

Interactive comment on “Long-term observation of mass-independent oxygen isotope anomaly in stratospheric CO₂” by S. Kawagucci et al.

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Received and published: 4 January 2008

This discussion paper presents a large number of new measurements of the ¹⁷O isotope anomaly in stratospheric CO₂ in air collected by a balloon-borne cryogenic whole air sampler between 1991 and 2004. It is an interesting and important new dataset, but several significant weaknesses in analysis, interpretation, and presentation need to be addressed.

General comments:

The most significant scientific weakness in my opinion is their interpretation (Lines 1-10, Pg 15729) of their dataset that transport alone controls the isotopic compositions of CO₂ for air with N₂O mixing ratios larger than 50 ppbv – or, in other words, over

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much of the stratosphere. However, their own dataset suggests that this is not the case since, for example, the $d_{17O}:d_{18O}$ slope appears to change between the higher vs. the lower N_2O data (when taken together with the other available datasets). If the isotopic compositions of CO_2 for the majority of their stratospheric samples are determined by mixing of tropospheric CO_2 with upper stratosphere/mesospheric CO_2 , as the authors claim here, then how could the slope change somewhere in between? Rather, in my opinion, the evidence of the combined datasets suggests that the isotope photochemistry first suggested by Yung et al. [1991, 1997] is occurring throughout the stratosphere while an additional isotopic fractionation process comes into play higher in the stratosphere. In coming to their – I believe – erroneous conclusion that transport alone controls the isotopic composition of CO_2 throughout most of the stratosphere, the authors may also be misinterpreting a (perhaps poorly worded) sentence in Boering et al. [GRL, 2004] in which we stated that the very tight correlation between D_{17O} of CO_2 and N_2O mixing ratios is not necessarily or not simply the result of a common connection to $O(1D)$, as others had suggested prior to the 2004 publication. By this, we meant that the strikingly tight correlation we observed was much more the result of the relative chemical time scales for production of the $17O$ anomaly in CO_2 (via the sequence of reactions $O+O_2+M$, $O_3+h\nu$, and $O(1D)+CO_2$) and the destruction of N_2O (90% by photolysis and 10% by reaction with $O(1D)$) versus the stratospheric transport time scales than due to any arguably "coincidental" connection with $O(1D)$. In other words, the tight *correlation* is due to a combination of the relative chemical and transport rates, as described in general for all long-lived tracers by Plumb and Ko [1992], and is NOT due to the *commonality* of $O(1D)$ chemistry (as others had suggested prior to 2004). This is not to say, however, that the observed * $17O$ anomaly* in stratospheric CO_2 results from transport alone and not in situ $O(1D)$ photochemistry (as the authors here claim). That a tight *correlation* (between 2 long-lived tracers) would remain in the "absence" of "this commonality" in our 2004 publication is thus in retrospect a poor choice of words and was not meant to imply that photochemical transfer of the $17O$ anomaly in O_3 to CO_2 via $O(1D)$ is not occurring throughout the stratosphere. Thus,

while the D17O production and N2O destruction rates are certainly fastest in the upper stratosphere, this does NOT mean that in situ photochemistry involving O3, O(1D), and CO2 is not altering the 17O and 18O isotopic compositions of CO2 in much of the stratosphere to one degree or another. It just does so on a time scale that is relatively slow compared with vertical and horizontal transport rates in the lower stratosphere. It is in this latter context that we so heavily emphasized the tight correlation between D17O-CO2 and N2O and the Plumb and Ko "long-lived tracer" concept in the 2004 GRL paper: we argued that a rapid and localized chemical event – such as production of the 17O anomaly in CO2 during solar proton events that can affect ozone chemistry at the poles, which was suggested as one possibility by Lammerzahl et al. [2002] to explain their high D17O-CO2 values at low altitudes near the north pole – was not consistent with the tight correlation we observed between D17O-CO2 and N2O, a well-known long-lived tracer. D17O-CO2 correlates well with N2O and thus effectively with integrated time in the stratosphere and not altitude; thus a high value for D17O-CO2 at low altitudes is not unexpected or unusual if N2O shows the air has resided in the stratosphere long enough for D17O-CO2 to have "accumulated." Furthermore, a localized, rapid chemical production as Lammerzahl et al. had suggested would most likely result in large scatter in the D17O-CO2:N2O correlations and not the tight correlation we observed.

A second weakness that should be addressed is that the authors suggest, based on their and other's datasets, that an additional isotope fractionation mechanism must be operative in the upper stratosphere/lower mesosphere due to a smaller d17O:d18O slope in the upper stratosphere than the lower stratosphere, but they fail to discuss or give credit to their own previous work [Kawagucci, Anal. Chem., 2005] or to recent modeling work by Liang et al. [PNAS, 2007]. Liang et al. model a plausible contribution to a lower slope at higher altitudes/for older air due to the influence of photolysis of O2 in the mesosphere, which in their model significantly alters the isotopic composition of O(1D), and, hence, of CO2 in the middle and upper stratosphere. I believe the differences in slopes, even if they are at the limits of statistical interpretation, are

an important contribution of the new observations presented here and should be thoroughly discussed, including providing a deeper discussion of the context provided by previous measurements and modeling studies and of presentation of one or more hypotheses for an isotope fractionation mechanism beyond simply saying "an additional fractionation mechanism may exist."

A third weakness that needs attention is that the authors' use of the term "year-to-year variation" throughout the manuscript is ambiguous. Is "interannual variation" meant or is "long-term trend" meant? The distinction is important. Significant interannual variations arguably do exist, most notably in the vertical profiles shown, as the authors note, but also perhaps in the isotope: N₂O correlations. The latter is difficult to judge by the current version of Figure 2, however, since the data which had been binned by year in Figure 1 are now lumped together. Variations in transport from year to year (or even week to week for the altitude profiles!) likely contribute to each, as the authors do mention for altitude profiles in Figure 1. Yet they may also exist for the correlations with N₂O, and it would be interesting for the authors to investigate and discuss or mention this – that is, it would be interesting if the scatter seen in the D¹⁷O-CO₂ and d¹⁸O-CO₂ correlations with N₂O in Figure 2 is larger in some years than others, whether some outliers occur in a particular year, etc., and, if so, hypothesize why this might be. On the other hand, the fact that apparently no long-term trend is observed may be what the authors meant in numerous places in the manuscript, particularly since the term "long-term" appears in their title. However, if this is what is meant, it should be stated explicitly and backed up by a more careful analysis and discussion of the data, which are now lacking (or appear to be). Finally, the authors note on page 15727 (Line 9) that "the long-term observations over Sanriku confirm that no clear year-to-year variation exists in vertical profiles of D¹⁷O-CO₂; beyond small fluctuations;" First, the fluctuations due to transport look quite large to me. Second, use of the word "confirm" is odd: did a previous publication show this (and, again, are the authors discussing interannual variations or a temporal trend)? If so, it should be discussed. Does a previous hypothesis suggest that there should be a temporal trend in D¹⁷O-CO₂? I

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can't think of one but use of the word confirm could suggest there was one. If neither of these situations is correct, then the word "demonstrate" should be used, if indeed this holds up to additional analysis.

Another weakness to be addressed concerns the discussion of recent modeling by Liang et al. [PNAS, 2007]. The discussion in its current form is not informative and some details given appear to be wrong, such as the model "underestimating" the D17O-CO₂ vs N₂O correlation when the Liang et al. Figure 5 appears to overestimate it (using the Boering et al. 2004 data as a "transfer standard" via Figure 2a in the current discussion paper). It would be much more helpful and interesting to either clarify the comparisons – without denigrating the model results and pointing out what works as much as what doesn't – or, even better, to include the model results in a figure with the new observations if Liang et al. would provide their published results for comparison.

Finally, some important data, information, and other parameters are missing from the manuscript – data that will be required for the datasets to be useful in the future. First, it is critical to this and future applications of the data that the N₂O mixing ratio data be included in Table 1. Second, the specific parameters the authors used to calculate d17O from their isotope equilibration technique must be included explicitly in the manuscript (e.g., λ , K, 17-R-PDB, …). It is not enough that these parameters may appear in their technique paper [Kawagucci, Anal. Chem., 2005], as accepted values may change, different groups may use different values, and it may not be clear in the future which papers and datasets used which parameters. Third, how do the D17O-CO₂ fluxes to the troposphere compare with those from Boering et al. [GRL, 2004] calculated using the D17O-CO₂:N₂O relationship? What is the d18O-CO₂ flux and how does that compare with estimates used by the tropospheric d18O-CO₂ community [e.g., Cuntz et al., JGR, 2003; Peylin et al., 1999].

Specific and technical comments:

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In addition to the scientific and analytical points above, I provide several additional specific comments below to help strengthen the presentation and discussion.

* In a number of places, the present version does not make clear the new contributions of the new data and their analysis much beyond stating that they are the "first" or by putting previous studies in an unnecessarily negative light. A concerted effort to correct these throughout the discussion paper will strengthen it and is needed most particularly in the discussion section just prior to the conclusions and in the conclusion sections. How do the authors show or hypothesize that their new data will resolve the "still open questions"? What other data could be obtained or modeling sensitivities pursued that could likely help resolve the open questions? Indeed, what are the open questions more specifically and specifically what questions have the authors addressed and/or raised anew?

* Abstract and other places: "The correlations fade away..." This is a poor term to use for several reasons. First, I would argue that a huge increase in D17O-CO₂ as N₂O disappears is definitely not "fading away". This "anti-correlation," in fact, looks even stronger to the eye simply because of the increase is dynamic range of the tracers even if the r² value might decrease). Thus, I recommend use of a different term (and a more scientific one in any case) is called for to avoid this perception problem.

Introduction:

* The term "recently" is used to refer to a paper that is 25 years old; Perhaps "however" would be a better transition.

* "Tropospheric CO₂ has a[n] almost constant d18O value; with no 17O anomaly through a rapid exchange with seawater (Thiemens et al., 1991)." First, the anomaly in the troposphere may be non-zero – see Hoag et al. [GRL, 2005]. Second, exchange with leaf water is a more important determinant of tropospheric d18O-CO₂ than seawater – see Francey and Tans [Nature, 1987] and Ciais et al. [JGR, 1997].

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* More information should be given in this discussion paper on both the type of sampling canister(s) used and how the samples were stored and for how long. Since it is certainly true that sampling and storage issues are of concern (and are likely responsible, for example, for the large scatter in the Boering et al. 2004 d18O-CO₂ values), at least a few details should be given and discussed here. It is not acceptable for readers to have to consult previous publications for such basic and important information as this. Further, at least the very rudimentary details of how the continuous flow – isotope equilibration technique works should also be given here. Virtually no (useful) information is given here on the technique when there is certainly room (in addition to motivation) for some critical information without readers having to look up previous publications. And, as noted above, values for the critical parameters used for calculating D17O from the equilibrated and non-equilibrated 45/44 and 46/44 ratios should be explicitly given.

* First sentence of section 3.1: A sample cannot collected "in the stratosphere" but also be "just below the tropopause." The sentence could simply read: "49 whole air samples from above or just below the tropopause" instead of "49 whole air samples in the stratosphere, including 4 samples just below or around the tropopause, were obtained";

* 15727, Line 11: I suggest "for the past 14 years beyond [cut "small"] fluctuations caused by variations in transport. In contrast, vertical profiles of the CO₂ mixing ratio [for the same flights??] show a clear increasing trend of about 1.4 ppmv per year"; How was 1.4 derived? If only roughly consistent with the tropospheric trend, why not use 1.5?

* Throughout: Correlations *with* N₂O, not "to N₂O". "High-latitudinal" should be "high-latitude"

* "Lower stratospheric air above 25 km": This seems like an oxymoron to me. Indeed, there seems to be no "middle stratosphere" in this discussion paper, which I usually

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take to be about ~28-35 or so km (although the definition is in the often in the eye of the investigator's platform!). It would help avoid ambiguity and unintentional meanings if use of the terms lower and upper stratosphere are defined.

* It seems trivial but it makes for difficult reading: "an almost positive (or almost negative) linear trend." The word "almost" is in the wrong place, as a value or correlation can't be "almost positive" or "almost negative" but they can be "almost linear". These should therefore read "a positive, almost linear correlation" (if that is what is meant!).

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 15723, 2007.

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