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Jena Reference Air Set (JRAS): a multi-point scale anchor for isotope measurements of CO_2 in air

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Abstract

The need for a unifying scale anchor for isotopes of CO_2 in air was brought to light at the WMO CO_2 Experts Meeting in Tokyo 2001. During discussions about persistent discrepancies in isotope measurements between the worlds leading laboratories it was concluded that a unifying scale anchor for VPDB of CO_2 in air was desperately needed. Now, 10 yr later, the 2011 CO_2-Experts-Meeting in Wellington has decided that the Jena Reference Air Set or JRAS is recommended as official scale anchor for isotope measurements of CO_2 in air.

The JRAS gases consist of reference CO_2 mixed into CO_2 free air. To safeguard both stability and longevity of the CO_2, it is directly generated from two solid reference calcites. That the reference CO_2 is supplied in air is unique to JRAS. This is made to ensure that any measurement bias arising from the extraction procedure is eliminated. As every lab has its own procedure for extracting the CO_2 this is of paramount importance if the local scales are to be unified.

For a period of four years, JRAS has been evaluated through the IMECC program, which made it possible to distribute sets of JRAS gases to 11 laboratories worldwide. A summary of the results is reported here along with a description of the production and maintenance of the JRAS scale anchors.

1 Introduction

1.1 State of affairs

Prior to the WMO meeting in Tokyo 2001, a project funded by the International Atomic Energy Agency (IAEA) called CLASSIC (Circulation of Laboratory Air Standards for Stable Isotope inter-Comparisons) had revealed significant discrepancies between four of the world leading laboratories (Allison et al., 2003). The results from the CLASSIC project were based on five high-pressure cylinders filled with chemically modified air and two canisters with pure CO_2. These gases had been circulated during two campaigns (1996–1998, 1999–2000) between CAR/CSIRO (Aspendale, Australia), INSTAAR/NOAA (Boulder, USA), Scripps Institute of Oceanography (La Jolla, USA), and the Center for Atmospheric and Oceanic Studies (Sendai, Japan).

The results reported from the pure CO_2 canisters exposed differences between the laboratories exceeding the inter-laboratory target precision of 0.01 ‰ for $\delta^{13}C$, leading the authors of the report to state: "The mean differences in reported values are consistent with uncertainties in assignment of the isotopic composition of in-house pure CO_2 working standards onto the VPDB-CO_2 scale."

For the analysis of air in the high pressure cylinders the results were not much better. Although the differences between two campaigns within the laboratories met the target precision, the average differences relative to the CAR results for $\delta^{13}C$ between the laboratories ranged from −0.022 ‰ to +0.118 ‰ and for $\delta^{18}O$ the range was −0.804 ‰ to +0.112 ‰. Quoting the report: "As with GS20B[1], the mean difference between laboratories is consistent with problems in assignment onto the VPDB-CO_2 reference scale."

At the root of this problem was and still is the fact that both methods for scale anchoring and the choice of anchor vary from laboratory to laboratory. A further complicating factor was that all available scale anchors were pure CO_2, forcing the laboratories to anchor their scales by comparing the CO_2 they extracted from air to pure reference CO_2 – a comparison that adds any possible bias caused by the extraction of CO_2 from air to the local scale. As the extraction method is unique to the laboratory the resulting local scale will hence differ from laboratory to laboratory.

In addition to this weakness in scale definition, results were hampered by the cross-contamination or eta-effect that has been plaguing isotope mass spectrometers over years (Meijer et al., 2000; Verkouteren et al., 2003a,b) and, thus, causing scale contraction. Further inconsistencies were found in the correction procedures for the ^{17}O contribution used when translating ion currents to delta values (Brand et al., 2010) and

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[1] The pure CO_2 canister.

in the algorithms applied for removing the inevitable presence of N_2O in the CO_2 gas extracted from air cryogenically (Sirignano et al., 2004; Ghosh et al., 2004).

2 The Jena Reference Air Set – JRAS

A JRAS set consists of two 5-l glass flasks containing CO_2 from two different calcites mixed into CO_2-free air. The first of the two calcites, MAR-J1, has characteristics (isotopic composition, trace elements, grain size) that are almost identical to NBS 19, the primary scale anchor for VPDB. The second calcite, OMC-J1, was chosen as a compromise after a long and unsuccessful search for an ideal candidate to serve as a second anchor point. Ideally, this point should be close to that of atmospheric CO_2; however, OMC-J1 provides an adequate range between the two anchor points with a δ^{13}C value of −4 ‰ on the VPDB scale (Ghosh et al., 2005).

By using solid calcites, enough material can be prepared and stored without risk of isotopic alteration to ensure both longevity and stability of the JRAS scale anchors.

In order to keep the variability arising from the preparation of the reference CO_2 at a minimum, a computer-controlled system has been designed and built at the MPI-BGC (Ghosh et al., 2005). The system prepares CO_2 by digestion of the calcites in highly concentrated phosphoric acid and mixes it into CO_2-free air in batches large enough to provide three 5-l flasks (p = 1.5 bar) at a time. Figure 1 shows the δ^{13}C variability of the produced CO_2 between these batches over time. The preparations should not vary by a large amount in order to maintain the anchor point fixed in time. It is important to note that – because the isotopic composition of the flasks is measured and assigned during this procedure – the preparation variability is not propagated into an uncertainty of the scale anchor.

The local δ^{13}C scale at the BGC Isolab has been established based on repeated analysis of preparations of primary calcites, NBS 19 and LSVEC, using the automated preparation system (Ghosh et al., 2005; Brand et al., 2009). This scale, JRAS-06, which is firmly anchored at +1.95 ‰ and −46.6 ‰ exactly on the VPDB scale and is continuously maintained, has been used to assign the values of the JRAS sets.

3 Results

3.1 Test and evaluation

The JRAS concept has been evaluated from 2007 to 2011 as a part of the European Commission funded program – Infrastructure for Measurements of the European Carbon Cycle, IMECC. Thanks to IMECC the isotope laboratory at MPI-BGC has been able to produce and distribute 50 JRAS sets. Thirteen laboratories from all over the world volunteered to participate in the IMECC-JRAS project (Table 1). Each of the laboratories received a JRAS set which, when exhausted, was replaced with a new set. The number of analyses performed varied between the participating laboratories due to differences in workload and instrument availability. The project as a whole totaled over 250 analyses of the JRAS scale anchors.

In the spring of 2010 the JRAS project was augmented with 5-l glass flasks containing calibrated (dry ambient) air; this was a result of requests made during discussions at the 15th WMO CO_2 Experts Meeting in Jena 2009. While these air samples do not constitute an immediate scale anchor, they add an important data point right at the isotope composition of atmospheric CO_2, thus allowing for a three-point comparison of the scales.

The JRAS results were evaluated by comparing the analytical results on the local scales with the values assigned on the JRAS-06 scale. MPI-BGC also participated in the evaluation by intermittently measure JRAS gases as independent samples. The results are shown in Fig. 2, where the linear regression represents the agreement between the measurements and the JRAS-06 scale. The additive term in the equation signifies an offset between the two scales and the factor/slope describes differences in standardization strategies between laboratories or serves as a quantification of any scale contraction occurring. As both the term and the factor are negligible the BGC results validate the ability of Isolab to maintain the JRAS-06 scale.

Figure 3 is an extrapolation of the results from the JRAS measurements in the BGC Isolab to cover the whole isotopic range of the two primary scale anchors, NBS 19 and LSVEC. This plot gives a visual characterization of scale discrepancies caused by different standardization schemes or possibly scale contraction issues. For MPI-BGC the deviation of the scale is insignificant, amounting to 0.04 ‰ only over a scale distance of almost 50 ‰. However, when we plot the results from all participating laboratories that included the air samples in their measurements, the deviations become larger (Table 2, Fig. 4).

The offsets between local scales and VPDB-CO_2 (term a in Table 2) determined by the JRAS project are not much different from those reported from the CLASSIC project. In other words the situation has remained largely unchanged over the last decade. With the JRAS project the scale comparison is going further than during CLASSIC by using a multi point scale anchor and thereby testing the local scales for scale contraction issues. Scale contraction (i.e. the scale offset is linearly dependent on the delta value) can be caused by differences in standardization methods/materials or cross contamination in the mass spectrometer. The results from JRAS clearly suggest that these issues are real and significant (slope b in Table 2), although not for all laboratories. For example; the factor b values of the regressions for University of Heidelberg and NIWA are so small that the slope is insignificant thus explaining the sign of the slopes, which otherwise would indicate a virtual scale expansion. In Fig. 4 the results are extrapolated to demonstrate the relationship between the scales and $\mathrm{VPDB}_{\mathrm{gas}}$.

The results for oxygen isotopes can be evaluated in the same way as those for δ^{13}C. Here the offsets are expected to be larger, reflecting the commonly observed uncertainties in oxygen isotope measurements (Table 3, Fig. 5). Factors contributing to the uncertainty are the correction for N_2O present in the analyzed gas (Sirignano et al., 2004; Ghosh and Brand, 2004), the δ^{18}O value used for digesting the calcite during standardization (Wendeberg et al., 2011) and the ^{17}O correction (Brand et al., 2010).

The latter have been the focus of the WMO recommendations for several years, where the need for a unified use of the Assonov correction has been emphasized (Assonov et al., 2003).

4 Conclusions

Ten years after the need for a unifying scale anchor for CO_2 in air was formulated, the participants of the 16th WMO CO_2 Experts Meeting in Wellington 2011 have decided to recommend the JRAS gases for use as the official scale anchor for measurement of atmospheric CO_2 on the VPDB scale. This along with a unified use of the ^{17}O correction will hopefully contribute greatly to harmonize the various local scales.

The MPI-BGC lab will continue to aid in this process, now as a WMO-endorsed Central Calibration Lab, by providing calibration for high-pressure tanks based on the JRAS procedure.

Acknowledgement. We would like to thank all participants in the various laboratories for extending their best efforts into this (rather tedious) endeavor. In particular we would like to acknowledge their openness in communicating their results to the general public.

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Table 1. Laboratories that participated in the JRAS project.

Laboratoire des Sciences du Climat et de l'Environnement	Gif sur Yvette Cedex	France
Dep. of Enivonmental Physics – AGH-Univ. of Science and Technology	Kraków	Poland
Institute of Environmental Physics – University of Heidelberg	Heidelberg	Germany
Scripps Institute of Oceanography – University of California-San Diego	La Jolla	USA
CSIRO – Marine and Atmospheric Research	Aspendale Victoria	Australia
Environment Canada – Stable Isotope Research Laboratory	Downsview Ontario	Canada
National Institute for Environmental Studies	Tsukuba	Japan
Institute for Reference Materials and Measurements	Geel	Belgium
Climate and Environmental Physics – University of Bern	Bern	Switzerland
Institute of Arctic and Alpine Research – University of Colorado	Boulder Colorado	USA
Center for Atmospheric and Oceanic Science – Indian Institute of Science	Bangalore	India
Max Planck Institute for Biogeochemistry	Jena	Germany
National Institute of Water and Atmospheric Research	Wellington	New Zealand

Table 2. δ^{13}C results. Linear regression resulting from comparing local scales to JRAS-06.

	$y = a + bx$		
	a	b	R^2
INSTAAR, University of Colorado, USA	−0.0721	0.9836	0.99997
NIES, Japan	−0.0199	0.9963	1
Scripps Institute of Oceanography, USA	0.1198	0.9795	0.99999
University of Heidelberg, Germany	−0.0321	1.0016	0.99999
NIWA, New Zealand	0.0503	1.0026	0.99994
MPI-BGC, Germany	0.0007	0.9992	1

Table 3. δ^{18}O results. Linear regression resulting from comparing local scales to JRAS-06.

	$y = a + bx$		
	a	b	R^2
INSTAAR, University of Colorado, USA	0.0399	0.9667	0.99997
NIES, Japan	−0.09	0.9895	0.99999
Scripps Institute of Oceanography, USA	−0.3153	0.9426	0.99722
University of Heidelberg, Germany	0.151	1.0024	0.9999
NIWA, New Zealand	−0.0709	0.9549	0.99872
MPI-BGC, Germany	−0.0064	0.9963	0.99998

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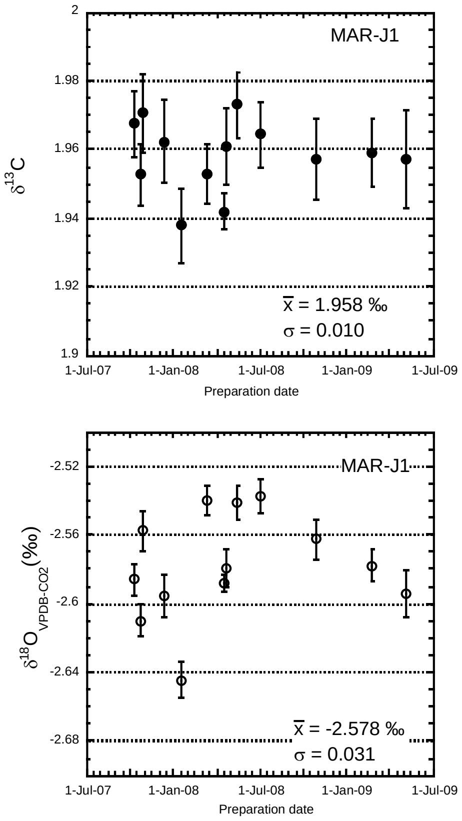

Fig. 1. Production variability of the JRAS gases over time. Each data point represents an average of nine measurements of the prepared CO_2-air mix, three per flask within a batch. Thus the overall standard deviation reflects the combined variability between the prepared CO_2 as well as the uncertainty related to the extraction and mass spectrometric measurements performed in the MPI BGC laboratory.

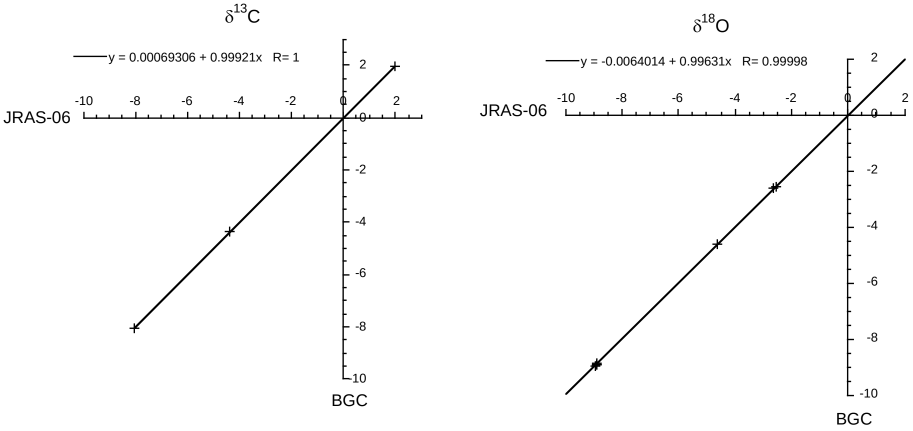

Fig. 2. Comparison of MPI-BGC measurements of JRAS gases treated as independent samples to the originally assigned values on the JRAS-06 scale. Left panel shows the δ^{13}C data and the right the corresponding δ^{18}O data.

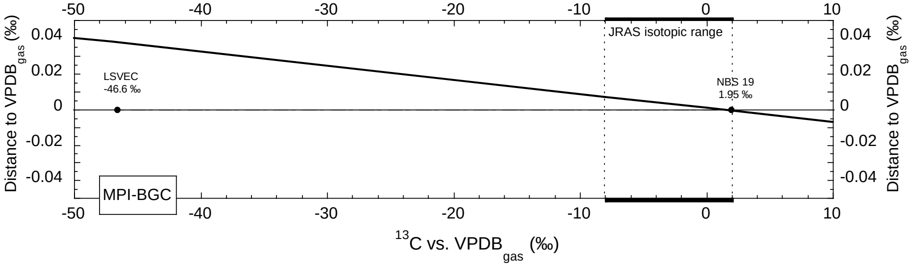

Fig. 3. Extrapolation of the MPI-BGC results to the range spanned by NBS 19 and LSVEC.

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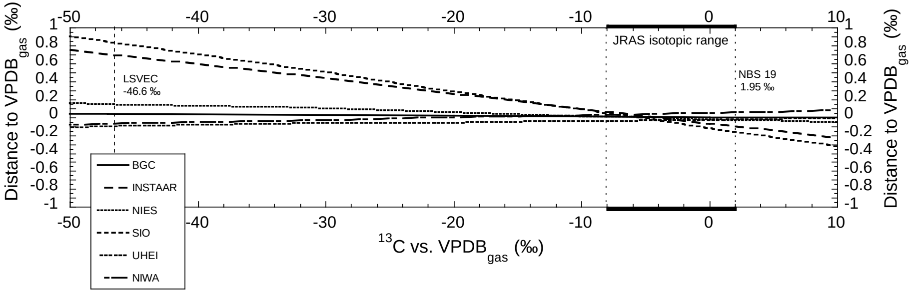

Fig. 4. Extrapolation based on linear regression of the JRAS δ^{13}C data.

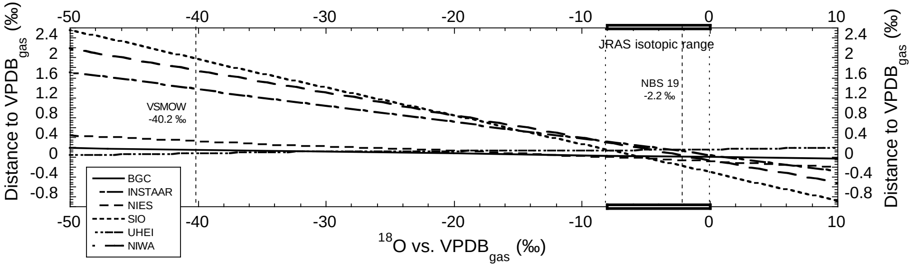

Fig. 5. Extrapolation based on linear regression of the JRAS δ^{18}O data.