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Long-term observation of mass-independent oxygen isotope anomaly in stratospheric CO_2

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Abstract. Stratospheric and upper tropospheric air samples were collected during 1994–2004 over Sanriku, Japan and in 1997 over Kiruna, Sweden. Using these archived air samples, we determined the triple oxygen-isotope composition of stratospheric CO_2 and the N_2O mixing ratio. The maximum $\Delta^{17}O_{CO_2}$ value of +12.2‰, resembling that observed previously in the mesosphere at 60 km height, was found in the middle stratosphere over Kiruna at 25.6 km height, suggesting that upper stratospheric and mesospheric air descended to the middle stratosphere through strong downward advection. A least-squares regression analysis of our observations on a $\delta^{18}O_{CO_2}$-$\delta^{17}O_{CO_2}$ plot ($r^2>0.95$) shows a slope of 1.63±0.10, which is similar to the reported value of 1.71±0.06, thereby confirming the linearity of three isotope correlation with the slope of 1.6–1.7 in the mid-latitude lower and middle stratosphere. The slope decrease with increasing altitude and a curvy trend in three-isotope correlation reported from previous studies were not statistically significant. Using negative linear correlations of $\Delta^{17}O_{CO_2}$ and $\delta^{18}O_{CO_2}$ with the N_2O mixing ratio, we quantified triple oxygen-isotope fluxes of CO_2 to the troposphere as +48‰ GtC/yr ($\Delta^{17}O_{CO_2}$) and +38‰ GtC/yr ($\delta^{18}O_{CO_2}$) with ∼30% uncertainty. Comparing recent model results and observations, underestimation of the three isotope slope and the maximum $\Delta^{17}O_{CO_2}$ value in the model were clarified, suggesting a smaller O_2 photolysis contribution than that of the model. Simultaneous observations of $\delta^{18}O_{CO_2}$, $\delta^{17}O_{CO_2}$, and N_2O mixing ratios can elucidate triple oxygen isotopes in CO_2 and clarify complex interactions among physical, chemical, and photochemical processes occurring in the middle atmosphere.

1 Introduction

The value of $\delta^{17}O$, (defined as $[(^{17}O/^{16}O)_{sample}/(^{17}O/^{16}O)_{VSMOW}-1]\times1000$ (‰), where VSMOW is an international oxygen isotope standard) varies during many isotopic fractionation processes, but the relation between $\delta^{17}O$ and $\delta^{18}O$ values is usually conserved according to the mass-dependent relation of $\delta^{17}O=0.516\times\delta^{18}O$ (Matsuhisa et al., 1978; Santrock et al., 1985). Mass-independent triple oxygen-isotopic fractionation processes, which engender a non-zero value of $\Delta^{17}O$ ($=\delta^{17}O-0.516\times\delta^{18}O$), so-called ^{17}O anomaly, have been found in several chemical reactions, such as in the photochemical production of O_3 from O_2 (Thiemens and Heidenreich, 1983; Mauersberger, 1987). Note that this equation is an often-used linearization as described for example in Young et al. (2002), Miller et al. (2002), and Miller et al. (2007).

Tropospheric CO_2 has an almost constant $\delta^{18}O$ value (∼+41‰) with a small ^{17}O anomaly which results from rapid oxygen isotope exchange between tropospheric CO_2 and surface water such as leaf water and seawater (Thiemens et al., 1991; Ciais et al., 1997; Hoag et al., 2005). In contrast, anomalously high $\delta^{18}O$ values and a positive ^{17}O anomaly have been observed in stratospheric CO_2 over Texas and New Mexico (Thiemens et al., 1991), in southern high-latitude regions (Thiemens et al., 1995a), over Sanriku in Japan (Gamo et al., 1989;, 1995; Aoki et al., 2003; Kawagucci et al., 2005), over Kiruna in Sweden (Alexander et al., 2001; Lämmerzahl et al., 2002), Aire-sur-l'Adour in France (Lämmerzahl et al., 2002), in northern high-latitudinal regions (Boering et al., 2004), and also in the upper stratosphere and lower mesosphere over New Mexico (Thiemens et al., 1995b). The ^{17}O anomaly observed for middle atmospheric (stratospheric and mesospheric) CO_2 is generally thought to be derived from a

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series of chemical reactions of which O_3 formation is the principal source of extra heavy δ^{18}O and Δ^{17}O (Mauersberger, 1987; Yung et al., 1991; Lacoursiere et al., 1999; Perri et al., 2003):

$$O_3 + h\nu(< 310\,\text{nm}) \rightarrow O_2 + O(^1D) \tag{R1a}$$

$$O_2 + h\nu(< 175\,\text{nm}) \rightarrow O(^3P) + O(^1D) \tag{R1b}$$

$$\begin{aligned} CO_2 + O(^1D) \rightarrow CO_3^* &\rightarrow CO_2 + O(^3P) \\ &\text{or} \quad CO_2 + O(^1D) \end{aligned} \tag{R2}$$

In addition to those field observations, several laboratory experiments and model calculations have been conducted to elucidate detailed mechanisms of mass-independent oxygen isotope fractionation of CO_2, O_3, and O_2 in the middle atmosphere (Wen and Thiemens, 1993; Johnston et al., 2000; Chakraborty and Bhattacharya, 2003; Liang et al., 2007; Shaheen et al., 2007). In addition, the flux of oxygen anomaly in CO_2 from the stratosphere to the troposphere is an important parameter for the tropospheric CO_2 budget, which is useful to investigate carbon circulation between the atmosphere and the biosphere (Cuntz et al., 2003; Boering et al., 2004; Hoag et al., 2005).

Although several observational studies have revealed anomalous oxygen isotopic compositions in stratospheric CO_2, few samples or parameters have been obtained for each observation, rendering further detailed quantitative analyses difficult. For example, some reports have presented results from fewer than 10 stratospheric air samples (Thiemens et al., 1991, 1995a; Alexander et al., 2001). In more extensive studies, interesting correlations have been reported for the lower stratosphere of $\delta^{18}O_{CO_2}$-$\delta^{17}O_{CO_2}$ (Lämmerzahl et al., 2002), $\delta^{18}O_{CO_2}$-N_2O mixing ratio (Aoki et al., 2003), and $\Delta^{17}O_{CO_2}$-N_2O mixing ratio (Boering et al., 2004). However, no report has described a comprehensive dataset to elucidate these unique relations in the same observation, which hinders further comparison of direct data to modeling studies.

The correlation plot between δ^{18}O and δ^{17}O is useful to discuss mass-independent isotope fractionation processes because vertical deviation from a terrestrial fractionation line (TFL: slope=0.516) corresponds to the ^{17}O anomaly. Several previous studies of the triple oxygen isotope composition of middle atmospheric CO_2 have revealed a linear correlation between δ^{18}O and δ^{17}O. However, slopes of the linear correlation lines and the degree of the mutual relation differ among studies. For example, Lämmerzahl et al. (2002) reported a close linear relation with a slope of 1.71 ± 0.06 (2σ) in the lower/middle stratosphere air over Aire-sur-l'Adour (44° N) and Kiruna (68° N); in contrast, Thiemens et al. (1995b) reported a slope of 1.18 ± 0.17 for the upper stratosphere/lower mesospheric air over New Mexico (32° N). This difference in slope was interpreted as a gradual decrease in slope occurring concomitantly with increasing altitude (Kawagucci et al., 2005; Liang et al., 2007), although such a change in slopes has not been observed to date.

As described in this paper, we report triple oxygen isotope compositions of CO_2 and its relation with the N_2O mixing ratio of the middle-latitude lower/middle stratospheric CO_2 samples collected during 11 years' air sampling over Sanriku, Japan and Kiruna, Sweden. The long-term stratospheric air sampling program over Sanriku was started in 1985 (Gamo et al., 1989). It continued during 1994–2004, while additional stratospheric air sampling was carried out over Kiruna in February 1997 within the polar vortex. Oxygen isotope fluxes in CO_2 from the stratosphere to the troposphere and triple oxygen isotope fractionation processes in the middle atmosphere are discussed using the comprehensive dataset of triple oxygen isotope composition of stratospheric CO_2 and the mixing ratio of N_2O.

2 Sampling and analysis

2.1 Sampling and sample storage

Stratospheric whole air samples were collected during six balloon flights over Sanriku, Japan (39° N, Table 1) during 1994–2004 using a balloon-borne cryogenic sampler developed by the Japan Aerospace Exploration Agency (JAXA). Using the same sampling system, additional vertical sampling was carried out at Kiruna, Sweden (68° N) on 22 February 1997 (Table 1). Details of our air sampler and sampling procedure have been reported elsewhere (Nakazawa et al., 1995; Honda et al., 1996; Aoki et al., 2003; Honda, 2001). Herein, we describe them briefly. The air sampling system can collect multiple whole-air samples into pre-evacuated 760 cm^3 stainless steel sample bottles. Chemical and isotopic compositions in the sampled air are only slightly affected by the collection process (Honda et al., 1996; Honda, 2001). Preliminary experimental tests showed that a possible change of $\delta^{18}O_{CO_2}$ caused by isotope exchange between CO_2 and water on the inner walls of the sample bottle is comparable to our analytical precision of 0.05‰ (Honda, 2001; Gamo et al., 1995; Aoki et al., 2003). For $\Delta^{17}O_{CO_2}$, such preliminary experimental tests were not carried out, but we consider that this sampling process also provides results within our analytical precision of 0.5‰, as discussed previously (Boering et al., 2004).

In the laboratory, each whole air sample in the stainless steel bottle of the sampler was divided into several aliquots. From each aliquot, CO_2 was extracted and separated from water vapor and other components using cryogenic trapping, which is commonly used in CO_2 isotope analysis. The separated CO_2 gas was then sealed into a glass ampoule that had been combusted at 400°C and kept in a desiccator to avoid contamination by water and organic matter. These CO_2 samples had been stored for more than a decade before current isotope analysis. Although the storage period is quite long, the change in $\delta^{18}O_{CO_2}$ is expected to be negligible because very little water remains in the ampoules.

Table 1. Measured oxygen isotopic compositions of CO_2 are shown with the sampling location, date, altitude, and N_2O mixing ratio. A sample denoted with # is regarded as mesosphere-derived air. Five samples marked with * are regarded as tropospheric air. Errors of δ^{18}O, δ^{17}O, and Δ^{17}O are estimated respectively as at most, 0.05‰, 0.5‰, and 0.5‰.

Location	Date	Altitude (km)	N_2O (ppbv)	δ^{18}O (‰)	δ^{17}O (‰)	Δ^{17}O (‰)	
Sanriku (39° N)	31 Aug 94	18.2	289	41.89	22.6	1.0	
		20.4	266	42.29	23.2	1.4	
		22.3	196	43.22	24.9	2.6	
		24.7	158	43.67	25.8	3.3	
		26.8	135	43.75	25.6	3.0	
		29.2	127	43.50	25.7	3.2	
		31.1	92	44.29	27.8	5.0	
		34.7	72	44.75	27.6	4.5	
	8 Jun 95	20.3	209	43.67	24.8	2.3	
		22.3	223	41.92	23.1	1.4	
		24.5	129	45.35	28.1	4.7	
		26.7	108	45.21	27.9	4.5	
		28.8	66	46.13	30.3	6.5	
		30.6	50	46.31	30.5	6.6	
		32.4	43	47.50	31.3	6.8	
		33.8	35	46.73	30.3	6.1	
	28 Aug 00	15.0	316	39.71	20.5	0.0	*
		17.1	315	41.80	22.3	0.7	
		18.7	282	41.97	21.4	−0.3	
		20.9	209	42.92	25.0	2.9	
		22.7	192	43.23	25.4	3.1	
		25.8	144	44.13	27.1	4.4	
	30 May 01	14.9	300	41.22	21.7	0.4	
		16.8	292	41.04	21.7	0.5	
		18.8	280	40.02	20.5	−0.2	
		27.6	154	42.58	25.4	3.4	
		29.4	107	44.03	27.7	5.0	
	4 Sep 02	15.2	316	42.24	21.6	−0.2	*
		16.4	315	40.44	20.8	−0.1	*
		18.7	296	42.15	23.1	1.3	
		20.6	231	43.16	25.1	2.8	
		22.9	210	43.90	26.7	4.1	
		24.0	208	43.19	26.0	3.7	
		27.7	95	44.79	28.2	5.1	
		30.3	50	45.68	30.5	6.9	
		34.0	19	47.08	31.2	6.9	
	6 Sep 04	14.7	318	41.63	21.4	−0.1	*
		16.5	317	42.11	22.2	0.5	
		18.7	287	42.27	22.3	0.5	
		21.2	238	42.90	24.9	2.7	
		23.4	183	43.79	25.1	2.5	
		25.7	180	43.55	25.0	2.5	
		27.8	124	43.64	27.3	4.7	
		30.5	53	45.11	29.1	5.8	
		31.5	30	46.47	30.8	6.8	
		32.8	30	46.61	31.6	7.6	
		35.6	16	46.90	31.3	7.1	
Kiruna (68° N)	22 Feb 97	10.2	300	43.67	22.6	0.0	*
		13.0	273	42.07	22.9	1.2	
		14.1	259	42.21	23.8	2.1	
		15.9	198	43.23	24.0	1.7	
		16.4	175	43.63	25.6	3.1	
		17.2	171	43.79	25.4	2.8	
		18.2	164	43.82	25.8	3.2	
		20.1	124	45.62	27.4	3.9	
		21.8	76	45.58	29.4	5.9	
		23.6	25	48.34	33.6	8.7	
		25.6	9	52.49	39.3	12.2	#

After 2001, we changed the sample storage method. Aliquots of the whole-air samples were transferred directly into pre-evacuated 1000 cm^3 stainless steel gas canisters at a positive pressure of 2 atm without CO_2 separation. They were stored for more than three years before analyses. It is noteworthy that the quality of our whole-air sampling and handling procedures was verified by concurrent analyses of multiple compositions, such as concentrations of CO_2, N_2O, and CH_4, and $\delta^{13}C_{CO_2}$. The sample air was regarded as defective and eliminated from this study when an apparent anomaly was observed in any chemical or isotope signature.

2.2 Oxygen isotope analysis using CF-IRMS

Both $\delta^{18}O_{CO_2}$ and $\delta^{17}O_{CO_2}$ values of the stratospheric CO_2 were analyzed simultaneously using a new continuous flow-isotope ratio mass spectrometry (CF-IRMS) technique. Details of the analytical method and $\delta^{17}O$ calculation were reported in Kawagucci et al. (2005). Herein, we describe them briefly. The CO_2 and other molecules in a sample gas are separated using gas chromatography with helium as the carrier gas. After separation, CO_2 is split and analyzed on-line using two procedures: 1) direct introduction into the IRMS (Finnigan MAT252) for isotope analysis, and 2) eliminating the ^{17}O anomaly in the CO_2 by exchanging the oxygen atoms with high-temperature CuO, with subsequent isotope analysis using IRMS. This CF-IRMS measurement yield two isotope values for "raw" CO_2 and "exchanged" CO_2 and results in four isotope ratios of $45/44_{raw}$, $46/44_{raw}$, $45/44_{ex}$, and $46/44_{ex}$. The $\delta^{17}O$ value is calculable accurately using these measured isotope ratios and several constants of λ=0.516 (Santrock et al., 1985), K=0.0099235 (Santrock et al., 1985), $^{13}R_{VPDB}$=0.0112372 (Craig, 1957), and $^{18}R_{VSMOW}$=0.0020052 (Baertschi, 1976). The total analytical errors of this method in determining $\delta^{18}O_{CO_2}$, $\delta^{17}O_{CO_2}$, and $\Delta^{17}O_{CO_2}$ values are estimated respectively as, at most, ±0.05‰, ±0.5‰, and ±0.5‰. The N_2O mixing ratio was also determined using a gas chromatographic technique with analytical precision of 2 ppbv using another aliquot from the same stratospheric air sample (Aoki et al., 2003).

3 Results and discussion

3.1 Spatial distribution of $\Delta^{17}O_{CO_2}$

We obtained 53 whole stratospheric air samples and five tropospheric air samples during seven launches over Sanriku and Kiruna (Table 1). Figure 1 portrays altitude profiles of $\Delta^{17}O_{CO_2}$ for each balloon launch. The ^{17}O anomalies reached maximum values of +7.6‰ and +12.2‰, respectively, over Sanriku and Kiruna. For comparison, similar altitude profiles reported in the previous studies are presented in that figure as well (Thiemens et al., 1995b; Alexander et al., 2001; Lämmerzahl et al., 2002).

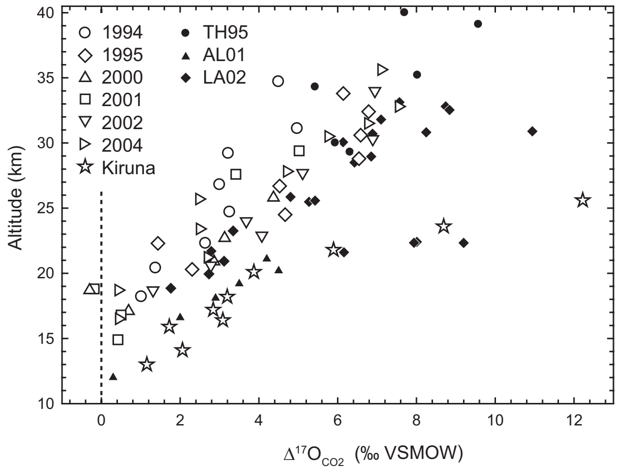

Fig. 1. Vertical profiles of $\Delta^{17}O_{CO_2}$. Open symbols represent our observation over Sanriku (categorized by the sampling year) and Kiruna. Filled symbols represent observations referred from previous studies: TH95 (Thiemens et al., 1995b), AL01 (Alexander et al., 2001), and LA02 (Lämmerzahl et al., 2002). A vertical dotted line indicates no ^{17}O anomaly.

The measurements over Sanriku revealed a nearly linear altitude dependence of $\Delta^{17}O_{CO_2}$. Some deviations from the linearity might reflect dynamic variation in the stratosphere. The vertical distribution of $\Delta^{17}O_{CO_2}$ over Kiruna exhibited a different profile: ^{17}O anomalies higher than 20 km height increased more quickly with increasing altitude than those lower than 20 km height, which agrees well with the results of previous studies of the stratosphere over Kiruna (Alexander et al., 2001; Lämmerzahl et al., 2002). In particular, large $\Delta^{17}O_{CO_2}$ values (>+5‰) even in the lower/middle stratosphere (20–26 km), observed in this study and by Lammerzahl et al. (2002), are noteworthy. The characteristic vertical profile of $\Delta^{17}O_{CO_2}$ over Kiruna resembles the typical one observed for long-lived tracers, such as N_2O and CH_4 mixing ratios within a polar vortex: Upper stratospheric and mesospheric air descends to the lower/middle stratosphere through strong downward advection (Waugh and Hall, 2002), resulting in upper stratospheric and mesospheric characteristics observed even in the lower/middle stratosphere. Indeed, $\Delta^{17}O_{CO_2}$ at 25.6 km height in our observation over Kiruna reached +12.2‰ (Table 1, Fig. 1), which is significantly greater than those over Sanriku at a similar height and which is as large as the highest value previously observed at 60 km height over New Mexico (Thiemens et al., 1995b). That result suggests the probable transport of a mesospheric air mass into the middle stratosphere over the Kiruna area.

3.2 Triple oxygen isotopic compositions

The triple oxygen isotopic compositions ($\delta^{18}O_{CO_2}$ and $\delta^{17}O_{CO_2}$) determined in this study are depicted in Fig. 2.

For comparison, those reported in other studies are shown in the figure as well (Thiemens et al., 1995b; Lammerzahl et al., 2002; Boering et al., 2004). A least-squares linear regression between $\delta^{18}O_{CO_2}$ and $\delta^{17}O_{CO_2}$ for the stratospheric samples (excluding five tropospheric samples) yields a slope of 1.63±0.10 (2σ) with a small deviation ($r^2 > 0.95$; $n=53$), which agrees with the slope (1.71±0.06; $r^2 > 0.99$; $n=23$) observed previously in the lower/middle stratosphere (Lammerzahl et al., 2002) within combined 2-sigma errors. The agreement, or non-significant difference, of the slopes was further tested using statistical analysis, ANCOVA, with a 95% confidence level ($F_{(1,72)}=0.87$; $p<0.05$). We conclude that the slope on the triple oxygen isotope plot within mid-latitude lower/middle stratospheric CO_2 (39–68° N; <36 km) is always constant for the observation term. In contrast, Thiemens et al. (1995b) reported a slope of 1.18±0.17 ($r^2 > 0.96$; $n=12$) in their observation of both $\delta^{18}O_{CO_2}$ and $\delta^{17}O_{CO_2}$ values in upper stratospheric/lower mesospheric CO_2, which is much lower than observations of the lower/middle stratosphere reported herein and by Lammerzahl et al. (2002). Furthermore, ANCOVA tests demonstrate significant differences in the regression between results reported by Thiemens et al. (1995b) and Lammerzahl et al. (2002) ($F_{(1,31)}=53.78$; $p>0.05$) and between results of the former study and this study ($F_{(1,61)}=26.29$; $p>0.05$).

The observed difference in the slopes implies that $\delta^{18}O_{CO_2}$ and $\delta^{17}O_{CO_2}$ values might not have a simple linear relation, but rather an altitude-dependent difference by which the slopes become smaller as altitude increases (Kawagucci et al., 2005). Liang et al. (2007) also reported a gradual slope decline with increasing altitude using a theoretical model that incorporated a considerable impact of O_2 photolysis to $O(^1D)$ in the mesosphere. Kawagucci et al. (2005) reported that the slopes in the $\delta^{18}O_{CO_2}$ and $\delta^{17}O_{CO_2}$ correlation line seem to be different for altitudes greater than and less than 25 km over Sanriku, although the difference was not statistically significant. Using the current dataset over Sanriku, which includes more data than reported in Kawagucci et al. (2005), the separate linear fit for the lower division (<25 km) yields a slightly larger slope of 1.60±0.13 ($r^2 > 0.88$; $n=22$) than that for the higher division (>25 km) of 1.46±0.11 ($r^2 > 0.90$; $n=21$). However, ANCOVA tests for these slopes reveal no significant difference at a 95% confidence level ($F_{(1,39)}=0.71$; $p<0.05$). In addition, a least-squares quadratic fit for our stratospheric dataset showed a correlation coefficient of $r^2 > 0.95$, which is the same as that for a linear fit ($r^2 > 0.95$), meaning that it is not possible to identify the gradual slope decline in the lower/middle stratosphere from our dataset. For those reasons, it is difficult to prove the gradual slope decline in the stratosphere, even from our dataset. Further observation of the triple oxygen isotopes in the upper stratosphere/lower mesosphere is necessary to prove the gradual decline in the slope.

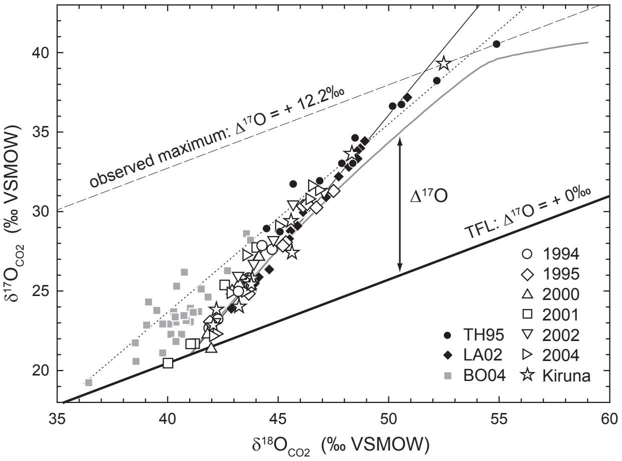

Fig. 2. $\delta^{18}O_{CO_2}$-$\delta^{17}O_{CO_2}$ plot. Symbols are similar to those used for Fig. 1. Filled squares (BO04) represent datasets obtained from Boering et al. (2004). The terrestrial fractionation line (TFL: slope=0.516) and also an isoclinic line for $\Delta^{17}O_{CO_2}$=+12.2‰ that marks the maximum value of the atmospheric observations are shown respectively as a bold solid line and a dashed line. Thin solid and dotted lines respectively represent least square linear fits for our dataset and the dataset described by Thiemens et al. (1995b). A gray solid curve represents the model simulation result (from Fig. 5 in Liang et al., 2007) for comparison.

3.3 Correlation between N_2O mixing ratio and oxygen isotopes in CO_2

The physical processes in the stratosphere that are responsible for the characteristic spatial distribution of $\Delta^{17}O_{CO_2}$ in both Sanriku and Kiruna (Fig. 1) can be studied by plotting $\Delta^{17}O_{CO_2}$ against the N_2O mixing ratio (Boering et al., 2004). The present data, except for the five tropospheric samples and the sample showing the largest ^{17}O anomaly of +12.2‰ over Kiruna (Table 1), exhibited a linear negative correlation between $\Delta^{17}O_{CO_2}$ and N_2O mixing ratio ($r^2 > 0.90$) (Fig. 3a), with some deviations from the fit line which are larger than the analytical errors. The linear correlation suggests that the relative reaction rates between the heavy oxygen isotope accumulation in CO_2 (R1–R2) and photochemical N_2O destruction are almost uniform in the lower and middle stratosphere. On the other hand, the sample showing the largest ^{17}O anomaly of +12.2‰ in the middle stratosphere over Kiruna (Table 1, Fig. 1) deviates from the general linear correlation of N_2O-$\Delta^{17}O_{CO_2}$ (Fig. 3a). It overlaps with the values from the mesosphere (Thiemens et al., 1995b), suggesting its mesosphere origin, as discussed above. In addition to $\Delta^{17}O_{CO_2}$, $\delta^{18}O_{CO_2}$ showed a negative linear correlation with the N_2O mixing ratio (Fig. 3b), as presented in Aoki et al. (2003). Deviations comparable to those in the N_2O-$\Delta^{17}O_{CO_2}$ correlation were also observed in the N_2O-$\delta^{18}O_{CO_2}$ correlation, although the degree of the deviations was much smaller than for those described in Boering et al. (2004) (Fig. 3).

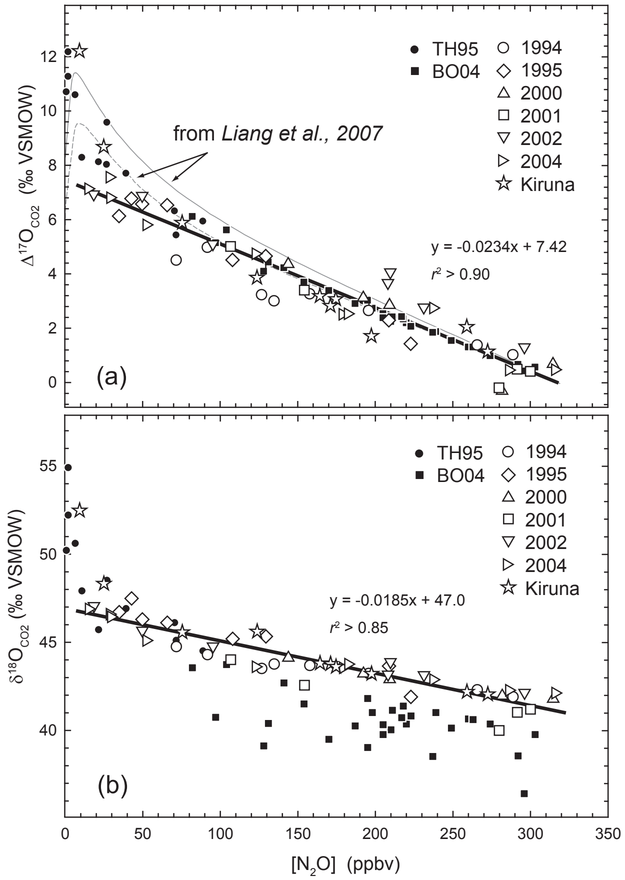

Fig. 3. N_2O mixing ratio and **(a)** $\Delta^{17}O_{CO_2}$ or **(b)** $\delta^{18}O_{CO_2}$ plots. Symbols are the same as those shown in Figs. 1 and 2. Solid bold lines represent linear square regression lines for our stratospheric observation, excluding a sample showing $\Delta^{17}O_{CO_2}$=+12.2‰ and $\delta^{18}O_{CO_2}$=+52.49‰, used for isotope flux estimations. Solid and dash curves in Fig. 3a represent model simulation results referred from Liang et al. (2007).

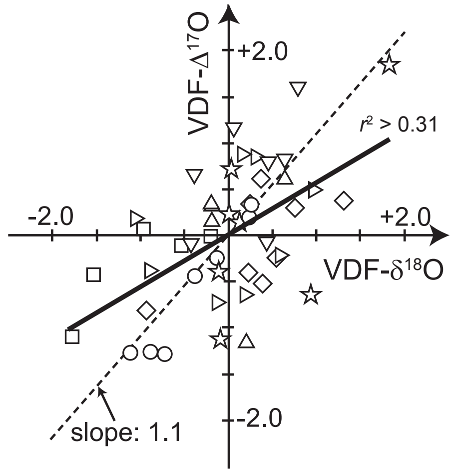

Fig. 4. A correlation plot between VDF-δ^{18}O and VDF-Δ^{17}O. Symbols are the same as those used for Fig. 1. A solid line is least-squares fitting line. A dashed line denotes a theoretical line with a slope of 1.1.

The observed deviations from the linear correlations in the plots of N_2O-$\Delta^{17}O_{CO_2}$ and N_2O-$\delta^{18}O_{CO_2}$ could reflect either some changes in the major natural (photo)chemical processes in the stratosphere, in which the relative destruction rate of N_2O against the heavy oxygen isotope accumulation rate in CO_2 (R1–R2) have varied, or some additional isotope fractionation processes for CO_2 other than the Reactions (R1)–(R2). The N_2O destruction rate is almost entirely (~90%) governed by UV radiation, although the accumulation rate of heavy oxygen isotopes in CO_2 (R2) is controlled by the O(^{1}D) concentration governed by both the O_3 concentration and its photolysis rate (R1a). Therefore, independent changes in the reaction rates in response to variations in stratospheric chemical conditions, such as abundances of O_3 and O(^{1}D) that would control the accumulation rate with no relation to N_2O destruction, for example, might cause deviation from linear N_2O-$\Delta^{17}O_{CO_2}$ and N_2O-$\delta^{18}O_{CO_2}$ correlation. However, isotope fractionation processes other than the (R1)–(R2) reactions, most of which fractionate under the mass-dependent relation that is usual for almost all physical and chemical processes (e.g. Thiemens et al., 1999), cause changes only in the N_2O-$\delta^{18}O_{CO_2}$ correlation. Consequently, a comparison of the deviations between the N_2O-$\Delta^{17}O_{CO_2}$ and N_2O-$\delta^{18}O_{CO_2}$ correlations is useful to examine potential additional isotope fractionation processes. For this purpose, we introduce new parameters, VDF-Δ^{17}O and VDF-δ^{18}O, which correspond to the vertical deviation of each datum from the fit lines of either N_2O-$\Delta^{17}O_{CO_2}$ or N_2O-$\delta^{18}O_{CO_2}$ plot (Fig. 3) using the following equations:

$$\text{VDF-}\Delta^{17}\text{O}=\Delta^{17}\text{O}_{\text{CO}_2}-(-0.0234\times[\text{N}_2\text{O}]+7.42)$$

$$\text{VDF-}\delta^{18}\text{O}=\delta^{18}\text{O}_{\text{CO}_2}-(-0.0185\times[\text{N}_2\text{O}]+47.0)$$

Calculated VDF values for stratospheric samples are within ±2‰, as presented in Fig. 4, although the VDF values for the sample showing the largest ^{17}O anomaly of +12.2‰ are out of that range (>+5‰), indicating a distinguishable origin as discussed above. By plotting VDF-Δ^{17}O against VDF-δ^{18}O, we can distinguish whether those deviations are explainable according to changes in the relative destruction rate of N_2O or not. That is to say, if the relative reaction rate change were the only process responsible for the deviations, the correlation between the VDF-δ^{18}O and VDF-Δ^{17}O values would be expected to be linear with a slope of +1.1–1.2 (Fig. 4), as calculated from the constant fractionation slope of +1.6–1.7 between $\delta^{18}O_{CO_2}$ and $\delta^{17}O_{CO_2}$ (Fig. 2) and the Δ^{17}O definition of $\Delta^{17}O=\delta^{17}O–0.516\times\delta^{18}O$. Although the observed VDF-Δ^{17}O values exhibit a correlation with the VDF-δ^{18}O values, showing a positive slope of +0.6 (Fig. 4), the linearity is not good (r^2>0.31). Therefore, we conclude that, aside from changes in the relative reaction rate in the stratosphere that produce the slope of +1.1–1.2, some additional isotope fractionation processes having different slopes on the plot between the VDF values, such as the slope of 0 (mass-dependent fractionation processes), were involved in the observed isotopic compositions of CO_2 as well.

One such additional isotope fractionation process is, unfortunately, sample alteration during sampling and storage despite careful handling. For example, oxygen isotope exchange with stratospheric H_2O, which includes highly ^{18}O-depleted $\delta^{18}O$ from CO_2 (Johnson et al., 2001), that takes place in canisters reduces $\delta^{18}O_{CO_2}$ values, with little accompanying $\Delta^{17}O_{CO_2}$ variation (Boering et al., 2004). In this case, the maximum extent of $\delta^{18}O$ change can be estimated as 1.5‰ from Fig. 4. That is to say, we can obtain linear correlation of the slope of 1.1–1.2 on the plot between VDF-$\delta^{18}O$ and VDF-$\Delta^{17}O$, by adding, at most, 1.5‰ correction on VDF-$\delta^{18}O$. Therefore, we adopt the value for the maximum extent of errors in $\delta^{18}O_{CO_2}$ for subsequent discussions.

3.4 Net oxygen isotope flux to the troposphere

The linear correlations of $\Delta^{17}O_{CO_2}$ and $\delta^{18}O_{CO_2}$ with the N_2O mixing ratio enable us to quantify net isotope fluxes of $\Delta^{17}O$ and $\delta^{18}O$ in CO_2 from the stratosphere to the troposphere. A slope of the fitting line between two long-lived tracers is known to be equal to the ratio of their net vertical fluxes (Plumb and Ko, 1992); furthermore, the net vertical flux of N_2O is estimated as the global N_2O loss rate of 13 MtN/yr with uncertainty of ±25% (Prather and Ehhalt, 2001). Using the dataset in the stratosphere (excluding five tropospheric and one mesosphere-derived samples)(Table 1), least-squares linear fitting is applied to correlation plots of N_2O-$\Delta^{17}O_{CO_2}$ and N_2O-$\delta^{18}O_{CO_2}$. The fittings yielded slopes of -0.0234 ± 0.0022 (‰/ppbv, $r^2>0.90$) and -0.0185 ± 0.0022 (‰/ppbv, $r^2>0.85$), respectively, for N_2O-$\Delta^{17}O_{CO_2}$ and N_2O-$\delta^{18}O_{CO_2}$. The best fit lines are shown as solid lines with the formulas presented in Fig. 3a and b. Assuming that the CO_2 mixing ratio in the stratosphere during our observation period is constant (370 ppmv), the resulting net isotope fluxes of $\Delta^{17}O_{CO_2}$ and $\delta^{18}O_{CO_2}$ are estimated as +48‰ GtC/yr and +38‰ GtC/yr, respectively. We estimate that the calculated isotope fluxes might include ∼30% uncertainty because of the uncertainty in the estimated N_2O loss rate used here, uncertainty in the least-squares linear fitting, and the assumption of a constant CO_2 mixing ratio. The isotope flux of $\Delta^{17}O_{CO_2}$ estimated in this study resembles that reported by Boering et al. (2004).

3.5 Comparison of current observation and model calculation

Liang et al. (2007) first investigated the considerable contribution of O_2 photolysis in the upper mesosphere to the oxygen isotope composition of middle atmospheric CO_2. They simulated correlation of N_2O-$\Delta^{17}O_{CO_2}$ and $\delta^{18}O_{CO_2}$-$\delta^{17}O_{CO_2}$ using a 1D vertical model. That innovative model, however, has not been tested yet, especially in terms of its adequacy for assessing effects of O_2 photolysis on CO_2. Herein, we verify the theory in Liang's model to compare the simulation results with the observation results. The simulation results are included in the current correlation plots of $\delta^{18}O_{CO_2}$-$\delta^{17}O_{CO_2}$ and N_2O-$\Delta^{17}O_{CO_2}$ portrayed in Figs. 2 and 3a, for which two different eddy diffusion constants were used for comparison (original values: solid curves in Figs. 2 and 3a; increased by 30% for altitudes of less than 40 km: dashed curve only in Fig. 3a) (see Liang et al., 2007).

On the $\delta^{18}O_{CO_2}$-$\delta^{17}O_{CO_2}$ plot (Fig. 2), the slope of the solid curve shows good fit for the lower stratosphere, but it declines gradually and underestimates $\Delta^{17}O_{CO_2}$ concomitantly with increasing altitude (increasing $\delta^{18}O_{CO_2}$) in the model (Fig. 2) in comparison to observations from various latitudes and altitudes (Thiemens et al., 1995b; Lammerzahl et al., 2002; this study). In particular, the maximum $\Delta^{17}O_{CO_2}$ value in the simulation result, which corresponds to ca. 55 km height, does not reach that in the observation results (isoclinic line in Fig. 2). Furthermore, on the N_2O-$\Delta^{17}O_{CO_2}$ plot, the change of the eddy diffusion constant from the original value (solid curve) to the increased value (dashed curve) results in an excellent fit between the model and observation at a range of $[N_2O]>\sim50$ ppbv, corresponding to the lower/middle stratosphere, although the discrepancy in the maximum $\Delta^{17}O_{CO_2}$ values between the model and observation is more significant. The cause of the underestimation of the maximum $\Delta^{17}O_{CO_2}$ in the model will be discussed later. In addition to that disagreement, at a range of $[N_2O]<\sim50$ ppbv, the observation result over Sanriku demonstrates smaller ^{17}O anomalies in CO_2 compared to the model simulation result. The wide ranges of the observed $\Delta^{17}O_{CO_2}$ values at the range of $[N_2O]<\sim50$ ppbv would be informative for middle/upper stratospheric chemistry and physics, although only a fragmentary dataset of chemical and isotopic compositions in the middle/upper stratosphere is available for comparison to those in the lower/middle stratosphere ($[N_2O]>$ca. 50 ppbv). Additional intensive observation throughout the whole stratosphere will elucidate the complex chemistry and air transport in the upper stratosphere.

Oxygen isotope fractionation in middle atmospheric CO_2 occurs through isotope exchange between CO_2 and $O(^1D)$ produced by photolysis of O_3 and O_2 (Yung et al., 1991; Liang et al., 2007). The possibility of oxygen isotope fractionation from the CO_2 photodissociation reaction has also been proposed (Bhattacharya et al., 2000), although the actual contribution of the isotope fractionation was considered to be negligible throughout the middle atmosphere (Liang et al., 2007). Oxygen isotope fractionation in the series of reactions of CO_2 with $O(^1D)$ through photolysis of O_3 (R1a–R2), which dominates in the stratosphere, engenders a steep slope of ∼1.7, as observed in the lower/middle stratospheric CO_2

(Fig. 2). This engenders the strengthening ^{17}O anomaly with increasing altitude. On the other hand, Liang et al. (2007) pointed out that photolysis of O_2 might dominate $O(^1D)$ production in the upper mesosphere and that the three isotope slopes of the Reactions (R1b)–(R2) in this region might be as low as 0.3. Consequently, $\Delta^{17}O_{CO_2}$ will decrease again with increasing altitude if this pattern pertains in the upper mesosphere (Figs. 2 and 3a). Therefore, we conclude herein that the underestimation of maximum $\Delta^{17}O_{CO_2}$ value (Figs. 2 and 3a) in the model simulation implies some problems related to the treatment of O_2 photolysis (R1b–R2) in the model. A possible reason is overestimation of the contribution of O_2 photolysis in the model. In this case, changing the parameters in the model would yield a better fit of the simulated with the observed data without changing the underlying theory of the model.

4 Concluding remarks

Decade-long observations of triple oxygen isotope composition in stratospheric CO_2 over Sanriku and Kiruna within the polar vortex revealed the following:

1. Observed $\delta^{18}O_{CO_2}$ and $\delta^{17}O_{CO_2}$ showed a good linear correlation ($r^2 > 0.95$) with a slope of 1.63 ± 0.10 (2σ), which is consistent with that observed in the middle-latitude lower/middle stratosphere (Lammerzahl et al., 2002). However, it differs clearly from that observed in the upper stratosphere/lower mesosphere (Thiemens et al., 1995b). The reason for the difference in the slopes remains unknown.

2. Both N_2O-$\Delta^{17}O_{CO_2}$ and N_2O-$\delta^{18}O_{CO_2}$ plots showed a negative linear correlation, as previously reported respectively by Boering et al. (2004) and Aoki et al. (2003). Based on those linear relations, CO_2 oxygen isotope fluxes from the stratosphere to the troposphere are estimated as +48‰ GtC/yr ($\Delta^{17}O_{CO_2}$) and +38‰ GtC/yr ($\delta^{18}O_{CO_2}$) with ∼30% uncertainties.

3. A comparison between a recent model study and observations revealed underestimation of the maximum $\Delta^{17}O_{CO_2}$ value in the model. One reason might be overestimation of O_2 photolysis considered in the model.

Results of the current study show that long-term observations of $\delta^{18}O_{CO_2}$, $\delta^{17}O_{CO_2}$, and N_2O mixing ratios are informative when combined with a model study that particularly addresses correlations of N_2O-$\Delta^{17}O_{CO_2}$ and $\delta^{18}O_{CO_2}$-$\delta^{17}O_{CO_2}$. These results can elucidate triple oxygen isotope fractionations in CO_2 and help to untangle complex interactions among physical, chemical, and photochemical processes in the middle atmosphere.

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