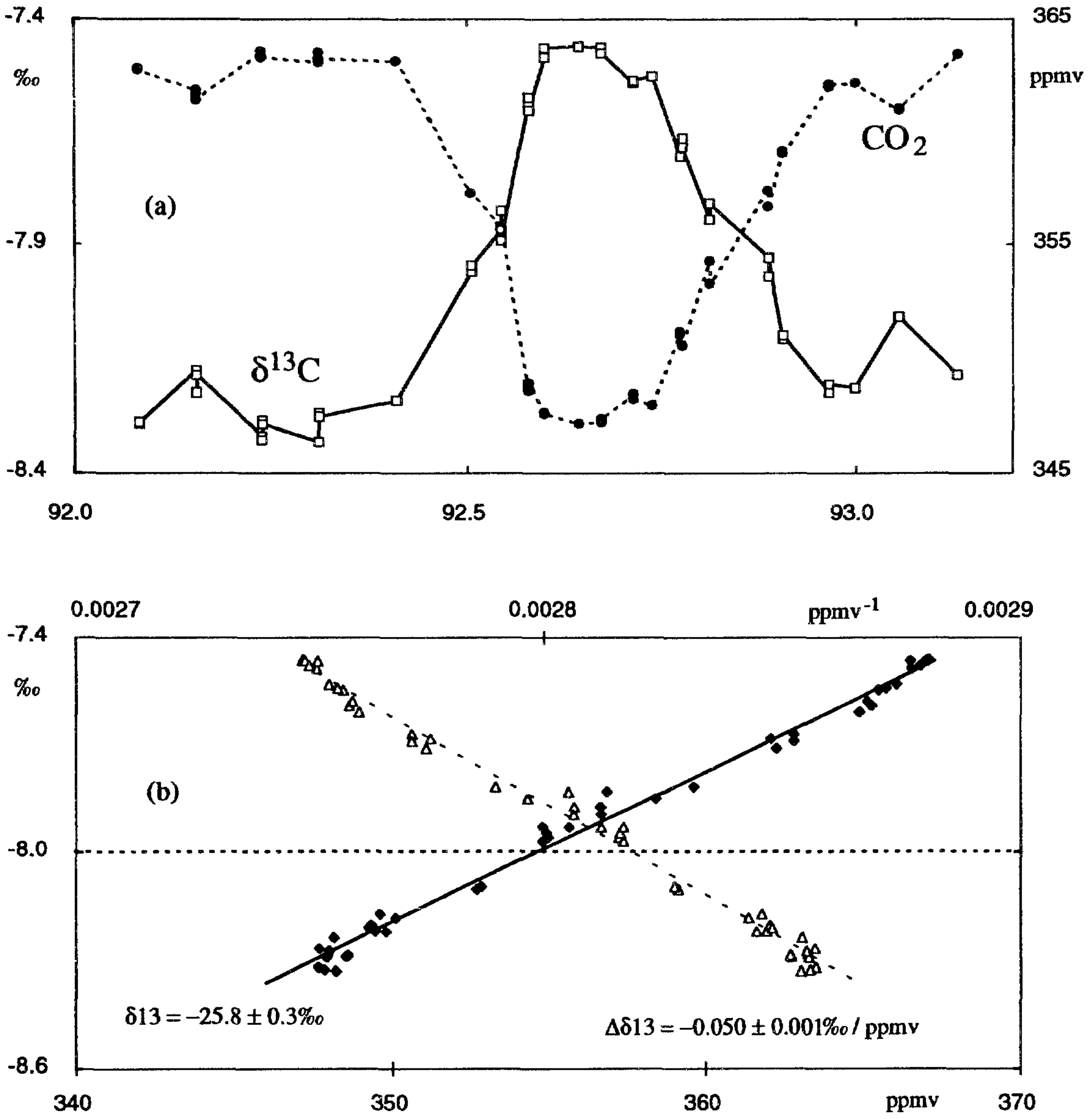

FIGURE 4. (a) One year cycle in CO_2 (solid circles: ppmv - right ordinate) and $\delta^{13}C$ (open squares : per mil - left ordinate) measured at Alert, Canada (82°N), showing the correlation between CO_2 concentration and $\delta^{13}C$ isotopic composition. (b) Plot of $\delta^{13}C$ vs. CO_2 concentration (open triangles) shows plant $\delta^{13}C$ signature of -0.050 ± 0.001 ‰ per ppmv. Plot of $\delta^{13}C$ vs. inverse CO_2 concentration (solid diamonds) indicates the extinction $\delta^{13}C$ of the removed CO_2 to be -25.8 ± 0.3 ‰.

1.6.2. Air archives - Antarctic ice-sheets

GASLAB collaborates in the drilling of Antarctic ice-cores and extracts air trapped in the ice. Depending on the site of drilling, air as recent as a few decades or as ancient as a few hundred thousand years, can be accessed. More recent air samples, from a few to ten years, can be extracted from the firn layer, the accumulating snow layer which is compacting to form ice. Measurements of $\delta^{13}C$ for CO_2 in this firn air show reasonable agreement, after correction for gravitational separation, with modern atmospheric $\delta^{13}C$ measurements and with $\delta^{13}C$ measurements made on the air extracted from ice-cores. (It is

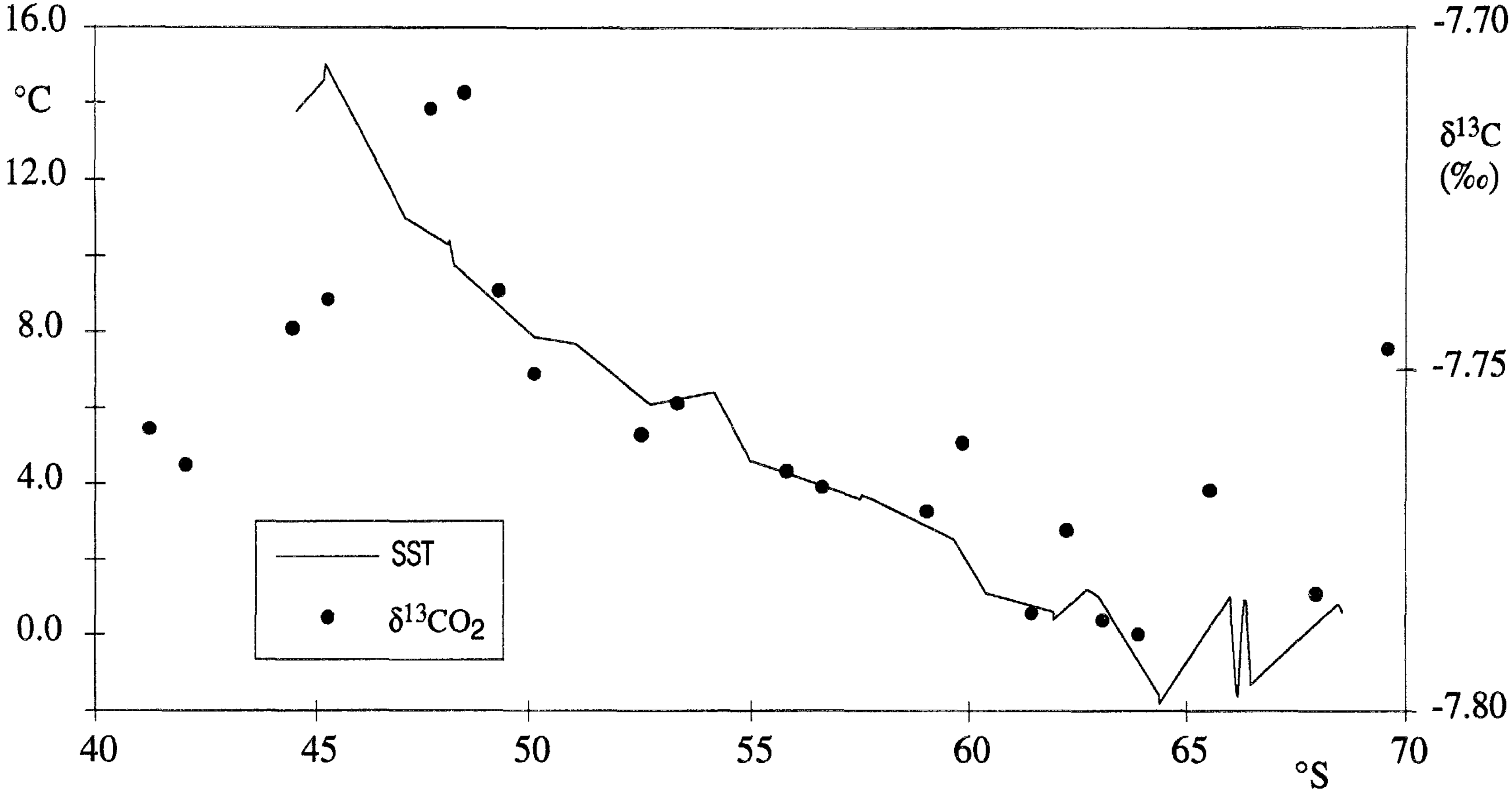

FIGURE 5. Plot of sea surface temperature (SST, °C) (solid line : left axis) and $\delta^{13}C$ (‰) of atmospheric CO_2 (circles : right axis) vs. latitude (°S).

anticipated that even better agreement will be achieved when full correction for non-equilibrium diffusion effects is made). Combination of the modern, firn and ice-core records provides a detailed history of $\delta^{13}C$ in CO_2 from pre-industrial times to the present and over glacial time-scales. Measurement of other isotopic ratios, such as $\delta^{15}N$ and $\delta^{18}O$ for N_2 and O_2 respectively, assist in understanding the mechanisms which drive gas inclusion in ice formation.

1.6.3. Other isotopes

If sufficient air is available (5 L or more) the $\delta^{13}C$ of atmospheric CH_4 can be measured using extraction techniques developed jointly with David Lowe of the New Zealand National Institute of Water & Atmospheric Research Ltd. (NIWA) and Paul Quay of the University of Washington, USA. CH_4 is combusted with atmospheric O_2 to form CO_2 and H_2O which are trapped cryogenically. The CO_2 is then separated from the H_2O and analysed. Long term measurements from Cape Grim are not yet available but preliminary analysis gives good agreement with the atmospheric record constructed for Baring Head, New Zealand [9].

1.7. Problems

A number of problems have been identified in the $\delta^{13}C$ measurement of the atmospheric CO_2. Box 1 summarises the "pitfalls" we have identified and which are described below.

BOX 1. Pitfalls in $\delta^{13}C$ measurement : The CSIRO experience.

Precision target			
	Individual sample		0.010 ‰
	Annual average		0.005 ‰
Gas standards			
	CO_2 flasks (o-ring taps)		≈ +0.02 ‰ L / year
	Air tanks		±0.10 ‰ ?
Mass spectrometer fractionations			
	Reservoir "bleed" effect		≈ 0.003 ‰ / hour
	"Sample size" effect :	Δr ~ 1 ‰ *	$\Delta_{2\text{-}6V} < 0.05$ ‰
		Δr ~ 20 ‰	$\Delta_{2\text{-}6V} \approx 0.4$ ‰
Ion corrections			
	^{17}O algorithms	Δr ~ 1 ‰	≈ 0.05 ‰
	N_2O		≈ 0.22±0.01 ‰
Sampling site bias			
	Cape Grim cliff		≈ ±0.01 ‰
	Boundary layer		≈ -0.01 ‰
	Interannual		?

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* $\Delta r = \delta 45 = r13(\text{sample}) - r13(\text{reference})$

1.7.1. Precision

Measurement of $\delta^{13}C$ can be used to constrain the sources and sinks for atmospheric CO_2. The deconvolution of atmospheric $\delta^{13}C$ data, for example, puts very severe constraints on the measurement for both spatial and temporal differences of $\delta^{13}C$ [7,10]. Enting et al. conclude that temporal precision, i.e. the trend, of $\delta^{13}C$ is the more important constraint. Our precision target for an individual $\delta^{13}C$ isotopic analysis is 0.01‰. For an annual average, the precision target drops to 0.005‰ based on averaging to reduce the precision of individual measurements. This assumes that most errors are random.

1.7.2. Gas standards

We maintain a suite of pure CO_2 standards (Table I) which are used both for measuring samples and monitoring the long-term stability of our standards. Occasional measurement of carbonate standards, such as NBS19, also serve to check the precision of our standards. Measurements over 15 years have shown that differences between sub-samples of the pure CO_2 standards are less than 0.02‰. Further, we have evidence that our standards are either all maintaining close to initial values, or that all standards are

TABLE I. The pure CO_2 reference gases used in GASLAB. All $\delta^{13}C_{VPDB}$ and $\delta^{18}O_{VPDB}$ values are in per mil, ‰.

Standard Name	Flask	Acquired	$\delta^{13}C_{VPDB}$	$\delta^{18}O_{VPDB}$
ST01†	15L glass	1977	-6.384	-13.230
ST02†	15L glass	1978	-6.383	-13.121
ST03†	50L glass	1978	-6.396	-13.176
ST04†	15L glass	1990	-6.405	-13.178
ST05†	15L glass	1990	-6.400	-13.158
CG06#	0.3L s/steel	1992	-37.2	-6.7
GS-19‡	0.25L s/steel	1992	-7.502	-0.193
GS-20‡	0.25L s/steel	1992	-8.622	-0.991
OZTECH-3*	1L steel	1990	-3.759	-21.511
OZTECH-30*	1L steel	1990	-30.281	1.315
OZTECH-40*	1L steel	1990	-40.651	-29.744

† CARBA CO_2 cylinder HC453
# Air Liquide, Melbourne, Australia. Approximate values.
‡ University of Groningen
* Oztech Trading Co.

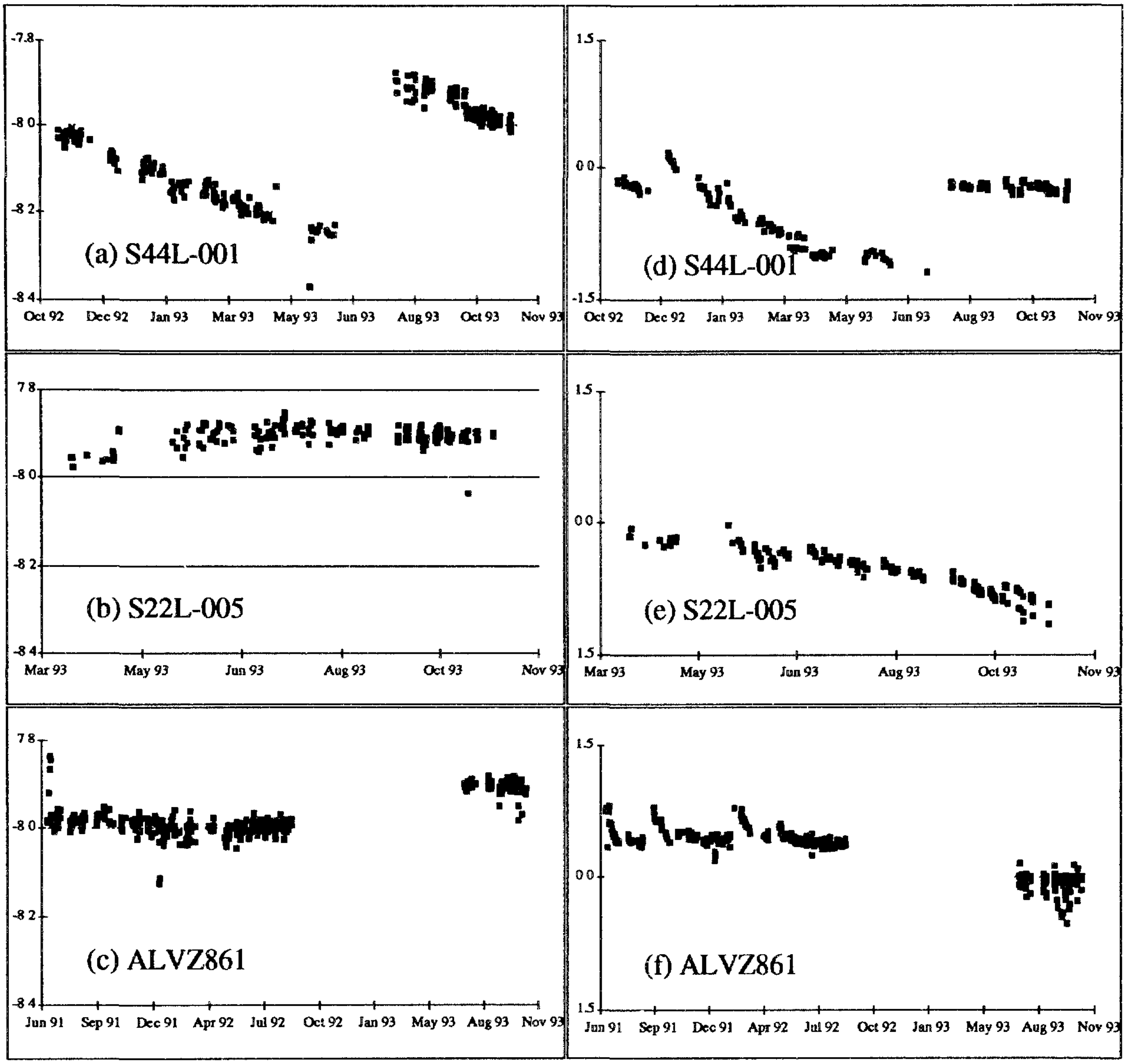

FIGURE 6. Air standards used to check the performance of the MAT252 mass spectrometer. Note that the time scales vary. The $\delta^{13}C$ measurements are shown in panels **(a)**, **(b)** and **(c)**. The $\delta^{18}O$ measurements are shown in panels **(d)**, **(e)** and **(f)**. All measurements are in per mil, ‰, against VPDB. The discontinuity observed for cylinder S44L-001 is due to refilling the cylinder in July, 1993. The discontinuity observed for cylinder ALVZ861 is an instrumental effect.

drifting at identical rates. External checks on the isotopic composition of some of the standards indicates the former. Further, we believe that observed shifts in CO_2 are due to the polymer o-ring seals used on some of the containers.

We also maintain a suite of air standards for use as calibration gases. The air standards have not been calibrated to the same precision as the CO_2 standards but have been monitored using the pure CO_2 standards. Significant variation in the behaviour of the air standards has been observed and indicates that the storage vessels are an important variable. Figure 6 presents the results of long-term monitoring of three of our air standards, ALVZ861, a 60L high pressure (45 bar) cylinder, S22L-005, a 22L low pressure

(2 bar) cylinder, and S44L-001, a 44L low pressure (2 bar) cylinder. ALVZ861 appears stable for both $\delta^{13}C$ and $\delta^{18}O$, S22L-005 maintained good $\delta^{13}C$ but $\delta^{18}O$ was drastically affected, and S44L-001 showed significant drift in both $\delta^{13}C$ and $\delta^{18}O$. We attribute these drifts in isotopic composition to small leaks in the container.

1.7.3. Mass spectrometer fractionations

A number of mass spectrometer effects have been observed which can introduce errors into the measurement of isotopic composition. We identify two of these effects as the "reservoir bleed effect" and the "sample size effect".

The "reservoir bleed effect" is observed during long periods of analysis where the reference gas fractionates. We estimate this effect is greatest when the reference gas has been allowed to "bleed" for long periods of time to the ion source or to waste. Measurements have characterised the maximum value of this effect to be about 0.0028‰ per hour, based on a 24 hour test using two gases of similar isotopic composition (Figure 7). We minimise this effect by refilling the reference gas reservoir every few hours during analysis.

The "sample size effect" results in different isotopic compositions being measured for the same sample against reference gas when measured at smaller analysis voltages, e.g. Vsa(m/e 44) < 2 volts, than normally used, e.g. > 3 volts. The magnitude of the effect is dependent on the difference in isotopic composition of the sample and reference gases (C. Flehoc, M.A. Leuenberger, R.J. Francey and C.E. Allison, private communication). Where the difference in isotopic composition is small ($\delta45$ only a few ‰) the difference observed in measuring small samples is less than 0.05‰. When reference and sample gas are very different (e.g. about 20‰) the observed difference is as large as 0.4‰. The effect most likely originates in mixing of the sample and reference gas in the ion source region. For normal samples analysed by GASLAB this effect is not a problem because of (i) the small difference in $\delta^{13}C$ between our CO_2 standards, based on HC453 CO_2, and air values, and (ii) the consistency of our sample sizes.

1.7.4. Ion corrections

Ion corrections are an important consideration in the construction of an atmospheric trace gas isotopic record. A number of problems in the ion correction procedures have been identified and are discussed below, in Part 2 of this paper.

1.7.5. Sampling site bias

Other effects have been observed which reflect a particular bias introduced into the isotopic composition during sample collection. For instance, vegetation near the sampling site may introduce $\delta^{13}C$ variation due to an increase or decrease in photosynthetic activity. Observed $\delta^{13}C$ may thus represent local phenomena rather than large scale features, such as ocean/atmosphere exchange. As deconvolution studies [5,6,7] require high precision in $\delta^{13}C$, effects such as this need to be identified and described on an individual basis.

Part 2: Data Reduction

Data reduction is an important aspect of stable isotope measurements. Because relative rather than absolute measurements are made errors can propagate through

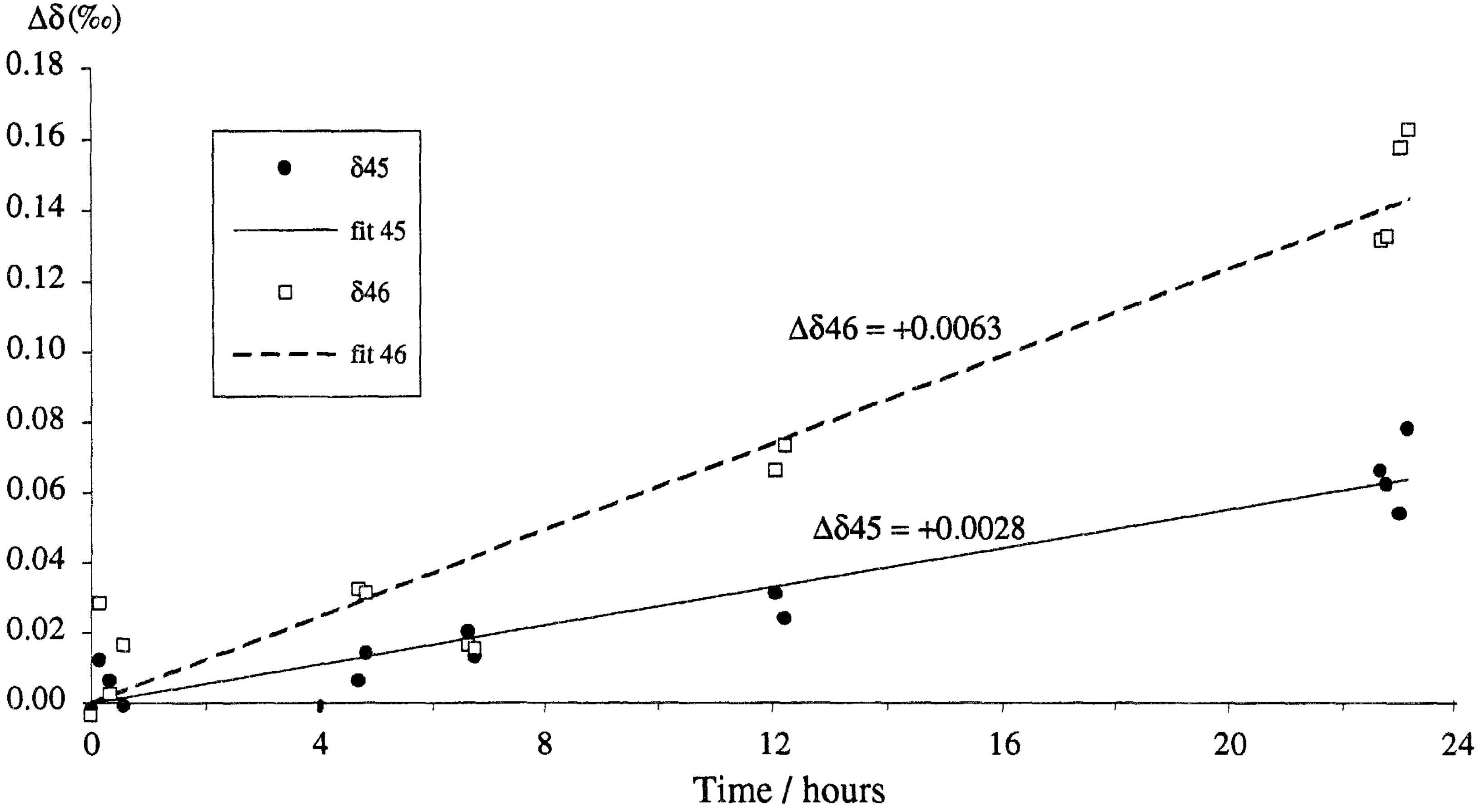

FIGURE 7. The reference gas bleed effect measured over a 24 hour period for sample and reference gas of similar isotopic composition. The solid and dashed lines represent linear best fits to the δ45 (solid circles) and δ46 (open squares) respectively. The Δδ values are in units of per mil per hour (‰ / hour).

calculations and comparisons can be made which do not have common points of reference. Due to the incremental nature of the development of our data reduction procedure, an historical approach is used to describe the procedure. Some material has been presented earlier in Part 1.

2.1. *Introduction*

The CSIRO Division of Atmospheric Research has a number of research projects which use the facilities of the Cape Grim Baseline Air Pollution Monitoring station (jointly administered by the Bureau of Meteorology and CSIRO-DAR) in north-west Tasmania.

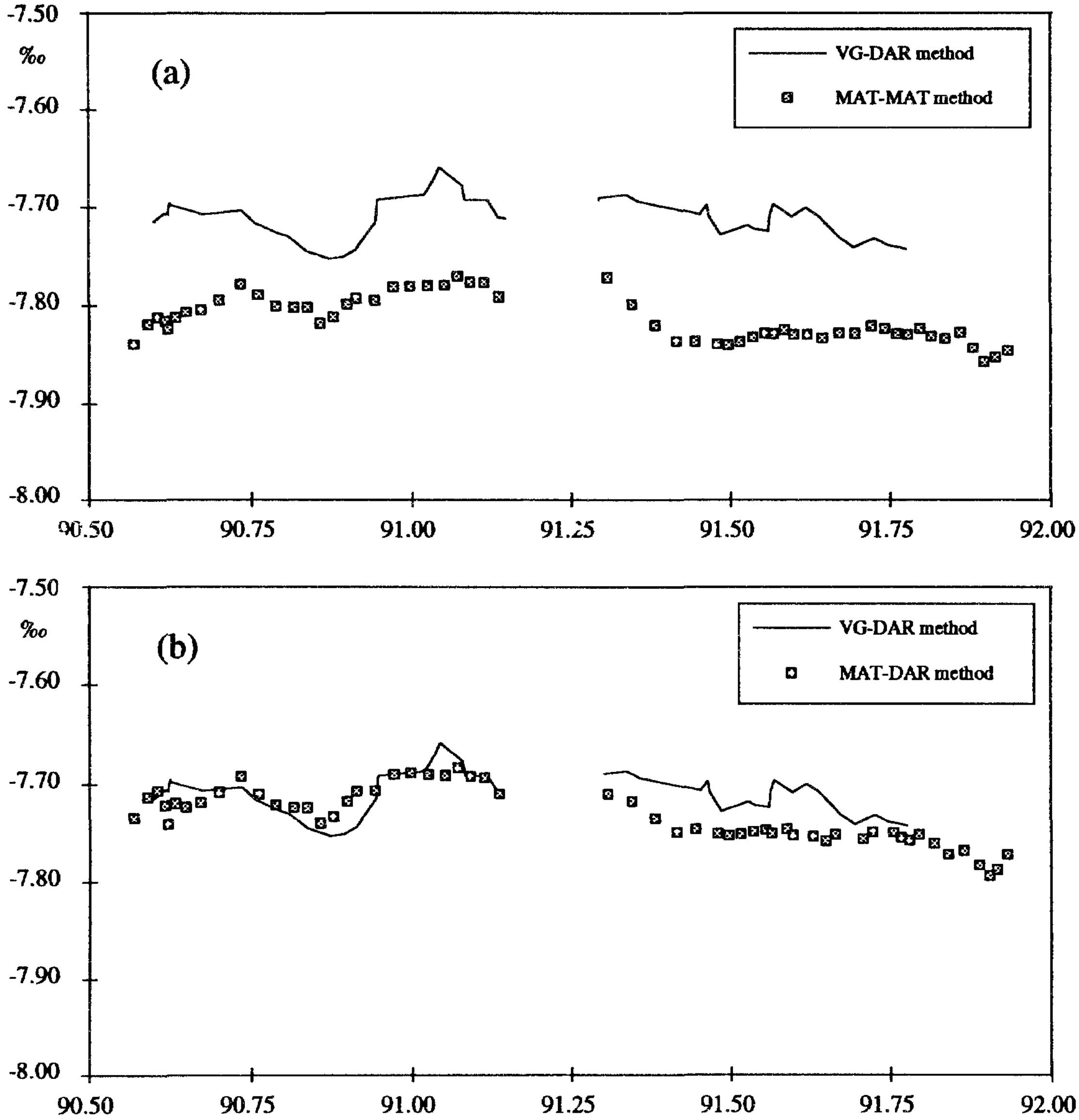

FIGURE 8. The Cape Grim in situ $\delta^{13}C$ isotopic record for the period of the mass spectrometer comparison. The VG602D data (represented by solid lines) and the MAT252 data (squares) represent 4-6 week averages. The break in both records in early 1991 is due to rejection of data from that time period. **(a)** The $\delta^{13}C$ records constructed using the CSIRO-DAR data reduction procedure for the VG602D data and the Finnigan MAT252 recommended ion correction procedure for the MAT252 data. **(b)** The $\delta^{13}C$ records constructed using the CSIRO-DAR data reduction procedure for both data sets.

One such program is the Cape Grim in situ CO_2 stable isotope program which has been operating in its present form since 1982. About 3 mL of CO_2 is extracted cryogenically from air, stored in a 100 mL glass flask and transported back to DAR for analysis.

From 1982, the Cape Grim CO_2 samples were analysed on a VG602D stable isotope mass spectrometer. In August, 1990, a Finnigan MAT252 stable isotope mass spectrometer was installed to replace the VG602D and CO_2 samples were analysed on both instruments for a period of over one year.

When the data for this comparison period was analysed, there was clear disagreement for the same samples concerning both $\delta^{13}C$ and $\delta^{18}O$. The $\delta^{18}O$ record appears to converge during the period of the mass spectrometer comparison and is assigned to an instrumental effect (Figure 2(b)). The $\delta^{13}C$ record shows a significant constant offset, illustrated in Figure 8(a).

A number of potentially important factors, including sample storage time were considered, however, with normal turn-around time and procedures, these were too small to be of concern.

The main cause for the disagreement was identified to be the different data reduction procedures recommended by the respective instrument manufacturers. Investigation of the data reduction procedures showed that systematic differences could be expected, as observed, and that the magnitude of the differences was dependent on the difference in isotopic composition of the sample CO_2 from the reference gas. A modified data reduction procedure was established and applied to both sets of data. The effect of this new procedure is shown in Figure 8(b).

After describing the two different data reduction procedures, the data reduction procedure now in use is described.

2.2. *General background*

The goal of the data reduction procedure is to enable r13, the $^{13}C/^{12}C$ ratio, and r18, the $^{18}O/^{16}O$ ratio, to be measured. The ratios r13 and r18 in a sample gas are usually expressed by reference to the same ratios in a standard or reference gas using the δ-notation.

$$\delta^{13}C = \left[\frac{r13_S}{r13_R} - 1\right] \qquad 1$$

$$\delta^{18}O = \left[\frac{r18_S}{r18_R} - 1\right] \qquad 2$$

The subscripts S and R to refer to ratios in the sample and reference gas respectively. We also use the lower case letters "s" and "r" to designate specific sample and reference gases as respectively, e.g. s13, r13, etc .... When used by itself, an "r" term without a complementary "s" term, represents a ratio in any CO_2 sample. We also reserve the upper case "R" to refer to a ratio in a calibrated reference material, such as R13, R45 for the absolute ratios in a calibration material such as NBS19.

Due to the presence of isobaric species in CO_2, $\delta^{13}C$ and $\delta^{18}O$ are not measured directly. Instead, combinations of ^{12}C, ^{13}C, ^{16}O, ^{17}O and ^{18}O form three ion currents measured at mass-to-charge ratios (m/e) 44, 45 and 46, referred to as I44, I45 and I46 respectively.

I44: $^{12}C^{16}O_2$

I45: $^{13}C^{16}O_2$; $^{12}C^{16}O^{17}O$

I46: $^{12}C^{16}O^{18}O$; $^{12}C^{17}O_2$; $^{13}C^{16}O^{17}O$

As I44 contains only the most abundant species, ^{12}C and ^{16}O, the ratio of the ion currents due to the less abundant species, i.e. I45 and I46, with respect to the most abundant ion current, I44, are reported as r45 and r46.

$$r45 = I45/I44 \tag{5}$$

$$r46 = I46/I44 \tag{6}$$

Due to the symmetry of the CO_2 molecule, there are two configurations for CO_2 containing one ^{17}O or ^{18}O atom. Combining the symmetry considerations, the combinations of CO_2 molecules contributing to the ion currents and the relationship for r45 and r46 allows us to express r45 and r46 as combinations of the ratios r13, r17 and r18.

$$r45 = r13 + 2r17 \tag{7}$$

$$r46 = 2r18 + 2r13r17 + (r17)^2 \tag{8}$$

Specifically, the quantities we measure for a sample CO_2 gas are the difference in s45 and s46 from the r45 and r46 of the reference CO_2 gas expressed in the δ-notation.

$$\delta 45 = \left[\frac{s45}{r45} - 1\right] \tag{9}$$

$$\delta 46 = \left[\frac{s46}{r46} - 1\right] \tag{10}$$

2.3. *The VG602D procedure*

The VG602D data reduction procedure used at CSIRO DAR has been described in detail elsewhere [11], but is briefly summarised here.

The VG602D mass spectrometer has a two Faraday cup collector system which measures directly the ratio of I45 to I44 to provide δ45 but measures the ratio of I46 to the sum (I44 + I45) to provide δ46. A "slit-correction" is applied to convert this measured "δ46" into a true δ46.

The relationship between ^{17}O and ^{18}O in the sample and reference gases is the equilibrium expression given by Craig [12].

$$\frac{s17}{r17} = \sqrt{\frac{s18}{r18}} \qquad 11$$

For sample gas with isotopic composition close to the reference gas, as with atmospheric samples, this is approximated as follows.

$$\delta 17 = \delta 18/2 \qquad 12$$

Also used is the approximate relationship given by Mook and Grootes [13] for converting measured $\delta 45$ and $\delta 46$ into $\delta^{13}C$ and $\delta^{18}O$.

$$\delta^{13}C = \frac{R45\delta 45}{R13} - \frac{R17\delta 46}{R13} \qquad 13$$

$$\delta^{18}O = \delta 46\left[1 - \frac{R45R17}{R18}\right] \qquad 14$$

2.4. *The MAT252 procedure*

The MAT252 has discrete collectors for each ion beam (I44, I45 and I46) and no "slit-correction" is necessary. The data reduction procedure used is based on the method of Santrock et al. [14] which differs considerably from the VG602D method in implementation.

The relationship between r17 and r18 is expressed as

$$r17 = k(r18)^{\alpha}, \qquad 15$$

where $\alpha = 0.516$ and $k = 0.0099235$. This compares with the expression used for the VG602D (Equation 11) where $k = [r17/(r18)^{\alpha}]$ and $\alpha = 0.5$. The value of k used (0.0099235) represents the hypothetical VPDB material.

Equation 15 is combined with Equations 7 and 8 to give the following expression

$$-3k^2(s18)^{2\alpha} + 2ks45(s18)^{\alpha} + 2s18 - s46 = 0, \qquad 16$$

which is solved numerically to give s18. The relationship of Equation 15 is used to provide s17, and s13 is calculated from Equation 7. These are then expressed as $\delta^{13}C$ and $\delta^{18}O$ using Equations 1 and 2.

2.5. *Common conversion*

Two common corrections are applied to the $\delta^{13}C$ and $\delta^{18}O$ obtained using the VG602D and MAT252 methods. The first converts the ion corrected $\delta^{13}C_S$ and $\delta^{18}O_S$ to the international VPDB material via $\delta^{13}C_R$ and $\delta^{18}O_R$ measured for the reference gas.

$$\delta^{13}C(VPDB) = \delta^{13}C_S + \delta^{13}C_R + 0.001(\delta^{13}C_S\delta^{13}C_R) \qquad 17$$

$$\delta^{18}O(VPDB) = \delta^{18}O_S + \delta^{18}O_R + 0.001(\delta^{18}O_S\delta^{18}O_R) \qquad 18$$

A second correction is applied to correct for the presence of N_2O which is removed cryogenically with the CO_2.

$$\delta^{13}C(N_2O) = \delta^{13}C(VPDB) + 0.233(N2O/CO2) \qquad 19$$

$$\delta^{18}O(N_2O) = \delta^{18}O(VPDB) + 0.338(N2O/CO2) \qquad 20$$

N2O is the concentration of N_2O in parts per billion (ppbv) and CO2 is the concentration of CO_2 in parts per million (ppmv). The constants 0.233 and 0.338 are dependent upon the relative ionisation efficiencies of N_2O and CO_2 and have been determined using the VG602D [3]. The corrections to the VPDB scale and for N_2O are applied identically to both VG602D and MAT252 data.

2.6. Comparison of VG602D and MAT252 data

To compare the two data reduction procedures a set of input data was generated and "corrected" using the two procedures. The input data and the results are presented in Table II.

Where the values of δ45 and δ46 are similar, the difference between data obtained using the two methods is small. However, when the δ45 and δ46 are dissimilar, either of opposite sign or with appreciable difference in magnitude, the difference becomes quite large.

Using values for δ45 and δ46 of -1‰ and 13‰, typical for Cape Grim CO_2 analysed against our major reference gas, we observed a difference in calculated $\delta^{13}C$ of -0.05‰ and $\delta^{18}O$ of +0.05‰. The $\delta^{13}C$ difference is almost exactly that observed as the

TABLE II. Comparison of the results obtained from the ion correction procedures used for data from the VG602D and MAT252 mass spectrometers. All values are in per mil, ‰. Where the magnitude and sign of the input δ45 and δ46 are equal, the difference between the two methods is small. For large differences in magnitude and/or sign the differences are appreciable. Values given in the final row are typical for atmospheric air measured against our working reference gas ST03.

Input		**VG602D**		**MAT252**		**difference**	
δ45	δ46	$\delta^{13}C_{VPDB}$	$\delta^{18}O_{VPDB}$	$\delta^{13}C_{VPDB}$	$\delta^{18}O_{VPDB}$	$\delta^{13}C_{VPDB}$	$\delta^{18}O_{VPDB}$
-20.000	-20.000	-20.676	-19.956	-20.701	-19.976	-0.025	-0.020
-10.000	-10.000	-10.338	-9.978	-10.351	-9.988	-0.013	-0.010
0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
10.000	10.000	10.338	9.978	10.353	9.988	0.015	0.010
20.000	20.000	20.676	19.956	20.708	19.975	0.032	0.019
-20.000	20.000	-22.028	19.956	-22.204	20.071	-0.175	0.115
20.000	-20.000	22.028	-19.956	22.211	-20.070	0.183	-0.114
-1.000	13.000	-1.507	12.972	-1.560	13.018	-0.053	0.046

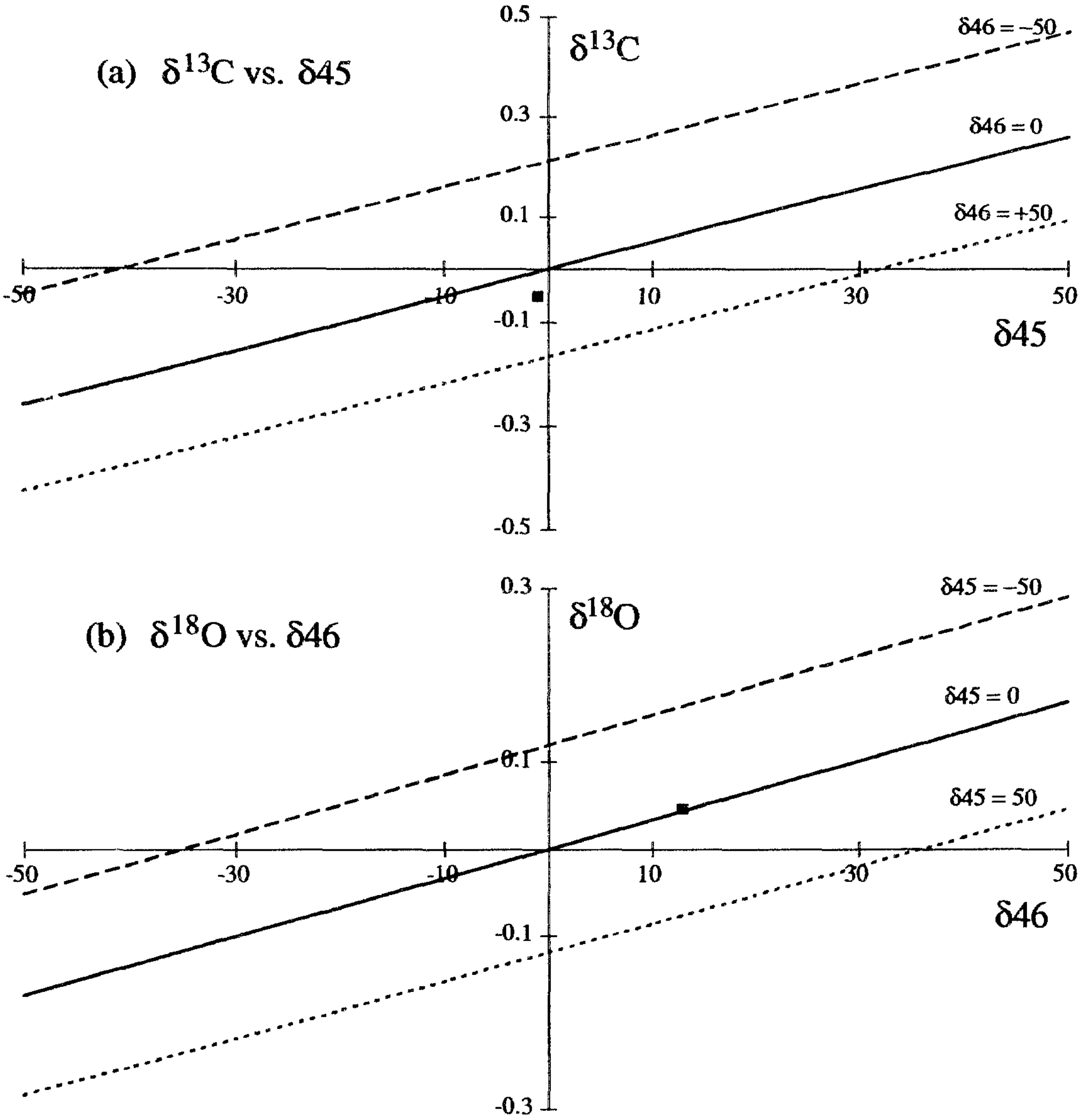

FIGURE 9. Calculated differences between the original VG602D and MAT252 methods plotted as **(a)** $\delta^{13}C$ vs. $\delta 45$ for various values of $\delta 46$, and **(b)** $\delta^{18}O$ vs. $\delta 46$ for various values of $\delta 45$. The solid square on each plot represents a typical sample of atmospheric CO_2 measured against our working reference gas ST03. The expected differences are about -0.05 ‰ and +0.05 ‰ for $\delta^{13}C$ and $\delta^{18}O$ respectively.

discrepancy in the Cape Grim in situ record (see Figure 8). The Cape Grim in situ $\delta^{18}O$ record is not sufficiently precise over the comparison period to identify the expected difference.

Other calculations showed the difference between the two methods to be systematic as demonstrated in Figure 9.

2.7. Origin of discrepancy

The discrepancy arises from the different values for the isotopic ratios of the reference material in each data reduction procedure.

TABLE III. Comparison of $\delta^{13}C$, $\delta^{18}O$ and isotopic ratios for the hypothetical VPDB CO_2, the CSIRO-DAR reference CO_2, HC453, and the NBS19 CO_2. For VPDB and NBS19 the ratios are calculated for CO_2 generated from the carbonate using 100 % phosphoric acid at 25°C. All isotopic ratios are in per mil, ‰.

	V-PDB	HC453	NBS19
$\delta^{13}C_{VPDB}$	0.000	-6.396	1.95
$\delta^{18}O_{VPDB}$	0.000	-13.176	-2.20
r13	0.01123720	0.01116533	0.01125911
r17	0.0003808033	0.0003782863	0.0003803842
r18	0.002088349	0.002060833	0.002083755

For the ion correction we need to consider two reference gases, VPDB CO_2, the hypothetical international reference gas, and HC453, the CSIRO DAR reference CO_2. The isotopic compositions used for these gases in each methods are presented in Table III.

Significant differences are apparent which arise as a consequence of three factors:

1. The problems associated with assigning the isotopic composition of VPDB CO_2, assigned by back calculation from NBS19.
2. The assumed relationship between ^{17}O and ^{18}O.
3. Which of the two data reduction procedures, specifically the α of Equation 15, is most appropriate.

To remove, or at least minimise, the influence of these factors we have developed a new approach to the reporting of isotopic measurements.

2.8. Reporting of isotopic measurements

Our method for reporting isotopic measurements is to relate all sample measurements back to the hypothetical VPDB CO_2 as $\delta 45$ and $\delta 46$ measurements. This means that the calculation of $\delta^{13}C$ and $\delta^{18}O$, and the assumption about the relationship between ^{17}O and ^{18}O, is required only once, and then only to report final results using the VPDB scale.

Measurements of the isotopic ratios in a sample are made against a reference material calibrated against NBS19, the accepted international reference material which defines the VPDB scale. The sample analysis and reference calibration measurements are all measured as $\delta 45$ and $\delta 46$ so it becomes a simple procedure to construct the $\delta 45$ and $\delta 46$ of the sample with respect to NBS19. For example, if a sample (SA) is analysed against a reference gas (WS) to give $\delta 45(SA\text{-}WS)$ and $\delta 46(SA\text{-}WS)$, and WS has been measured directly against NBS19 to give $\delta 45(WS\text{-}NBS19)$ and $\delta 46(WS\text{-}NBS19)$, we evaluate $\delta 45(SA\text{-}NBS19)$ and $\delta 46(SA\text{-}NBS19)$ as follows.

$$\delta 45(SA\text{-}NBS19) = (\delta 45(SA\text{-}WS) + 1)(\delta 45(WS\text{-}NBS19) + 1) \qquad 21$$

$$\delta 46(SA\text{-}NBS19) = (\delta 46(SA\text{-}WS) + 1)(\delta 46(WS\text{-}NBS19) + 1) \qquad 22$$

These δ45 and δ46 define directly the isotopic composition of the sample against VPDB as the NBS19 reference material defines the VPDB scale. Note the δs are not in units of per mil.

To report isotopic composition as $\delta^{13}C$ and $\delta^{18}O$ it is necessary to perform ion corrections, which requires that we:

1. Define the absolute isotopic abundances of ^{13}C, ^{17}O and ^{18}O in VPDB.
2. Assign isotopic composition to NBS19 relative to VPDB.
3. Define the relationship between ^{17}O and ^{18}O in the sample pool.

This procedure is described in detail in the Annex to the Report of Working Group 2, in this volume [15]. As indicated in the Annex, the data reduction procedure has been tested by a number of laboratories and identical results have been obtained in all cases.

Part 3: Summary and acknowledgments

An overview of the CSIRO DAR stable isotope program has been presented. The use of high precision stable isotope data in establishing the various contributions of the biosphere and oceans as sources and/or sinks for atmospheric CO_2 has been illustrated. Some of the problems associated in maintaining a high-precision stable isotope measurement program have been identified. Strong emphasis has been placed on the data reduction procedure used to present results.

GASLAB was established and is operated by CSIRO with significant financial support from the Australian government departments with responsibility for the environment, science, energy/industry and foreign affairs, and with additional support from private industry.

Sample collection is almost entirely dependent upon collaborative agreements with many agencies and universities (especially the Bureau of Meteorology and the Antarctic Division in Australia) and similar agencies in the USA, Canada, UK, India and New Zealand. International support for some aspects of GASLAB's operation has come from the IAEA and the UK TIGER program.

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RECOMMENDATIONS FOR THE REPORTING OF STABLE ISOTOPE MEASUREMENTS OF CARBON AND OXYGEN IN CO_2 GAS [1]

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Abstract : *Recommendations are made for the reporting of stable isotope measurements of carbon and oxygen in CO_2 gas. The isotopic composition of the hypothetical Vienna PDB calcite and CO_2 gas are determined from the primary standard calcite NBS19. An ion correction procedure is described which eliminates many of the errors which can arise during inter-calibration exercises. Data are presented which allow implementations of the data reduction procedure to be tested.*

1. Introduction

Measurements of the stable isotopes of CO_2 are used in global carbon budget analyses to constrain sources and sinks for atmospheric CO_2 [2,3]. With a requirement for high precision in both spatial and temporal data, there is a need to report atmospheric $\delta^{13}CO_2$ in a way that permits comparison of different collection sites (spatial) to a precision of around 0.01‰, or better, and comparison of the long term behaviour (temporal) to a precision of 0.005‰ or better, with only slightly relaxed requirements for $\delta^{18}O$. However, difficulties arise when comparing CO_2 isotopic measurements from the fact that the quantities measured are $\delta 45$ and $\delta 46$ but most laboratories report $\delta^{13}C$ and $\delta^{18}O$ for the CO_2.

The reported quantities are not directly comparable between laboratories due to different ion correction algorithms and/or different assumptions about the isotopic composition of the primary standards. Uncertainties in ion correction algorithms, in reference gases and the potential uncertainties due to inadequate calibration or correction of measurements currently prevent comparisons between different laboratories to this precision.

In the absence of universally accepted protocols, the following data reduction procedure offers a means of minimizing the uncertainties.

2. General background

The goal of the data reduction procedure is to enable r13, the $^{13}C/^{12}C$ ratio, and r18, the $^{18}O/^{16}O$ ratio, to be measured. The ratios r13 and r18 in a sample gas are usually expressed by reference to the same ratios in a standard or reference gas using the δ-notation.

$$\delta^{13}C = \left[\frac{r13_S}{r13_R} - 1\right] \tag{1}$$

$$\delta^{18}O = \left[\frac{r18_S}{r18_R} - 1\right] \tag{2}$$

The subscripts S and R refer to ratios in the sample and reference gas respectively. We also use the lower case letters "s" and "r" to designate specific sample and reference gases respectively, e.g. s13, r13, etc .... When used by itself, an "r" term without a complementary "s" term, represents a ratio in any CO_2 sample. We also reserve the upper case "R" to refer to a ratio in a calibrated reference material, such as R13, R45 for the absolute ratios in a calibration material such as NBS19. We use the upper case "S" to refer to the hypothetical VPDB material.

Due to the presence of isobaric species in CO_2, $\delta^{13}C$ and $\delta^{18}O$ are not measured directly. Instead, combinations of ^{12}C, ^{13}C, ^{16}O, ^{17}O and ^{18}O form three ion currents measured at mass-to-charge ratios (m/e) 44, 45 and 46, referred to as I44, I45 and I46 respectively.

I44 : $^{12}C^{16}O_2$

I45 : $^{13}C^{16}O_2$; $^{12}C^{16}O^{17}O$

I46 : $^{12}C^{16}O^{18}O$; $^{12}C^{17}O_2$; $^{13}C^{16}O^{17}O$

As I44 contains only the most abundant species, ^{12}C and ^{16}O, the ratio of the ion currents due to the less abundant species, i.e. I45 and I46, with respect to the most abundant ion current, I44, are reported as r45 and r46.

$$r45 = I45/I44 \tag{3}$$

$$r46 = I46/I44 \tag{4}$$

Due to the symmetry of the CO_2 molecule, there are two configurations for CO_2 containing one ^{17}O or ^{18}O atom. Combining the symmetry considerations, the combinations of CO_2 molecules contributing to the ion currents and the relationship for r45 and r46 allows us to express r45 and r46 as combinations of the ratios r13, r17 and r18.

$$r45 = r13 + 2r17 \tag{5}$$

$$r46 = 2r18 + 2r13r17 + (r17)^2 \tag{6}$$

Specifically, the quantities we measure for a sample CO_2 gas are the difference in s45 and s46 from the r45 and r46 of the reference gas expressed in the δ-notation.

$$\delta 45 = \left[\frac{s45}{r45} - 1 \right] \qquad 7$$

$$\delta 46 = \left[\frac{s46}{r46} - 1 \right] \qquad 8$$

Isotopic ratios are often expressed in units of "per mil", ‰, obtained by multiplying the δ-values above by 1000.

3. Primary standard

The assignment of isotopic ratios to the primary CO_2 standard is crucial. As almost all measurements of CO_2 are reported using the PDB scale, and the original PDB material is no longer available, we use the non-existent Vienna-PDB as our primary standard. We use NBS19, with IAEA recommended values of $\delta^{13}C = +1.95‰$ and $\delta^{18}O = -2.20‰$ relative to the hypothetical Vienna-PDB(VPDB) [4], as the reference material through which measurements are related to VPDB.

To calculate R45 and R46 for NBS19, we need to first assign S13, S17 and S18 to VPDB calcite. We use Craig's measurements of the original PDB material [5] to assign r13, r17 and r18 for CO_2 from the original PDB material.

r13 = 0.0112372
r17 = 0.00037995
r18 = 0.002079

To assign S13 to VPDB, we assume that the ratio of ^{13}C to ^{12}C in VPDB calcite is identical to that assigned to the original PDB material by Craig, i.e. S13 = 0.0112372.

To assign S18 to VPDB, we use the ^{18}O to ^{16}O ratio in VSMOW (Vienna Standard Mean Ocean Water) of 0.00200520 [6] and the IAEA recommended value for $\delta^{18}O$ of VPDB with respect to VSMOW of +30.9‰ [4]. This gives S18 = 0.002067160680.

To assign S17 to VPDB, we assume the ratio between S17/S18 in VPDB is related to the ratio r17/r18 in PDB by the equilibrium approximation of Craig [5].

$$S17/r17 = [S18/r18]^{0.5} \qquad 9$$

We use this approximation, the calculated value of S18, and the ratios r17 and r18 in the original PDB CO_2 to calculate S17 = 0.000378866601.

To assign R13, R17 and R18 to NBS19 calcite we use the IAEA recommended values for $\delta^{13}C$ and $\delta^{18}O$ (+1.95‰ and -2.20‰) and assume the r17/r18 equilibrium approximation describes the relationship between the $^{17}O/^{18}O$ ratios in VPDB and NBS19.

We summarise the stable isotope ratios for the calcites as:

VPDB calcite : S13 = 0.01123720000
S17 = 0.0003788666010
S18 = 0.002067160680,

NBS19 calcite : R13 = 0.01125911254
R17 = 0.0003784496180
R18 = 0.002062612927.

There is no change in r13 in converting the calcite to CO_2, however we need to apply the fractionation factor of 1.01025, for ^{18}O fractionation during CO_2 evolution at 25°C with 100% phosphoric acid [7] , and the equilibrium approximation to calculate the r17 and r18.

VPDB CO_2 : S13 = 0.01123720000
S17 = 0.0003808033420
S18 = 0.002088349077

NBS19 CO_2 : R13 = 0.01125911254
R17 = 0.0003803842280
R18 = 0.002083754709

For the data reduction procedure we need to calculate S45 and S46 for VPDB, R45 and R46 for NBS19, and $\delta45$ and $\delta46$ values for NBS19 with respect to VPDB.

VPDB CO_2 : S45 = 0.01199880669
S46 = 0.004185401492

NBS19 CO_2 : R45 = 0.01201988100
R46 = 0.004176219688
$\delta45$(w.r.t. VPDB) = +1.756367272‰
$\delta46$(w.r.t. VPDB) = -2.193768974‰

We note that the precision quoted here is not justified by measurement, but it is important to assign a high precision to "accepted values" for the primary standard to avoid propagation of errors. We have chosen to use 10 significant figures.

4. Sample reporting

The ratios r45 and r46 in a CO_2 sample can be determined accurately, without assumptions about ion correction algorithms, from measured $\delta45$ and $\delta46$ values [1]. The expressions for accurately relating the r45, r46 in a sample to the S45, S46 in VPDB via $\delta45$ and $\delta46$ measured for the sample gas against the primary working standard (indicated by the subscripts *i*) are given below.

$$r45_S = \left(\frac{\delta 45_{\,i}}{1000} + 1\right)\left(\frac{\delta 45_{\,i-1}}{1000} + 1\right)\ldots\left(\frac{\delta 45\mathrm{NBS19}}{1000} + 1\right) S45 \qquad 10$$

$$r46_S = \left(\frac{\delta 46_{\,i}}{1000} + 1\right)\left(\frac{\delta 46_{\,i-1}}{1000} + 1\right)\ldots\left(\frac{\delta 46\mathrm{NBS19}}{1000} + 1\right) S46 \qquad 11$$

The expressions accommodate a number of possible intermediate pure CO_2 reference gases (indicated by subscripts *i, i-1, ...*) without compromise of the isotopic composition. The terms containing δ45NBS19 and δ46NBS19 refer to the calibration of a reference gas directly to NBS19 CO_2 gas evolved at 25°C using 100% phosphoric acid.

Until such time as consistent protocols are widely accepted, the reporting of isotopic composition for precise inter-laboratory comparisons should provide the δ45 and δ46 measured for the sample(s) along with similar information relating to the reference gas(es) including calibration to the primary standard NBS19. Where ion correction is performed and these results are presented, we recommend the ion correction algorithms used be described clearly. Further, for ion correction, we recommend the use of the procedure described in the following section.

5. Ion correction

In atmospheric CO_2 measurements, the ion corrections normally required are

(1) correction for the co-extraction of N_2O with CO_2,
(2) conversion of the measured δ45 to $\delta^{13}C$ by correction for a $^{12}C^{17}O^{16}O$ contribution to m/e 45, and
(3) conversion of the measured δ46 to $\delta^{18}O$ by correction for $^{13}C^{17}O^{16}O$ and $^{12}C^{17}O_2$ contributions to m/e 46.

The correction for N_2O affects mainly the m/e 44 ion current and has been described by Mook et al. [8]. We address only items (2) and (3) here.

The main difficulty in performing ion corrections lies in correcting for the presence of ^{17}O. The method described here is an exact calculation of r13, r17 and r18 from the δ45 and δ46 measured for a sample. The only approximation which is required is the relationship between the r17/r18 ratio in the sample and reference gases. The relationship we use is the equilibrium expression of Craig (Equation 9).

$$r17_S/r17_R = [r18_S/r18_R]^{0.5}$$

Santrock et al. [9] suggest using a different relationship based on using an exponent (α) of 0.516 instead of 0.5 (square root relationship). We recommend use of α = 0.5 because of its simplicity and theoretical basis but note that at the precision levels required for some studies very real variations in the $^{17}O/^{18}O$ ratio are likely [10, 11]. We therefore recommend that where specific deviations from the above relationship are chosen that they be documented on an individual basis.

To perform the ion correction, we use δ45 and δ46 which have been converted to r45 and r46 after correction to VPDB CO_2 as described above using Equations 10 and 11. The details of the ion correction method have been described previously [12].

We rearrange Equations 5, 6 and 9 to give a quadratic in r17.

$$(2S18/(S17)^2 - 3)(r17)^2 + 2r45r17 - r46 = 0 \qquad 12$$

This is then solved for r17 as

$$r17 = \frac{-B + \sqrt{B^2 - 4AC}}{2A}, \qquad 13$$

where $A = 2S18/(S17)^2 - 3$, $B = 2r45$ and $C = -r46$. It then follows that

$r13 = r45 - 2r17$, and

$r18 = (r46 - 2r13r17 - (r17)^2)/2$.

These are then converted to $\delta^{13}C$ and $\delta^{18}O$.

$$\delta^{13}C = (r13/S13 - 1)1000‰ \qquad 14$$

$$\delta^{18}O = (r18/S18 - 1)1000‰ \qquad 15$$

6. Advantages of the data reduction procedure

This data reduction procedure has a number of advantages:

1. The quantities measured in the experiment, δ45 and δ46, are used to relate the isotopic composition of the sample directly to the isotopic composition of the hypothetical VPDB. Direct comparison of δ45 and δ46 against VPDB means that measurements from different laboratories can be compared directly without the complication of different ion correction algorithms.

2. This method avoids problems which may arise from using intermediate CO_2 working standards which have been produced by processes which may involve $^{17}O/^{18}O$ fractionations which are determined by different values of α.

3. The ion correction procedure recommended is exact and can be easily changed if modification to the isotopic ratios in the primary VPDB standard are required, or if changes to δ-values assigned to reference gases are made.

7. Data reduction test data

To aid in the implementation of this data reduction procedure a set of test data is provided. The test data consists of the following:

1. A working standard gas CO_2 (WS) has been directly measured against NBS19 CO_2 gas (evolved at 25°C with 100% phosphoric acid) to have $\delta 45 = -7.0000‰$ and $\delta 46 = -1.0000‰$.

2. A series of samples have the following δ45 and δ46 (both in ‰) when measured against WS:

Sample	δ45	δ46
1	-20.0000	-20.0000
2	-20.0000	0.0000
3	-20.0000	20.0000
4	0.0000	-20.0000
5	0.0000	0.0000
6	0.0000	20.0000
7	20.0000	-20.0000
8	20.0000	0.0000
9	20.0000	20.0000.

The data reduction procedure described above produces the following results (all in ‰) for δ45, δ46, $\delta^{13}C$ and $\delta^{18}O$:

Sample	δ45	δ46	δ45(VPDB)	δ46(VPDB)	$\delta^{13}C$	$\delta^{18}O$
1	-20.0000	-20.0000	-25.1508	-23.1277	-26.0681	-23.0985
2	-20.0000	0.0000	-25.1508	-3.1916	-26.7489	-3.1402
3	-20.0000	20.0000	-25.1508	16.7446	-27.4230	16.8184
4	0.0000	-20.0000	-5.2559	-23.1277	-4.8233	-23.1415
5	0.0000	0.0000	-5.2559	-3.1916	-5.5042	-3.1836
6	0.0000	20.0000	-5.2559	16.7446	-6.1782	16.7746
7	20.0000	-20.0000	14.6390	-23.1277	16.4214	-23.1845
8	20.0000	0.0000	14.6390	-3.1916	15.7406	-3.2270
9	20.0000	20.0000	14.6390	16.7446	15.0665	16.7307.

These calculations have been tested and verified by a number of independent groups.

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