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 $\delta^{47}$ composition and by establishing a relation between $\delta^{47}$ and $\Delta_{47}$ of the CO$_2$ at a given temperature. $\delta^{47}$ is basically the sum of $\delta^{45}$ and $\delta^{46}$ or $\delta^{13}$C and $\delta^{18}$O measured with respect to the working reference gas. Figure S1 shows the plots between $\delta^{47}$ and $\Delta_{47}$ at temperatures of 17, 32 and 1000 °C, with a wide range of $\delta^{47}$ values (measured against the same working reference gas). The variation in $\delta^{47}$ 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 $\Delta_{47}$ values of the sample CO$_2$ are made by this slope assuming true $\Delta_{47}$ values corresponding to $\delta^{47}$=0 (Dennis et al., 2011). $\Delta_{47}$ value corresponding to $\delta^{47}$=0 for a sample is obtained using the relation $\Delta_{47,0} = \Delta_{47,(ms)} + \delta^{47} \cdot (-0.0017)$, where $\Delta_{47,(ms)}$ is the $\Delta_{47}$ 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 $\Delta_{47,ARF} = 1.0996 \Delta_{47,\text{EGvsWG}0} + 0.9145$, where $\Delta_{47,\text{EGvsWG}0}$ is the $\Delta_{47}$ value of the equilibrated CO$_2$ corresponding to $\delta^{47}$=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 $\Delta_{47}$ value is expressed in ARF using the relation $\Delta_{47,ARF} = 1.0996 \Delta_{47,0} + 0.9145$. As the dependence of $\Delta_{47}$ on $\delta^{47}$ 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 $\Delta_{47}$ 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 $\Delta_{47}$, respectively (Table S1). The accuracy of $\Delta_{47}$ 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$_2$O 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 al., 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$_2$O 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$_2$O. The two peaks are well separated even for a high N$_2$O content. In reality the N$_2$O content is very less (<1 ppmv), the separation would be much better than that shown here.

S4. Local meteorological parameters

Table S3 shows $\Delta_{47}$ 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 $\Delta_{47}$ 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 $\Delta_{47}$ due to contribution from fossil fuel combustion
We estimated the contribution in $\Delta_{47}$ 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 $\Delta_{47}$ values observed at the two sites and compared to the expected $\Delta_{47}$ values considering air CO$_2$ is a mixture of two components, viz., background CO$_2$ and vehicle emitted CO$_2$. The observed $\Delta_{47}$ 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.
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$_2$O (54:45 each in µmol).

Table S1. Reproducibility of stable isotope analysis including $\Delta_{47}$ from three aliquots of air CO$_2$ extracted from a compressed air cylinder.

<table>
<thead>
<tr>
<th>Sl.No.</th>
<th>$\delta^{13}$C(‰) (VPDB)</th>
<th>$\delta^{18}$O (‰) (VSMOW)</th>
<th>$\delta^{47}$ (‰)</th>
<th>Std. Err.</th>
<th>$\Delta_{47}$(‰) (ARF)</th>
<th>Std. Err</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-8.37</td>
<td>25.51</td>
<td>13.03</td>
<td>0.02</td>
<td>0.8737</td>
<td>0.007</td>
</tr>
<tr>
<td>2</td>
<td>-8.44</td>
<td>25.71</td>
<td>13.18</td>
<td>0.02</td>
<td>0.8557</td>
<td>0.014</td>
</tr>
<tr>
<td>3</td>
<td>-8.54</td>
<td>25.56</td>
<td>12.85</td>
<td>0.02</td>
<td>0.8489</td>
<td>0.012</td>
</tr>
<tr>
<td>Ave.</td>
<td>-8.45</td>
<td>25.60</td>
<td>13.02</td>
<td></td>
<td>0.859</td>
<td></td>
</tr>
<tr>
<td>Std. dev.</td>
<td>0.07</td>
<td>0.08</td>
<td>0.14</td>
<td></td>
<td>0.010</td>
<td></td>
</tr>
<tr>
<td>Std. Err</td>
<td>0.04</td>
<td>0.05</td>
<td>0.07</td>
<td></td>
<td>0.006</td>
<td></td>
</tr>
</tbody>
</table>
Table S2. Clump and bulk isotopes and temperature estimated from $\Delta_{47}$ values for AS-2 cylinder CO$_2$ equilibrated at 25±2 °C and 15±2 °C with waters of different $\delta^{18}$O values.

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>$\delta^{13}$C(‰) (VPDB)</th>
<th>$\delta^{18}$O(‰) (VSMOW)</th>
<th>$\delta^{47}$(‰)</th>
<th>Std. Err.</th>
<th>$\Delta_{47}$ (ARF)</th>
<th>Std. Err</th>
<th>$\Delta_{47}$ Temp. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-32.59</td>
<td>41.26</td>
<td>-12.35</td>
<td>0.02</td>
<td>0.923</td>
<td>0.016</td>
<td>25</td>
</tr>
<tr>
<td>2</td>
<td>-32.53</td>
<td>41.17</td>
<td>-12.39</td>
<td>0.02</td>
<td>0.926</td>
<td>0.017</td>
<td>25</td>
</tr>
<tr>
<td>3</td>
<td>-32.68</td>
<td>33.93</td>
<td>-2.91</td>
<td>0.02</td>
<td>0.929</td>
<td>0.015</td>
<td>24</td>
</tr>
<tr>
<td>4</td>
<td>-32.54</td>
<td>34.11</td>
<td>-2.60</td>
<td>0.01</td>
<td>0.923</td>
<td>0.010</td>
<td>25</td>
</tr>
<tr>
<td>5</td>
<td>-32.39</td>
<td>16.99</td>
<td>-19.12</td>
<td>0.01</td>
<td>0.962</td>
<td>0.012</td>
<td>18</td>
</tr>
<tr>
<td>6</td>
<td>-32.40</td>
<td>64.45</td>
<td>24.34</td>
<td>0.01</td>
<td>0.972</td>
<td>0.006</td>
<td>16</td>
</tr>
</tbody>
</table>

At 25±2 °C, $\delta^{18}$O$_{water} \sim 0$‰

At 25±2 °C, $\delta^{18}$O$_{water} \sim -8$‰

At 15±2 °C, $\delta^{18}$O$_{water} \sim -25$‰ and 22‰

Table S3. $\Delta_{47}$ 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.

<table>
<thead>
<tr>
<th>Date time</th>
<th>$\Delta_{47}$ (%) (ARF)</th>
<th>Press. (mb)</th>
<th>Temp. (°C)</th>
<th>RH (%)</th>
<th>Wind speed (m/s)</th>
<th>Wind direction (degree)</th>
</tr>
</thead>
<tbody>
<tr>
<td>17/10/2013 10:00</td>
<td>0.893</td>
<td>1017</td>
<td>24</td>
<td>71</td>
<td>1.1</td>
<td>81</td>
</tr>
<tr>
<td>17/10/2013 14:30</td>
<td>0.883</td>
<td>1014</td>
<td>26</td>
<td>69</td>
<td>1.1</td>
<td>77</td>
</tr>
<tr>
<td>17/10/2013 17:20</td>
<td>0.89</td>
<td>1014</td>
<td>26</td>
<td>69</td>
<td>1.1</td>
<td>77</td>
</tr>
<tr>
<td>30/10/2013 10:00</td>
<td>0.878</td>
<td>1017</td>
<td>22</td>
<td>90</td>
<td>0.6</td>
<td>86</td>
</tr>
<tr>
<td>30/10/2013 14:30</td>
<td>0.887</td>
<td>1017</td>
<td>22</td>
<td>90</td>
<td>0.6</td>
<td>86</td>
</tr>
<tr>
<td>4/11/2013 10:30</td>
<td>0.89</td>
<td>1014</td>
<td>29</td>
<td>67</td>
<td>1.0</td>
<td>117</td>
</tr>
<tr>
<td>9/11/2013 10:30</td>
<td>0.912</td>
<td>1017</td>
<td>22</td>
<td>90</td>
<td>0.6</td>
<td>86</td>
</tr>
<tr>
<td>9/11/2013 14:00</td>
<td>0.914</td>
<td>1013</td>
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<td>67</td>
<td>1.0</td>
<td>117</td>
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<td>9/11/2013 18:30</td>
<td>0.918</td>
<td>1014</td>
<td>22</td>
<td>90</td>
<td>0.6</td>
<td>86</td>
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<tr>
<td>19/11/2013 10:00</td>
<td>0.923</td>
<td>1020</td>
<td>19</td>
<td>50</td>
<td>0.9</td>
<td>89</td>
</tr>
<tr>
<td>9/11/2013 14:00</td>
<td>0.912</td>
<td>1017</td>
<td>22</td>
<td>90</td>
<td>0.6</td>
<td>86</td>
</tr>
<tr>
<td>9/11/2013 18:00</td>
<td>0.888</td>
<td>1017</td>
<td>22</td>
<td>90</td>
<td>0.6</td>
<td>86</td>
</tr>
<tr>
<td>27/01/2014 10:30</td>
<td>0.894</td>
<td>1018</td>
<td>19</td>
<td>60</td>
<td>1.6</td>
<td>82</td>
</tr>
<tr>
<td>27/01/2014 15:20</td>
<td>0.91</td>
<td>1018</td>
<td>19</td>
<td>60</td>
<td>1.6</td>
<td>82</td>
</tr>
<tr>
<td>27/01/2014 18:00</td>
<td>0.896</td>
<td>1018</td>
<td>19</td>
<td>60</td>
<td>1.6</td>
<td>82</td>
</tr>
</tbody>
</table>
Table S4. Average $\Delta_{47}$ 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$_2$.

<table>
<thead>
<tr>
<th>Sampling location</th>
<th>Average $\Delta_{47}$ (ARF)</th>
<th>CO$_2$ Conc. (ppmv)</th>
<th>Expected $\Delta_{47}$ (ARF)*</th>
<th>Difference $\Delta_{47}$†</th>
</tr>
</thead>
<tbody>
<tr>
<td>Roosevelt Road</td>
<td>0.807</td>
<td>500</td>
<td>0.798</td>
<td>0.009</td>
</tr>
<tr>
<td>Academia Sinica Campus</td>
<td>0.897</td>
<td>411</td>
<td>0.923</td>
<td>0.026</td>
</tr>
</tbody>
</table>

*Linear summation of the equilibrium $\Delta_{47}$ values of background air (395 ppmv) and car exhaust.  
†Difference between the expected and observed $\Delta_{47}$ values assuming air CO$_2$ as a mixture of background and car exhaust CO$_2$. $\Delta_{47}$ value of car exhaust CO$_2$ was taken to be 0.273‰ (see Table 2 in main text).
References

