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

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Abstract

Anomalous oxygen isotopic compositions of stratospheric CO_2 were first reported in 1989, although their detailed behavior in the middle atmosphere is still open question. We collected 60 stratospheric air samples over Sanriku, Japan from 1991 to 2004 and Kiruna, Sweden in 1997. Using these accumulated air samples, we performed long-term observations of triple oxygen isotope compositions of stratospheric CO_2. It is the first simultaneous observation in the stratosphere of both relations between $\Delta^{17}O_{CO2}$ and [N_2O], and $\delta^{18}O_{CO2}$ and $\delta^{17}O_{CO2}$, accurately. Observations confirmed simultaneous linear correlations between $\delta^{18}O_{CO2}$, $\Delta^{17}O_{CO2}$, and [N_2O] within [N_2O]>50 ppbv: the correlations faded away along with decreasing [N_2O] from 50 ppbv. For dividing observation results by [N_2O]=50 ppbv, the divided datasets show that 1) both $\Delta^{17}O_{CO2}$ and $\delta^{18}O_{CO2}$ are conservative parameters within the N_2O-rich division, 2) the slope of least squares regression on $\delta^{18}O$–$\delta^{17}O$ plot for the N_2O-rich division is significantly steeper than that of the N_2O-depleted one, and 3) the N_2O-depleted division shows a discrepancy with recent model calculations, suggesting unconsidered isotope fractionation processes on complicated oxygen interactions in the CO_2-O_3-O_2 system in the upper stratosphere and mesosphere.

1 Introduction

Although $\delta^{17}O$ values vary during most isotopic fractionation processes, relationship between $\delta^{17}O$ and $\delta^{18}O$ values are usually conserved according to a mass-dependent relation of $\delta^{17}O=0.516\times\delta^{18}O$ (Matsuhisa et al., 1978; Santrock et al., 1985). Recently, mass-independent triple oxygen isotopic fractionation processes, which bring non-zero $\Delta^{17}O$ ($=\delta^{17}O-0.516\times\delta^{18}O$) values, so-called ^{17}O anomaly, have been found in photochemical reactions, such as in the photochemical production of O_3 from O_2 (Thiemens and Heidenreich, 1983; Mauersberger, 1987).

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Tropospheric CO_2 has a almost constant $\delta^{18}O_{VSMOW}$ value (+41‰) with no ^{17}O anomaly through a rapid oxygen isotope exchange with seawater (Thiemens et al., 1991). On the contrary, anomalously heavy $\delta^{18}O$ and positive ^{17}O anomaly have been observed in the stratospheric CO_2 over Texas and New Mexico (Thiemens et al., 1991), southern high-latitudinal regions (Thiemens et al., 1995a), Kiruna in Sweden (Alexander et al., 2001; Lämmerzahl et al., 2002), Aire-sur-l'Adour in France (Lämmerzahl et al., 2002), and northern high-latitudinal regions (Boering et al., 2004). A positive ^{17}O anomaly in CO_2 has been also observed in upper stratosphere and lower mesosphere over New Mexico (Thiemens et al., 1995b). It is generally thought that the ^{17}O anomaly observed in the stratospheric CO_2 is brought through a series of reactions, where O_3 is a source of extra heavy $\delta^{18}O$ and $\Delta^{17}O$ anomaly (Mauersberger, 1987; Yung et al., 1991):

$$O_3 + h\nu(< 310\,\text{nm}) \rightarrow O_2 + O(^1D) \quad \text{(R1)}$$

$$CO_2 + O(^1D) \rightarrow CO_3^* \rightarrow CO_2 + O(^3P) \quad \text{(R2)}$$

In parallel with the field observations, several laboratory experiments and model calculations have been conducted to elucidate detailed mechanism of the mass-independent oxygen isotope fractionation of CO_2, O_3, and O_2 in the middle atmosphere (e.g. Chakraborty and Bhattacharya, 2003; Liang et al., 2007).

Although several observations have reported anomalous oxygen isotopic compositions in stratospheric CO_2, only limited number of samples or parameters, which makes further detailed quantitative analysis difficut, has been obtained in each observation. For example, results from only few stratospheric air samples (less than 10) were presented (Thiemens et al., 1991, 1995a; Alexander et al., 2001). Only Lämmerzahl et al. (2002) and Boering et al. (2004) have reported a notable correlation of $\Delta^{17}O_{CO2}$ respectively with other tracers, such as $\delta^{18}O_{CO2}$ over Aire-sur-l'Adour and Kiruna (Lämmerzahl et al., 2002) and with N_2O mixing ratio ($[N_2O]$) over the northern high-latitudinal region (Boering et al., 2004).

Since 1985, we have continued stratospheric whole air sampling over Sanriku, Japan. This is so far the only long-term stratospheric whole air sampling and a portion of the $\delta^{18}O$ data in the lower stratospheric CO_2 has been reported (Gamo et al., 1989, 1995). In this paper, we report triple oxygen isotope compositions and its relationship to $[N_2O]$ obtained in the past 14 years long-term sampling in addition to a stratospheric air sampling carried out over Kiruna in February 1997, when the sampling area was inside a polar vortex. A novel analytical method we recently developed was used to determine $\Delta^{17}O_{CO2}$ (Kawagucci et al., 2005).

2 Sampling and analysis

During 1991–2004, vertical samples of stratospheric whole air were collected during seven observations in early or late summer over Sanriku, Japan (39° N)(Table 1) using a balloon-borne cryogenic sampler developed by the Japan Aerospace Exploration Agency (JAXA). Utilizing the same sampling system, an additional vertical sampling was carried out at Kiruna, Sweden (68° N) on 22 February 1997 (Table 1). The air sampling system is capable of collecting whole air samples with little transformation of chemical and isotopic compositions. Detailed descriptions of the sampler and sampling procedures have been reported elsewhere (Nakazawa et al., 1995; Honda et al., 1996; Aoki et al., 2003).

After taking aliquots from the sampled whole air in the sampler, both $\delta^{18}O_{CO2}$ and $\delta^{17}O_{CO2}$ values in the sampled stratospheric air were simultaneously analyzed using a continuous-flow isotope ratio mass spectrometer, which requires no preparation processes such as separation of CO_2 from other components and fluorination conversion of CO_2 to O_2 in determining $\Delta^{17}O_{CO2}$ in a small amount of whole air sample (Kawagucci et al., 2005). Analytical precisions for the analyzed $\delta^{18}O_{CO2}$, $\delta^{17}O_{CO2}$, and $\Delta^{17}O_{CO2}$ in this study were estimated at most, ±0.05‰, ±0.5‰, and ±0.5‰, respectively. In addition, the N_2O mixing ratios were also determined using other aliquots from the same

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stratospheric air samples. Some of the $\delta^{18}O_{CO2}$, $\delta^{17}O_{CO2}$, and N_2O mixing ratio data have been already reported previously (Aoki et al., 2003; Kawagucci et al., 2006).

3 Results

3.1 Sanriku

49 whole air samples in the stratosphere, including four samples just below or around the tropopause, were obtained during seven launches in the past 14 years (Table 1). Figure 1 plots vertical profiles of $\Delta^{17}O_{CO2}$. Significantly positive ^{17}O anomalies in CO_2 with at most +7.6‰ were found over Sanriku, although no ^{17}O anomaly was observed near the tropopause. The long-term observations over Sanriku confirm that no clear year-to-year variation exists in vertical profiles of $\Delta^{17}O_{CO2}$ for the past 14 years beyond small fluctuations, which is caused by natural air transport, although vertical profiles of the CO_2 mixing ratio in the stratosphere show a clear increasing trend by a ratio of ca. 1.4 ppmv per year (Aoki et al., 2003).

Figures 2a, b show correlations of $\Delta^{17}O_{CO2}$ and $\delta^{18}O_{CO2}$ to $[N_2O]$. All data obtained during the past 14 years are plotted. Both $\Delta^{17}O_{CO2}$ and $\delta^{18}O_{CO2}$ exhibit almost negative linear correlations with $[N_2O]$ and no year-to-year variation was observed. The observed negative linear correlation between $\Delta^{17}O_{CO2}$ and $[N_2O]$ supports the first observation about the correlation over northern high-latitudinal region (Boering et al., 2004), while the linear correlation between $\delta^{18}O_{CO2}$ and $[N_2O]$ is first observed in this study. Additionally, the $\delta^{18}O$ and $\delta^{17}O$ values in stratospheric CO_2 exhibit an almost positive linear trend with no year-to-year variation (Fig. 3).

3.2 Kiruna

We obtained 11 whole air samples from the stratosphere over Kiruna, including one sample collected around the tropopause (Table 1). A vertical profile of the $\Delta^{17}O_{CO2}$

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(Fig. 1) showed that above 20 km altitude ^{17}O anomalies became much larger with increasing altitude compared to those below 20 km altitude. The profile is similar to the typical one observed for long-lived tracers within a polar vortex, where upper stratospheric air descends into lower stratosphere because of strong downward advection (Waugh and Hall, 2002). As a result, air with characteristics of upper stratosphere could be observed even in lower stratosphere in this region (Waugh and Hall, 2002). In our observation, $\Delta^{17}O_{CO2}$ at 25.6 km height was +12.2‰ (Table 1), which is as large as previously observed in the mesosphere (Thiemens et al., 1995b). Therefore, we consider that the observed lower stratospheric air above 25 km height in Kiruna had been brought from mesosphere by a strong downward advection. One should notice that correlations of $\Delta^{17}O_{CO2}$ and $\delta^{18}O_{CO2}$ to $[N_2O]$ changed significantly at a $[N_2O]$ ~50 ppbv (Fig. 2). At a condition of $[N_2O]$>50 ppbv, both $\Delta^{17}O_{CO2}$ and $\delta^{18}O_{CO2}$ showed linear correlations similar to those observed over Sanriku, however, at the condition of $[N_2O]$<50 ppbv , the correlations faded away along with decreasing $[N_2O]$ from 50 ppbv.

4 Discussion

It has been known that physical height (altitude) is not a conserved parameter to describe vertical structure in the stratosphere because of the complex air mass transition in different times and locations. For this reason, it is not possible to compare $\Delta^{17}O_{CO2}$ values among different years and locations based on sampling altitudes. In contrast, N_2O is known to be used as a tracer of air mass in the lower stratosphere since N_2O is a long-lived trace gas and emitted only from earth's surface (Waugh and Hall, 2002). The observed negative linear correlation between $\Delta^{17}O_{CO2}$ and $[N_2O]$ within $[N_2O]$>50 ppbv over Sanriku and Kiruna suggests that the $\Delta^{17}O_{CO2}$ value is also regarded as a long-lived tracer. Similar linear correlation between $\Delta^{17}O_{CO2}$ and $[N_2O]$ has been also reported in the northern high latitudinal region (Boering et al., 2004).

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In addition, we also found the negative correlation between $\delta^{18}O_{CO2}$ and [N_2O] in the lower stratospheric air (i.e., air masses with [N_2O]>50 ppbv), suggesting that $\delta^{18}O_{CO2}$ is also a long-lived tracer like N_2O in the lower stratosphere. These observed linear relationship of $\Delta^{17}O_{CO2}$ and $\delta^{18}O_{CO2}$ to [N_2O] within air containing N_2O>50 ppbv indicate that both $\Delta^{17}O_{CO2}$ and $\delta^{18}O_{CO2}$ undergo physicochemical processes similar to those long-lived N_2O undergoes in the air mass with N_2O>50 ppbv in the stratosphere. Namely, in-situ photochemical reactions as suggested previously (e.g., R2) are not responsible for the mass-dependent and mass-independent oxygen isotope fractionations in CO_2 , but simple physical mixing of different air masses is responsible for the fractionation within air masses containing N_2O>50 ppbv in the stratosphere.

On the other hand, the correlations of $\Delta^{17}O_{CO2}$ and $\delta^{18}O_{CO2}$ to [N_2O] in the air masses containing [N_2O]<50 ppbv over Sanriku and Kiruna showed a relationship which is different from those observed in the air mass with [N_2O]>50 ppbv (Fig. 2). Similar change at [N_2O]~50 ppbv in the correlations of $\Delta^{17}O_{CO2}$ and $\delta^{18}O_{CO2}$ to [N_2O] have been observed in the upper stratosphere and lower mesosphere over New Mexico (Thiemens et al., 1995b) as plotted with our observations in Fig. 2. One should notice that the data observed over New Mexico quite nicely overlap with our observation. Therefore, we divided our observation results over Sanriku and Kiruna at [N_2O]=50 ppbv and referred air masses in the N_2O-rich division (>50 ppbv) as "lower stratosphere-like air" and those in the N_2O-depleted division (<50 ppbv) as "upper stratosphere/lower mesosphere-like air."

Figure 3 plots a correlation between $\delta^{18}O$ and $\delta^{17}O$, which is useful to discuss mass-independent isotope fractionation processes since vertical deviation from the terrestrial fractionation line (TFL: slope = 0.516) corresponds to ^{17}O anomaly. Using a least-square regression analysis, slopes of the correlation lines in the lower stratosphere-like air and the upper stratosphere/lower mesosphere-like air were calculated (Fig. 3). Their slopes were 1.75±0.17 (lower stratosphere-like air) and 1.17±0.24 (upper stratosphere/lower mesosphere-like air), respectively, which shows there is a clear difference

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in the slopes. Even if [N_2O]=30 ppbv or 70 ppbv was employed as a dividing point of the air mass type, the difference qualitatively remained similar. It should be pointed out that the slope in the lower stratosphere-like air in this study agrees well with that observed in the lower stratosphere over Aire-sur-l'Adour and Kiruna (1.71±0.03) (Lämmerzahl et al., 2002), while the upper stratosphere/lower mesosphere-like air observed in this study agrees well with that observed in upper stratosphere and mesosphere over New Mexico (1.21±0.19) (Thiemens et al., 1995b). The clear difference in slopes suggests presence of isotope fractionation process(es) for triple oxygen isotope compositions in the upper stratosphere/lower mesosphere-like CO_2 in addition to those for the lower stratosphere-like CO_2, which is long-lived and its triple oxygen isotope compositions is controlled by only physical process such as air mass movement.

Characteristic oxygen isotope fractionation in CO_2 through the stratosphere and mesosphere has been proposed in a recent model calculation study (Liang et al., 2007), which considered O_2 photolysis as a dominant $O(^1D)$ source on (R2) above upper mesosphere (~70 km height), while in the current observation only air masses in the stratosphere and the lower mesosphere below 60 km height have been sampled. The model calculation also qualitatively reproduced observed relationships of $\delta^{18}O_{CO2}$–$\delta^{17}O_{CO2}$ in the stratosphere (see Figs. 4 and 5 in Liang et al., 2007), however, the deviation of the model calculation from the observations including current study gradually increased as [N_2O] decreased, resulting in underestimated $\Delta^{17}O_{CO2}$ value in both $\delta^{18}O_{CO2}$–$\delta^{17}O_{CO2}$ plot and $\Delta^{17}O_{CO2}$–[N_2O] plot. These deviations in the low [N_2O] conditions suggests existence of process(es) during oxygen isotope exchanges in CO_2-O_3-O_2 system in the upper stratosphere and mesosphere, which is not considered in the current model study.

5 Conclusions

Our observations revealed and reconfirmed following new and important facts related to stratospheric CO_2.

1) Simultaneous observation of $\delta^{18}O_{CO2}$, $\Delta^{17}O_{CO2}$, and [N_2O] confirmed a negative linear correlation between [N_2O] and $\Delta^{17}O_{CO2}$, and newly revealed a similar correlation between [N_2O] and $\delta^{18}O_{CO2}$ within [N_2O]>50 ppbv, indicating that $\Delta^{17}O_{CO2}$ and $\delta^{18}O_{CO2}$ are long-lived.

2) No clear year-to-year variation was found in the correlations of $\Delta^{17}O_{CO2}$ to altitude, [N_2O], and $\delta^{18}O_{CO2}$.

3) Relationship between $\delta^{18}O_{CO2}$ and $\delta^{17}O_{CO2}$ found to be divided into two different linear ones when the samples are divided at [N_2O]=50 ppbv, suggesting existence of oxygen isotope fractionation process of CO_2 in the N_2O-depleted air.

4) Discrepancy between observations and the recent model calculation was found in the N_2O-depleted air, suggesting existence of oxygen isotope fractionation(s) during complicated oxygen interactions in CO_2-O_3-O_2 system at the upper stratosphere and mesosphere.

Present study confirmed several features of oxygen isotope behaviors in stratospheric CO_2 which have been previously reported and also found possible existence of unaccounted oxygen isotope fractionation process(es). However, detailed oxygen isotope fractionations in a CO_2-O_3-O_2 system at the stratosphere and mesosphere have not yet fully understood and still remain an open question.

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Table 1. Measured oxygen isotopic compositions of CO_2 are shown with the sampling location, date, and altitude. Several samples indicated by * are obtained just below or around the tropopause. Errors of $\delta^{18}O$, $\delta^{17}O$, and $\Delta^{17}O$ are estimated respectively as, at most, 0.05‰, 0.5‰, and 0.5‰.

Location	Date	Altitude (km)	$\delta^{18}O$ (‰)	$\delta^{17}O$ (‰)	$\delta^{17}O$ (‰)	
Sanriku (39° N)	29 Aug 91	33.3	46.37	30.8	6.9	
		35.3	45.18	29.8	6.5	
	31 Aug 94	18.2	41.89	22.6	1.0	
		20.4	42.29	23.2	1.4	
		22.3	43.22	24.9	2.6	
		24.7	43.67	25.8	3.3	
		26.8	43.75	25.6	3.0	
		29.2	43.50	25.7	3.2	
		31.1	44.29	27.8	5.0	
		34.7	44.75	27.6	4.5	
	8 June 95	20.3	43.67	24.8	2.3	
		22.3	41.92	23.1	1.4	
		24.5	45.35	28.1	4.7	
		26.7	45.21	27.9	4.5	
		28.8	46.13	30.3	6.5	
		30.6	46.31	30.5	6.6	
		32.4	47.50	31.3	6.8	
		33.8	46.73	30.3	6.1	
	28 Aug 00	15.0	39.71	20.5	0.0	*
		17.1	41.80	22.3	0.7	
		18.7	41.97	21.4	−0.3	
		20.9	42.92	25.0	2.9	
		22.7	43.23	25.4	3.1	
		25.8	44.13	27.1	4.4	
	30 May 01	14.9	41.22	21.7	0.4	
		16.8	41.04	21.7	0.5	
		18.8	40.02	20.5	−0.2	
		27.6	42.58	25.4	3.4	
		29.4	44.03	27.7	5.0	
	4 Sep 02	15.2	42.24	21.6	−0.2	*
		16.4	40.44	20.8	−0.1	*
		18.7	42.15	23.1	1.3	
		20.6	43.16	25.1	2.8	
		22.9	43.90	26.7	4.1	
		24.0	43.19	26.0	3.7	
		27.7	44.79	28.2	5.1	
		30.3	45.68	30.5	6.9	
		34.0	47.08	31.2	6.9	
	1 Sep 04	14.7	41.63	21.4	−0.1	*
		16.5	42.11	22.2	0.5	
		18.7	42.27	22.3	0.5	
		21.2	42.90	24.9	2.7	
		23.4	43.79	25.1	2.5	
		25.7	43.55	25.0	2.5	
		27.8	43.64	27.3	4.7	
		30.5	45.11	29.1	5.8	
		31.5	46.47	30.8	6.8	
		32.8	46.61	31.6	7.6	
		35.6	46.90	31.3	7.1	
Kiruna (68° N)	22 Feb. 97	10.2	43.67	22.6	0.0	*
		13.0	42.07	22.9	1.2	
		14.1	42.21	23.8	2.1	
		15.9	43.23	24.0	1.7	
		16.4	43.63	25.6	3.1	
		17.2	43.79	25.4	2.8	
		18.2	43.82	25.8	3.2	
		20.1	45.62	27.4	3.9	
		21.8	45.58	29.4	5.9	
		23.6	48.34	33.6	8.7	
		25.6	52.49	39.3	12.2	

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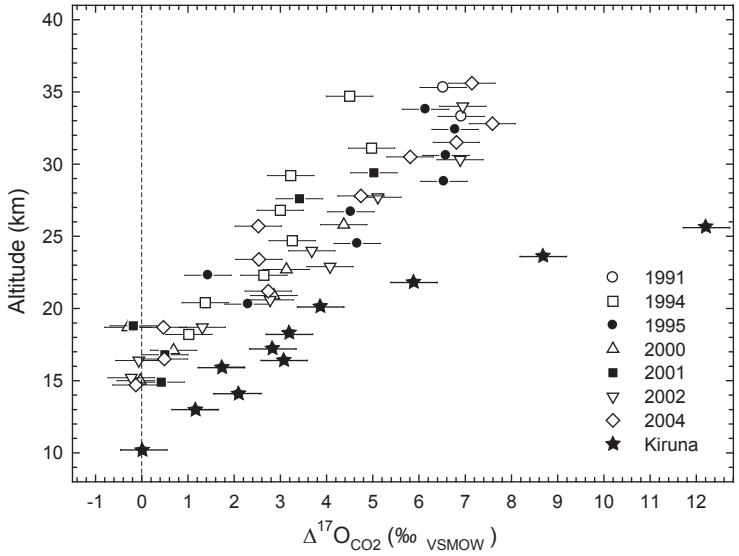

Fig. 1. Vertical profiles of $\Delta^{17}O_{CO2}$ values. Datasets over Sanriku are categorized by the sampling year and season (open symbols, late summer; filled symbols, early summer) and that over Kiruna is represented by a filled star. A vertical dashed line indicates no ^{17}O anomaly. Analytical precisions of 0.5‰ are represented as horizontal bars.

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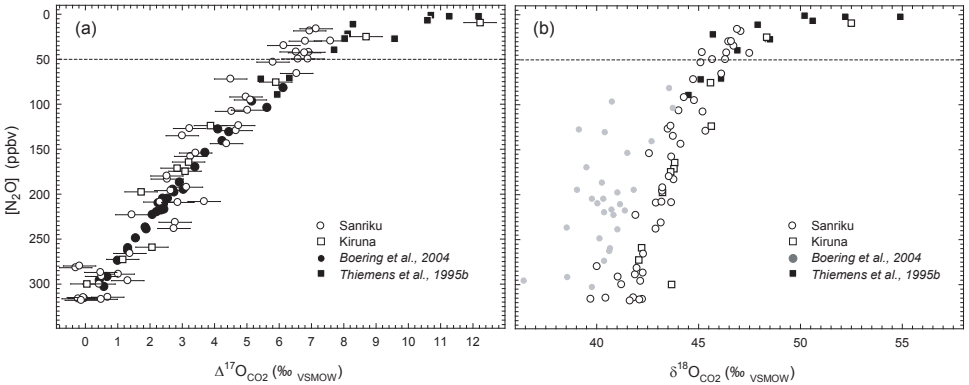

Fig. 2. (a) $\Delta^{17}O_{CO2}$–N_2O mixing ratio plot. **(b)** $\delta^{18}O_{CO2}$–N_2O mixing ratio plot. Vertical axes for the N_2O mixing ratio are in reverse. Open circles and squares in both figures respectively represent observations over Sanriku and Kiruna. Black circles in (a) and gray circles in (b) represent datasets from Boering et al. (2004). Black squares in both figures represent datasets obtained from Thiemens et al. (1995b). Analytical precisions for each parameter are represented as cross bars; errors are comparable to symbol sizes in some instances.

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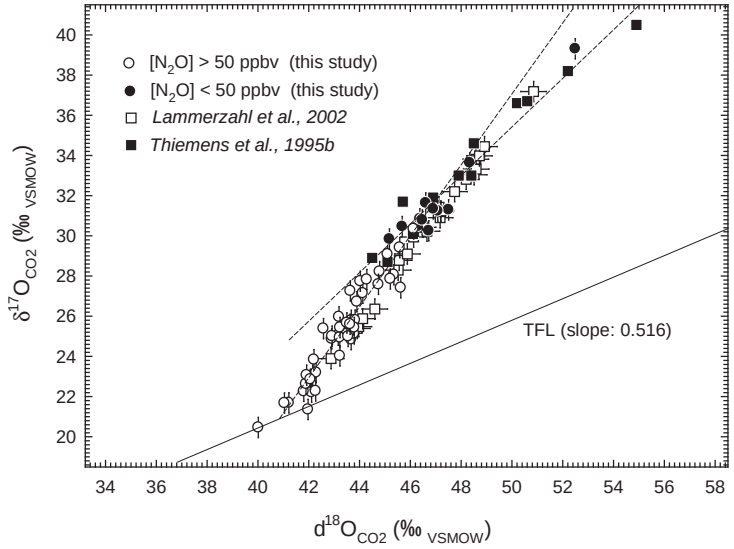

Fig. 3. $\delta^{18}O_{CO2}$–$\delta^{17}O_{CO2}$ plot. A terrestrial fractionation line (TFL: slope = 0.516) is shown as a solid line. Our observations over Sanriku and Kiruna are divided based on N_2O mixing ratios, such as open circles ([N_2O]>50 ppbv) and solid circles ([N_2O]<50 ppbv). Dashed lines represent least square fittings, which have slopes of 1.75±0.17 (N_2O-enriched) and 1.17±0.24 (N_2O-depleted). Open and solid squares respectively represent datasets from Lämmerzahl et al. (2002) and Thiemens et al. (1995b). Analytical precisions for each parameter are represented as cross bars; errors are comparable to symbol sizes in some instances.

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