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Near Surface CO_2 Triple Oxygen Isotope Composition

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ABSTRACT

The isotopic composition of carbon dioxide in the atmosphere is a powerful tool for constraining its sources and sinks. In particular, the ^{17}O oxygen anomaly [$\Delta^{17}O = 1000 \times \ln(1 + \delta^{17}O/1000) - 0.516 \times 1000 \times \ln(1 + \delta^{18}O/1000)$], with a value $> 0.5‰$ produced in the middle atmosphere, provides an ideal tool for probing the exchange of carbon dioxide between the biosphere/hydrosphere and atmosphere. The biosphere/hydrosphere and anthropogenic emissions give values $\leq 0.3‰$. Therefore, any anomaly in near surface CO_2 would reflect the balance between stratospheric input and exchange with the aforementioned surface sources. We have analyzed $\Delta^{17}O$ values of CO_2 separated from air samples collected in Taipei, Taiwan, located in the western Pacific region. The obtained mean anomaly is $0.42 \pm 0.14‰$ (1-σ standard deviation), in good agreement with model prediction and a published decadal record. Apart from typically used $\delta^{13}C$ and $\delta^{18}O$ values, the $\Delta^{17}O$ value could provide an additional tracer for constraining the carbon cycle.

Key words: Oxygen anomaly, Biogeochemistry, Carbon and water cycling

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1. INTRODUCTION

Carbon dioxide is an important climate-relevant greenhouse gas in the atmosphere (IPCC 2007; Lacis et al. 2010) and thus, its sources and sinks are of societal interest. Information obtained from concentration measurements alone is limited because of poor spatial and temporal resolution of existing observation networks (Chahine et al. 2008; GLOBALVIEW-CO2 2008). The atmospheric CO_2 concentration is increasing at a rate of about 2 ppmv per year, the present level being close to 400 ppmv. About 88% of anthropogenic emissions are due to fossil fuel burning and cement manufacturing while land use change is responsible for the rest (IPCC 2007). Not all of the emitted CO_2 remains in the atmosphere. Land and ocean absorb ~50% of the total emissions (Tans et al. 1990; Gurney et al. 2002; IPCC 2007). However, the partitioning of the uptakes between the land and ocean is highly debated (Denning et al. 1995). Regions that absorb are not identified satisfactorily (Tans et al. 1990; Denning et al. 1995; IPCC 2007; Peters et al. 2007). Current understanding of the sources and sinks of CO_2 is based primarily on $\delta^{13}C$ values (Ciais et al. 1995; Francey et al. 1995) and models that assimilate CO_2 observations (Tans et al. 1990; Denning et al. 1995; Gurney et al. 2002). The $\delta^{13}C$ values are used to differentiate the uptake fluxes by land and ocean (Ciais et al. 1995; Francey et al. 1995) while $\delta^{18}O$ values are useful for estimating terrestrial gross primary production (GPP) (Farquhar et al. 1993; Ciais et al 1997). The $\delta^{17}O$ values have not yet been used widely, mainly because of the measurement difficulty due to its low abundance. Using a recently developed procedure, systematic and precise analysis of both $\delta^{17}O$ and $\delta^{18}O$ values have become possible.

Natural variations in the three oxygen isotopes usually obey a pattern where the change in the $^{17}O/^{16}O$ ratio is nearly half that in the $^{18}O/^{16}O$ ratio. There are however instances where this rule is violated to varying degrees. Such anomalous oxygen isotope variations, termed as mass independent fractionation (MIF), can often provide new insight into the processes occurring in nature. The MIF in atmospheric CO_2

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is defined as $\Delta^{17}O = 1000 \times \ln(1 + \delta^{17}O/1000) - \lambda \times 1000 \times \ln(1 + \delta^{18}O/1000)$ where the δ-values are expressed relative to VSMOW (Vienna Standard Mean Ocean Water) in parts per thousand and λ is the coefficient or slope that relates $\delta^{17}O$ and $\delta^{18}O$ variations. To obtain the ^{17}O anomaly or $\Delta^{17}O$ (in a given reference scale), one has to choose an appropriate coefficient (slope) λ value which usually lies in the 0.520 to 0.528 range (Miller et al. 2007). The $\Delta^{17}O$ concept is useful in practical applications because small fractionations due to experimental gas handling processes cancel out (Thiemens 2006). In the present work, we chose λ as 0.516 based on considering the main controlling factors of atmospheric CO_2 isotopes. This value is close to the value defining fractionation in evaporative and diffusional processes (Barkan and Luz 2007; Luz and Barkan 2010) and also applies to the fractionation that occurs in transpiration at ~75% (globally averaged) relative humidity (Landais et al. 2006). This slope is however different from the one (0.523) occurring in the water-CO_2 equilibrium process (Barkan and Luz 2012; Hofmann et al. 2012). The choice of λ is still being debated as λ-values differ for different processes and from a budgetary scenario each contribution will have to be integrated depending on its strength to arrive at a "mean" value appropriate for λ. As the CO_2 cycle in nature is intimately related to the hydrological cycle the choice of reference VSMOW is quite natural.

MIF in stratospheric ozone (Mauersberger 1981; Thiemens et al. 1991) is thought to be partially transferred into carbon dioxide (Thiemens et al. 1995; Hoag et al. 2005; Liang et al. 2007, 2008a) via the reaction $O(^1D) + CO_2$, where $O(^1D)$ is formed by the photodissociation of O_3 in the Hartley-Huggins band (Thiemens et al. 1991; Yung et al. 1997; Lämmerzahl et al. 2002; Boering et al. 2004). Note that the photochemical processes involving O_2, O_3, and CO_2 introduce the positive anomaly in CO_2 and also a small corresponding negative anomaly in O_2. A small but measurable MIF in the tropospheric O_2 and dissolved O_2 in the ocean has been successfully used to examine the biospheric productivity (Luz et al. 1999; Luz and Barkan 2000; Juranek and Quay 2005).

The anomalous stratospheric CO_2 is brought to the troposphere by large scale circulation (Brewer-Dobson circulation) and synoptic eddy mixing, providing another opportunity for studying the biogeochemical cycles involving CO_2 at the lower level (Hoag et al. 2005; Liang et al. 2008b). The CO_2 and O_2 cycles in the troposphere are intimately connected by photosynthesis and respiration whose magnitude can be inferred from their isotopic characteristics. The oxygen isotope anomaly in CO_2 or the anomaly budget of atmospheric CO_2 is controlled by three major biospheric/hydrospheric processes: photosynthetic consumption and attendant isotopic exchange with leaf water, respiration, and exchange with ocean and other water bodies (Fig. 1). The exchange with leaf water, being very rapid, determines the net $\Delta^{17}O$ value of tropospheric CO_2. According to Luz et al. (1999), globally the tropospheric CO_2 essentially inherits the $\Delta^{17}O$ value of the surface water which has a magnitude of 0.155‰ taking atmospheric oxygen as a reference passing through a line with slope of 0.521. Based on the above considerations, various calculations have been performed to investigate the stratospheric CO_2 contribution to tropospheric/biospheric CO_2. For example, a two-box model has

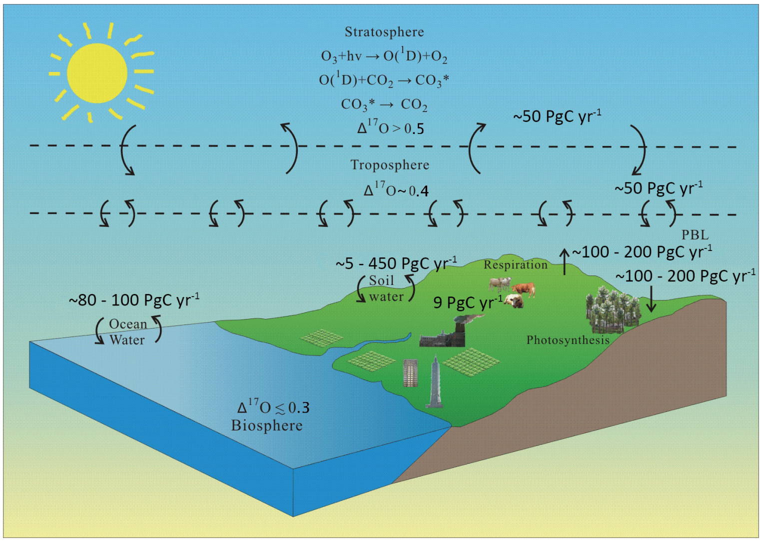

Fig. 1. Schematic diagram (not to scale) of the exchange processes between the biosphere, troposphere, and stratosphere with various $\Delta^{17}O$ values. There is wide difference in the cross boundary fluxes of carbon published by various authors (Cuntz et al. 2003; Boering et al. 2004; Hoag et al. 2005; IPCC 2007; Liang et al. 2008a; Wingate et al. 2009; Beer et al. 2010; Welp et al. 2011). As a guide we adopt the following flux values: Ocean to Atmosphere: 80 - 100 PgC yr^{-1}; Photosynthesis: 100 - 200 PgC yr^{-1}; Respiration: 100 - 200 PgC yr^{-1}; fossil fuel burning: 9 PgC yr^{-1}; Soil invasion: 5 - 450 PgC yr^{-1}; Planetary Boundary Layer (PBL) to free Troposphere: 50 PgC yr^{-1}; Troposphere to Stratosphere: 50 PgC yr^{-1}. (Color online only)

been used to estimate the magnitude of the resultant CO_2 anomaly in the troposphere (Hoag et al 2005). The predicted size of the $\Delta^{17}O$ anomaly is ~0.15‰ above that originating from the biosphere and hydrosphere. The elevated anomaly compares well with the average value found in 10 years of measurements made at La Jolla, CA, USA (Thiemens et al. 2014). Liang et al. (2008a) extended this model and suggested that the stratospheric-tropospheric exchange modifies the isotopic composition of CO_2, and also influences its seasonal cycle. The results from a phase correlation study of O_3 and CO supported this conclusion and suggested that the stratosphere-troposphere exchange carries stratospheric air into the troposphere at select places (Liang et al. 2008b). This would be especially important in regions where intrusion events like typhoons/monsoons occur frequently (such as Taiwan), and the magnitude of the anomaly could be enhanced during those episodes (Liang and Mahata 2015).

Taiwan is an island ~400 km long and ~140 km wide located at the interface of the Asian continent and Pacific Ocean. Mountainous terrain occupies more than 60% of the island. The Taipei basin (~250 km^2) is situated at the northern tip of the island and is bounded by Yangmingshan to the north, Linkou mesa to the west and the Xueshan Range ridge to the southeast. Taiwan is part of the Western Pacific island arc and its meteorology is influenced primarily by low pressure systems from the Pacific and South China Sea and high pressure systems from mainland China and the Tibetan Plateau. Taiwan has a strong topographic gradient, with mountains higher than 3000 m at the central ridge down to the coastal sea level within a distance of less than 100 km. Summer and winter monsoons are the two major climate systems responsible for the seasonal rainfall in Taiwan. The moisture from these two monsoons originate from three different air masses (CWB 1991; Araguás-Araguás et al. 1998): Polar Continental (PC), Equatorial Maritime (EM), and Tropical Maritime (TM). The northeasterly PC air mass from the Asian continent flows over the island in the winter (December - March). During the summer (June - September), the southwesterly EM air mass from the South China Sea and the east-southeasterly TM air mass from the western Pacific dominate the island (CWB 1991; Araguás-Araguás et al. 1998). In summer and fall Taiwan is significantly affected by typhoons, making the weather more dynamic and highly turbulent. All of these meteorological conditions make this region a possible site for stratospheric air incursion down to ground and sea levels (Liang and Mahata 2015). The Taipei basin has a particularly shallow boundary mixed layer in the winter (~500 m in daytime) (Chou et al. 2007) which is generally lower than the surrounding mountains (~1000 m to the north and southeast), making the air mass confined and isolated in the basin for about a week. As a result, diurnal variations in $\Delta^{17}O$ values can be attributed to either local biogeochemistry/anthropogenic activities, stratospheric intrusions, or a combination of the two. Lateral transport as a source for $\Delta^{17}O$ variability can be mostly ignored. We report here the results of our study on $\Delta^{17}O$ values of CO_2 separated from a set of air samples collected in Taipei city.

2. MEASUREMENT PROCEDURE

Two liter air samples were collected at the Academia Sinica campus in Taipei, Taiwan (121°36’51’’E, 25°02’25’’N) from the roof of a building (~25 m above ground and 75 m above the sea level) and processed using a glass vacuum system consisting of five traps. Two traps were used for moisture removal, and the remaining were used for CO_2 collection followed by purification by repeated freeze-thaw technique at liquid nitrogen temperature (-196°C) and dry ice temperature (-77°C). CO_2 was separated from other condensable species like N_2O, CH_4, and hydrocarbons by Gas Chromatography using a Porapak Q column. The cerium oxide exchange method (Mahata et al. 2012) was employed to determine the $\Delta^{17}O$ value of CO_2. All isotopic measurements were performed in a Thermo FINNIGAN MAT-253 mass spectrometer in dual inlet mode. The method accuracy was determined using CO_2 samples with known $\Delta^{17}O$ values and further checked using a recently developed high precision method (Mahata et al. 2013, 2016). The $\Delta^{17}O$ determination precision was better than ~0.1‰ as tested by repeatedly measuring gas samples from a tank of air. As an additional check of the precision in the context of ambient air-CO_2 analysis, we collected in several cases two air samples at the same time from the same location and analyzed them following the same protocol. The largest difference between such pairs was 0.15‰ and can be taken to be a better measure of the precision of the whole method.

3. RESULTS AND DISCUSSION

The $\delta^{18}O$ values (relative to VSMOW) of the CO_2 samples collected during September 2010 to February 2013 range from 38.67 - 41.45‰ (Table 1 and Fig. 2). The mean value (40.38‰) is slightly less than the average global tropospheric value in this latitudinal belt (~41‰) which may reflect exchange with local meteoric water sources which are -4.2 ± 2‰ in winter (Peng et al. 2010). Air pollution and local plant activity could have an effect (Nakazawa et al. 1997). Consistent with this expectation a large variation is also observed in $\delta^{13}C$ values over the -8.19 to -12.43‰ range [relative to VPDB (Vienna Pee Dee Belemnite)]. The relatively higher negative values (-9.13 ± 0.87‰) than the background indicate larger than normal respired CO_2 contribution from plant and soil biota and anthropogenic emissions (Newman et al. 2008).

The $\delta^{17}O$ and $\delta^{18}O$ analysis results are summarized in Table 1 and Fig. 3 where all available measurements by the UCSD (University of California, San Diego) group from the troposphere are also shown for comparison. A least-squared linear regression fit, with zero intercept, to the present tropospheric data shows a slope of 0.527 ± 0.030 which is steeper than the terrestrial mass fractionation line (slope = 0.516) but smaller than the stratospheric slope (~1.2 - 1.7) (Thiemens et al. 1995; Lämmerzahl et al. 2002; Boering et al. 2004). The difference from the terrestrial mass fractionation is small and suggests that the near surface CO_2 in this region is largely affected by local biogeochemistry with only a small amount of stratospheric contribution. This slope is comparable with the recently published tropospheric CO_2 data with slope of 0.523 (Thiemens et al. 2014) with the consideration that our measurements were performed with larger uncertainty. The averaged $\Delta^{17}O$ value is 0.42 ± 0.14‰ (1-σ standard deviation), which suggests that the stratospheric CO_2 signature, if any, is barely detectable. The frequency distribution of the $\Delta^{17}O$ values show a near normal distribution but there are some high $\Delta^{17}O$ sample values with higher frequency of occurrence (Fig. 4) than dictated by uncertainty. They are probably the samples with stratospheric influence. In this work we focus on the grand average $\Delta^{17}O$ value. A large spread in the data may or may not reflect the real variability and further verification is required.

Apart from the above interpretation we should consider the possibility that the triple isotope signature of biological CO_2 sources from this region (i.e., the λ-value) could be different from that assumed. This would change the calculated numerical value of $\Delta^{17}O$. For example, our analysis considers that the anomaly in the tropospheric CO_2 can be calculated with a single coefficient of 0.516 in the logarithmic expression of $\Delta^{17}O$ given above. However, the CO_2 in the near surface region can come from diverse sources with possibly different coefficients. If there is substantial contribution from a source whose fractionation process has a coefficient higher than 0.516 (like water-CO_2 equilibrium process), we would obtain artificially higher $\Delta^{17}O$ values with a choice of 0.516. As mentioned before, recent studies (Barkan and Luz 2012; Hofmann et al. 2012) show that the coefficient for water-CO_2 equilibrium system is 0.523. It is also known that for various combustion processes (Horváth et al. 2012) λ varies and could be significantly different from 0.516.

The oxygen isotope distribution in tropospheric CO_2 is largely controlled by water-CO_2 equilibrium process, resulting in $\delta^{18}O \approx 41‰$ (VSMOW). Following Hoag et al. (2005), we could have assumed that CO_2 from the biosphere and hydrosphere is in equilibrium with water. In that case, using slope 0.523 would decrease our values by $\Delta^{17}O = (0.523 - 0.516) \times 41‰ = 0.29‰$. Our measured mean $\Delta^{17}O$ of 0.42‰ would then reduce to 0.13‰ representing a local mean anomaly above the reference water-CO_2 value of zero. This value is in good agreement with prediction (0.15‰) (Hoag et al. 2005) albeit made on a global scale.

Table 1. $\delta^{13}C$ (VPDB), $\delta^{18}O$, and $\Delta^{17}O$ values (VSMOW) in ‰ of CO_2 separated from air samples collected in the campus of Academia Sinica, Taipei, Taiwan. $\Delta^{17}O = 1000 \times \ln(1 + \delta^{17}O/1000) - 0.516 \times 1000 \times \ln(1 + \delta^{18}O/1000)$. The average values along with the standard deviation for the whole set are given in the last two rows.

Collection Date	Time	$\delta^{13}C$	$\delta^{17}O$	$\delta^{18}O$	$\Delta^{17}O$
10/11/2010	15:00	-8.40	21.34	40.59	0.58
10/22/2010	20:10	-8.61	20.71	40.06	0.23
10/25/2010	14:15	-8.62	20.66	39.74	0.34
10/26/2010	10:10	-8.59	20.82	39.63	0.55
10/26/2010	14:30	-9.31	20.61	39.45	0.44
10/29/2010	0:20	-8.56	20.78	40.20	0.23
10/29/2010	3:10	-8.64	21.08	40.18	0.54
10/29/2010	9:00	-8.74	21.00	40.03	0.53
10/29/2010	12:45	-8.92	21.65	41.34	0.51
10/29/2010	19:20	-9.26	20.56	39.83	0.20
11/19/2010	11:00	-8.64	20.54	39.62	0.28
11/19/2010	20:30	-8.68	20.71	39.85	0.33
11/20/2010	0:35	-10.38	20.16	38.79	0.32
11/20/2010	14:25	-8.47	21.35	40.83	0.48
11/22/2010	10:15	-8.44	20.88	40.11	0.37
11/22/2010	17:45	-9.35	20.51	39.35	0.38
11/22/2010	21:40	-9.61	20.24	39.22	0.19
11/22/2010	23:50	-8.58	21.21	40.47	0.51
12/1/2010	17:20	-8.50	21.40	40.62	0.63
12/2/2010	9:30	-12.43	20.22	38.67	0.44
12/27/2010	20:50	-9.47	21.00	40.40	0.35
12/28/2010	0:30	-10.07	21.38	40.47	0.68
12/28/2010	17:30	-10.95	20.62	39.73	0.30
12/29/2010	10:10	-8.61	21.50	40.75	0.66
12/29/2010	17:00	-8.71	21.43	41.40	0.27
12/29/2010	21:05	-10.70	21.12	40.24	0.54
1/18/2011	11:00	-9.55	20.75	39.65	0.47
5/15/2011	19:15	-9.40	21.17	40.60	0.42
5/17/2011	12:50	-8.47	21.65	41.19	0.59
5/25/2011	14:15	-10.29	21.18	40.61	0.42
6/3/2011	14:05	-9.91	20.77	39.68	0.48
7/14/2011	11:50	-8.96	21.47	40.74	0.64
10/27/2011	20:10	-9.09	21.64	41.11	0.62
3/28/2011	21:15	-9.14	21.30	40.83	0.42
3/29/2011	19:05	-8.91	21.35	41.14	0.33
10/11/2012	14:40	-8.30	21.49	40.99	0.53
10/12/2012	15:00	-8.19	21.43	41.45	0.25
10/13/2012	12:00	-8.37	21.36	41.26	0.27
10/15/2012	11:20	-8.31	21.54	41.33	0.42
10/16/2012	15:00	-8.37	21.36	41.12	0.34
11/21/2012	11:00	-10.55	20.89	39.65	0.61
11/21/2012	17:30	-10.57	20.77	39.64	0.49
11/22/2012	12:00	-9.23	20.96	40.18	0.42
11/28/2012	10:45	-9.04	20.93	40.37	0.29
12/4/2012	10:50	-8.76	21.23	40.81	0.37
12/4/2012	16:45	-8.76	21.16	40.85	0.27
12/6/2012	11:00	-8.45	21.43	41.01	0.46
12/6/2012	17:15	-8.64	21.57	41.20	0.50
12/7/2012	11:00	-8.20	21.48	40.85	0.60
12/7/2012	17:30	-8.83	21.51	41.04	0.53
12/14/2012	12:30	-8.46	21.21	41.08	0.21
2/12/2013	10:15	-10.79	20.48	39.76	0.16
Mean		**-9.13**	**21.07**	**40.38**	**0.42**
Stdev		**0.87**	**0.40**	**0.70**	**0.14**

Despite the good progress made in monitoring the trends in the carbon cycle and understanding their drivers,

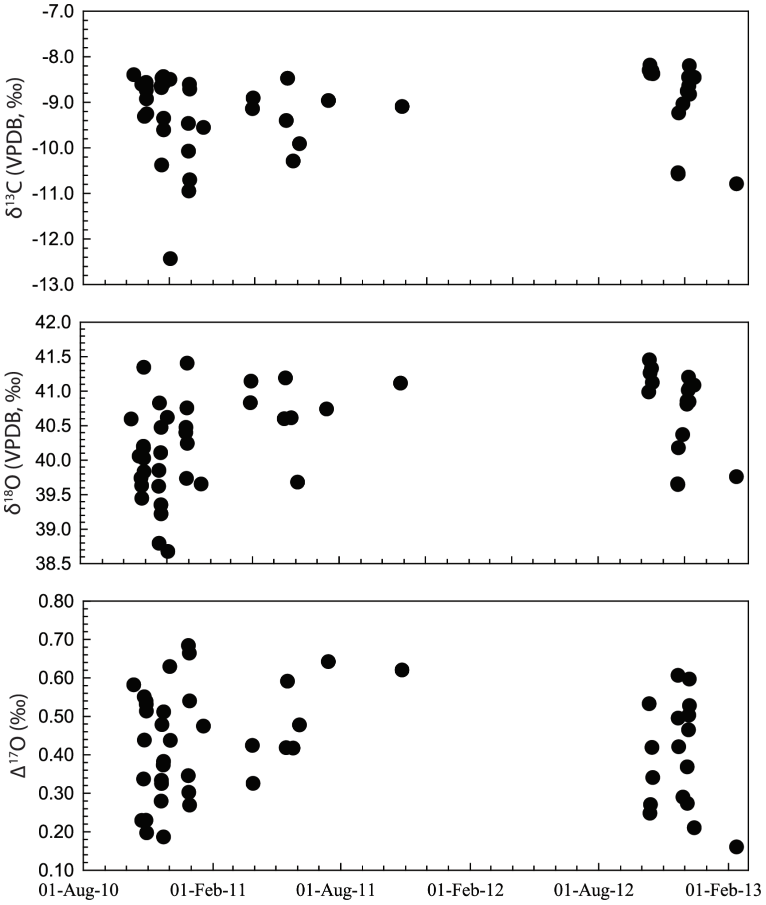

Fig. 2. Time series of $\delta^{13}C$, $\delta^{18}O$, and $\Delta^{17}O$ values obtained during the study period.

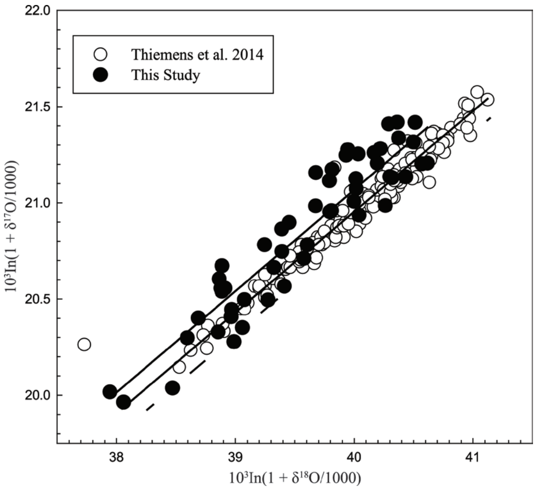

Fig. 3. Triple isotope plot of oxygen of tropospheric CO_2 showing data from this work (filled symbols) and Thiemens et al. (2014) (open symbols fitted with line: slope = 0.523). The terrestrial fractionation line (TFL; slope = 0.516) and the linear fit (slope = 0.527 ± 0.03) to the present data are shown by the dashed and solid lines, respectively.

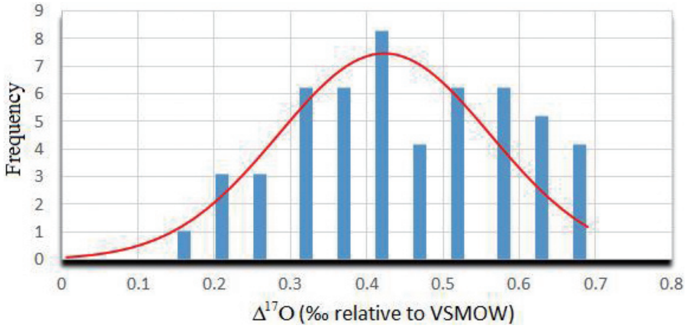

Fig. 4. A plot of the sample frequency against $\Delta^{17}O$ values of CO_2 (in ‰ relative to VSMOW) with superimposed normal distribution (red curve) fitted to the data. A few samples have high $\Delta^{17}O$ values above the normal curve. These samples probably indicate stratospheric air incursion with high $\Delta^{17}O$ values. (Color online only)

questions remain about accurate quantitative fluxes across the sources and sinks of CO_2. The observed hemispheric gradient was shown to be due to the seasonal exchange with land biota which implies a larger sink of CO_2 in the northern hemisphere (Tans et al. 1990; Denning et al. 1995). Recently, moderate North American carbon sinks have been suggested and is estimated to be 0.65 $PgCy^{-1}$ (Peters et al. 2007). Better constraints could be obtained using $\Delta^{17}O$ value measurements of atmospheric CO_2.

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