**Atmospheric
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Discussions**

Interactive
Comment

Interactive comment on "Long-term observation of mass-independent oxygen isotope anomaly instratospheric CO$_2$" *by* S. Kawagucci et al.

S. Kawagucci et al.

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We are grateful for the referee comments on our discussion paper from anonymous referee. We have carefully studied the comments and revised the manuscript accordingly as follows.

(1) Referee comment (p. S7133, line 5 to 11) N2O mixing ratio dataset is presented in new Table 1. All the stratospheric samples (n=53), excluding 5 tropospheric samples (labeled by * in Table 1), are presented in new figures 1, 2a, 2b, and 3.

(2) Referee comment (p. S7133, line 11 to 14) As pointed out by referee, d18O values in 1991 samples are different between past and present studies. We consider that the difference was derived from wrong sample re-collection after the analysis or incorrect standardization in past study. Anyway, we omit the data for the 1991 samples in re-

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vised manuscript in order to avoid any confusion. We consider that our dataset other than the 1991 samples has no problem because the probable causes to make the difference (described below) have no relation with the observation after 1992. First, stratospheric CO_2 samples obtained in 1991 were once analyzed and subsequently re-collected by cryogenic concentration for archive. Assuming incomplete re-collection of CO_2, concentrated (archived) CO_2 would be isotopically heavier than original CO_2. This assumption is adequate to explain the observed difference of d18O between past and present studies. Samples obtained after 1992 had not been analyzed until the triple oxygen isotope analyses in this study so that affects on sample re-collecting should be not considerable. Secondly, a significant difference of analytical methods between past and present studies is in treatment of some gases other than CO_2, such as N_2O, for example, which are inescapably contaminated into a glass ampoule at cryogenic CO_2 purification procedure. The analytical method in this study consists based on a Continuous-Flow mass spectrometry, which enables us to introduce CO_2 into mass spectrometer completely separated from the other gas species (Kawagucci et al. (2005)). On the other hand, a method in Gamo et al. (1995) was based on Dual-Inlet mass spectrometry, by which the sample CO_2 was introduced into mass spectrometer simultaneously with the contaminated molecules. Simultaneous introduction of CO_2 and other gases should change both ionization efficiency of CO_2 and ion quantities of m/z 44, 45, and 46, resulting in a biased data from truly pure CO_2 analysis. In Dual-Inlet method, standardization of d18O was carried out by analyzing d18O-known pure CO_2 gas although d18O analyses of stratospheric CO_2 were done using CO_2 with inescapably contaminated gases. So, the discrepancy of d18O between past and present studies may be derived from the biases caused by the contaminated molecules although quantitative effect of these biases is not estimated.

(3) Referee comment (p. S7133, line 15 to 21) As pointed out, 7 samples obtained in 1991, 2000, and 2001 are omitted in present paper. Reason of the omit is described in revised paper as [It should be noted that quality of our whole air sampling and handling the sample air had been checked by concurrent analyses of multiple composi-

tions, such as concentrations of CO2, N2O, and CH4 and d13C-CO2. When apparent anomaly was observed in any chemical compositions, the sample air was regarded as a defect and eliminated from this study.]

(4) Referee comment (p. S7133, line 22 to p. S7134, line 11) We carefully re-calculate our dataset again in revised manuscript. For statistic comparison, least square regression results we calculate are always presented with 1-sigma and a correlation efficient (r2).

(5) Referee comment (p. S7134, line 11 to p. S7135, line 4) One of objectives in this study is to verify the gradual slope change on triple oxygen isotope plot that have been thought in previous studies (Kawagucci et al., 2005; Liang et al., 2007). In discussion paper, our approach was improper for achievement of the objectives. So, we change discussion in revised manuscript. The slope change in our dataset was checked by two approaches, such as a quadratic fitting and dataset dividing by sampling altitude as done in Kawagucci et al. (2005), but a correlation the triple oxygen isotopes in this study is certainly constant. The existence of gradual slope decline is still open question. Observation of triple oxygen isotopes in CO2 continuously through middle atmosphere and/or intensively in upper stratosphere/lower mesosphere will help to clarify the slope changing.

(6) Referee comment (p. S7135, line 10 to 16) A systematic error of the sampler and an error during sample storing for more than 10 years of d18O are distinguishable terms in this study as described below. In brief, both the errors are comparable within the analytical precision. Although a cryogenic sampler for collecting stratospheric air used in Gamo et al. (1989, Tellus) involved systematic error for d18O of 1permil during sample storage in the sampler, the sampler used in this study (and also Gamo et al. (1995, GRL); Aoki et al. (2003, Tellus)), presented by Honda (2001), is different from that used in Gamo et al. (1989). Air sample storage examination during 21 days in the new sampler has effect for d18O as small as analytical precision of 0.05permil (Honda, 2001 (Bulletin of Institute of Space and Astronautical Science (in Japanese with English ab-

stract), 115, 1-93)). In addition, for D17O, such experimental test was not carried out, but we consider that it is probably within our analytical precision of 0.5permil as discussed previously (Boering et al., 2004). Whole air sample in the stainless bottle of the sampler was divided into several aliquots and CO2 gas in the aliquot was extracted and separated from water vapor and other components by cryogenic trapping as commonly used in CO2 isotope analysis. The separated CO2 gas was then sealed into a glass ampoule that had been combusted at 400oC and kept in a desiccator in order to avoid contamination of water and organic matter. These CO2 samples had been stored for most over a decade before current isotope analysis. Although the storage period is quite long, variation in d18O due to oxygen isotope exchange with water during the sample storage is negligible since negligible water is left in the ampoules due to complete water separation during the CO2 ampoule preparation.

(7) Referee comment (p. S7136, line 2 to 16) As pointed out, data division by N2O=50ppbv was arbitrariness so that we deleted such discussion. Except for the sample observed over Kiruna (obtained from 25.6 km and showing [N2O] = 9 ppbv), D17O andd18O showed a linear negative correlation with N2O mixing ratio with correlation coefficients of $r2 > 0.90$ and > 0.85, respectively. The linear correlations are used to quantify CO2 oxygen isotope fluxes.

(8) Referee comment (p. S7136, line 17 to 19) Our discussion was repeated of Boering et al. (2004) as referee#1 said. We give credit to the original paper as: [Boering et al. (2004) pointed out that the correlation between D17O and N2O would result from comparable time scales of the reaction (R1-R2) and N2O destruction reactions, which are dominated (˜90%) by photolysis and partly (˜10%) contributed by reactions to O(1D).].

(9) Referee comment (p. S7136, line 20 – p. S7137, line 15) The discussion using data division by N2O mixing ratio is deleted from revised manuscript. What we want to describe using the data division is presented in (5) in this reply.

(10) Referee comment (p. S7137, line 16 – 21) To make our manuscript more quantitatively, estimations of isotope fluxes of D17O and d18O from stratosphere to troposphere are carried out. A slope of two long-lived tracers is known to be equal to the ratio of their net vertical fluxes (Plumb and Ko, 1992) and net vertical flux of N2O is estimated as the global N2O loss rate of 13 MtN/yr with an uncertainty of +/- 25% (Prather and Ehhalt, 2001). CO2 oxygen isotope fluxes from stratosphere to the troposphere were estimated from the observed linear correlations (see (7) in this reply) as +48 permil GtC/yr (D17O) and +38 permil GtC/yr (d18O).

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