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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Long-term observation of mass-independent oxygen isotope anomaly instratospheric CO_2" *by* S. Kawagucci et al.

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General Comment

The authors present the analysis of old and new data of the oxygen isotopic composition of stratospheric carbon dioxide that were gathered over several years between 1991 and 2004, mostly over Sanriku (Japan). The strength of the data set comprising 60 samples is its temporal coverage and access to the simultaneous measurement of nitrous oxide, a tracer of stratospheric transport.

While the particular findings of this study do not seem to be entirely new (*e.g.* the correlation of $\delta^{18}O$ with N_2O (previously reported by Aoki et al. (2003)), the correlation of $\Delta^{17}O$ with N_2O (previously reported by Boering et al. (2004)), a tight correlation of

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$\delta^{17}O \approx 1.7\,\delta^{18}O$ (previously reported by Lämmerzahl et al. (2002)) and a different $\delta^{17}O$ - $\delta^{18}O$ relation for air masses from high altitudes (previously reported by Thiemens et al. (1995)), the entity of observations makes the difference. The existing database is largely extended and the increased number of measurements allows to draw a more reliable picture of the isotope composition of CO_2 in the middle stratosphere, opening up the possibility to better understand the mechanisms behind. So far, first modeling attempts have been made, but more data, especially at high altutides, are needed. It is beyond doubt that the paper addresses relevant scientific questions within the scope of ACP.

In particular, the observations might bring together aspects of two earlier data sets that apparently are not consistent: The negative linear correlation of $\Delta^{17}O(CO_2)$ with N_2O in the lower stratosphere (Boering et al. (2004)) and the tight correlation of $\delta^{17}O$ and $\delta^{18}O$, which was demonstrated by Lämmerzahl et al. (2002), but absent in the ER-2 measurements of Boering et al. (2004). With the new data one has to conclude that the ER-2 measurements are affected by an additional mass dependent fractionation (of yet unspecified origin), reconciling respective key aspects of the two earlier measurements.

While the data themselves are highly interesting, their presentation and discussion suffers from shortcomings that require a major revision. These drawbacks are summarized here and disussed in more detail in the "Specific Comments" section.

Firstly, the data analysis is not transparent and cannot be reproduced: Not all data points that appear in Table 1 are shown in Figure 3. Using the data given in Table 1, the three isotope slopes are 1.64 ± 0.094 and 1.34 ± 0.094 (with standard errors reported) and not 1.75 and 1.17 for the respective cases of high and low N_2O mixing ratios. In addition, the hypothesis of different slopes in the different regimes of N_2O is not backed up by the data – only if certain subsets are chosen. Anyway, the low number (n $\approx$ 12) of "upper stratospheric air" samples, requires a much more careful

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and detailed analysis before a decisive conclusion can be drawn. Otherwise these values might be over-interpreted.

Secondly, the discussion of the data completely neglects systematic errors which could be larger than the analytical accuracy given in the paper. In particular, air samples that have been stored for ~ 15 years seem to be prone to contamination. Sample treatment and integrity needs to be discussed in more detail. Even more so, because contamination problems have been reported (Brenninkmeijer et al. (2003), Lämmerzahl et al. (2002), Honda (2004), Gamo et al. (1989)). Apparently they have a great impact on the results

Thirdly, the sources of original findings/data are not always identified. For example, it was pointed out in the manuscript that in-situ reactions cannot be responsible for the isotope composition of CO_2 in the lower startosphere. That needs to be the result of vertical transport. As far as I know, this point has been made first by Boering et al. (2004), also based on the correlation with $\Delta^{17}O$. Likewise, missing in Table 1 is a clear identification of data that have been published before (*e.g.* by Kawagucci et al. (2005), Gamo et al. (1995), Gamo et al. (1989), Aoki et al.(2003)). This issue should be also clarified in the introduction, where the merits of the new data are illustrated.

Finally, arguments are not presented in a clear and conclusive manner. For example, the apparent change in the correlation between isotopic data of CO_2 with N_2O at low values of N_2O seems to be interpreted as indicative for a change of the physics or chemistry of CO_2 alone. However, it is more likely that the change in the correlation behavior is due to changing conditions for N_2O rather than for CO_2, even though the latter possibility may not be strictly ruled out. The discussion is incomplete also with respect to other crucial questions. It is claimed that lower stratospheric CO_2 is completely determined by transport. What about the seasonal change of tropospheric CO_2? What does it mean that the data of Boering et al. (2004) do not show the isotope correlation of $\delta^{17}O \approx 1.7\,\delta^{18}O$, which is in contradiction to the new observations? What other processes might have played a role? It seems that these were effective at lower

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stratospheric heights. Could these yet unidentified effects also lead to a decline in the $\delta^{17}O$-$\delta^{18}O$ slope at higher altitudes?

Specific Comments

1. Data Selection, Statistical Analysis and Reproducibility of Results

Unfortunately, N_2O data are missing in Table 1, so that it is cumbersome and error prone to verify which data points belong to the classes with $N_2O >$ and $<$ 50 ppb. From Figure 2, the data points 1, 2, 16, 17, 18, 37, 38, 47, 48, 49, 59 and 60 have been identified at low N_2O data ($N_2O < 50$ ppb). One must also notice that the data points 19, 30, 31, 39 and 50 do not appear in Figure 3 (it seems that the values labelled "tropospheric" in Table 1 have been omitted in Fig. 3, while they are retained in Fig. 2). One should also note that the first two data points from a flight in August 1991, which have been measured before (Gamo et al. (1995)), seem to be higher by 0.5 . . . 1 permil than the originally published $\delta^{18}O$ values. What has caused this shift (beyond measurement precision) and what are the implications?

From comparison with earlier publications (Gamo et al. (1995), Kawagucci et al. (2005)) it also seems that not all collected and analysed samples available have been listed in Table 1. For example, Kawagucci et al. (2005) have measured the data of flights over Japan in 1991, 2000 and 2001 by the newly developped CF-IRMS technique. They report the results on 20 samples (their Fig. 5), whereas only 13 data points from presumably the same flights are shown here. This seemingly selection of data needs to be justified.

In order to investigate the significance of a difference in slopes, one may apply linear regression coupled by an analysis of covariance (ANCOVA). I have used four different data sets for this type of analysis: (A) – all data in Table 1, (B) – all data without the

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"tropospheric" values, (C) – all data without the 1991 data points and (D) – all data without the "tropospheric values" and without the 1991 data points (= (B) ∩ (C)). The results are displayed in the following table (slope errors come from separate fits to the data, errors in the differences from ANCOVA):

Data Set	$\Delta(\delta^{17}O)/\Delta(\delta^{18}O)$	Fit Value	Std. Error
(A)	low N_2O	1.638	0.094
	high N_2O	1.336	0.094
	difference	0.302	0.167
(B)	low N_2O	1.683	0.088
	high N_2O	1.336	0.094
	difference	0.347	0.145
(C)	low N_2O	1.638	0.094
	high N_2O	1.383	0.103
	difference	0.255	0.178
(D)	low N_2O	1.683	0.088
	high N_2O	1.383	0.103
	difference	0.300	0.154

Two observations may be made: First, the slope values quoted in the manuscript (1.75 and 1.17) cannot be reproduced. Second, only if one choses a particular subset of the entire data (case (B)) the difference between slopes is significant ($P(>|t|) = 2.0\,\%$). In all other cases it is not ($P(>|t|) \approx 5.7 \ldots 15.8\,\%$). Because of the sensitivity of the conclusion with respect to the selection of a particular subset, the data (as presented in Table 1) cannot be used to demonstrate a difference between two atmospheric regions. Moreover, since the separation of the data into two different classes seems to be arbitrary (not motivated by external criteria, see also section 3), a less arbitrary method would be desirable. If one makes the assumption that the transition (if any) between two regimes is occuring gradually, then fitting a quadratic polynomial to the

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whole data set and testing for the significance of the quadratic term would probably be a less arbitrary approach than the one presented here. If one does so, one finds that the quadratic term is not significant – independent of the data set ((A)-(D)) used for the analysis.

To summarize here, the data selection process, the method to analyze the data as well as the results are questionable. The conclusion that the isotope data indicate a transition between two different isotopic regimes appears to be an over-interpretation and might follow from a biased approach.

2. **Systematic Errors**

The discussion of systematic errors has been completely omitted even though storage of air samples can have large effects on $\delta^{18}O$ (and $\delta^{17}O$). For a 50 days storage time a 1 permil shift has already been observed in early cryo sampler experiments (Gamo et al. (1989)). Since the description given on p. 15726 seems to imply that some samples had to be stored for more than 10 years, contamination effects might well be relevant and need to be considered. The resulting systematic uncertainties should be higher than the analytical errors indicated. Another pointer in the same direction was given by (Lämmerzahl et al. (2002)). These authors have reported that three out of four samples that showed a significant deviation from a linear $\delta^{18}O$ - $\delta^{17}O$ relation were always the first of two replicates. The fourth data point (that had not been followed by a duplicate measurement) could not be checked. If there are no atmospheric processes to explain the high variability in the ER-2 data set from (Boering et al. (2004)), systematic errors in sample storage, preparation and analysis may be a possible explanation. Therefore, the effect of these systematic errors on the individual conclusions should be clearly stated. For example it is expected that $\Delta^{17}O$ is quite robust against such effects (apart from direct contamination with tropospheric carbon dioxide), whereas δO values are much more prone to such problems.

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3. Presentation of Results, Discussion and Interpretation

Provided that section 3 (Results) of the manuscript is meant to present the data collected and analysed by the authors and not the discussion of other data, the statement that correlations between oxygen isotope data of CO_2 and the mixing ratio of N_2O are fading away needs clarification. Within the scatter all except one data point of Fig. 2a support a linear correlation throughout the entire data set. In particular, 10 out of 12 data hypothesized to show a change in physico-chemical conditions ($N_2O < 50$ pppb, indicated by the dashed line in Figs. 2 a and b) do completely follow the lower atmospheric trend. It therefore does not seem to be justified to describe this as a "fading away" of the $\Delta^{17}O$-N_2O correlation. There might be a trend in the $\delta^{18}O$-N_2O data, but if significant, it looks more like a small change than a fade away. Actually, a logarithmic N_2O scale might help to understand the behaviour at low N_2O better. Overall, the evidence given by the data here seems to be weak. It looks as if essentially one or may be two data points could indicate a deviation from the low N_2O trend, but the significance of this observations needs to be demonstrated, even though it might be expected on physical grounds. Anyway, this may not at all tell anything about CO_2 (see below).

The discussion of data with $N_2O > 50$ ppb is misleading (lines $1 - 10$, page 15729). It appears that the reasoning of (Boering et al. (2004)) is reapeated, without giving credit to the original paper.

The discussion of data with $N_2O < 50$ ppb is insufficient (lines > 11, page 15729). What is the reason for separating the CO_2 data into two different classes of N_2O? It may be inferred on the basis of this and other measurements (Thiemens et al. (1995)) that on a linear plot δO *vs.* N_2O a deviation from linearity towards low N_2O exists. But how would this need to be interpreted? In principle, the upturn may be due to two reasons: The physical chemistry of CO_2 *or* that of N_2O is changing with altitude

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(or both change differently at the same time). It seems to be unlikely to assume that the line can be extrapolated just to N_2O = 0, because that would imply that at higher altitudes the sinks of N_2O identically reflect the source of the isotopic composition of CO_2. Probably it would also imply that timescales for the two processes are the same, which they are not. A priori, the change of the correlation may not tell anything about differences in the isotope chemistry of CO_2 at different altitudes. Because N_2O undergoes a change in loss (from diffusion controlled to chemical) roughly at these altitudes, we might only be able to conclude that $\delta O(CO_2)$ is an even longer-lived tracer than N_2O! Certainly, a more careful analysis and discussion is required to understand the details and implications of a changing correlation pattern between isotope data of CO_2 and mixing ratios of N_2O. It must be noted, however, that it is entirely misleading to build a separation of O isotope values of CO_2 according to the N_2O mixing ratio on the correlation plots in Figure 2, without demonstrating that these demonstrate an effect in CO_2. As discussed before, such a conclusion is not backed up by the isotope data of CO_2 alone.

Finally, the paper could be more quantitative at times. For example no numbers are given for the $\Delta^{17}O(CO_2) \sim N_2O$ relation, even though it seems to be quite universal and coincides beautifully with the measurements of Boering et al. (2004). Likewise, what is the slope in the linear range of the $\delta^{18}O(CO_2) \sim N_2O$ diagram? The paper could gain from explicitly stating these numbers that might be useful as a benchmark for atmospheric isotope modeling.

Technical

Here, some minor suggestions are made that could help improving the manuscript.

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