Calcite-CO$_2$ mixed into CO$_2$-free air: a new CO$_2$-in-air stable isotope reference material for the VPDB scale

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Received 11 December 2004; Revised 20 February 2005; Accepted 20 February 2005

In order to generate a reliable and long-lasting stable isotope ratio standard for CO$_2$ in samples of clean air, CO$_2$ is liberated from well-characterized carbonate material and mixed with CO$_2$-free air. For this purpose a dedicated acid reaction and air mixing system (ARAMIS) was designed. In the system, CO$_2$ is generated by a conventional acid digestion of powdered carbonate. Evolved CO$_2$ gas is mixed and equilibrated with a prefabricated gas comprised of N$_2$, O$_2$, Ar, and N$_2$O at close to ambient air concentrations. Distribution into glass flasks is made stepwise in a highly controlled fashion. The isotopic composition, established on automated extraction/measurement systems, varied within very small margins of error appropriate for high-precision air-CO$_2$ work (about ±0.015% for δ$^{13}$C and ±0.025% for δ$^{18}$O). To establish a valid δ$^{18}$O relation to the VPDB scale, the temperature dependence of the reaction between 25 and 47°C has been determined with a high level of precision. Using identical procedures, CO$_2$-in-air mixtures were generated from a selection of reference materials; (1) the material defining the VPDB isotope scale (NBS 19, δ$^{13}$C = +1.95‰ and δ$^{18}$O = −2.2‰ exactly); (2) a local calcite similar in isotopic composition to NBS 19 (‘MAR-J1’, δ$^{13}$C = +1.97‰ and δ$^{18}$O = −2.02‰), and (3) a natural calcite with isotopic compositions closer to atmospheric values (‘OMC-J1’, δ$^{13}$C = −4.24‰ and δ$^{18}$O = −8.71‰). To quantitatively control the extent of isotope-scale contraction in the system during mass spectrometric measurement other available international and local carbonate reference materials (L-SVEC, IAEA-CO-1, IAEA-CO-8, CAL-1 and CAL-2) were also processed. As a further control pure CO$_2$ reference gases (Narcis I and II, NIST-RM 8563, GS19 and GS20) were mixed with CO$_2$-free synthetic air. Independently, the pure CO$_2$ gases were measured on the dual inlet systems of the same mass spectrometers. The isotopic record of a large number of independent batches prepared over the course of several months is presented. In addition, the relationship with other implementations of the VPDB-scale for CO$_2$-in-air (e.g. CG-99, based on calibration of pure CO$_2$ gas) has been carefully established. The systematic high-precision comparison of secondary carbonate and CO$_2$ reference materials covering a wide range in isotopic composition revealed that assigned δ-values may be (slightly) in error. Measurements in this work deviate systematically from assigned values, roughly scaling with isotopic distance from NBS 19. This finding indicates that a scale contraction effect could have biased the consensus results. The observation also underlines the importance of cross-contamination errors for high-precision isotope ratio measurements.

As a result of the experiments, a new standard reference material (SRM), which consists of two 5-L glass flasks containing air at 1.6 bar and the CO$_2$ evolved from two different carbonate materials, is available for distribution. These ‘J-RAS’ SRM flasks (‘Jena-Reference Air Set’) are designed to serve as a high-precision link to VPDB for improving inter-laboratory comparability.

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The term ‘SRM’ normally refers to a long-lasting reference material with physical properties assigned by a recognized referencing body. For a particular pair of reference air, the longevity requirement might not be met. However, due to the fact that the underlying materials (carbonate) have the required long life, this term is used because the material serves the same function. As an alternative, the term ‘SRMM’ for ‘standard reference material and method’ might be adopted.

The isotopic composition and concentration of CO$_2$ in atmospheric air are useful parameters, required for deriving carbon-flux information between atmospheric, terrestrial, and marine compartments. In the terrestrial regime, plant photosynthesis strongly discriminates against $^{13}$C while oceanic uptake and release of CO$_2$ do not significantly fractionate its isotopes relative to atmospheric values. As a consequence, the isotopic variation in atmospheric CO$_2$ is rather small and approaches the detection limit of modern analytical techniques.
requires a comparable precision in the analysis of $\delta^{13}C$ values as well as in the determination of CO$_2$ mole fractions. Current fossil fuel emissions of ~6 Gt C per year result in a long-term change of the CO$_2$ mixing ratio of 1.6 ppm per year and a $\delta^{13}C$ change of about $-0.025\%$ per year. While CO$_2$ mixing ratio analyses typically can be made with a precision of 0.1 ppm or better, $\delta^{13}C$ precision is near 0.015% at best.

In recent years, there has been growing concern about climate change and consequent proposals to limit atmospheric levels of greenhouse gases, in particular CO$_2$. An obvious requirement is to improve inter-laboratory calibration, with new laboratories participating in routine measurements, thus permitting consistently high precision for merging data from a variety of sources. Wider comparison of CO$_2$ stable isotopic composition data between laboratories is possible provided an air-CO$_2$ reference material (reflecting the composition of air) is made available with a short, direct link to the international $\delta^{13}C$ and $\delta^{18}O$ isotope ratio scales (VPDB). This link also requires a high precision of about 0.015% in the case of $\delta^{13}C$ and 0.03% for $\delta^{18}O$.

Attempts to link the isotopic composition of CO$_2$ in air to the VPDB scale

Several attempts have been made to tightly link the air-CO$_2$ carbon and oxygen isotopic scales to VPDB. The VPDB scale replaced the PDB scale in 1987. VPDB was defined by assigning $\delta^{13}C_{\text{VPDB}} = +1.95\%$ and $\delta^{18}O_{\text{VPDB}} = 2.2\%$ (exactly) to the reference material NBS 19. In order to report air-CO$_2$ isotopic results to this scale, isotope laboratories generate carbon dioxide by reaction of NBS 19 calcite with 100% orthophosphoric acid (Fig. 1, left panel). CO$_2$ is extracted cryogenically from air samples. By measuring carbon and oxygen isotope ratios of the resulting CO$_2$ gases against each other with isotope ratio mass spectrometry (IRMS), stable isotope ratios are assigned to the respective laboratory air standards. Clean air in high-pressure tanks, often sampled in remote areas with low pollution, usually serves as a working reference. Carbon isotope ratios of pure CO$_2$ are obtained by correcting for the $^{17}O$ contribution to the m/z 45 ion current and by removing N$_2$O, which would cause isobaric interference. This classical way of assigning isotopic values to CO$_2$ in air samples and to reference materials was also employed by the stable isotope laboratory at CSIRO Atmospheric Research (CAR) in Aspendale, Australia, which has published isotope ratios in air since 1982. CSIRO started with the calibration of a laboratory reference CO$_2$ gas (‘HC 453’) using NBS 19 and other reference materials. These values were used subsequently for assigning $\delta$-values to CO$_2$ in air in high-pressure tanks, which led to the now more widely recognized CG-99 scale. Details of the implementation of the CG-99 scale at the isotope laboratory in Jena (‘BGC-IsoLab’) are given later.

In order to reduce discrepancies in high-precision carbon and oxygen isotopic measurements on CO$_2$ in air samples between different laboratories, CSIRO (with support from the IAEA) initiated an intercomparison experiment termed CLASSIC, in which ten high-pressure cylinders of air were prepared of which five were circulated. In addition, two lecture bottles of pure CO$_2$ were also circulated. The results of this inter-comparison exercise, spanning measurements over almost 4 years, were presented at the 11th IAEA/WMO meeting of CO$_2$ experts in Tokyo. Significant differences in the mean carbon and oxygen isotopic compositions reported by the different laboratories were observed. Three major observations were made: (1) Differences in the reported values were up to 10 times larger than the target precisions for merging data from different networks; (2) $\delta^{13}C$ as well as $\delta^{18}O$ data of pure CO$_2$ measured several years apart within a given laboratory showed poor consistency; (3) data for air-CO$_2$ were much more consistent than for pure CO$_2$. In addition, isotopic results from pure CO$_2$ gas samples were not consistent with those from air-CO$_2$ analyses across participating laboratories. From the CLASSIC experiment, a clear need for the development of a reliable and long-lasting CO$_2$-in-air isotope ratio reference material emerged.

![Figure 1](image-url). Comparison of the classical strategy for relating CO$_2$-in-air to the international VPDB scale and the one pursued in this work.
Discrepancies for carbon or oxygen results may have arisen from a number of problems in assigning isotopic compositions onto the VPDB scale:

1. Errors in the preparation of CO2 gas from NBS 19 and initial assignment on the VPDB-CO2 scale.b
2. Propagation of initial assignment errors to subsequent air working standards and hence to the sample.
3. Systematic effects like 17O correction, drift correction and, most importantly, cross contamination during gas switching in the ion source of the mass spectrometer leading to a scale contraction ('Z-effect').10–12

Some of the uncertainties can be addressed by an improved strategy of linking local laboratory CO2-in-air scales to NBS 19. Following this goal, an experiment was devised for implementing into the primary referencing scheme the principle of identical treatment 13 of sample and reference material (Fig. 1, right panel).

In this approach, CO2 is extracted from NBS 19 and from other carbonates following a standard operating procedure (SOP). Instead of using the CO2 gas directly for comparative isotopic measurements it is mixed into CO2-free synthetic air.c

The resulting mixture of air now contains CO2 from a precisely known and long-lasting source (the carbonate), which can be used to calibrate working reference air. As a consequence, the critical step of cryogenic extraction of CO2 is performed on the same apparatus in an identical fashion for sample and reference air; therefore, differences cancel in the final result. The cryogenic extraction step is conceptually replaced by the less critical step of mixing CO2 with CO2-free air.14

Implementation of the ‘CG-99’ scale in Jena

The current Jena CO2-in-air stable isotope scale is based on air standards alone. A local version of the Cape Grim isotope scale (‘CG-99’)9 was implemented using six high-pressure reference air cylinders filled with Southern Hemisphere air of slightly altered chemical and isotopic composition. The cylinders were supplied by CSIRO (CAR). The mixing gas ratios for CO2, N2O and CH4, as well as the carbon and oxygen isotopic composition of CO2 in these cylinders, have been determined and assigned at CSIRO. The corresponding measurements were made at the end of 1999. The cylinder ‘CA01656’ with isotopic and mixing ratios closest to that of ambient air was chosen for positioning our measurements on the international scale (see Fig. 2). The respective assigned isotopic compositions of CO2 versus VPDB (on the CG-99 scale) were

\[
\delta^{13}C = \frac{\text{ratio}}{\text{VPDB}} - 1 = \frac{8.078}{100} = 0.08078\%
\]

\[
\delta^{18}O = \frac{\text{ratio}}{\text{VPDB}} - 1 = \frac{0.017}{100} = 0.00017\%
\]

The data in Fig. 2 exhibit a systematic shift in the Jena and the CSIRO measurements, which is approximately linear with the isotopic deviation from the origin. The effect is more pronounced for \(\delta^{18}O\) where the isotopic differences between the tanks are larger. The Jena laboratory measures a given \(\delta^{18}O\) isotopic
The slope of the $\delta^{13}$C relation (4.8%) appears even larger. The span of the scale, however, is small (0.6%) and, therefore, the regression value is considered as non-significant. From the $\delta^{18}$O measurements, a slope of about 0.015 would appear more reasonable. This would result in a $\delta^{13}$C scaling difference of 1.5% between the Jena and the Melbourne isotope-ratio measurement systems.

**EXPERIMENTAL**

**ARAMIS setup and flask preparation**

The air preparation system ARAMIS (acid reaction and air mixing system), schematically depicted in Fig. 3, has been constructed using internally electropolished ¼” o.d. stainless steel tubing (ULTRON, Dockweiler, Neustadt-Glewe, Germany; www.dockweiler.com). The twin water trap is a tube-in-tube design consisting of two outer 0.5” o.d. ULTRON tubes (30 cm in length), also electropolished, and two inner ¼” tubes extending almost to the bottom of the outer tubes. During the reaction, the water traps are immersed in an ethanol/dry ice slurry.

Oil-free vacuum is generated by two membrane pumps (Pfeiffer, model MVP 015-4; 1.5 m³/min) and a 60 L/s hybrid-turbo pump (Pfeiffer model TMH071). A set of four gauges is installed for reading pressure in the extraction line and close to the mixing chamber. Gauges G1 and G2/2 have coarse vacuum readouts whereas gauge G3 (Baratron, MKS, Andover, MA, USA; www.mksinst.com) is designed for pressures up to 2100 mbar. Prior to starting a new batch, the whole system, including the final glass flasks, is evacuated to less than 3 × 10⁻⁷ mbar.

The preparation of reference air samples involves a tight protocol. Carbonate powder is reacted in the reaction chamber for a preset time of 60 min. The gas is expanded from the reactor through the cryotrap to a mixing chamber (volume ~4.5 L) and allowed to equilibrate for 90 min. Then the mixing chamber is isolated from most of the remaining sample preparation line. Mixing with CO₂-free air from the high-pressure cylinder and transfer to the carousel holding the final glass containers is performed in a stepwise fashion until the final pressure of 1600 mbar is achieved. As an alternative to generating CO₂ from carbonate powder, pure CO₂ gas can be introduced via dedicated inlet valves. The rest of the procedure is identical.

A number of tests and checks have been performed and several improvements to the system were made in order to establish a satisfactory protocol for the air standard preparation:

- Influence of the sample chamber material
- Influence of the water content of the phosphoric acid
- Optimization of the fraction of acid to carbonate
- Influence of temperature
- Correction for N₂O
- Timing of the reaction and mixing process
- Yield control
- Comparison of results for pure CO₂ gases with dual inlet measurements using manual gas introduction.

**Materials**

**MAR-J1 and OMC-J1 carbonates**

Laboratory carbonate reference materials were prepared from a (limestone) marble slab (‘MAR-J1’, Marble-Jena #1) purchased from a local vendor and from a calcite slab from the Meieberg section of the Otavi platform in northern Namibia (OMC-J1; Otavi Meieberg Calcite-Jena #1), which was kindly provided by Paul Hoffmann. The slabs were broken into chips, crushed into fine grains, and sieved into fractions.

MAR-J1: The <250 µm size fraction weighing about 900 g was labeled ‘MAR-J1’. The texture and appearance of the powder are similar to those of NBS 19 carbonate material. Other
fractions, 250–315 μ (~500 g) and 315–400 μ (~300 g), were designated as ‘MAR-J2’ and ‘MAR-J3’ and stored for future use. Quantitative analysis using ICP-MS and ICP-OES indicated an average CaCO₃ content of 98.0 and 2.0% MgCO₃. Al, Fe, Cu, Mn, Na, K together were less than 0.1%. NBS 19 (TS limestone) is very similar: in line with literature XRF data we obtained 98.1% CaCO₃ and 1.8% MgCO₃. Non-carbonate traces were 0.08% in total. The similarity of the two materials is further confirmed by observing the carbonate reaction yield (see below and Fig. 7) with NBS 19 and MAR-J1 resulting in the same amounts of CO₂ gas.

OMC-J1: The compositional analysis of the Otavi-Meieberg calcite using ICP-AES and ICP-OES has given 98.7% CaCO₃ and 0.9% MgCO₃ with non-carbonate cationic impurities summing up to 0.4%. The crushing, milling and sieving left us with 1270 g powder with a grain size <100 μ (‘OMC-J1’), 700 g between 100 and 200 μ (‘OMC-J1’), and 1800 g between 200 and 400 μ (‘OMC-J2’). In order to avoid oxygen exchange with ambient moisture or CO₂ all fractions are kept in glass or PE jars topped with Ar.

Other carbonate reference materials, including L-SVEC (LiCO₃), IAEA-CO-1 (calcite), IAEA-CO-8 (calcite), CAL-1 and CAL-2 (both from laboratory precipitation of CO₂), were treated in an identical fashion during our experiments.

Pure CO₂ reference gases
In parallel to CO₂ from carbonates, well-characterized pure CO₂ samples were also used to establish independent information for the carbonate and the mixing processes and for controlling scale-contraction effects. These pure CO₂ reference materials included Narcis I and Narcis II (6 mm o.d. tubes), GS19 and GS20 (lecture bottles), HC453 (two 50-ml glass bottles with Teflon valves), NIST RM 8563 (9 mm o.d. tubes), as well as Eire, Rose and Yaka (CNRS local CO₂ standards in stainless steel containers). Most of these reference gases are close to atmospheric isotopic composition values with the notable exceptions of Narcis II, which is very close in isotopic composition to that of NBS 19 CO₂ and RM 8563, which is rather negative on the VPDB δ¹³C scale (~4.6‰).

The Jena CO₂ working reference gases are Cathy (δ¹³C approx. ~38‰) and Cindy (approx. ~4‰), both in high-pressure tanks. Air-CO₂ samples are always measured against Cindy in the reference container of the dual inlet system of our mass spectrometer. The final isotope results, however, are based on the isotopic analysis of co-processed air standards. Hence the precise value of Cindy should not be relevant for sample calibration.

CO₂-free air
CO₂-free air was manufactured to our specifications by Linde (Germany). The gas mixture in a 50-L high-pressure cylinder has mixing ratios of N₂, O₂, Ar and N₂O (0.39 ppm) near those in air. Using established gas chromatography (GC) techniques at MPI-BGC, this CO₂-free synthetic air was examined for impurities. The CO₂ concentration was lower than 0.1 ppm. This was further confirmed by running complete blank preparations on the ARAMIS system; these were performed in a completely identical fashion as the normal preparations.

Preparation of CO₂ from carbonate reference material
The traditional method of producing CO₂ from carbonates for stable isotopic analysis involves reaction with phosphoric acid:

\[
\text{CaCO}_3 + H_3PO_4 \leftrightarrow \text{CaHPO}_4 + \text{CO}_2 + H_2O \quad (1)
\]

thereby generating CO₂, H₂O and hydrous calcium phosphate as products of the reaction. This standard method is still followed in many stable isotope laboratories around the world. The original procedure, as suggested by McCrea (1950), and modified by Coplen et al. (1983), includes recipes for preparing the acid, for the timing, and for the temperature of the reaction. The reaction was carried out isothermally at 25°C inside a specially designed glass reaction vessel (with a side arm for the acid), which was evacuated prior to the start of the reaction. Constant temperature was maintained by immersing most of the reaction chamber into a water bath. Our procedure of CO₂ preparation basically follows the conventional concept with a number of modifications for improving control over the repeatability of the overall procedure.

Phosphoric acid
Phosphoric acid is commercially available as a 85–100% purity analytical reagent. ‘Pure’ H₃PO₄ is a mixture of hydrated polyacids, also containing free water molecules. These can exchange oxygen with CO₂ in the liquid phase. This process is less probable when the acid has a nominal H₃PO₄ content above 100%. Highly concentrated acid being hygroscopic also absorbs water formed during the reaction (Eqn. (1)) more readily.

In order to generate a higher concentrated orthophosphoric acid either boiling the acid under vacuum or adding a sufficient amount of phosphorous pentoxide (P₂O₅) or a combination of both can be used. The purity of the acid is determined by measuring the density/specific gravity. Using tabulated literature data the relationship between specific density D₄ and weight-% H₃PO₄ at 25°C can be easily calculated from:

\[
D_4 = 0.0114 \times \% H_3PO_4 + 0.723 \quad (2)
\]

100% acid corresponds to a density of 1.86 g/mL. It is worth noting that the H₂O/H₃PO₄ phase diagram exhibits several minima including one at 105% with a freezing point of 16°C. The viscosity, however, is a steady function of the nominal H₃PO₄ concentration and strongly temperature-dependent. An overview of H₃PO₄ properties is given in Ref. 28. Owing to its high viscosity, working with highly concentrated acids at room temperature is very difficult and complete degassing of CO₂ from the acid can take hours. In order to ensure that the CO₂ generated from carbonates is quantitatively available for mixing with CO₂-free air, the routine carbonate reactions were carried out at 47 ± 0.1°C.

Concentrated acids (85–106%) were prepared with a density ranging from 1.69–1.935 g/mL. For the ‘normal’
105% acids, 100 g of P₄O₁₀ together with 20 mg K₂Cr₂O₇ (for oxidizing possible organic impurities in the acid) were dissolved in 1000 mL of orthophosphoric acid (99.9%, Merck, Darmstadt, Germany) while heating to 70°C and stirring for 24 h. Density should be 1.93 g/mL. The solution is allowed to cool slowly. The final density at room temperature is measured again using a digital densitometer (Anton Parr GmbH, Graz, Austria; model DMA 35N). The acids are covered with argon and stored in air-tight glass containers prior to use. Stability of the acid was repeatedly checked with the densitometer. No significant alterations were found over a period of 8 months.

Using a set of acids with different densities, the dependence of the final δ¹³C and δ¹⁸O values upon density was studied. For this experiment, less concentrated acids were either made by adding appropriate amounts of P₄O₁₀ to the 100% acid, or commercial 85% H₃PO₄ was used as supplied. Results are summarized in Fig. 4. As expected, δ¹³C shows a negligible influence from acid density variations, whereas the results for δ¹⁸O are mixed: neglecting the data point at the lowest density, a slope of −2.2% per density unit is observed. However, the values at 1.69 g/mL indicate that oxygen exchange is not a simple function of the acid density. Since it cannot be guaranteed that oxygen in the acids originates from the same source, the finding probably reflects different oxygen signatures of H₂O exchanging with CO₂ in the liquid phase. Hence, it is expected that this behavior varies with every new batch of phosphoric acid. It should be noticed that the density does not level out completely at higher values for the density. Between acid densities of 1.915 and 1.935 g/mL, we still observe a mean difference of 0.05% for the final δ¹⁸O from the same calcite material. For high-precision δ¹⁸O work, this finding requires a tight control of the acid density. It complements the experience of other laboratories and illustrates the difficulties encountered when generating CO₂ from carbonates with a reliable high-precision δ¹⁸O composition.

Timing of the reaction
To maintain the precision of the CO₂ results over years and even decades, precise control of reaction timing is mandatory. Of particular importance is the time allowed for the carbonate reaction itself. In order to determine when the reaction has come to completion and variation in the isotopic results is no longer observed, this parameter was studied within a range of 40–90 min at 47°C. (For 25°C, the times usually employed are much longer, up to 24 h). Results are plotted in Fig. 5. In this set of experiments, an initial change in the oxygen isotopic composition of the released CO₂ was observed. The carbon isotopic compositions remained constant within measurement uncertainty. Based on this set of experiments, 60 min was established as the default duration time for the acid-digestion reaction.

The sequence of events in preparing a set of reference air samples from carbonate powder has been established as follows:

- CO₂ is produced using the classical reaction with concentrated H₃PO₄ at constant temperature (47 ± 0.1°C). CO₂ is evolved in the closed chamber for 60 min.
- Keeping the water trap at −77°C (dry ice/ethanol mixture), expansion of CO₂ from the reaction chamber to the mixing chamber (MC) is done in a stepwise fashion within 5 min.
- Following equilibration of CO₂ throughout the system for 90 min, the CO₂ in the MC is isolated from the rest of the preparation system, sacrificing 2.2% of the evolved CO₂.
- An inlet close to the MC is used to introduce CO₂-free air from a high-pressure tank. Synthetic air is added to the CO₂ in the MC until a pressure of ~1450 mbar is reached.

![Figure 4](https://example.com/figure4.png)

**Figure 4.** Dependence of δ¹³C and δ¹⁸O of CO₂ evolved from MAR-J1 on acid density (water content) at a reaction temperature of 47°C.
In order to specify the quantity of acid required for consistency in isotopic composition, an experiment was performed where the acid volume was altered, keeping the quantity of carbonate powder constant (\(\sim 60\) mg in this case).

Mostly, the carbonate-digestion reaction is performed in reaction vessels made from Pyrex glass. However, the reaction is exothermic and glasses have a low thermal conductivity (\(\sim 1.0\) W m\(^{-1}\) K\(^{-1}\)) compared with most metals (300–400 W m\(^{-1}\) K\(^{-1}\)). Moreover, the time taken to reach thermal equilibrium can be rather long. In order to check the role of the material, two different kinds of chambers were employed: one made from pure copper and the other from glass.

The copper reaction chamber was manufactured from a block of copper in the local workshop at MPI-BGC. The volume of the reaction chamber is about 30 mL. The vessel is connected to the vacuum line using a flat base glass lid and a Viton O-ring clamp. The copper chamber is housed in a tightly fitting brass housing regulated to provide a constant temperature (\(\pm 0.1^\circ\)C) using a Pt-100 feedback resistor. About 10 mL of acid is filled into the reaction chamber and stirred. The acid-filled reaction chamber is kept under vacuum for more than 1 h. After this time, the stirrer is switched off, the reaction chamber is opened, and a quartz boat with the carbonate powder is added. The quartz boat is designed to allow free floating on the acid. The glass joint is fitted back to the reaction chamber, the stirrer is switched back on, and the evacuation sequence is repeated. The carbonate reaction is initiated manually by applying a small magnet bar from outside. The magnetic field interacts with the stirring bar, thereby tilting the quartz boat.

Experiments were performed using both the copper and a glass chamber. Results are presented in Fig. 6. A systematic depletion in \(\delta^{18}O\) isotopic ratios of CO\(_2\) with decreasing amount of acid was observed. The figure shows that, as the acid amount is increased from 5 to 10 mL, a variation in \(\delta^{18}O\) from \(-2.15\) to \(-1.95\)% for the glass chamber is observed. The variation is considerably smaller for the copper vessel. No appreciable shifts were detectable in the \(\delta^{13}C\) ratios using either chamber. Based on these experiments, the copper vessel and a volume of 10 mL of acid were adopted as standard parameters.

**Yield of the entire preparation over time**

The overall yield of a single preparation can be determined from the CO\(_2\) mixing ratios in the final flasks. These are measured using established GC procedures in our GasLab section\(^{31,32}\), where CO\(_2\) in air samples is routinely quantified with a long-term precision of better than 0.1 ppm. Figure 7 shows the yield of a number of recent carbonate preparations, which on average was 97.9 ± 2.8%. In this figure, available CO\(_2\) was calculated from the known or estimated mineral compositions. Uncertainties in the yield determination arise from variations in the 5-L flask volumes and from the exact amount of CO\(_2\) that can be expected from the carbonate. NBS 19, MAR-J1, and OMC-J1 are similar calcites, which are mainly comprised of CaCO\(_3\) but also hold traces of MgCO\(_3\). From the yield study it was concluded that the time for releasing CO\(_2\) from the acid is one of the most critical parameters. An expansion of 20 min resulted in a yield of only

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**Acid volume and reaction chamber**

The ratio of carbonate powder versus acid volume is an important parameter in acid-digestion reactions. Usually, a large excess of acid of the order of 1:100 is used. Apart from the critical exchange of oxygen isotopes with water in the acid, the release of CO\(_2\) from the acid is slow (even at the higher temperature of 47\(^\circ\)C employed in this study). Retention of reaction water also requires sufficient contact time.

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**Figure 5.** Isotopic composition of CO\(_2\) evolved from MAR-J1 carbonate at 47\(^\circ\)C as a function of reaction time.

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The mixture of CO\(_2\) and synthetic air inside the MC is allowed to equilibrate for another 20 min.

- The mixture is then expanded from the MC through a 0.0625\(^\circ\) (o.d.) capillary into three evacuated 5-L flasks attached to a multi-port Valco valve acting as a passive distributor only.
- The cycle is repeated twice with higher pressure readings of up to 1750 mbar. Usually less than 2\% of the CO\(_2\) remains in the MC.
- Synthetic air is added to the three flasks until a pressure of 1600 mbar is reached.
- The last step is a 10 min equilibration of the final flasks before closing their individual valves.

The resulting air-CO\(_2\) mixtures in the three separate 5-L flasks are analyzed for the CO\(_2\) isotopes together with regular air samples within a single sequence on one of our BGC-AirTrap/IRMS systems.\(^{30}\)
86%, significantly lower than average. The standard gas release delay was set to 90 min, after which time a further change in yield could not be observed. IAEA-CO-8 was a special case: assuming similar compositions as other carbonates the observed amount of CO₂ was too low. The yield could only be brought in line with the other carbonates by assuming a 20% non-carbonate impurity.

**The mass spectrometers**

All stable isotope ratio analyses have been made on either of two Finnigan MAT 252 (ThermoFinnigan, Bremen, Germany) mass spectrometers (‘Matty’ and ‘Cora’), both provided with a homemade CO₂ extraction system (‘BGC-AirTrap’\(^3\)) for automated analysis of carbon and oxygen isotope ratios of CO₂ in air samples. Although very different in age, both instruments have identical technical standard and specifications, and they are operated in a very similar fashion:

- Ion source lenses and exit slits are made from Ta to minimize sputter related memory during gas switching;\(^1\)
- The ion source window (‘VISC’, variable ion source conductance) is fully open in routine analysis;
- With rare exceptions, the instruments are dedicated to routine CO₂-in-air operation;
- Instruments are operated with a reduced emission current (0.5–0.7 mA instead of the maximum sensitivity setting of 1.5 mA);
- Refill of reference gas is made through a permanently attached inlet line; both mass spectrometers are fed with the same working reference gas (\(\delta^{13} \text{C} \approx 4\% \text{ vs. VPDB}\));
- Instruments are operated with a low ion current intensity during routine analyses (\(\approx 5 \times 10^{-7} \text{ A}\));
- Asymmetric crimps on sample and working reference gas sides minimize reference gas variation over a long sequence.

A positive side effect of these operational parameters is extreme longevity of the filament. Replacement of the filament has not been necessary within the time frame reported in this study (4 years on ‘Matty’ and 2.5 years on ‘Cora’). Vacuum is broken only once per year for
maintenance of the pumping system. Operating vacuum with no gas admitted is better than $10^{-8}$ mbar. With analyte gas entering the ion source, a pressure of $2 - 4 \times 10^{-8}$ mbar is observed. Background ion currents from fore vacuum oil are below the limit of detection.

\textbf{$\eta$-Effect}

Due to the low emission and ion currents, the VISC window open and good vacuum quality conditions, the memory during gas switching, commonly termed the ‘$\eta$-effect’, is extremely low for both mass spectrometers. Figure 8 exhibits data from an experiment on ‘Matty’ where the ion source conditions were altered by wide margins and a difference of about 32\% was measured for $d_{45}$CO$_2$ of CO$_2$ using normal dual inlet methods. Since the CO$_2$ fluxes through the capillaries were not identical in all cases, comparison of absolute values does not allow firm conclusions to be drawn. Instead, the variation of the observed isotopic change with switch-over time (often referred to as ‘idle time’) shows that the memory effect from one gas to the next is very small. A significant increase in the measured difference between the two gases is seen mainly for ion source conditions with the VISC window closed and emission high (Fig. 8, solid diamonds). However, even for this worst case scenario, the total memory using idle times of 2 s does not exceed 0.03\%. For all other conditions, the cross talk is smaller, and, for the standard operating conditions (Fig. 8, dashed line), it is below the detection limit for this kind of experiment. A convenient and fast experiment to estimate the amount of gas left over from the previous gas is to close the changeover valve while monitoring the ion currents. Such a signal decay observation from ‘Cora’ is shown in Fig. 9. Starting with a (higher than normal) m/z 45 ion current of 4600 mV (±150 pA), a remaining signal of 0.4 mV is observed after 14 s. This time corresponds to commonly used changeover operations during measurement. The $\eta$-value therefore is $8.7 \times 10^{-5}$, resulting in a hypothetical compression of a true 32\% difference by 0.006\%. In this experiment, a wash-out effect of old gas by the new gas (which would lead to an even smaller $\eta$-value) is not considered.

\textbf{17O correction}

Raw isotopic results for CO$_2$ are $\delta^{45}$CO$_2$ and $\delta^{46}$CO$_2$ values (see Note in the previous paragraph). These must be converted into pure $\delta^{13}$C and $\delta^{18}$O results by subtracting the isobaric interferences from the $^{17}$O-containing CO$_2$ moieties. On m/z 46, the isobaric contribution is small because it originates from two minor isotopes in the same molecule ($^{12}$C$^{17}$O$^{16}$O and $^{12}$C$^{17}$O$_2$). For m/z 45, however, the interference from $^{12}$C$^{17}$O$^{16}$O comprises about 7\% of the ion current and correction must be carried out with great care. The original ‘Craig’ correction has been repeatedly challenged because it uses mathematical approximations for the correction and the original ratios used in the correction equation have been revised. For a recent comprehensive review and recommendations for the $^{17}$O/$^{18}$O ratio in VPDB, please refer to Ref. 36. In this study we have used the mathematically exact algorithm from Santrock et al. and the ratio set given in Ref. 13. In order to evaluate the influence of different correction parameters, the data were also compiled using alternative ratio sets (see Results section).

d_{45}CO_2 = (45R_{obs}/45R_{ref} - 1) \times 1000, \text{ with } 45R \text{ being the ratio of the respective m/z 45 to m/z 44 ion currents.}

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**N₂O correction**

Mass spectrometric analysis requires extraction of CO₂. In this procedure, N₂O is also frozen out at the temperature of liquid nitrogen (−196°C) and cannot be separated further by cryogenic means. Hence, a correction must be applied. The synthetic air used in this study contained 0.39 ppm of N₂O. In a separate set of experiments, the influence of the N₂O correction has been studied. Details of this study have been published elsewhere, and will therefore be mentioned here only briefly. Synthetic air with and without N₂O was used. In addition, the relative ratios of CO₂ and N₂O in preparations of air samples using the ARAMIS setup were adjusted within a wide range, resulting in a high-precision N₂O correction. From the study it was concluded that N₂O can be corrected for using a weighted-mass-balance algorithm, provided that the respective mixing ratios are precisely known and the relative ionization-efficiency ratio has been determined for the particular mass spectrometer and its ion source settings. The remaining error for δ¹³C on the VPDB scale is estimated to be smaller than 0.01‰. For further information, see Ref. 14, and the literature cited therein.

**BGC-AirTrap**

In the automated CO₂ (± N₂O) extraction system (‘BGC-AirTrap’), glass flasks with sample air are attached to a Valco 16-port valve. CO₂ is sampled from the flasks in 600-mL aliquots by transferring a flow of 60 mL/min through a vacuum line consisting of a mass flow controller, a dry-ice/water trap and a CO₂ trap at −196°C using liquid nitrogen. Via a 0.14-mm i.d. capillary the CO₂ trap volume (~15 mL) directly serves as an inlet to the changeover valve; it is available once residual air has been removed and the CO₂ (± N₂O) has completely thawed and equilibrated.

For routine analysis, referencing is performed using a working standard air (Westf.10-2000) in a 50-L cylinder filled to a pressure of 250 bar. The cylinder contains synthetic air with atmospheric CO₂ and N₂O concentrations. The CO₂ isotopic ratios (~2.77‰ for δ¹³C and −14.67‰ for δ¹⁸O) are considerably different from those of air. The working standard and primary reference gases are permanently attached to different positions of the Valco 16-port multiport valve (ports 1 and 2 are assigned for the working reference air and port 9 for the primary reference gas). The remaining 13 ports are used for routine sample flasks.

**Figure 9.** Signal decay (m/z 45) after closing the inlet valve. At the time of measurement (14 s after gas switching in this example), 0.0087% of the previous gas is still present in the ion source and contributes to the measurement. Similar results were obtained for m/z 46.
\[ \delta^{18}O \text{ as a function of the reaction temperature} \]

The role of temperature on the oxygen isotopic composition of CO\(_2\) produced during reaction of carbonate material with phosphoric acid was recognized prior to 1950.\(^{24}\) Based on a number of experiments, it was concluded that isotopic precision could be obtained by using a procedure in which carbonate samples were reacted with 100% H\(_3\)PO\(_4\) at constant temperature. Evolved CO\(_2\) is retained in the reaction vessel until dissolution is complete. Due to the fact that only 2/3 of the carbonate oxygen is released as CO\(_2\), fractionation of oxygen isotopes takes place between the CO\(_2\) and residual H\(_2\)O (Eqn. (1)). Sharma and Clayton\(^ {39}\) determined the oxygen isotope fractionation factor between CO\(_2\) and calcite during acid digestion at different temperatures. At 25°C, this factor has a value of 1.01025 according to Ref. 39. More recently, a revision of this factor was suggested, based on

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**Figure 10.** Quality-assurance performance chart of $\delta^{13}C$ in ‘Westf 10-2000’ on the VPDB scale as measured vs. reference ‘CA01656’ over a 4-year period. The two mass spectrometric systems (‘Matty’ and ‘Cora’) are completely independent. Solid lines are 10-point running averages. The difference $\Delta\delta^{13}C$ between the two gases is $\sim 5\%$.

**Figure 11.** Quality-assurance performance chart of $\delta^{18}O$ in ‘Westf 10-2000’ on the VPDB-CO\(_2\) scale as measured vs. reference ‘CA01656’ over a 4-year period. An offset of $\sim 0.03\%$ in the first 9 months of operation of ‘Cora’ is attributed to an initially enhanced $\eta$ effect. The systems are fed by the same gases. The two gases differ in $^{18}O$ by $14\%$.
new experimental results showing a different value of 1.01050 for the calcite-acid fractionation factor ($\alpha_T$) at the same temperature.\textsuperscript{40} Swart \textit{et al.}\textsuperscript{41} as well as Boettcher,\textsuperscript{42} estimated the oxygen isotopic fractionation between calcite and CO$_2$ during phosphoric acid digestion as a function of temperature in the range of 20–90°C. Since phosphoric acid reacts with carbonates only sluggishly at 25°C,\textsuperscript{43–45} most of these studies aimed at accurate determination of the isotopic fractionation associated with the carbonate reaction at higher temperatures. In order to decrease the reaction time, to react more stable carbonate materials like dolomites or siderites, and to increase the degassing of CO$_2$ from the acid, higher temperatures of up to 90°C have been employed. However, for aiming at high precision for single preparations and high accuracy over extended periods of time the temperature dependence of the reaction is still not known with sufficient accuracy for operating above 25°C.

In order to evaluate the temperature dependence of the $^{18}$O/$^{16}$O ratio with higher resolution and precision, a number of reactions of MAR-J1 with 105% phosphoric acid were performed, varying the temperature between 28°C and 47°C using the ARAMIS line. The results are presented in Fig. 12. The value at 25°C was estimated from the regression equation:

$$\delta^{18}O = -0.0357638 \times T + 8.727$$

obtained by plotting $\delta^{18}O$ of CO$_2$ vs. temperature (in K). As expected, the temperature dependence of $\delta^{13}C$ in the range studied is less than the observed uncertainty (0.019%). In order to determine $\alpha_T$ at a particular temperature, two measurements are necessary. The first involves analyzing CO$_2$ from acid digestion. The second requires a reaction producing CO$_2$ from all carbonate oxygen, using a technique such as reaction with BrF$_5$\textsuperscript{39}

In order to relate the observed $\delta^{18}O$ data to $\delta^{18}O$ in the mineral, the values were normalized to 25°C using a fractionation factor of 1.01050.\textsuperscript{40} Swart \textit{et al.}\textsuperscript{41} used the fractionation factor from Sharma and Clayton\textsuperscript{39} (1.01025) and obtained a relationship between $\alpha_T$ and temperature for the common acid bath and for the sealed vessel methods with a slope similar to ours. Linear regression of the data in Fig. 12 shows a relation between $\alpha_T$ and temperature (in K) given by:

$$\alpha_T = 0.0005237 \times \left(\frac{10^6}{T^2}\right) + 1.0046$$

Figure 13 shows the fractionation of $^{18}$O/$^{16}$O data between carbonate and CO$_2$ at six temperatures. Also shown in this figure is the relationship from Swart \textit{et al.}\textsuperscript{41} anchored at a different fractionation factor for 25°C (for an anchor of 1.01025, the corresponding intercept in Eqn. (4) would be 1.00435). While the slope observed here is close to but slightly different from that of Swart \textit{et al.}, the experiments were conducted with a tight temperature control (±0.1°C). As a consequence, the results in Fig. 13 exhibit a consistent precision for $\delta^{13}C$ and $\delta^{18}O$ of MAR-J1 CO$_2$ at 47°C. This factor, a rigorous timeline for completion of the reaction, and the high long-term precision of the mass spectrometric measurements were important factors for improving measurement precision related to the temperature dependence of the calcite/acid reaction. The precision is adequate for calibrating a CO$_2$-in-air isotope reference material directly based on the primary reference material NBS 19. Since our standard reaction temperature is 47°C, all carbonate $\delta^{18}O$ values have been adjusted to the 25°C fractionation using the value of 1.00078. However, not all materials were calcites. In those cases (L-SVEC, CAL-1, CAL-2), no information about the precise temperature function was available. Consequently, the $\delta^{18}O$ values may be slightly in error. The $\delta^{13}C$ values are not affected by temperature.

RESULTS

Isotope ratio results and discussion

Including the test experiments reported herein and results for the preliminary data set\textsuperscript{46} presented at the 12th IAEA/WMO
meeting of CO₂ experts, Toronto, Canada, Sept. 2003, more than 190 separate batches or preparations were made. A δ¹³C offset for NBS 19 of 0.146‰ (measured on the Jena-CG-99 scale) was observed which remained unexplained at the time. Among the experimental changes and improvements made since the Toronto meeting are:

- Removal of the mass-flow controller. During gas flow a small variation in the isotopic composition was observed, which was due to diffusion effects. Mixing is now made in a stepwise fashion with appropriate delay times in between for equilibration, thereby transferring close to 96% of the available CO₂ into the final 5-L flasks.
- Removal of a small leak at the turbo pump.
- Rigorous yield investigations showed that expansion of CO₂ from the reactor to the mixing chamber had to be increased from 20 to 90 min.
- Longer evacuation times before starting a preparation with the 5-L flasks attached to the carousel.

The overall results did not change by much but the observed offset for NBS 19 on the CG-99 scale was changed consistently to 0.076‰ for δ¹³C. For δ¹⁸O we obtained an offset value of 0.041‰. The results given in Table 1 summarize data that have been obtained under consistent conditions (since batch #151). Please note that the results in Table 1 do not include the measurements described in the preliminary data set except for the recalculated HC453. The oxygen isotope results are listed as measured, i.e. they have not been scaled to a given isotopic distance of reference materials as required for reporting against VSMOW.⁴⁷ Although this leads to a scale compression in our case, adjusted δ¹⁸O results are presented in Table 2, where also a comparison of the final data on the VPDB scale with literature values is made. In order to calibrate oxygen stable isotope ratio data from carbonate measurements to the SLAP/VSMOW difference, Coplen has suggested the use of the δ¹⁸O difference between NBS 18 (−23.00‰) and NBS 19 (−2.20‰) for scaling.⁴⁸ The third column in Table 2 has been generated using the δ¹⁸O measurement of IAEA-CO-1 instead of NBS 18 as the second scaling anchor with a δ¹⁸O value of −22.70‰ vs. VPDB. The value arises from Stichler’s intercomparison,¹⁷ where the δ¹⁸O difference between IAEA-CO-8 and NBS 18 was +0.30‰. Further justification arises from the preliminary data set where both materials were included and a Δ¹⁸O difference of 0.27‰ between the two calcites was obtained. The literature δ¹⁸O values from Ref. 23 in Table 2 have been adjusted to comply with the NBS 18/NBS 19 isotopic difference.

I: Carbonates

The upper part of Table 1 lists the data obtained for all carbonate preparations. Seven independent preparations were made using NBS 19 calcite with a δ¹³C average of 2.026‰ (±0.012‰) and δ¹⁸O on the Jena-CG-99 scale. The uncertainties in brackets are the inter-batch 1-s values. Since offset values of NBS 19 are fixed and define the VPDB scale, we adopt the observed differences (0.076‰ for δ¹³C and 0.041‰ for δ¹⁸O) to correct all data generated using the ARAMIS system.

With MAR-J1, 29 separate batches were prepared resulting in 88 flasks with a volume of 5 L. The average value for δ¹³C is 2.050‰, 0.024‰ higher than the NBS 19 result. The preliminary data set had both values almost identical, but the statistical basis was much smaller. With 29 independent results for MAR-J1 and 7 independent results for NBS 19, the difference of 0.024‰ is statistically correct within ±0.007‰ using error propagation of the mean errors: ±SQRT(Σ(F² × σ²/n)), F is Student’s uncertainty correction for a confidence level of 90%.
Table 1. Summary table for isotopic measurements of calcite and CO₂ reference materials; all values in [%]

<table>
<thead>
<tr>
<th>Minerals (reacted with H₂PO₄ and mixed into CO₂-free air)</th>
<th># of batches</th>
<th># of 5-L flasks</th>
<th>δ¹³C [CG-99-J]</th>
<th>Std. dev (interbatch)</th>
<th>Std. dev (inrabatch)</th>
<th>δ¹⁸O [CG-99-J]</th>
<th>Std. dev (interbatch)</th>
<th>Std. dev (inrabatch)</th>
<th>δ¹³C [VPDB]</th>
<th>δ¹⁸O [VPDB]</th>
<th>Std. dev (no scaling)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NBS 19*</td>
<td>7</td>
<td>21</td>
<td>2.026</td>
<td>0.012</td>
<td>0.010</td>
<td>−2.159</td>
<td>0.015</td>
<td>0.023</td>
<td>1.930</td>
<td>−2.390</td>
<td></td>
</tr>
<tr>
<td>MAR-J1</td>
<td>29</td>
<td>88</td>
<td>2.050</td>
<td>0.015</td>
<td>0.011</td>
<td>−1.979</td>
<td>0.025</td>
<td>0.020</td>
<td>1.974</td>
<td>−2.020</td>
<td></td>
</tr>
<tr>
<td>L-SVEC</td>
<td>3</td>
<td>9</td>
<td>−46.535</td>
<td>0.029</td>
<td>0.018</td>
<td>−26.426</td>
<td>0.010</td>
<td>0.033</td>
<td>−46.607</td>
<td>−26.466</td>
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</tr>
<tr>
<td>IAEA-CO-1</td>
<td>3</td>
<td>9</td>
<td>2.586</td>
<td>0.020</td>
<td>0.007</td>
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<td>0.038</td>
<td>0.017</td>
<td>2.492</td>
<td>−2.328</td>
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<tr>
<td>IAEA-CO-8</td>
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<td>6</td>
<td>5.689</td>
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<td>0.009</td>
<td>−22.895</td>
<td>0.043</td>
<td>0.021</td>
<td>−5.764</td>
<td>−22.935</td>
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</tr>
<tr>
<td>CAL-1</td>
<td>6</td>
<td>2</td>
<td>45.972</td>
<td>0.01</td>
<td>0.012</td>
<td>12.581</td>
<td>0.053</td>
<td>0.053</td>
<td>2.496</td>
<td>−12.622</td>
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<tr>
<td>CAL-2</td>
<td>1</td>
<td>3</td>
<td>46.535</td>
<td>0.029</td>
<td>0.018</td>
<td>26.426</td>
<td>0.033</td>
<td>0.023</td>
<td>46.607</td>
<td>−26.466</td>
<td></td>
</tr>
<tr>
<td>OMC-J1 (test drill)</td>
<td>3</td>
<td>9</td>
<td>−4.165</td>
<td>0.017</td>
<td>0.018</td>
<td>−8.664</td>
<td>0.012</td>
<td>0.029</td>
<td>−4.241</td>
<td>−8.705</td>
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<table>
<thead>
<tr>
<th>CO₂-gases (mixed into CO₂-free air)</th>
<th># of inlets</th>
<th># of runs</th>
<th>δ¹³C [CG-99-J]</th>
<th>Std. dev (interbatch)</th>
<th>Std. dev (inrabatch)</th>
<th>δ¹⁸O [CG-99-J]</th>
<th>Std. dev (interbatch)</th>
<th>Std. dev (inrabatch)</th>
<th>δ¹³C [VPDB]</th>
<th>δ¹⁸O [VPDB]</th>
<th>Std. dev (no scaling)</th>
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</thead>
<tbody>
<tr>
<td>Narcis I</td>
<td>2</td>
<td>3</td>
<td>−8.525</td>
<td>0.008</td>
<td>0.009</td>
<td>−0.668</td>
<td>0.020</td>
<td>0.008</td>
<td>−8.601</td>
<td>−0.709</td>
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</tr>
<tr>
<td>Narcis II</td>
<td>2</td>
<td>2</td>
<td>2.030</td>
<td>0.003</td>
<td>0.017</td>
<td>−2.557</td>
<td>0.020</td>
<td>0.025</td>
<td>1.954</td>
<td>−2.988</td>
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</tr>
<tr>
<td>NIST RM 8563</td>
<td>1</td>
<td>2</td>
<td>−41.541</td>
<td>0.017</td>
<td>−32.708</td>
<td>0.014</td>
<td>0.010</td>
<td>0.023</td>
<td>−7.564</td>
<td>−33.749</td>
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</tr>
<tr>
<td>GS19 (M)</td>
<td>2</td>
<td>4</td>
<td>−7.489</td>
<td>0.020</td>
<td>−0.994</td>
<td>0.020</td>
<td>−0.608</td>
<td>0.027</td>
<td>−7.569</td>
<td>−0.109</td>
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<tr>
<td>GS19 (D)</td>
<td>2</td>
<td>3</td>
<td>−7.749</td>
<td>0.006</td>
<td>0.008</td>
<td>−0.902</td>
<td>0.004</td>
<td>0.023</td>
<td>−8.716</td>
<td>−0.943</td>
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<tr>
<td>GS20 (M)</td>
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<td>4</td>
<td>−8.640</td>
<td>0.010</td>
<td>−0.854</td>
<td>0.001</td>
<td>0.003</td>
<td>−8.680</td>
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<tr>
<td>GS20 (D)</td>
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<td>2</td>
<td>−8.605</td>
<td>0.011</td>
<td>0.011</td>
<td>−1.848</td>
<td>0.035</td>
<td>0.025</td>
<td>−7.457</td>
<td>−1.889</td>
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<tr>
<td>Eire (D)</td>
<td>1</td>
<td>2</td>
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<td>0.003</td>
<td>−17.651</td>
<td>0.005</td>
<td>−18.057</td>
<td>0.005</td>
<td>−6.773</td>
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<tr>
<td>Rose (D)</td>
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<td>−7.381</td>
<td>0.016</td>
<td>0.011</td>
<td>−1.848</td>
<td>0.035</td>
<td>0.025</td>
<td>−7.457</td>
<td>−1.889</td>
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<tr>
<td>Yaka (D)</td>
<td>1</td>
<td>2</td>
<td>−6.698</td>
<td>0.005</td>
<td>−18.057</td>
<td>0.005</td>
<td>−18.057</td>
<td>0.005</td>
<td>−6.773</td>
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<tr>
<td>HC453 (BM504, enr.)</td>
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<tr>
<td>HC453 (recalc 1st set)</td>
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<td>−13.280</td>
<td>0.023</td>
<td>−6.634</td>
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</table>

<table>
<thead>
<tr>
<th>CO₂-gases (directly measured on dual inlet)</th>
<th># of inlets</th>
<th># of runs</th>
<th>δ¹³C [VPDB]</th>
<th>δ¹⁸O [VPDBgas]</th>
<th>Std. dev (no scaling)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Narcis I</td>
<td>1</td>
<td>2</td>
<td>0.001</td>
<td>−8.592</td>
<td>−0.679</td>
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<tr>
<td>Narcis II**</td>
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<td>2</td>
<td>0.005</td>
<td>1.954</td>
<td>−2.358</td>
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<tr>
<td>NIST RM 8563</td>
<td>2</td>
<td>8</td>
<td>0.002</td>
<td>0.065</td>
<td>−41.650</td>
</tr>
</tbody>
</table>

*The isotopic results for NBS 19 on the CG-99-J scale are used to correct all subsequent results to the VPDB scale.
**Difference between Narcis II and measured and VPDB values for Narcis II adopted from above.
Table 2. Comparison of isotopic values in this study and values in the literature. The $\delta^{18}O$ values from Ref. 23 have been rescaled to comply with the SLAP/VSMOW difference of 55.5%.

Minerals (reacted with H$_3$PO$_4$ and mixed into CO$_2$-free air)

<table>
<thead>
<tr>
<th>Material</th>
<th>Measured values $\delta^{13}C$ [VPDB]</th>
<th>$\delta^{18}O$ [VPDB] (no scaling)</th>
<th>Scale adjustment: $\delta^{13}C$ [VPDB]</th>
<th>$\delta^{18}O$ [VPDB]</th>
<th>Literature values $\delta^{13}C$ [VPDB]</th>
<th>$\delta^{18}O$ [VPDB]</th>
<th>Reference</th>
<th>Offsets $\delta^{13}C$ [VPDB]</th>
<th>$\delta^{18}O$ [VPDB]</th>
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</thead>
<tbody>
<tr>
<td>NBS 19</td>
<td>1.95</td>
<td>-2.2</td>
<td>-2.2</td>
<td>1.95</td>
<td>-2.2</td>
<td>0</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MAR-J1</td>
<td>1.974</td>
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<td>-2.022</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>L-SVEC</td>
<td>-46.607</td>
<td>-26.466</td>
<td>-26.191</td>
<td>-46.53</td>
<td>-26.430</td>
<td>23</td>
<td>-0.077</td>
<td>0.239</td>
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<tr>
<td>IAEA-CO-1</td>
<td>2.492</td>
<td>-2.328</td>
<td>-2.327</td>
<td>2.480</td>
<td>-2.437</td>
<td>17</td>
<td>0.012</td>
<td>0.110</td>
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<tr>
<td>IAEA-CO-8</td>
<td>-5.764</td>
<td>-22.935</td>
<td>-22.7</td>
<td>-5.749</td>
<td>-22.7</td>
<td>17, 25</td>
<td>-0.015</td>
<td>0.000</td>
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<tr>
<td>CAL-1</td>
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<td>-22.327</td>
<td>-22.099</td>
<td>-45.764</td>
<td>-22.036</td>
<td>18</td>
<td>-0.280</td>
<td>-0.063</td>
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<tr>
<td>CAL-2</td>
<td>-2.496</td>
<td>-12.622</td>
<td>-12.504</td>
<td>-2.558</td>
<td>-12.549</td>
<td>18</td>
<td>0.062</td>
<td>0.045</td>
<td></td>
</tr>
<tr>
<td>OMC-J1 (test drill)</td>
<td>-4.245</td>
<td>-8.716</td>
<td>-8.631</td>
<td></td>
<td></td>
<td></td>
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</tbody>
</table>

CO$_2$-gases (mixed into CO$_2$-free air)

<table>
<thead>
<tr>
<th>Material</th>
<th>Measured values $\delta^{13}C$ [VPDB]</th>
<th>$\delta^{18}O$ [VPDBgas]</th>
<th>Scale adjustment: $\delta^{13}C$ [VPDB]</th>
<th>$\delta^{18}O$ [VPDBgas]</th>
<th>Literature values $\delta^{13}C$ [VPDB]</th>
<th>$\delta^{18}O$ [VPDBgas]</th>
<th>Reference</th>
<th>Offsets $\delta^{13}C$ [VPDB]</th>
<th>$\delta^{18}O$ [VPDBgas]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Narcis I</td>
<td>-8.601</td>
<td>-0.709</td>
<td>-0.726</td>
<td>-8.550</td>
<td>-0.701</td>
<td>19</td>
<td>-0.051</td>
<td>-0.025</td>
<td>-0.012</td>
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<tr>
<td>Narcis II</td>
<td>1.954</td>
<td>-2.598</td>
<td>-2.593</td>
<td>1.936</td>
<td>-2.581</td>
<td>20</td>
<td>0.018</td>
<td>-0.012</td>
<td>-0.012</td>
</tr>
<tr>
<td>NIST RM 8563</td>
<td>-41.616</td>
<td>-33.749</td>
<td>-33.392</td>
<td>-41.560</td>
<td>-33.400</td>
<td>23</td>
<td>-0.056</td>
<td>-0.008</td>
<td>-0.014</td>
</tr>
<tr>
<td>GS19 (M)</td>
<td>-7.564</td>
<td>-0.135</td>
<td>-0.138</td>
<td>-7.550</td>
<td>-0.140</td>
<td>4</td>
<td>-0.014</td>
<td>-0.018</td>
<td>-0.014</td>
</tr>
<tr>
<td>GS19 (D)</td>
<td>-7.569</td>
<td>-0.109</td>
<td>-0.132</td>
<td>-7.550</td>
<td>-0.140</td>
<td>4</td>
<td>-0.019</td>
<td>0.008</td>
<td>-0.019</td>
</tr>
<tr>
<td>GS20 (M)</td>
<td>-8.716</td>
<td>-0.943</td>
<td>-0.957</td>
<td>-8.660</td>
<td>-0.980</td>
<td>4</td>
<td>-0.056</td>
<td>0.023</td>
<td>-0.056</td>
</tr>
<tr>
<td>GS20 (D)</td>
<td>-8.680</td>
<td>-0.895</td>
<td>-0.910</td>
<td>-8.660</td>
<td>-0.980</td>
<td>4</td>
<td>-0.020</td>
<td>0.070</td>
<td>-0.020</td>
</tr>
<tr>
<td>Eire (D)</td>
<td>-6.574</td>
<td>-17.692</td>
<td>-17.516</td>
<td>-6.410</td>
<td>-13.200</td>
<td>4</td>
<td>0.263</td>
<td>0.397</td>
<td>-0.011</td>
</tr>
<tr>
<td>Rose (D)</td>
<td>-7.457</td>
<td>-1.889</td>
<td>-1.893</td>
<td>-7.457</td>
<td>-1.893</td>
<td>4</td>
<td>0.263</td>
<td>0.397</td>
<td>-0.011</td>
</tr>
<tr>
<td>Yaka (D)</td>
<td>-6.733</td>
<td>-18.098</td>
<td>-17.918</td>
<td>-6.410</td>
<td>-13.200</td>
<td>4</td>
<td>0.263</td>
<td>0.397</td>
<td>-0.011</td>
</tr>
<tr>
<td>HC433 (BM504, enr.)</td>
<td>-6.147</td>
<td>-12.722</td>
<td>-12.603</td>
<td>-6.410</td>
<td>-13.200</td>
<td>4</td>
<td>0.263</td>
<td>0.397</td>
<td>-0.011</td>
</tr>
<tr>
<td>HC433 (recalc. 1st set)</td>
<td>-6.399</td>
<td>-13.239</td>
<td>-13.114</td>
<td>-6.410</td>
<td>-13.200</td>
<td>4</td>
<td>0.263</td>
<td>0.397</td>
<td>-0.011</td>
</tr>
</tbody>
</table>

CO$_2$-gases (directly measured on dual inlet)

<table>
<thead>
<tr>
<th>Material</th>
<th>Measured values $\delta^{13}C$ [VPDB]</th>
<th>$\delta^{18}O$ [VPDBgas]</th>
<th>Scale adjustment: $\delta^{13}C$ [VPDB]</th>
<th>$\delta^{18}O$ [VPDBgas]</th>
<th>Literature values $\delta^{13}C$ [VPDB]</th>
<th>$\delta^{18}O$ [VPDBgas]</th>
<th>Reference</th>
<th>Offsets $\delta^{13}C$ [VPDB]</th>
<th>$\delta^{18}O$ [VPDBgas]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Narcis I</td>
<td>-8.592</td>
<td>-0.679</td>
<td>-0.696</td>
<td>-8.550</td>
<td>-0.701</td>
<td>19</td>
<td>-0.042</td>
<td>0.022</td>
<td>-0.042</td>
</tr>
<tr>
<td>Narcis II*</td>
<td>1.954</td>
<td>-2.598</td>
<td>-2.593</td>
<td>1.936</td>
<td>-2.581</td>
<td>20</td>
<td>0.018</td>
<td>-0.017</td>
<td>-0.017</td>
</tr>
<tr>
<td>NIST RM 8563</td>
<td>-41.650</td>
<td>-33.517</td>
<td>-33.162</td>
<td>-41.560</td>
<td>-33.400</td>
<td>23</td>
<td>-0.090</td>
<td>0.243</td>
<td>-0.090</td>
</tr>
</tbody>
</table>
\(\delta^{18}O\) of MAR-J1 in Table 1 differs from that of NBS 19 by 
\(-0.18\%o\). Comparison with the preliminary data set for \(\delta^{18}O\) is 
not straightforward because the NBS 19 offset has changed by 
a larger amount (+0.041\%o instead of +0.188\%o). The 
preliminary data set may have been flawed for three 
reasons: (1) the initial evacuation time was much shorter 
and the final vacuum was inferior \((2 \times 10^{-4} \text{mbar} \text{ instead of } 3 \times 10^{-7} \text{mbar})\); (2) the precision of the 
preliminary data set for NBS 19 with five preparations was only 0.04\%o compared 
with 0.015\%o in this work with seven new batches; and (3) an 
improved yield control was established using an increased 
time for outgassing of the acid.

L-SVEC is interesting mainly because of its rather negative 
value for \(\delta^{13}C\) \((-46.48\%)\).\(^{17}\) A reduced precision can be 
expected for such a large difference between L-SVEC and 
NBS 19. However, the observed value of 0.029\%o for the 
inter-batch repeatability (three preparations) shows that the 
reproducibility is adequate. Our result for L-SVEC 
\((\delta^{13}C = -46.607\%)\) is slightly more negative than the 
literature value. This observation is also true for \(\delta^{13}C\) of other 
reference materials in Table 1 and is further illustrated in 
Fig. 14. As detailed above, the analysis system parameters 
were tuned to almost completely avoid cross talk \(\text{('\eta\text{-effect}') during gas exchange in the mass spectrometer. This effect has}

largely been neglected in the community for quite some time. 
As a consequence, listed \(\delta^{13}C\) literature values may suffer 
from scale contraction depending on the time of measurement 
and on the size of the \(\eta\text{-effect} during measurement. Verkouteren and Kleindinst}\(^{23}\) have attempted to minimize 

scale-contraction effects in their inter-laboratory comparison. 
Some of the materials circulated in this study were also 
processed on the ARAMIS system (NBS 19, L-SVEC, and RM 
8563). The mean \(\delta^{13}C\) for L-SVEC from six laboratories was 
\(-46.33 \pm 0.17\%)o with a tendency to more negative values 
when applying a more realistic \(^{17}O\) correction (see below).

For \(\delta^{18}O\) of L-SVEC an unscaled value of \(-26.466 \pm 0.01\%\) 
was observed, in close agreement with Stichler’s raw mean 
\((-26.46.0.456\%)\),\(^{17}\) but more positive than the value 
assigned in Ref. 23 \((-26.71 \pm 0.21\%)\). However, L-SVEC is 
pure synthetic \(\text{Li}_2\text{CO}_3\), not a calcite. All carbonates were 
reacted at 47°C and the temperature correction established 
for MAR-J1 calcite has been applied. Hence, the absolute \(\delta^{18}O\) 
value is likely to differ due to a different \(\eta\) for this material. 
Variations of up to 0.5\%o can be expected.\(^{40}\) The \(\delta^{18}O\) result 
after scale adjustment to comply with the SLAP/VMSOW 
difference is \(-26.191\%)o. It should be noted that the \(\delta^{18}O\) 
values in Ref. 23 \((-26.71\%)o for L-SVEC) have not been 
corrected for scaling effects.

IAEA-CO-1 is a calcite (Carrara marble) and may become a 
replacement for NBS 19 once this material is in short supply. 
The \(\delta^{13}C\) value of 2.492 \pm 0.020\%o in Table 1 from three 
preparations \(9 \text{flasks}\) is in good agreement with the outlier-
corrected literature value of 2.480 \pm 0.025\%o.\(^{17}\) For \(\delta^{18}O\) a 
value of \(-2.328 \pm 0.038\%)o was found, almost exactly 0.1\%o off 
of the consensus value at \(-2.437 \pm 0.073\%)o in Ref. 17. 
Statistically, the two values are still in agreement. The effect 
of scaling for this material is negligible.

The IAEA-CO-8 calcite has been selected as a reference 
material in order to supplement NBS 18. With a \(\delta^{13}C\) value of 
\(-5.749\%)o,\(^{17}\) IAEA-CO-8 would be a good material for the air-
\(\text{CO}_2\) scale. However, the value for \(\delta^{18}O\) is about 23\%o more 
negative than that of atmospheric \(\text{CO}_2\) and it is not a pure 

carbonate, rendering this material only a second choice.

The \(\delta^{13}C\) value for IAEA-CO-8 in Table 1 is \(-5.764\%)o and 
this differs from the previous value in the preliminary data 
set by 0.032\%o. The \(\delta^{13}C\) value for MAR-J1 was 0.029\%o more 
negative, which illustrates the internal consistency of the two 
data sets. With a deviation of \(-0.015\%o, the new result is close 
to the IAEA value, possibly due to a small scale contraction 
effect in the latter. Ambiguities may arise from small
differences in the $^{17}$O correction, which can influence the precise value. Comparing the effect of different literature ratio sets used for the $^{17}$O correction (Table 3) reveals a rather strong influence of this procedure on the final $^{13}$C value. In particular, the standard correction (‘Allison’) $^{34}$ gives a result which is almost 0.05$\%$ more negative than the others. This is in line with a similar calculation for NBS 18 in Ref. 23, where $^{13}$C of NBS 18 was $-5.06\%$ in comparison with $-5.02\%$ for the average of the other calculations.

The unscaled $^{18}$O result from two independent preparations ($-22.935 \pm 0.043\%$) in Table 1 may be compared with the value in Stichler’s report $^{17}$ ($-22.667 \pm 0.187\%$). For a calcite, the temperature correction should result in an accurate $^{18}$O value for 25$^\circ$C (in contrast to that of L-SVEC). Moreover, the sign of the difference ($-0.268\%$) is opposite to the situation with IAEA-CO-1. It is in line with the $^{18}$O value for NBS 18 in Ref. 17 ($-22.97 \pm 0.067\%$). However, the discrepancy is not so critical, in particular when comparing the data of IAEA-CO-1 and IAEA-CO-8.

The results from the inter-laboratory comparison in Ref. 23, where $^{13}$C of NBS 18 was $-5.06\%$ in comparison with $-5.02\%$ for the average of the other calculations.

Table 3. Evaluation of selected data from Table 2 using different corrections$^{34–36}$ for the $^{17}$O contribution to the m/z 45 ion current$^{38}$

<table>
<thead>
<tr>
<th>Material</th>
<th>Measured values</th>
<th>Literature values</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\delta^{13}$C [VPDB]</td>
<td>$\delta^{18}$O [VPDBgas]</td>
</tr>
<tr>
<td>L-SVEC</td>
<td>$-46.607$</td>
<td>$-26.466$</td>
</tr>
<tr>
<td>CAL-1</td>
<td>$-46.044$</td>
<td>$-22.327$</td>
</tr>
<tr>
<td>OMC-J1</td>
<td>$-4.241$</td>
<td>$-8.705$</td>
</tr>
<tr>
<td>IAEA-CO-8</td>
<td>$-5.80$</td>
<td>$-22.935$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
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<th>Literature values</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\delta^{13}$C [VPDB]</td>
<td>$\delta^{18}$O [VPDBgas]</td>
</tr>
<tr>
<td>NIST RM 8563</td>
<td>$-41.616$</td>
<td>$-33.749$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Material</th>
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<th>Literature values</th>
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<tr>
<td></td>
<td>$\delta^{13}$C [VPDB]</td>
<td>$\delta^{18}$O [VPDBgas]</td>
</tr>
<tr>
<td>NIST RM 8563</td>
<td>$-41.650$</td>
<td>$-33.517$</td>
</tr>
</tbody>
</table>

probably resulted in accurate data when the offsets are adjusted to the values in this report, resulting in $-46.038\%$ for $^{13}$C and $-22.313\%$ for $^{18}$O values. Both results are in excellent agreement with the more recent preparations in Table 1.

CAL-2, a laboratory-precipitated carbonate, is used as a twin reference to CAL-1. Results for this material were also included in the preliminary data set. The $^{13}$C value had an offset from that in the MSC data of almost $+0.03\%$. Assuming that the relation between MAR-J1 and CAL-2 in the first data set is not affected by the changes to the data in this work, one can correct the $^{13}$C value in the preliminary data set by adding $0.029\%$, resulting in exactly $-2.5\%$ for CAL-2. The new result in Table 1 ($-2.496\%$) is very close to the corrected value from the first set, but different from that of MSC by almost $+0.06\%$. Apart from the above-mentioned ambiguity in the $^{17}$O correction, the reason for the discrepancy is not clear to us, in particular when comparing the data of IAEA-CO-1 and IAEA-CO-8.

Huang et al. $^{38}$ used NBS 18 ($^{13}$C = $-5.01\%$) as a control reference with a measured average $^{13}$C value of $-5.038\%$. A more recent study explicitly addressed cross mixing in measuring NBS 19 against other reference carbonate materials including NBS 18. $^{49}$ In direct comparison of 23 preparations of NBS 18 and 134 preparations of NBS 19, $^{13}$C of NBS 18 shifted from the accepted value to an average of $-5.06\%$ due to the $\eta$-correction. The same value was also found in the inter-comparison reported in Ref. 23. Taking the new value for NBS 18, the MSC result for CAL-2 shifts to $-2.606\%$ and the discrepancy between MSC and the result in Table 1 is further increased to 0.11%. The value is in better agreement with a determination by CSIRO ($-2.620\%$) cited in Ref. 18.

The scale-adjusted $^{18}$O results are in slightly better agreement ($-12.504\%$ vs. $-12.549\%$). However, the precision of our result for a single preparation is only $0.053\%$ in this case, so the values can be regarded as statistically identical. The CSIRO value for $^{18}$O was $-12.660\%$.

OMC-J1 has a $^{13}$C value between that of NBS 19 and that of atmospheric CO$_2$. While we were hoping to find
a natural calcite closer in isotopic composition to that of air-CO₂. OMC-J1 may still be a valuable resource for controlling and possibly avoiding systematic errors due to cross-contamination tendencies when measuring the δ¹³C of CO₂ in air samples. As a first test, three independent preparations were made with nine 5-L flasks. Isotopic results of −4.241 ± 0.017‰ for δ¹³C and −8.705 ± 0.012‰ for δ¹⁸O were obtained. OMC-J1 is near NBS 18 and IAEA-CO₂ in δ¹³C and similar to the texture of NBS 19. Hence, this material is well suited to calibrate local CO₂-in-air scales when it is used as a sibling standard reference material with MAR-J1. In comparison with NBS 18 and IAEA-CO₂, the δ¹⁸O of CO₂ released from OMC-J1 is about 15‰ closer to that of CO₂ in ambient air. Ambiguities arising from different ¹⁷O correction procedures, hence, are considerably less important (see Table 3). The scale-adjusted δ¹⁸O value is −8.631‰.

II. CO₂-gas standards, mixed into CO₂-free air
The middle section of Table 1 contains the data obtained from mixing CO₂ gas of different origins with CO₂-free air. Most materials under investigation are used in conjunction with air-CO₂ isotopic analysis and therefore are close to −8‰ relative to VPDB. Exceptions include Narcis II, which is close in δ¹³C to that of NBS 19 and NIST RM 8563, whose δ¹³C value is rather negative, yet it is very well characterized. Both of these gases are key players in our study because they allow an unambiguous comparison with dual inlet measurements and they allow firm conclusions to be drawn about the magnitude of scale contraction effects.

Narcis I was prepared by Hitoshi Mukai at the National Institute for Environmental Studies (NIES, Tsukuba, Japan) and has been measured by a large number of laboratories over a period of several years.¹⁹ The δ¹³C results between the laboratories varied from −8.61‰ to −8.44‰, with a median value of −8.55‰. For δ¹⁸O, the corresponding median value vs. VPDB-CO₂ was −0.701‰. All laboratories arrived at their reported values by measurement against a local CO₂ reference directly calibrated using NBS 19. In the ARAMIS system two separate preparations were made resulting in three flasks of different volume. One 6-mm o.d. sealed tube was used per preparation; the mixing volumes were adjusted to account for the small amount of CO₂ available. In this study the results on the VPDB scale, defined through the procedure described above, were −8.601‰ for δ¹³C and −0.709‰ (−0.726‰ scale-adjusted) for δ¹⁸O. While both values are close to the median values cited above, the δ¹³C value is statistically different by 0.05‰ or almost exactly 0.5% of the measured 10‰ difference between NBS 19 and Narcis I.

Narcis II was prepared by Hitoshi Mukai only recently. Circulation has started and first results have been obtained (H. Mukai, personal communication, 2004). The δ¹³C value observed in this work (+1.954‰) is very close to that of NBS 19. Its δ¹⁸O value is more negative (−2.598‰) than that of NBS 19 CO₂. Scale adjustment does not change this value significantly. The material had been prepared to be close in isotopic composition to NBS 19 and preliminary values determined by Hitoshi Mukai are 1.927 ± 0.005‰ for δ¹³C and −2.589 ± 0.013‰ for δ¹⁸O, in close agreement with the findings in this study. The difference (Δ¹³C) between Narcis I and Narcis II using the ARAMIS technique amounts to 10.555‰. This value may be compared with that of NIES (10.483‰) and one other laboratory (10.495‰) (H. Mukai, personal communication, 2004).

NIST RM 8563 is a benchmark pure CO₂ reference material, which has been carefully calibrated by taking scale-contraction effects²³ into account. It was during the development and calibration of this material that the importance of the η-effect for high-precision calibration of reference materials with a larger difference in isotopic composition was rediscovered.¹¹ Such an effect was commonly known in earlier times of IRMS as the ‘changeover leakage effect’, which was attributed to leak effects mainly and, with improved valves, was considered negligible. The δ¹³C value observed in this study is −41.616 ± 0.017‰ vs. −41.567 ± 0.009‰ in the ring test of Ref. 23. The δ¹⁸O value is in even closer agreement. The unscaled result of −33.749 ± 0.025‰ compares well with the original value of −33.76 ± 0.08‰ reported in Ref. 23. Adjustment for the NBS 18/NBS 19 difference for both numbers result in −33.392 and −33.400‰, respectively.

Two points should be noted: (1) The new result is from a single preparation delivering two flasks and (2) the results in Ref. 23 were obtained by correction for η-effects, which for all participating laboratories were considerably larger (ranging from 0.00025–0.00148 for δ¹³CO₂) than the ones presented in this study (<0.0001, see above and Fig. 9).

The pure CO₂ gases GS19 and GS20 have been available in lecture bottles since 1995.²¹ Both gases are close to atmospheric CO₂ in carbon and oxygen isotopic composition. Two sets of GS19 and GS20 were available, a fresh set from Groningen (‘GSxx (M)’) and an older set from CNRS (‘GSxx (D)’). The results for the respective gas mixtures are listed in Table 1. The δ¹³C results for both GS19 samples are nearly identical with an average of −7.566 ± 0.021‰ for the two. The literature value (−7.550‰) cited in Table 2 was taken from Table 1 in Ref. 4. The δ¹³C values from several inter-comparison exercises range from −7.502‰ to −7.580‰ with our value lying on the more negative side of the range. The same is true for GS20, in which δ¹³C values of −8.716‰ and −8.680‰ were obtained for the two different lecture bottles. The comparison value from Table 1 in Ref. 4 is more positive by 0.04‰. The literature values range from −8.542‰ to −8.690‰. The measured δ¹⁸O values for GS19 and GS20 are similar to results reported previously⁴,³⁰ for those gases. The small number of measurements, however, does not allow any further reaching conclusions to be drawn from the results.

HC453 was made available by Colin Allison (CSIRO Aspendale) in two 50-mL glass bottles. These were filled from one of the original glass vessels set aside at CSIRO before 1990. Two sets of measurements were made on this material, one during the earlier stages of the ARAMIS project (1st set) and the other (‘enr.’) within the batches reported in this study. The second measurement exhibited a significant enrichment of carbon and oxygen isotope ratios of the CO₂ for both bottles. Since they were sealed using Teflon stopcocks, we suspect that permeation of CO₂ through the polymer led to enrichment in δ¹³C and δ¹⁸O over time. The first set of

"Some early instruments even used automated adjustment of the gas switching time (‘idle time’) depending on the measured difference in isotopic composition (T. B. Coplen, personal communication)."
measurements, listed in the preliminary data set, has been recalculated based on the assumption that a major cause for the difference in the CG-99 scale offset was due to the short time for degassing of the acid, which does not apply to clean CO2. The recalculated values are very close in δ13C and in δ18O to the revised numbers given in Ref. 4. However, because of the uncertainty in the recalculation, further conclusions cannot be drawn from this coincidence.

Also included in the experiments were other local CO2 reference materials like Eire, Rose, and Yaka for testing the performance and providing data. Apart from the observed precision for these preparations, no further conclusions can be drawn at this time.

### III. CO2-gas standards with dual inlet and offset comparison

In order to compare the mixing technique with more classical isotope ratio measurements, three of the gases described in the previous section were also introduced as clean, pure CO2 gases into the dual inlet system of one of our Finnigan MAT 252 mass spectrometers (‘Cora’). For a high-precision isotopic measurement, the principle of identical treatment requires that the gases must be introduced sequentially into one side of the dual inlet and be measured at the same ion current level against the same reference gas in the other bellows. Narcis II is very close in isotopic composition to CO2 evolved from NBS 19. Instead of trying to generate CO2 from NBS 19 (outside the ARAMIS setup), which could have introduced another non-quantifiable error, Narcis II was used as the reference against which the other two gases, Narcis I and RM 8563, were analyzed. In order to be consistent with the other data in this study, the Narcis II δ values were taken from the middle section of Table 1. The main focus was to examine whether the difference between the gases is in line with the differences observed for the same gases mixed into CO2-free air. The results are given in the bottom section of Table 1.

For δ13C of Narcis I, a difference between the two δ13C values (δ13C of 10.546‰) was found, very close to the previously mentioned value of 10.55‰. This finding confirms that the entire process of mixing CO2 into CO2-free air and subsequent automated extraction of CO2 and N2O, corrections, etc., are free from artefacts for air and subsequent automated extraction of CO2 and N2O, etc., are free from artefacts for this case. In contrast, the deviation of 0.034‰ for the air-mixture. In light of the large isotopic covariance of 0.5 to 0.6% of the difference. We also find a relative scale contraction of 0.16% for L-SVEC and 0.6% for CAL-1. Even for Narcis I, an δ8O contribution of 0.5 to 0.6% is estimated using the NIES difference for Narcis II vs. Narcis I and the one in this study.

For δ18O the situation is more complicated. The first thing to notice is that the differences in the δ13C values of pure CO2 dual inlet measurements are larger than the equivalent δ13C data from the CO2-in-air mixture analyses. In this case, preference is given to the much better controlled mixture values. Manual analysis of CO2 gas on the dual inlet is comparatively rarely made and the possible contamination from moisture on surfaces is larger for this case. In contrast, air sample measurements are routinely carried out on a daily basis in the Jena laboratory. Moreover, good agreement is observed for the two Narcis gases, both of which are not far from NBS 19 CO2 and, hence, should not suffer from scale-contraction effects in the δ18O analysis. The differences between the scale-adjusted δ18O results and the corresponding values in the literature are depicted in Fig. 15. While the air-mix analysis of RM 8563 also is very close to the literature value, larger deviations occur for L-SVEC, and even for IAEA-CO-1. L-SVEC is not a calcite; hence, a different δ18O might be responsible for the difference. True oxygen isotope ratios may be recalculated once the δ18O temperature dependence of LiCO3 between 47°C and 25°C is determined with acceptable accuracy. Although the δ13C values found for IAEA-CO-1 may still be identical from a statistical point of view, the 0.1‰ difference appears unacceptably large and deserves further attention.

#### Alternative 17O corrections

As already mentioned briefly, the δ13C results in this study have been generated from δ13C CO2 raw data using a mathematically exact correction algorithm for the isobaric contribution of 17O to the m/z 45 ion current. The ratio set for 13C/12C in VPDB and for the oxygen ratios as well as the fractionation exponent were adopted from Ref. 13. In order to test the sensitivity of the data upon the selected ratio set, δ48O CO2 and δ46CO2 values were recalculated. Using these values, δ13C and δ18O results were recalculated using other ratio sets from the literature. The procedure is similar to the scenarios presented by Verkeruten and Kleindinst. They also stated that the currently recommended ratio set leads to a covariance of δ13C and δ18O values and probably has to be revised. Table 3 provides the data for this comparison. Allison et al., denote the IAEA recommended ratio set; Santrock et al., and Assonov and Brenninkmeijer refer to other ratio assumption sets in common use. The Assonov set has the smallest covariance between δ13C and δ18O. The data show very good agreement between the different δ18O corrections except for the Santrock ratio data, confirming that δ18O for VPDB is probably overestimated in this assumption set.
The CO₂-in-air reference material ('J-RAS')

Based on the expertise accumulated in preparing air-samples with CO₂ originating from carbonates, the Jena Isotope Laboratory is able to provide a set of CO₂-in-air samples as standard reference material (SRM) to interested laboratories. The set termed 'J-RAS' ('Jena-Reference Air Set') consists of two 5-L flasks filled to a pressure of about 1600 mbar. One flask has CO₂ originating from MAR-J1; the other is derived from OMC-J1. Each flask is filled within a batch of three flasks, and all flasks are analyzed for \( \delta^{13}C \) and \( \delta^{18}O \) in a routine fashion. Hence, several \( \delta \)-values are available for characterizing a particular J-RAS flask pair: (1) the original values of the calcites MAR-J1 and OMC-J1; (2) the mean values of the batch; and (3) the individual flask values. Moreover, the reaction is carried out at 47°C; therefore, the gas is offset in \( \delta^{18}O \) from a preparation made at 25°C. Table 4 lists the values needed to fully characterize a pair of J-RAS flasks, including the mixing ratios for CO₂ and N₂O (with the gray fields to be filled in). The average inter-batch precisions for the carbonates in Table 1 are slightly inferior (0.019‰ for \( \delta^{13}C \) and 0.022‰ for \( \delta^{18}O \)) compared with the intra-batch precisions (0.011‰ for \( \delta^{13}C \) and 0.021‰ for \( \delta^{18}O \)). The intra-batch values are identical to the 4-year external precisions reported in Figs. 10 and 11.

Hence, the batch \( \delta \)-values probably represent the best values for a particular flask (as if that flask had been measured three times), and therefore should be taken as the reference value. On the other hand, by measuring the flasks routinely before shipment, a record is generated, tying the carbonate and the CO₂-in-air scale closely together.

In order to qualify as a reference material, the air in the flasks has to remain stable over extended periods of time as well as be immune against changes originating from sample decanting. The flasks are made from Duran™ borosilicate glass with a single valve, coated with a black heat-shrink hose for safety, which also helps prevent isotopic variations that might be caused by light. The valve sealing material is PCTFE, which has the lowest permeability for light gases, and has proven to be best for long-term air storage.51,52 For initial conditioning, all flasks are kept under vacuum at 60°C for 48 h before being filled with dry air prior to usage. We have evaluated the flask integrity and the results are given in Fig. 16 (for changes over time) and Fig. 17 (for alterations related to usage).

Figure 16 demonstrates that both \( \delta^{13}C \) and \( \delta^{18}O \) are stable within experimental error (~0.01‰ for \( \delta^{13}C \) and ~0.02‰ for \( \delta^{18}O \)) over at least 200 days. From independent experience

### Table 4. Isotopic composition and report of CO₂ in a Jena reference air set comprising two 5-L containers

<table>
<thead>
<tr>
<th></th>
<th>Mixing ratios</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>CO₂ [ppm]</td>
</tr>
<tr>
<td>NBS 19-gas</td>
<td></td>
</tr>
<tr>
<td>MAR-J1-flask</td>
<td>1.974</td>
</tr>
<tr>
<td>OMC-J1-flask</td>
<td></td>
</tr>
</tbody>
</table>

**Figure 15.** Deviations of \( \delta^{18}O \) values in Table 1 from literature values. All data have been normalized to the NBS 18/NBS 19 difference (~20.8‰) using a \( \delta^{18}O \) value of ~22.70‰ for IAEA-CO-8.
with 1-L air flasks it is expected that the $\delta^{18}O$ value will deteriorate over longer periods of time, possibly via oxygen exchange in the borosilicate matrix and with residual water. Hence, when storing for more than 1 year, this value must be regarded as outdated. Figure 17 shows data observed when aliquots of air are repeatedly removed from a flask for measurement. In this case, three flasks taken from a single batch were studied. The amount of air consumed for each analysis was 600 mL. All three flasks show identical behavior (measurement order from right to left) down to a pre-analysis pressure of 0.5 bar. Thus, ten analyses from each flask can be made. Below this pressure, variations are observed which are probably more related to the analysis system than to true changes in isotopic composition inside the flask: the mass-flow controller requires a certain pressure above the BGC-AirTrap system to withdraw the full 600-mL (STP) aliquot. This condition was violated below 500 mbar. Hence, the ion current signal was lower than normal and a (non-perfect) correction had to be applied.30

In order to use the J-RAS gases as a local link to the VPDB scale, they should be handled exactly as sample air. In a typical laboratory scenario, the flasks are connected to one of the sample ports where the routine air samples usually are attached. Also attached to one of the ports is a working reference air, typically in a high-pressure cylinder. Preliminary results obtained relative to the working air standard (including all necessary corrections) may then be used to assign new $\delta^{13}C$ and $\delta^{18}O$ values to the working reference air cylinder. This has the advantage that errors associated with this calibration, or with the fact that gases may behave differently in a high-pressure cylinder than in a low-pressure glass container, will tend to cancel for sample air in glass flasks. This is especially true for the $\delta^{17}O$ correction applied, as well as for errors associated with the removal of the N$_2$O interference. As long as the correction is applied to the working reference and to the air samples in a consistent fashion, it will cancel for comparable concentrations. As a check, it is recommended that the J-RAS flasks should be left at the sample ports and that the measurements should be repeated a number of times, this time using the revised values for the working reference. The measured values for the J-RAS gases should be identical to the assignment values within experimental error.

Independently, it is mandatory that the scale contraction of each mass spectrometer in use is either made extremely small (as in our systems) or is independently quantified and monitored in order to apply the necessary corrections. If this is not done, an offset of air-CO$_2$ isotope data between laboratories will still be observed due to the fact that $\delta^{13}C$ of OMC-J1 is $-4\%_o$ vs. VPDB instead of a more desirable $-8\%_o$, which is not available at present.

**SUMMARY, CONCLUSIONS AND OUTLOOK**

For generating a new CO$_2$-in-air stable isotope reference material from calcite, a referencing strategy conceptually avoiding cryogenic extraction in the fundamental calibration has been successfully implemented and tested. High precision for $\delta^{13}C$ and $\delta^{18}O$ measurements and a high level of comparability of data between pure CO$_2$ and CO$_2$-in-air analyses have been demonstrated on the same CO$_2$ reference materials, varying in $\delta^{13}C$ by more than 40\%.

The temperature dependence of the oxygen isotopic fractionation between CO$_2$ and calcite reacted with H$_3$PO$_4$ has been determined between 25°C and 47°C with high precision.
The cross contamination or η-effect has been the most probable candidate for scale contraction in individual laboratories in the past. Over the years this may have entered into the assignment of δ-values for secondary reference materials with the associated errors scaling with the isotopic distance from NBS 19.

Regarding the δ13C difference of 10‰ between atmospheric CO2 and NBS 19, calibrations in individual laboratories have arrived at different values for the δ13C of atmospheric CO2 with scale-contraction errors of up to 1‰. This error is larger than other errors associated with 17O corrections or with N2O correction.

From two different carbonate materials, we are able to routinely produce a reference air set (J-RAS) consisting of two 5-l glass containers at a pressure of up to 1600 mbar. This amount of air is sufficient for a large number of isotopic determinations, even when more than 500 mL (STP) of air is consumed in a single preparation. When extracting CO2 from these air-SRM containers on one of the sample ports, isotopic determination of a local working standard that is being used as the major referencing material in daily routine analysis can be made with a high level of precision. If systematic fractionation occurs in this procedure, or if other systematic errors are made with a high level of precision. If systematic fractionation occurs in this procedure, or if other systematic errors are present in the data evaluation and corrections applied, the errors will tend to cancel for other air samples provided that these are close to concentrations and isotopic compositions of ambient air with the exception that the air-SRM has an offset from the air δ13C value of about 10‰. The second flask is a sibling air-SRM with δ13C closer to that of air-CO2. The search for a calcite with carbon and oxygen isotope ratios of evolved CO2 even closer to that of air-CO2 should be continued.

The new material provides a close and firm high-precision link of air-CO2 to the VPDB scale based on mineral-RMs for the first time. Repeatability of the δ13C and δ18O values for different preparations (0.015 and 0.025‰, respectively) has met the requirements for high-precision inter-laboratory calibration of CO2-in-air isotope analyses. The new material will enable different laboratories around the globe to work on the same CO2-in-air implementation of the VPDB scale. This approach has been shown to be necessary because standardization using non-air standard reference materials has proven less accurate for the task, mainly owing to the fact that CO2 extraction is part of the primary calibration concept. Data comparability should improve from now on, allowing much closer integration.

Acknowledgements

Our appreciation goes to Manfred Groening of the IAEA Hydrology section in Vienna for supporting our project with an extra set of NBS 19 reference material. The IAEA also supported the presentation of the preliminary data set at the 12th WMO/IAEA meeting of CO2 experts in Toronto, 2003. We gratefully acknowledge the cooperation of the GasLab people at CSIRO in Melbourne, in particular Colin Allison, who kindly sent us two freshly filled glass ampoules filled with HC453 CO2 and Roger Francey for his support and encouragement. Hitoshi Mukai (Tsukuba) kindly provided the Narcis I and Narcis II CO2 samples. Harro Meijer (Groningen) contributed GS19 and GS20 CO2 and GS17 carbonate reference material as well as his valuable opinion on many of the issues described in this contribution. Marc Delmotte (Gif-sur-Yvette) kindly provided his set of CO2 reference gases. We are particularly grateful to Lin Huang (Toronto) for sharing her acid recipe and for sending us aliquots of CAL-1 and CAL-2 carbonate material. Paul Hoffmann (Boston) collected and kindly provided the Maieberg calcite. It was crushed, ground and sieved at the Institute for Geology and Mineralogy at Jena University (thanks to Robert Lippmann and Frank Linde). Chemical analysis of the carbonate materials was made by Michael Raessler at MPI-BGC (ICP-AES). In addition ICP-MS measurements were made by Nathan Delleska at Caltech. Armin Jordan (BGC-GasLab) thoroughly determined the CO2 and N2O mixing ratios on all air samples detailed in this report. Tyler B. Coplen (USGS Reston) has been of great help in making numerous suggestions to improve the manuscript and in critically reviewing the data presented in this paper. We thank Roland A. Werner (ETH Zürich) for cross reading the manuscript and suggesting a number of changes. The ARAMIS system was made possible by the TACOS project (EJ, EVRI-CT-2001-40015). The financial support for P. Ghosh and M. Patecki is highly appreciated.

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7. The CCO99 scale has more recently been refined at CAR by introducing new ‘CAR2003’ air and HC453 (2003) (CO2) assignments, with explicit corrections for cross-contamination effects in past measurements. Details were presented by C. Allison at the 12th WMO/IAEA meeting of CO2 experts in Toronto, Canada, 2003.


32. A quick overview can be found at http://www.bgc.mpg.de/service/iso_gas_lab/gaslab.shtml.


53. A spreadsheet for calculating the 17O contribution according to different ratio sets is available at: http://www.bgc.mpg.de/service/iso_gas_lab/activities/index.shtml.