Supplement of

Clumped isotopes in near surface atmospheric CO_2 over land, coast and ocean in Taiwan and its vicinity

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S1. Nonlinearity in the mass spectrometer

Clumped isotope measurements are affected nonlinearly in the mass spectrometer; there is significant difference between the measured and actual R^{47} values. Though the reason for this remains unclear, it can be corrected empirically. The correction is done with a CO_2 gas by varying its δ^{47} composition and by establishing a relation between δ^{47} and Δ_{47} of the CO_2 at a given temperature. δ^{47} is basically the sum of δ^{45} and δ^{46} or $\delta^{13}C$ and $\delta^{18}O$ measured with respect to the working reference gas. Figure S1 shows the plots between δ^{47} and Δ_{47} at temperatures of 17, 32 and 1000 ^{o}C, with a wide range of δ^{47} values (measured against the same working reference gas). The variation in δ^{47} is artificially made by equilibrating the cylinder CO_2 (AS-2: see the main text for detail) with water having $\delta^{18}O$ values of -106‰, -25‰, and +22 ‰. A slightly negative slope (-0.0017‰/‰) is observed in the linear regression fits (Figure S1). Nonlinearity corrections in Δ_{47} values of the sample CO_2 are made by this slope assuming true Δ_{47} values corresponding to δ^{47}=0 (Dennis et al., 2011). Δ_{47} value corresponding to δ^{47}=0 for a sample is obtained using the relation $\Delta_{47\text{-}0} = \Delta_{47(ms)} + \delta^{47}.(-0.0017)$, where $\Delta_{47(ms)}$ is the Δ_{47} value observed from the mass spectrometer. This value is then expressed in Absolute Reference Frame (ARF) using an empirical transfer function (Dennis et al., 2011). The empirical transfer function for the present case is $\Delta_{47\text{-}ARF} = 1.0996\Delta_{47\text{-}[EGvsWG]0} + 0.9145$, where $\Delta_{47\text{-}[EGvsWG]0}$ is the Δ_{47} value of the equilibrated CO_2 corresponding to δ^{47}=0 at any given temperature as shown in Figure S1. This function is established plotting the $\Delta_{47\text{-}[EGvsWG]0}$ values obtained at three different temperatures (Figures S1) against that predicted theoretically at the same temperatures. The sample Δ_{47} value is expressed in ARF using the relation $\Delta_{47\text{-}ARF} = 1.0996\Delta_{47\text{-}0} + 0.9145$. As the dependence of Δ_{47} on δ^{47} is small, no pressure baseline correction is applied (He et al., 2012). We monitor the pressure baseline with and without CO_2 in the mass spectrometer during analysis period. Without CO_2 in the mass spectrometer the signal for mass 47 is ~5 mV and when CO_2 is introduced into the mass spectrometer, the pressure background for mass 47 reduces to -6 to -8 mV and -0.2 to -0.5 mV, respectively, right before and after the appearance of the peak. This reduction happens for signal voltage of ~12000 mV for mass 44. As the drop in the background signal on the introduction of CO_2 is much less compared to the actual signal of mass 47, we do not apply pressure baseline correction.

S2. Error and reproducibility

The reproducibility of Δ_{47} for air CO_2 was checked using three aliquots of air collected from a compressed air cylinder (40 L cylinder at a pressure of ~2000 psi). The [CO_2] inside the cylinder was 387.7 ppm. CO_2 was extracted following standard cryogenic technique with GC cleaning discussed in the main text. The standard deviations for three measurements were 0.07, 0.08, and 0.01‰ for $\delta^{13}C$, $\delta^{18}O$, and Δ_{47}, respectively (Table S1). The accuracy of Δ_{47} for air CO_2 could not be checked due to lack of air standards. We checked accuracy with AS-2 CO_2 by equilibrating it with waters at different $\delta^{18}O$, viz., -106‰, -25‰, and +22 ‰ at 15 °C and 25 °C. The results are summarized in Table S2.

S3. Cleaning of CO_2 using Gas Chromatography

The separation of the CO_2 from other trace gas species, condensable at liquid nitrogen temperature (mostly N_2O and CH_4), was carried out using a home-made gas chromatography (GC) column (Porapak Q 80/100 mesh, 3.0m 0.3cm stainless steel, supplied by Supelco Analytical, Bellefonte, PA, USA) (Mahata et a., 2012) kept at -10 °C. The carrier gas was helium, the flow rate of which was maintained at 20 mL/min using a mass flow controller. Cleaned CO_2 after passing through the GC column was trapped at liquid nitrogen temperature in a stainless steel spiral tube of 1/8″ diameter. The performance of GC was checked with various proportions of CO_2 and N_2O and at different temperatures (25 to -20 °C). The GC column temperature and carrier gas flow rate were found to be optimal at -10 °C and 20 mL/min, respectively. Figure S2 shows a Thermal Conductor Detector (TCD) chromatogram at -10 °C for an artificially prepared mixture 54 μmole CO_2 and 45 μmole N_2O. The two peaks are well separated even for a high N_2O content. In reality the N_2O content is very less (<1 ppmv), the separation would be much better than that shown here.

S4. Local meteorological parameters

Table S3 shows Δ_{47} values along with the local meteorological parameters for the sub-urban and coastal stations. This is to check the effect of wind speed and direction on the Δ_{47} values of air CO_2. Meteorological parameters are taken from the nearest weather stations, Nankang (station code: C0A9G0; 25°03′27″ N, 121°35′41″ E, 42 m a.s.l.) and Keelung (station code: 466940; 25°08′05″ N, 121°43′56″ E, 26.7 m a.s.l.). Most of the time of the post summer and winter, Academia Sinica campus observes easterly and north-easterly winds, except in some days on which south-easterly and southerly winds are also observed. In the coastal station the winds are mainly northerly and north-easterly during the sampling period.

S5. Correction in Δ_{47} due to contribution from fossil fuel combustion

We estimated the contribution in Δ_{47} of air CO_2 from the fossil fuel combusted CO_2 in the urban and sub-urban station, i.e., Roosevelt Road and Academia Sinica Campus (Section 4.4). Table S4 shows the average Δ_{47} values observed at the two sites and compared to the expected Δ_{47} values considering air CO_2 is a mixture of two components, viz., background CO_2 and vehicle emitted CO_2. The observed Δ_{47} value at the urban street is similar to that obtained from the mixing of the two components while it significantly lower in the sub-urban site.

Figures

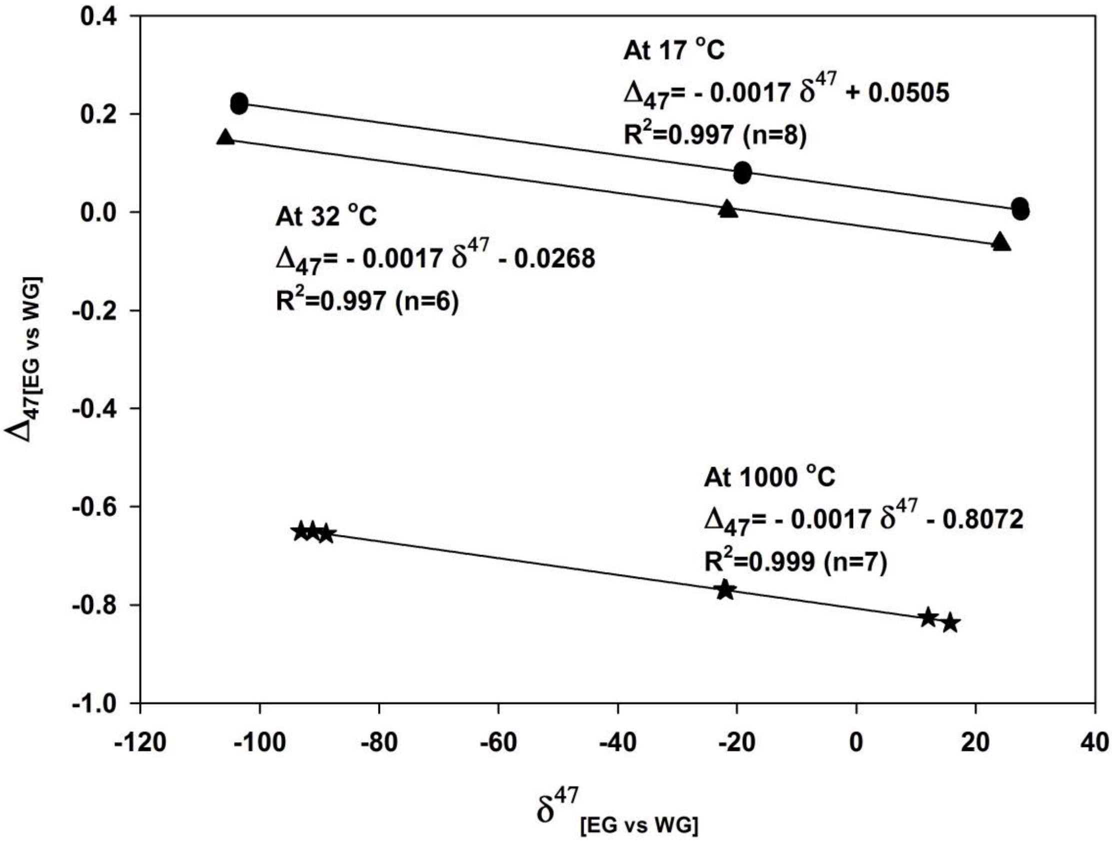

Figure S1. Least-squared linear regression for water-equilibrated and heated gases at 17 °C, 32 °C, and 1000 °C.

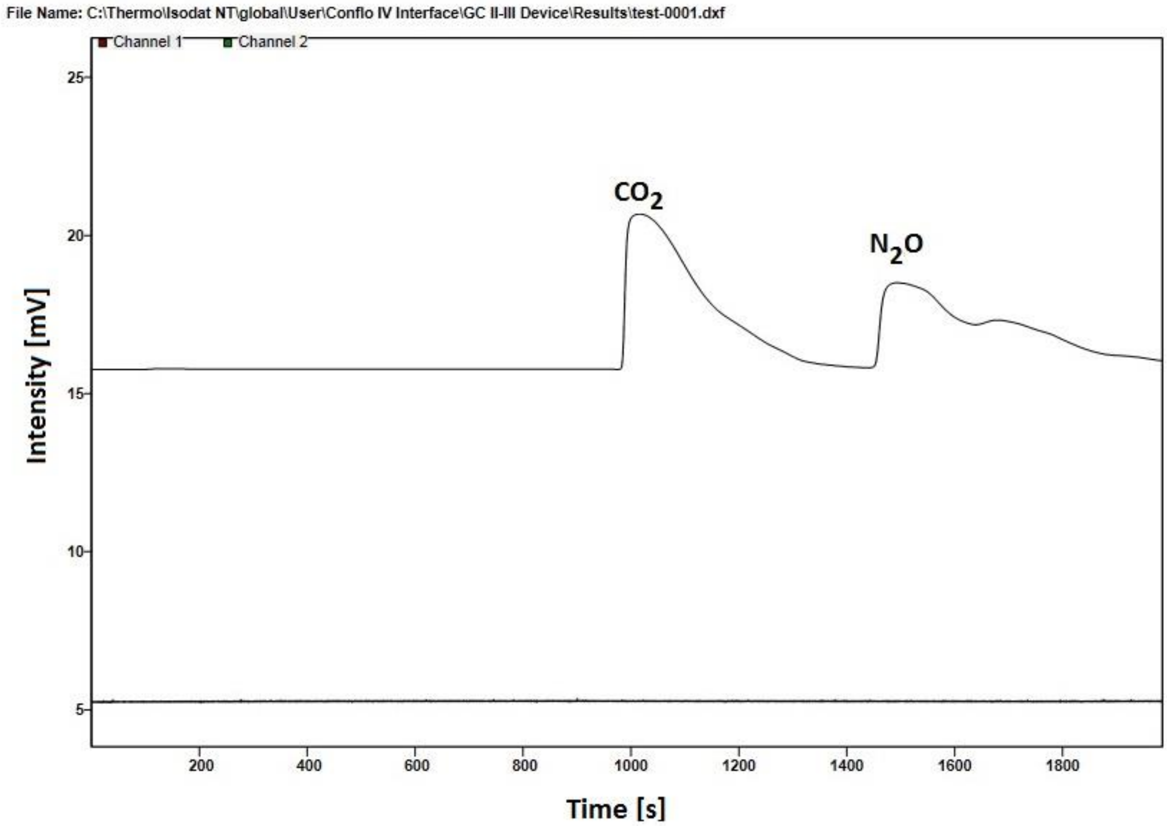

Figure S2. Thermal Conductor Detector (TCD) signals for a mixture of CO_2 and N_2O (54:45 each in µmol).

Table S1. Reproducibility of stable isotope analysis including Δ_{47} from three aliquots of air CO_2 extracted from a compressed air cylinder.

Sl.No.	$\delta^{13}C$(‰) (VPDB)	$\delta^{18}O$ (‰) (VSMOW)	δ^{47}(‰)	Std. Err.	Δ_{47}(‰) (ARF)	Std. Err
1	-8.37	25.51	13.03	0.02	0.8737	0.007
2	-8.44	25.71	13.18	0.02	0.8557	0.014
3	-8.54	25.56	12.85	0.02	0.8489	0.012
Average	-8.45	25.60	13.02		0.859	
Std. dev.	0.07	0.08	0.14		0.010	
Std. Err.	0.04	0.05	0.07		0.006	

Table S2. Clump and bulk isotopes and temperature estimated from Δ_{47} values for AS-2 cylinder CO_2 equilibrated at 25±2 ^{o}C and 15±2 ^{o}C with waters of different δ^{18}O values.

Sl. No.	δ^{13}C(‰) (VPDB)	δ^{18}O(‰) (VSMOW)	δ^{47}(‰)	Std. Err.	Δ_{47} (ARF)	Std. Err	Δ_{47} Temp. (^{o}C)
At 25±2 ^{o}C, $\delta^{18}O_{water}$ ~ 0‰							
1	-32.59	41.26	-12.35	0.02	0.923	0.016	25
2	-32.53	41.17	-12.39	0.02	0.926	0.017	25
At 25±2 ^{o}C, $\delta^{18}O_{water}$ ~ -8‰							
3	-32.68	33.93	-2.91	0.02	0.929	0.015	24
4	-32.54	34.11	-2.60	0.01	0.923	0.010	25
At 15±2 ^{o}C, $\delta^{18}O_{water}$ ~ -25‰ and 22‰							
5	-32.39	16.99	-19.12	0.01	0.962	0.012	18
6	-32.40	64.45	24.34	0.01	0.972	0.006	16

Table S3. Δ_{47} values along with the meteorological parameters (averaged over the sample collection duration) for semi-urban (Academia Sinica Campus) and Coastal (Keelung and Fuguei Cape) stations.

Date time	Δ_{47} (‰) (ARF)	Press. (mb)	Temp. (^{o}C)	RH (%)	Wind speed (m/s)	Wind direction (degree)
Academia Sinica Campus						
17/10/2013 10:00	0.893	1017	24	71	1.1	81
17/10/2013 14:30	0.883					
17/10/2013 17:20	0.89					
30/10/2013 10:00	0.878	1014	26	69	1.1	77
30/10/2013 14:30	0.887					
4/11/2013 10:30	0.89	1017	22	90	0.6	86
4/11/2013 14:30	0.881					
4/11/2013 18:30	0.885					
9/11/2013 10:30	0.912	1013	29	67	1.0	117
9/11/2013 14:00	0.914					
9/11/2013 18:30	0.918					
19/11/2013 10:00	0.923	1020	19	50	0.9	89
19/11/2013 14:00	0.912					
19/11/2013 18:00	0.888					
27/01/2014 10:30	0.894	1018	19	60	1.6	82
27/01/2014 15:20	0.91					
27/01/2014 18:00	0.896					

3/02/2014 11:00	0.954	1007	23	69	1.5	195
3/02/2014 14:30	NA					
3/02/2014 19:30	0.962					
17/02/2014 10:30	0.875	1015	22	68	0.5	131
17/02/2014 14:30	0.892					
17/02/2014 18:30	0.889					
19/02/2014 10:00	0.892	1017	13	89	0.4	113
19/02/2014 18:00	0.892					
20/02/2014 14:30	0.863	1024	13	57	0.8	39
20/02/2014 18:00	0.86					
22/02/2014 12:15	0.869	1020	19	72	0.8	70
22/02/2014 17:00	0.85					
24/02/2014 17:30	0.859	1016	24	53	1.2	203
Keelung coast						
3/10/2013 11:30	0.896	1011	24	70	7.7	13
3/10/2013 12:30	0.917					
13/11/2013 11:00	0.946	1014	19	91	5.3	51
21/11/2013 12:30	0.890	1017	21	72	1.8	60
28/11/2013 12:00	0.908	1022	14	66	7.2	12
Fuguei Cape coast						
13/11/2013 13:30	0.916	1014	19	91	5.3	51
21/11/2013 15:30	0.880	1017	21	72	1.8	60
28/11/2013 15:00	0.886	1022	14	66	7.2	12

Table S4. Average Δ_{47} value in air CO_2 at Roosevelt Road (urban) and Academia Sinica Campus (sub-urban) and that expected assuming mixtures of background and anthropogenic CO_2.

Sampling location	Average Δ_{47} (ARF)	CO_2 Conc. (ppmv)	Expected Δ_{47} (ARF)*	Difference $\Delta_{47}^{\dagger}$
Roosevelt Road	0.807	500	0.798	0.009
Academia Sinica Campus	0.897	411	0.923	0.026

*Linear summation of the equilibrium Δ_{47} values of background air (395 ppmv) and car exhaust.

†Difference between the expected and observed Δ_{47} values assuming air CO_2 as a mixture of background and car exhaust CO_2. Δ_{47} value of car exhaust CO_2 was taken to be 0.273‰ (see Table 2 in main text).

References

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