

Isotopic analysis of CO₂ in air samples: Requirements for a new CO₂-in-air standard and preparation of an air-CO₂ reference mixture from calcite material

Prosenjit Ghosh and Willi A. Brand[‡]

Max Planck Institute for Biogeochemistry, Jena, Germany

Abstract

An acid reaction and air mixing station (*ARAMIS*) is described which is capable to introduce CO₂ at ambient levels into an air mixture (without CO₂) at the precision level required for air monitoring of the CO₂ isotopes. The mixing station is used for generating CO₂ by a conventional acid reaction (at 47°C carbonate powder is reacted with pure ortho-phosphoric acid) and mixing the reaction gas with synthetic air. The mixture is distributed into a number of glass flasks (5l volume, 1.6 bar) attached to the system. The isotopic composition was recovered by measurement of the flask air samples using the two automated cryogenic extraction line / mass spectrometer systems in the Jena isotope facility.

Using the same protocol we have generated CO₂-in-air mixtures from NBS-19 and other internationally available carbonate standards for assigning isotopic values to our new carbonate reference material (MAR-J1). The isotopic record in a number of batches prepared over the course of several months is presented. In addition, the relationship with existing CO₂-in-air scales (e.g. CG-99, based on calibration of pure CO₂ gas) has been evaluated by direct CO₂ admixture to synthetic air using the same setup.

Introduction:

The isotopic composition and concentration of atmospheric air samples are useful parameters required for deriving the flux information of atmospheric CO₂ into terrestrial and marine compartments. In the terrestrial regime plant photosynthesis strongly discriminates against ¹³C, while oceanic uptake and release of CO₂ do not significantly fractionate these isotopes relative to atmospheric values. As a consequence, the isotopic signal in atmospheric CO₂ is rather small and approaches the detection limit of modern analytical techniques¹. Calculating fluxes with a small uncertainty requires a comparable precision in the analysis of δ¹³C values as well as in the determination of CO₂ mole fractions. Current fossil fuel emissions of ~6 Gt C yr⁻¹ result in a long term change of the CO₂ mixing ratio of 1.6 ppm yr⁻¹ and a δ¹³C change of about -0.025 ‰ yr⁻¹. While CO₂

[‡] author to whom correspondence should be addressed (wbrand@bgc-jena.mpg.de)

analyses typically can be made with a precision of 0.1 ppm or better, $\delta^{13}\text{C}$ precision is near 0.01 ‰ at best².

In recent years there is a growing concern about climate change and consequent proposed actions to limit atmospheric levels of green house gases, in particular CO_2 . An obvious requirement is much improved inter-laboratory calibration, with new laboratories participating in routine measurements, thus permitting high precision merging of 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 V-PDB. This link also requires a high precision of about 0.015 ‰ in the case of carbon and 0.03 ‰ in the case of oxygen isotopes³.

Background Information:

There were several attempts in the past to tightly link the air- CO_2 isotopic measurement scale to V-PDB. The V-PDB scale for carbon and oxygen stable isotopes replaced the PDB scale in 1987⁴. V-PDB was defined by assigning $\delta^{13}\text{C}_{\text{VPDB}} = +1.95$ ‰ and $\delta^{18}\text{O}_{\text{VPDB}} = 2.2$ ‰ (exact) to the international reference material NBS-19. In order to report to this scale, isotope laboratories generate carbon dioxide by reacting NBS-19 carbonate with 100 % phosphoric acid as well as extract CO_2 from air cryogenically. By measuring the resulting CO_2 gases against each other stable isotope values are assigned to the respective laboratory air standard (in a high pressure tank) used for routine measurement.

The stable isotope laboratory at CSIRO (Atmospheric Research, AR) in Aspendale, Australia, which has been involved in air- CO_2 isotopic measurement since 1982 started with the calibration of a laboratory reference CO_2 gas (HC 453) using NBS-19. The original values were -6.396 ± 0.029 ‰ and -13.176 ± 0.083 ‰ for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ respectively⁵. These values were used subsequently for assigning δ -values to standard air in high pressure tanks which led to the now more widely recognized CG-99 scale⁶.

More recently, in order to reduce the uncertainty associated with CO_2 isotopic measurements in different laboratories, CSIRO (AR) prepared 10 high pressure cylinders of air for the IAEA/WMO CLASSICS project (Circulation of Laboratory Air Standards for Stable Isotope inter-Comparisons) with the CO_2 concentration and stable isotope

composition spanning the present background atmosphere values. In addition, two containers of high-purity CO₂ were included in the circulation. All gases were circulated twice and measured independently by four laboratories using their individual analysis systems and protocols for routine isotopic determinations.

The results of this inter-comparison exercise were presented at the 11th IAEA/WMO CO₂ experts meeting in Tokyo³. Significant differences in the mean isotopic values reported by the different laboratories were found. Moreover, the data for determinations made two years apart from each other often exceeded the target precision for merging data considerably (0.015 ‰)^{2,3}. A number of possible causes for the observed discrepancies were discussed: (1) errors in the preparation of CO₂ gas from NBS-19 carbonate standard and initial assignment on the (V-)PDB-CO₂ scale, (2) propagation of initial assignment errors to subsequent working standards and hence to the sample and (3) systematic effects like ¹⁷O correction, drift correction and cross contamination during gas switching in the ion source of the mass spectrometer ('eta-effect').

In order to improve the link to primary reference material (NBS-19, but also NBS-18, IAEA-CO-1 and others) we have devised an experiment where we tried to strictly follow the rule of identical treatment. In this approach, CO₂ was extracted from NBS-19 carbonate following a standard procedure. Instead of using the CO₂ gas directly for comparative isotopic measurement we mixed it with CO₂-free synthetic air. The resultant mixture of air containing CO₂ was transferred into three 5 liter flasks at 1.6 bar pressure for routine mass spectrometric measurement. In this preparation we obtained a reproducibility of 0.019 ‰ in case of carbon and 0.034 ‰ in case of oxygen as a longer term reproducibility for different batches of CO₂ in air.

Jena 'CG99' isotope scale

In Jena we implemented a local CG-99 scale on the basis of 6 high pressure reference air cylinders filled and supplied by CSIRO (AR), Melbourne, Australia. These cylinders have assigned δ values based on the CG99 scale at CSIRO. The corresponding measurements were made at the end of 1999. The cylinder with identification number CA01656 was chosen for positioning our measurements on the international scale. It's assigned CO₂ isotopic composition was $\delta^{13}\text{C} = -8.078 \pm 0.017 \text{ ‰}$ and $\delta^{18}\text{O} = -0.847 \pm$

0.033 ‰. From the six cylinders, these values together with the mixing ratios of the trace gases were the closest to current atmospheric values. The other tanks of the suite serve as quality and drift control standards.

2. Experimental set up and flask preparation

The air preparation system ('ARAMIS', Acid Reaction and Air Mixing Station) in Figure 1, mounted on a mobile platform, is constructed mainly using ¼" stainless steel internally electropolished tubing (ULTRON, Dockweiler, Neustadt-Glewe, www.dockweiler.com).

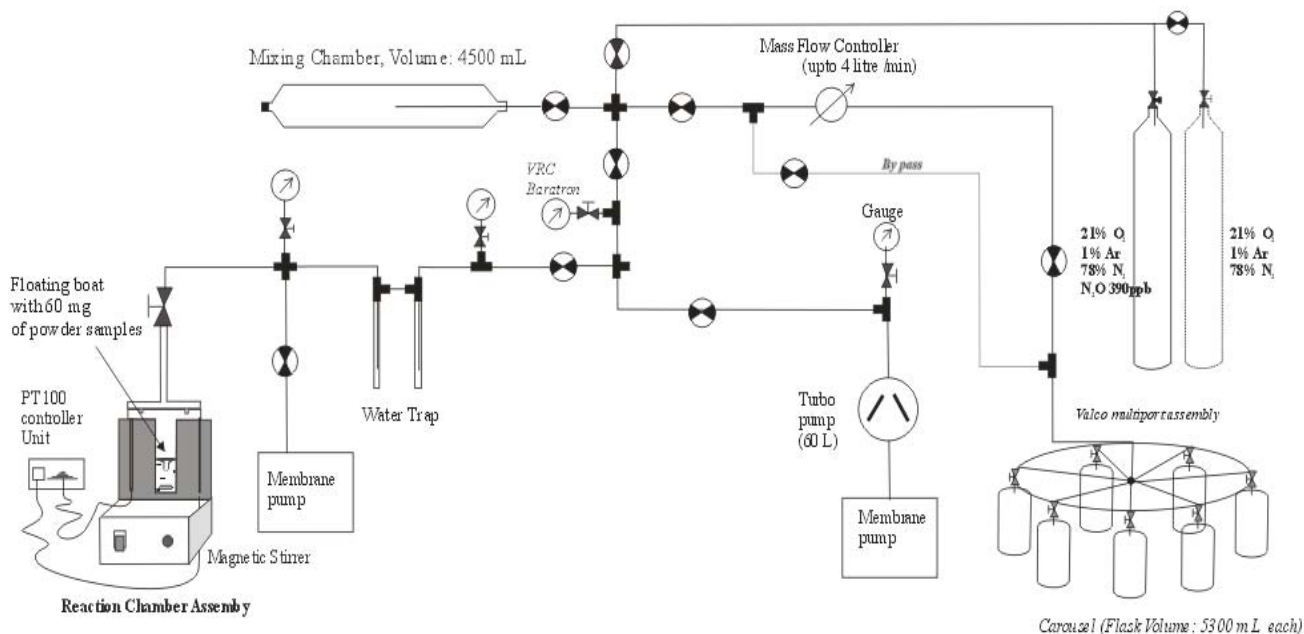


Figure 1; Layout of the Acid Reaction and Air Mixing System (ARAMIS)

The twin water trap comprises two ½" ULTRON tubes (30 cm in length) also internally electropolished. A set of three gauges were installed for pressure reading at three locations in the extraction line and close to the mixing chamber. Gauges 1 and 2 have coarse vacuum readouts whereas gauge 3 (Baratron, MKS, Andover, USA,

www.mksinst.com) is designed for pressures up to 2100 ± 2 mb. Prior to starting a new batch the whole setup is evacuated using a Pfeiffer membrane pump (model MVP 015-4; $1.5 \text{ m}^3/\text{min}$, located close to the reaction chamber) and subsequently by a 60 l/s hybrid-turbopump (Pfeiffer model TMH071 with MVP 015-04 backup pump).

The sequence of events in preparing a set of reference air samples is as follows:

- Carbon dioxide is produced using the classical calcite reaction with H_3PO_4 at constant temperature. The resulting CO_2 is allowed to equilibrate with the Mixing Chamber (MC) for 20 minutes keeping the water trap at -77°C (dry ice / ethanol mixture) . Here, expansion of CO_2 from the reaction chamber to the MC is done in a stepwise fashion (within 5 minutes following completion of reaction).
- An inlet close to the mixing chamber is included for introducing CO_2 -free air from a high pressure tank. Following equilibration of CO_2 throughout the system (20 mins) the CO_2 in the mixing chamber is isolated from the rest of the preparation system, sacrificing about $1/10^{\text{th}}$ of the gas.
- Synthetic air is then added to the CO_2 in the MC up to pressure of ~ 1450 mb. The mixture of CO_2 and synthetic air inside the MC is allowed to equilibrate for another 20 minutes.
- The mixture is then expanded from the MC through a mass flow controller (MKS model 1179AX53CS18V) into 3 evacuated 5 liter flasks attached to 3 ports of a multi-port (8 port) Valco valve using an initial flow rate of $3 \text{ l}/\text{min}$. The final pressure of the initial expansion is about 200 mb.
- Final addition of synthetic air into the three flasks is made at $3 \text{ l}/\text{min}$ until a pressure of 1.6 bar in the flasks is observed.
- The last step is a two hour equilibration with the MC and the 3 flasks communicating before closing the individual flasks.

The resulting air- CO_2 mixtures in the 3 separate 5 l flasks are measured together with ordinary air samples within a single sequence on one of our BGC-Airtrap/ IRMS systems⁷. δ -values are reported on the Jena-implementation of the CG99 scale.

3. Preparation of CO₂ from carbonate reference material

Carbonate powder

Laboratory carbonate reference powder was prepared from a (TS limestone) marble slab purchased from a local vendor (about A3 size). The slab was broken into chips, crushed into fine grains, and sieved. The <250 μ size fraction weighing about 0.9 kg was labelled 'MAR-J1' ('Marble-Jena1'). Texture and appearance of the powder is similar to the NBS19 carbonate material. Other fractions 250-315 μ (~0.5 kg) and 315-400 μ (~300 g), were designated as 'Mar-J2' and 'Mar-J3' and stored for future preparation. Other carbonate reference materials (NBS-19, NBS-18, Cal1, Cal2) were used in an identical fashion during our experiments.

Phosphoric acid

Preparation of the phosphoric acid involves 500 ml of ortho-phosphoric acid (99 %, MERCK, Darmstadt) and 25 g of phosphorus pentoxide, heated to 150°C for 2 hours. Final specific gravity at room temperature was 1.92 and 1.94. The acid is kept in a sealed container prior to use.

Reaction chamber

The reaction chamber was custom made from a block of copper in the workshop of the MPI-BGC. The volume of the reaction chamber is about 35 ml. The reaction chamber is connected to the vacuum line using a flat base glass lid and a Viton O-ring clamp. The reaction chamber is housed in a tight fit brass housing regulated to provide a constant temperature ($\pm 0.1^\circ\text{C}$) using a Pt-100 resistor. About 10 ml of acid is filled into the reaction chamber and stirred. The whole assembly of reaction chamber and acid fitted with glass joint is kept under vacuum for more than one hour. After this time the stirrer is switched off shortly, the reaction chamber is opened and a quartz boat with 60 mg of MAR-J1 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 and same sequence of evacuation is applied. The carbonate reaction is started manually by tilting the quartz boat using a permanent magnet applied from outside.

A similar set of experiments was performed with a glass reaction chamber. Compared to glass we noticed an improved temperature stability during the reaction using copper.

Temperature of reaction

The role of temperature on the oxygen isotopic composition of CO₂ produced during reaction has been recognized long ago⁸. Based on a number of experiments it was concluded that isotopic fidelity may be obtained by using a procedure in which carbonate samples are reacted with 100 % H₃PO₄ at 25°C, with the product CO₂ being retained in the reaction vessel until dissolution is complete. In order to decrease the reaction time and help degassing of the acid higher temperatures up to 90°C have been employed later (for a review see reference 1). However, the temperature dependence of the reaction is not known with sufficient accuracy^{9,10}. In order to evaluate the temperature dependence of the ¹⁸O/¹⁶O ratio with higher resolution and precision we conducted measurements at a number of temperatures between 25°C and 47°C using the ARAMIS line. The results indicated a strictly linear relationship with a slope of the observed δ¹⁸O of -0.03576 ‰/°C. There was no detectable dependence of the δ¹³C values within the studied temperature range and precision (0.019 ‰). Further details of these experiments will be presented elsewhere¹¹. Based on this experience we decided to set the default reaction temperature to 47°C.

Timing of the reaction

60 mg of MAR-J1 powder were weighed in for reaction with phosphoric acid. The reaction was allowed to proceed for time periods between 40 and 90 minutes. In this set of experiments we observed an initial change in the oxygen isotopic composition of the CO₂ produced. The carbon isotopic composition remained constant within the measurement uncertainty. Based on this set of experiment we established 60 minutes as the default duration time for our reaction. With this timing the isotopic results were both, consistent and reproducible. Further details about the experiment and the conclusions will be presented elsewhere¹¹.

4. Results

Mass spectrometric analysis involves extraction of $\text{CO}_2 + \text{N}_2\text{O}$. We made two sets of experiments adding two different types of synthetic air to CO_2 evolved from reaction of carbonate samples: air (1) had 390 ppb of N_2O and air (2) was without any N_2O . The online extraction system coupled with the mass spectrometer and the measurement protocol are described in detail elsewhere^{7,12}. Our laboratory uses air as working as well as quality control standards. These air standards in high pressure cylinders are processed together with regular air samples in our daily routine operation using the same experimental protocols.

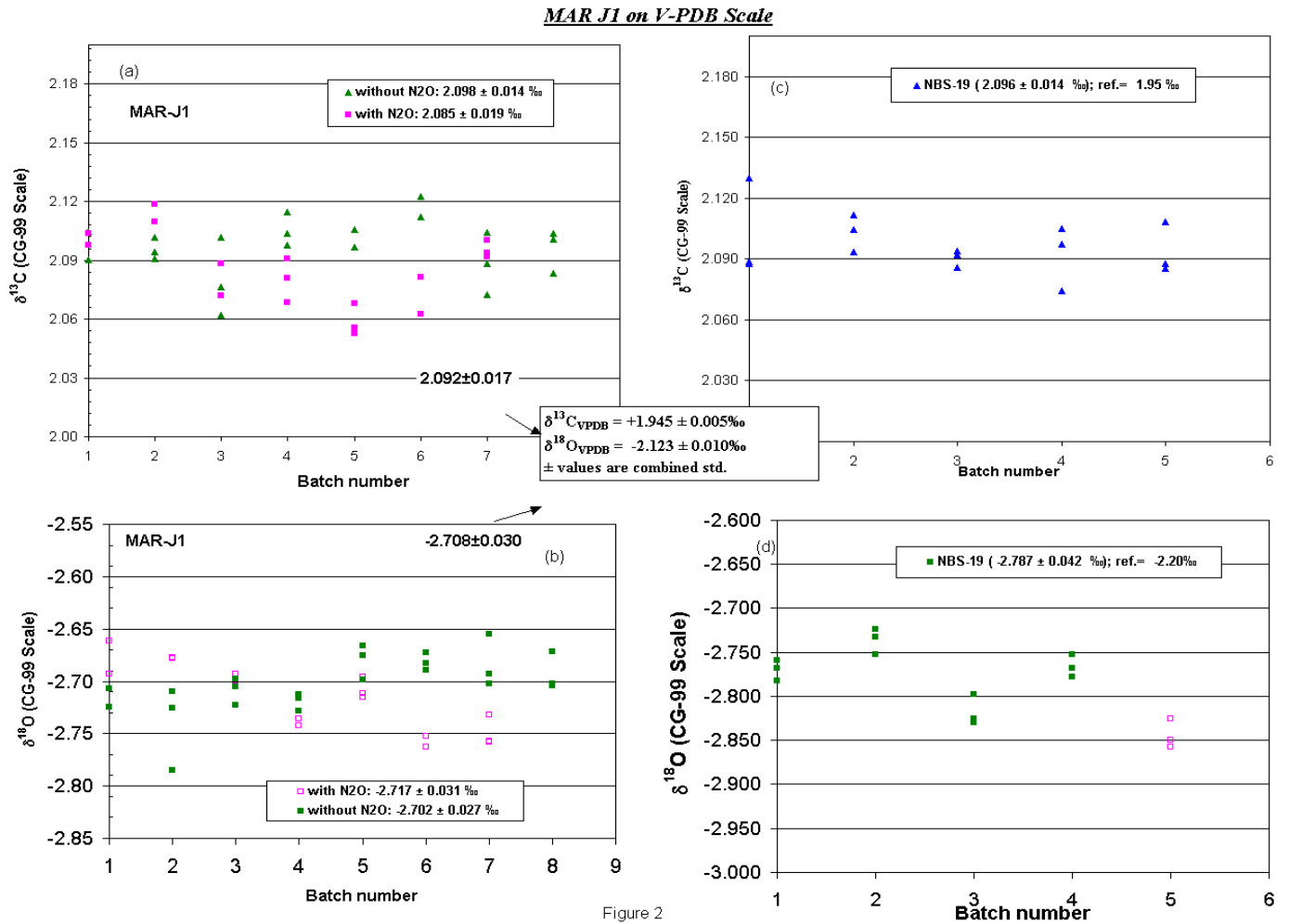


Figure 2; Determination of the isotopic composition of MAR-J1 using NBS19

Results from these air standards are used to monitor and correct systematic influences on all aspects of CO₂ extraction, sample handling, analysis, and ion correction.

δ¹³C of MAR-J1 analyses

Results from 15 batches of MAR-J1 flasks are shown in Figure 2a. Each batch comprises three samples. The set contains seven preparations made with synthetic air containing N₂O. Eight preparations were made without N₂O. Correction of the N₂O contribution was made using measured concentrations and a modified mass balance correction (for details see reference 12). There is no significant difference in the mean values of δ¹³C obtained from the analyses and the results are close to the target precision of 0.01 ‰ for air sample analyses. The means and standard deviations for MAR-J1 CO₂ with and without N₂O admixture were 2.085 ± 0.019 ‰ and 2.098 ± .014 ‰ respectively. We obtained an average value of 2.092 ± 0.019 ‰ from all analyses. The observed mean was consistent with the uncertainty arising from sample preparation.

δ¹³C of NBS-19 analyses

In a second series of experiments we prepared artificial mixtures of air with CO₂ from NBS-19. As already mentioned, the NBS-19 δ¹³C and δ¹⁸O values have been set to +1.95 ‰ and -2.2 ‰ respectively¹³. The isotopic composition of the CO₂ added in the mixture was established independently with repeated measurements giving a consistent precision of 0.02 ‰ for δ¹³C. The results plotted in Figure 2b show the intra-batch variability and heterogeneity in preparation. We obtained an average value of 2.096 ± 0.014 ‰ based on 5 batches of NBS-19 preparations. Comparison of MAR-J1 and NBS-19 preparation based on these analyses indicate indistinguishable δ¹³C values within analytical uncertainty for both materials. This implies that MAR-J1 is very close to NBS-19 in δ¹³C and that it can be used reliably as working carbonate reference material because of its isotopic homogeneity.

δ¹⁸O of MAR-J1 analyses

The δ¹⁸O results of batches of MAR-J1 are plotted in Figure 2c. The results obtained from individual sample are displayed in a similar way as in the case of carbon. The mean

and standard deviation of MAR-J1 CO₂ were 2.717 ± 0.031 ‰ and 2.702 ± 0.027 ‰ respectively with and without N₂O added to the mixture. We obtained an overall average value of 2.708 ± 0.03 ‰ from all analyses. The average is consistent with the uncertainty arising from sample preparation with and without N₂O.

δ¹⁸O of NBS-19 analyses

The δ¹⁸O of batches of NBS-19 are plotted in Figure 2d. The results obtained from individual samples denote a higher degree of heterogeneity between preparations in comparison to MAR-J1. However, the number of preparations is too small for judging the statistical significance of the observation. The mean for NBS-19 CO₂ without N₂O admixture was 2.787 ± 0.042 ‰.

5. The CG99 scale and other reference material measurements using the ARAMIS preparation line

In addition to NBS-19 we have analyzed a set of common carbonate standard reference materials (NBS-18, IAEA-CO-1, IAEA-CO-8) for further evaluating the scale offset seen in our measurements of NBS-19. Table 1 is a summary of all analyses made so far.

The CG99 scale offset we observed was 0.146 ‰ for carbon and 0.188 ‰ for oxygen respectively. In order to check for a possible scale contraction we have analysed NBS-18 carbonatite and obtained values consistent with the NBS-19 data when correcting the scale for the observed offset. The other carbonate standards provide a slightly less consistent picture when comparing accepted and obtained results.

The results for MAR-J1 are listed separately in order to show the different δ¹⁸O values present in the mineral and in the respective gas at 25°C and 47°C. The synthetic air mixture intended for use as CO₂-in-air SRM obviously is made by releasing CO₂ from MAR-J1 at 47°C.

In order to separate effects in the carbonate reaction from pure gas mixing effects we also mixed and analysed two batches of HC-453 CO₂. The results were internally consistent but the resulting offsets after scale adjustment were considerably different from zero (-0.059 ‰ and -0.266 ‰). We conclude from this finding that the original preparation⁵ combined with the transfer to the CG99 scale and cryogenic extraction of CO₂ from the

reference air⁶ differs from our carbonate preparation / gas mixing in terms of consistency. With the latter offsets closer to zero, a conclusion would have been possible that the observed CG99 scale offset might arise from the extraction process exclusively, not from the carbonate reaction. This is obviously not the case. However, all data presented in Table 1 are preliminary. We do not feel confident, yet, to draw farther reaching conclusions and we will continue to examine our system and our procedures for possible sources of fractionation at the precision level presented. Revised data and conclusions will be published separately.¹¹

Summary table

Standards (# of analyses)	Jena' CG-99 scale (measured)				corrected to VPDB (this work)				accepted or in use (VPDB)				Source of i
	$\delta^{13}\text{C}$		$\delta^{18}\text{O}$		$\delta^{13}\text{C}$		$\delta^{18}\text{O}$		$\delta^{13}\text{C}$		$\delta^{18}\text{O}$		
	Mean	StdDev	Mean	StdDev	Mean	StdDev	Mean	StdDev	Mean	StdErr	Mean	StdErr	
NBS-19 (15)	2.096	0.013	-2.012	0.041	1.95		-2.2		1.95		-2.2		Definition
CG99 scale offset	0.146	0.013	0.188	0.041									
other carbonate standards													
NBS-18 (5)	-4.857	0.011	-22.929	0.021	-5.002	0.011	-23.113	0.021	-5.01	0.05	-23.035	0.172	IAEA TECI
IAEA-CO-1 (6)	2.581	0.012	-2.332	0.027	2.434	0.012	-2.520	0.027	2.480	0.025	-2.437	0.073	IAEA TECI
IAEA-CO-8 (3)	-5.651	0.010	-23.458	0.022	-5.796	0.010	-23.642	0.022	-5.749	0.063	-22.667	0.187	IAEA TECI
CAL-1 (2)	-45.963	0.019	-22.272	0.012	-46.11	0.019	-22.462	0.012	-45.764	0.018	-22.036	0.033	VMO148
CAL-2 (2)	-2.383	0.000	-12.58	0.009	-2.529	0.000	-12.770	0.009	-2.558	0.009	-12.549	0.028	VMO148
NBS-19 (CO ₂ -gas)					1.950		-2.20 + (10.25)						
MAR-J1 (mineral)					1.945	0.017	-2.122	0.030	1.945	0.005	2.123	0.010	this work
MAR-J1 (gas, 25°C)					1.945		-2.123 + (10.25)						
MAR-J1 (gas, 47°C)					1.945		-2.123 + (9.475)						
Air standard (MARJ1 (47°) vs. VPDB-gas)					1.945		-2.897		1.945	?	-2.897	?	proposed
HC-453 (6)	-6.324	0.023	-13.280	0.015	-6.469	0.023	-13.466	0.015	-6.410	0.020	-13.200	0.030	VMO 148
Offset vs assigned					-0.059		-0.266						

8. Conclusions and outlook: open issues and plans for the future

Before a new CO₂-in-air standard reference material can be established we must arrive at a conclusive picture regarding the offset discussed above. Once this point is reached, we will be able to produce the SRM in the form of 5l glass containers at a pressure up to 2 bar. This amount of air is sufficient for a larger number of isotopic determinations even when about 500 ml (STP) of air are consumed in a single preparation. We plan to always ship two such flasks in order to provide a consistency check. 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 present in the data evaluation and corrections applied, the errors will tend to cancel for other air samples provided these are close to ambient concentrations and isotopic compositions with the exception that the air-SRM has an offset of about +10 ‰ for $\delta^{13}\text{C}$. It would be advantageous to also have a sibling air-SRM with $\delta^{13}\text{C}$ close to air-CO₂. This would, however, require a calcite with the texture and homogeneity of NBS19 that has a $\delta^{13}\text{C}$ value close to -8 ‰.

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