

## **A Clean Demonstration of Carbon-13 Isotope Depletion**

*The predictions of future rising temperatures and global warming have a key assumption that increasing atmospheric CO<sub>2</sub> comes entirely from the use of fossil fuels.*

*However an analysis of light and heavy CO<sub>2</sub> in the atmosphere, through measurements of the light (carbon-12) and heavy (carbon-13) isotopes of carbon, shows that this assumption may be too simple.*

*There are substantial periods when there is no change in the proportion of light to heavy CO<sub>2</sub> despite substantial fossil fuel emissions of light (carbon-12) CO<sub>2</sub> that would be expected to reduce the proportion of heavy (carbon-13) CO<sub>2</sub> in the atmosphere.*

*The largest reduction in the proportion of heavy (carbon-13) CO<sub>2</sub> occurs not where it would be expected at the latitudes with light (carbon-12) CO<sub>2</sub> fossil fuel emissions but further to the north.*

*The analysis shows that natural variability and in particular El Ninos may have a determining effect on the changing concentration and composition of CO<sub>2</sub> in the atmosphere not CO<sub>2</sub> emissions from fossil fuels.*

### **Introduction**

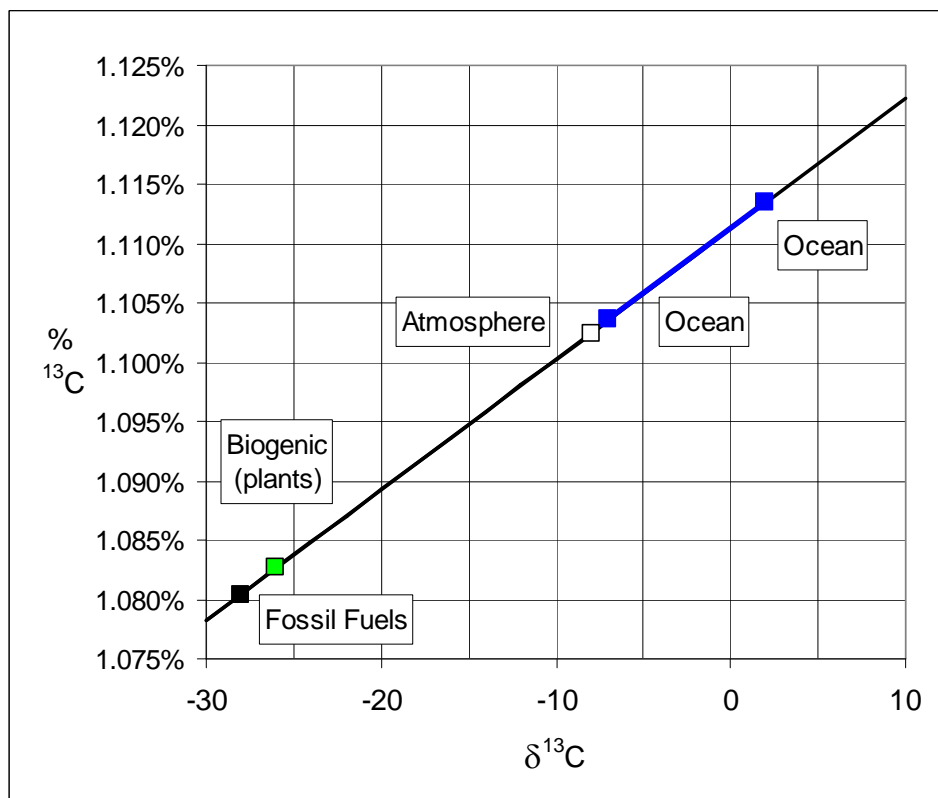
The variation in the relative amounts of CO<sub>2</sub> with carbon-12 and carbon-13 isotopes is a sensitive measure of changes in atmospheric CO<sub>2</sub>.

The chemical element carbon has two stable isotopes, Carbon-12 (<sup>12</sup>C) and Carbon-13 (<sup>13</sup>C). Both have 6 protons and six electrons but <sup>12</sup>C has six neutrons and <sup>13</sup>C has 7 neutrons. Thus <sup>13</sup>C is heavier than <sup>12</sup>C.

In general <sup>12</sup>C is 98.9% of natural carbon and <sup>13</sup>C 1.1%. However the rates at which chemical reactions and physical processes take place vary due to the masses of the isotopes. For carbon the result is fractionation of the isotopes. For instance in plant growth, the chemical reactions favour CO<sub>2</sub> with the light carbon isotope over the heavier isotope so that carbon found in plants has marginally less <sup>13</sup>C, in fact 1.083% <sup>13</sup>C, than the carbon in CO<sub>2</sub> in the atmosphere with 1.103% <sup>13</sup>C. This is a depletion of 0.020% <sup>13</sup>C. Fossil fuels, from decayed plant material, in particular coal, have a similar composition to plant material estimated to be 1.080% <sup>13</sup>C.

Extensive measurements of <sup>13</sup>C have been made alongside measurements of CO<sub>2</sub> concentration in the atmosphere. These measurements are expressed in units of δ<sup>13</sup>C which is related to the percentage of <sup>13</sup>C as shown in Figure 1. The 0.020% reduction in carbon passing from atmospheric CO<sub>2</sub> to plant material corresponds to a -20 unit change in δ<sup>13</sup>C.

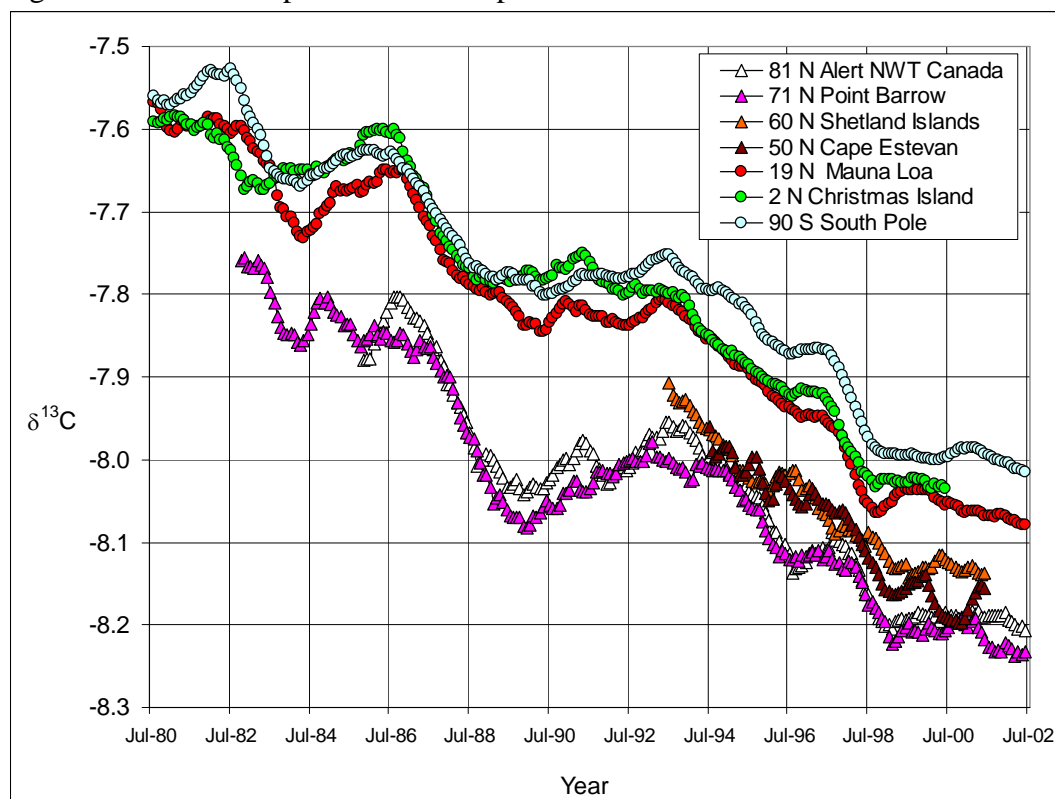
The measured values of δ<sup>13</sup>C can be divided as coming from two general sources of CO<sub>2</sub>, that from biogenic or fossil fuel sources with δ<sup>13</sup>C = -26 to -28 and from oceanic sources with δ<sup>13</sup>C = +2 to -7. Over time the atmosphere exchanges CO<sub>2</sub> with these sources and so has a δ<sup>13</sup>C determined by the magnitude of these exchanges.



**Figure 1** Relationship of % Carbon 13 ( $^{13}\text{C}$ ) in carbon to  $\delta^{13}\text{C}$ . Note the significant measured values.

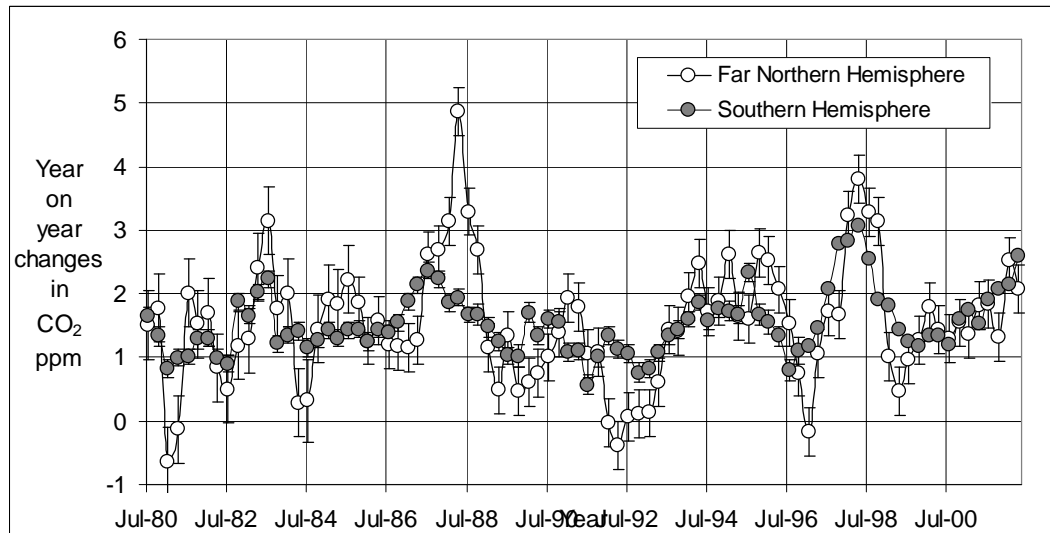
### Sources and Timing of Changes in $\text{CO}_2$ Composition

Figure 2 shows atmospheric  $\text{CO}_2$  isotope data with the seasonal variations removed.



**Figure 2**  $\delta^{13}\text{C}$  Measurements with seasonal variations removed.

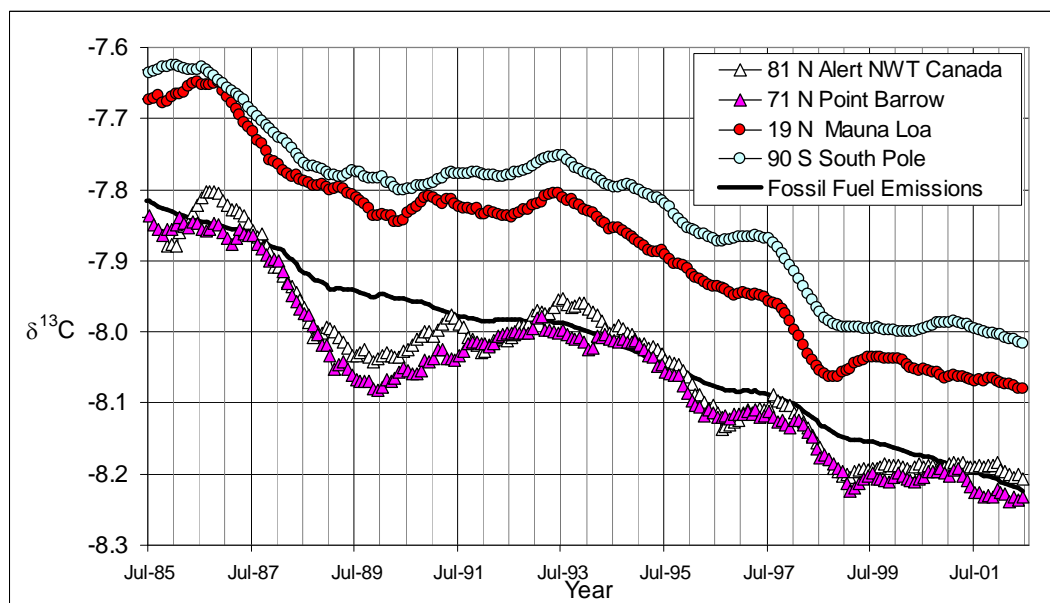
The El Nino periods are clearly identifiable at all stations despite a range of a factor of ten in seasonal variations (see Appendix).



**Figure 3** Year on year  $\text{CO}_2$  Measurements with seasonal variations removed. (SIO data)

Also there is a time delay for  $\delta^{13}\text{C}$  of about 5 months for the far north stations compared to the equatorial and southern regions. The delay is also present in the measurements of  $\text{CO}_2$  concentration in the atmosphere as shown in Figure 3.

These effects can be seen in greater detail in Figures 4 and 5 particularly for the 1987-88 and 1997-98 El Ninos.

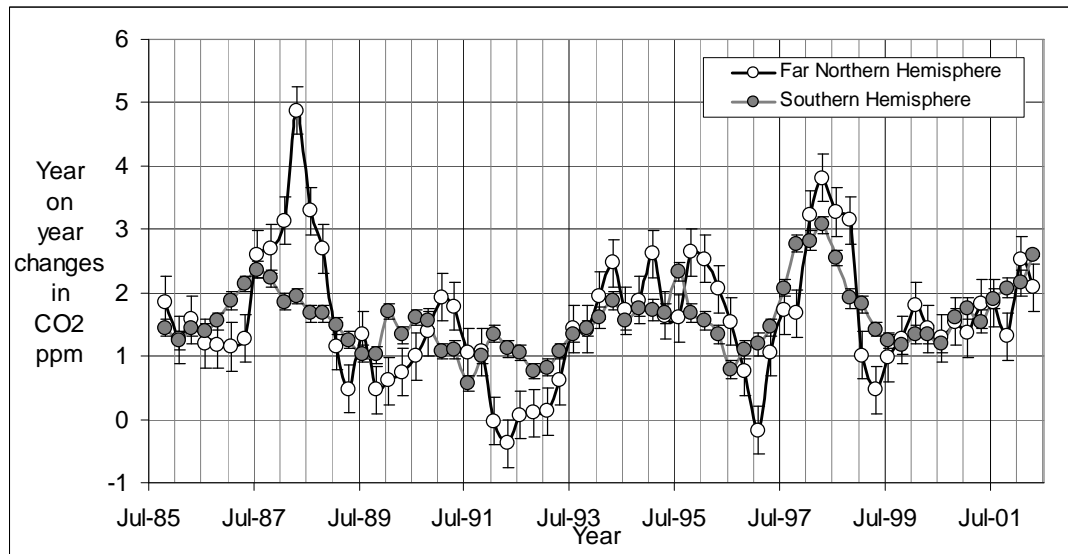


**Figure 4**  $\delta^{13}\text{C}$  Measurements with seasonal variations removed. The time delay in the far Northern Hemisphere is clearly visible as are periods with no significant change in  $\delta^{13}\text{C}$ . Contributions to the northern latitudes of fossil fuel emissions with  $\delta^{13}\text{C} = -26$  are calculated by adding the contributions in proportion to the monthly incremental increases of  $\text{CO}_2$ .

It is clear from measurements at Alert and Point Barrow that there are periods from 1989 to 1993, 1996 to 1998 and 1999 to 2002 where there is no change in isotopic composition. If fossil fuel emissions are responsible for increasing  $\text{CO}_2$  then a steady decrease in  $\delta^{13}\text{C}$  should have been seen at these times as the bulk of fossil fuel emissions occurs between latitudes  $30^\circ\text{N}$  and  $60^\circ\text{N}$  (see Figure 8). In Figure 4 the contributions to the northern latitudes from fossil fuel

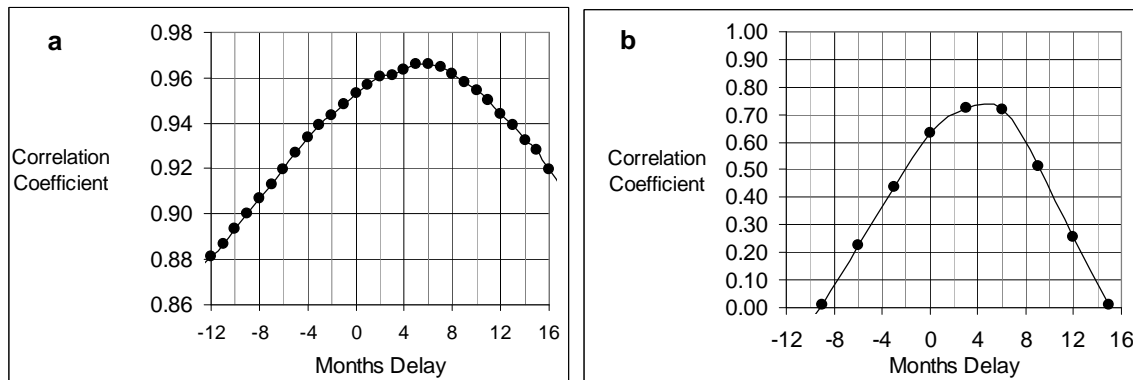
emissions with  $\delta^{13}\text{C} = -26$  have been calculated by adding the contributions in proportion to the monthly increases in  $\text{CO}_2$  (see the Appendix for a full explanation).

This analysis illustrates the dominance of El Nino processes



**Figure 5** Year on year  $\text{CO}_2$  Measurements with seasonal variations removed. The time delay in the far Northern Hemisphere is clearly visible. (SIO data)

The correlation coefficients have been calculated with changing time delay for the Southern Hemisphere (South Pole to Christmas Island) and the far Northern Hemisphere (Alert and Point Barrow). The maximum correlation occurs for a Southern Hemisphere delay of 5 months as shown in Figures 6a and 6b.

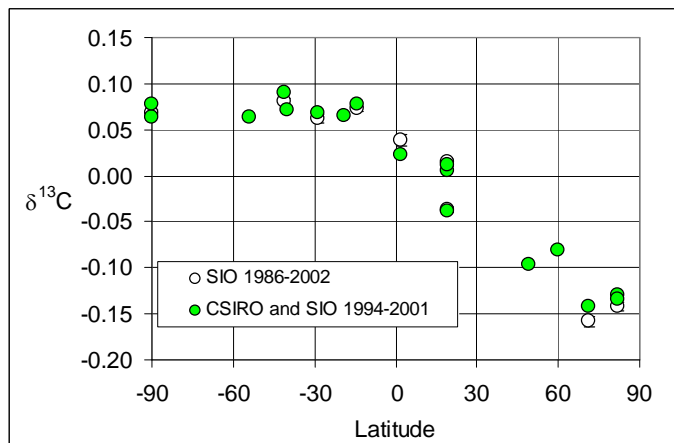


**Figure 6 a)**  $\delta^{13}\text{C}$  correlation and **b)**  $\text{CO}_2$  correlation of the Southern Hemisphere (South Pole to Christmas Island) delayed against the far Northern Hemisphere (Point Barrow and Alert). The far Northern Hemisphere changes occur some 5 months later than the changes in the Southern Hemisphere.

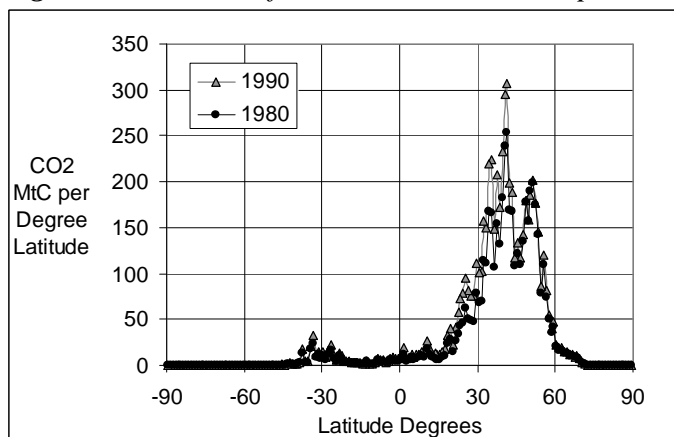
This is a strong indication that the changes in  $\delta^{13}\text{C}$  are driven by El Nino events.

### Location of Changes in $\text{CO}_2$ Composition

The annual variations in latitude can be seen by looking at the profile of each year against the mean value of all latitudes as shown in Figure 7. This indicates that the major source of the  $^{13}\text{C}$  isotope depletion comes from the far Northern Hemisphere. This is not the region of major  $\text{CO}_2$  emissions from fossil fuel as shown in Figure 8.



**Figure 7** Variation of  $\delta^{13}\text{C}$  with latitude compared to the yearly mean of all latitude values



**Figure 8** Estimated Atmospheric  $\text{CO}_2$  from fossil fuels. Source CDIAC

## Conclusion

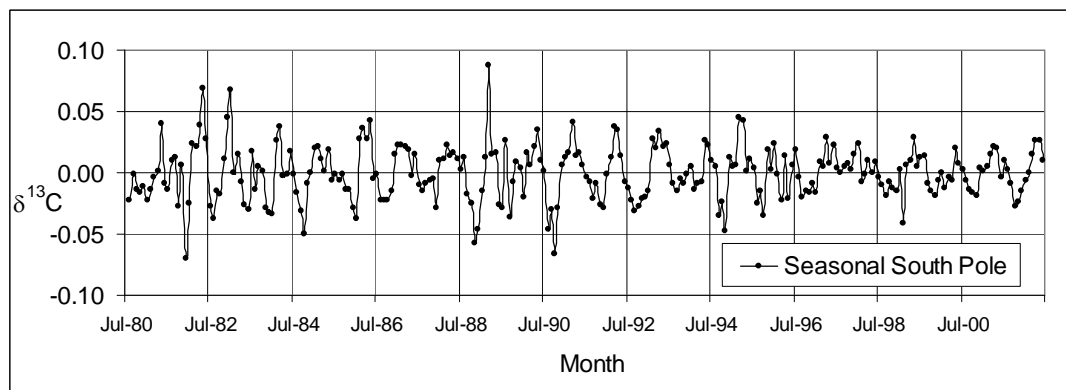
This analysis shows that the emissions of  $\text{CO}_2$  from fossil fuel are not the determining  $\text{CO}_2$  contribution for changes in the isotopic composition of atmospheric  $\text{CO}_2$ . There is a more complicated pattern of  $\text{CO}_2$  emissions.

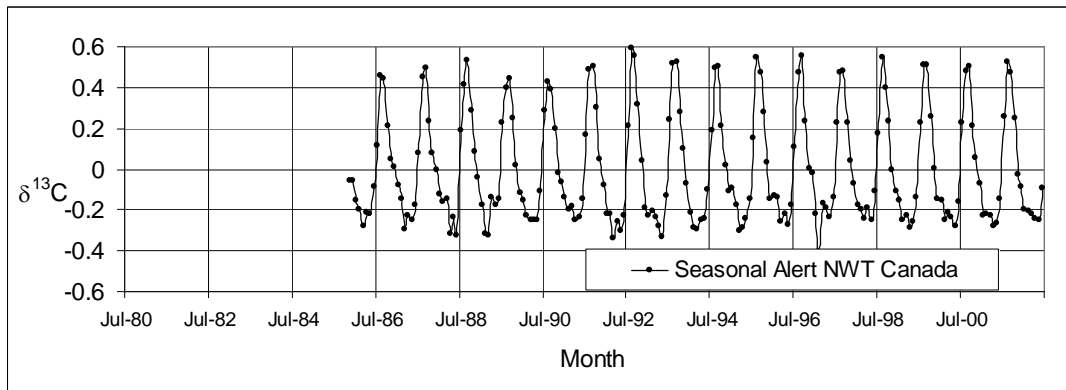
Tom Quirk

7 March 2009

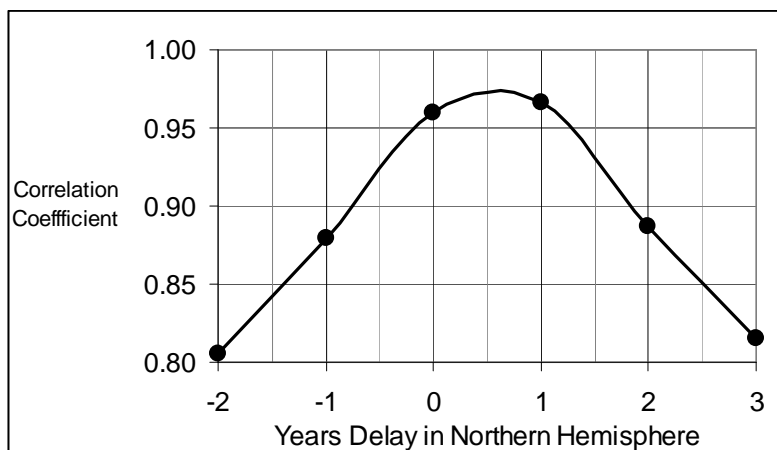
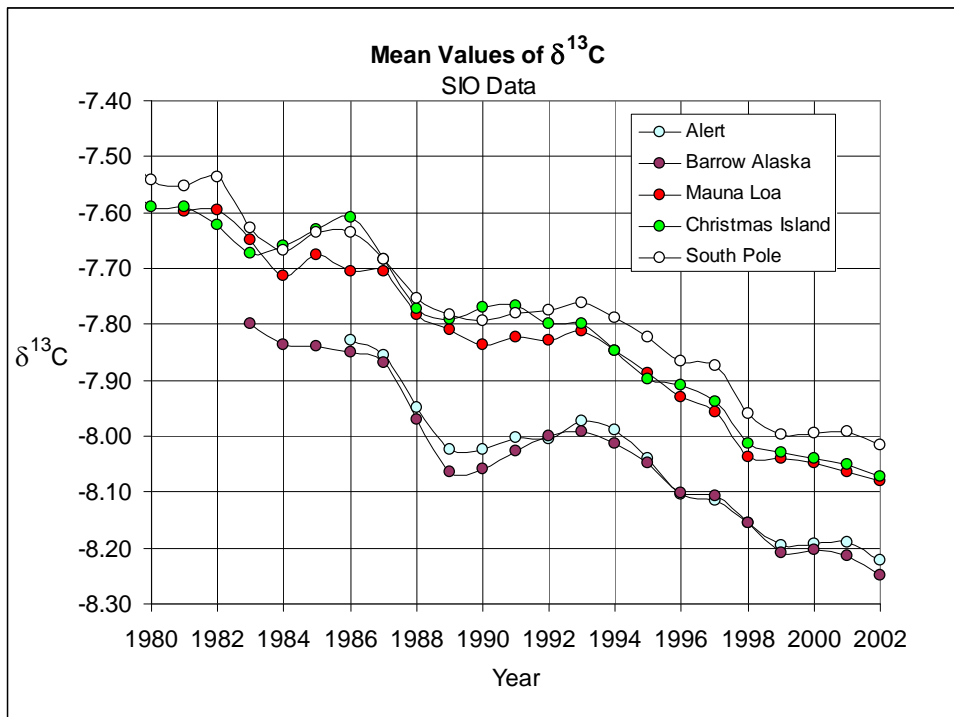
## APPENDIX

Note 1: The seasonal variations of the data set are very large as illustrated by the two stations shown below.





Note 2: As a check on the timing differences shown in the Figures 2 and 4, the mean annual values have been taken as calculated by SIO.



The data shows the same cascade pattern and the same time delay of the far Northern Hemisphere measurements as the extracted monthly values.

Note 3: Tom Quirk 2009 Sources and Sinks of CO<sub>2</sub> Energy & Environment 20, 1+2, pp 105-121.

Note 4: In Figure 4 the fossil fuel curve for the northern latitudes has been derived in the following way

The starting point for the time series is a measured  $\delta^{13}\text{C}$  and  $\text{CO}_2$  concentration in ppm. For each succeeding period the monthly increase in  $\text{CO}_2$  is added and an assumed  $\delta^{13}\text{C}$  for that increment. The weighted average for the end of the period is then calculated and the procedure repeated for the following periods:

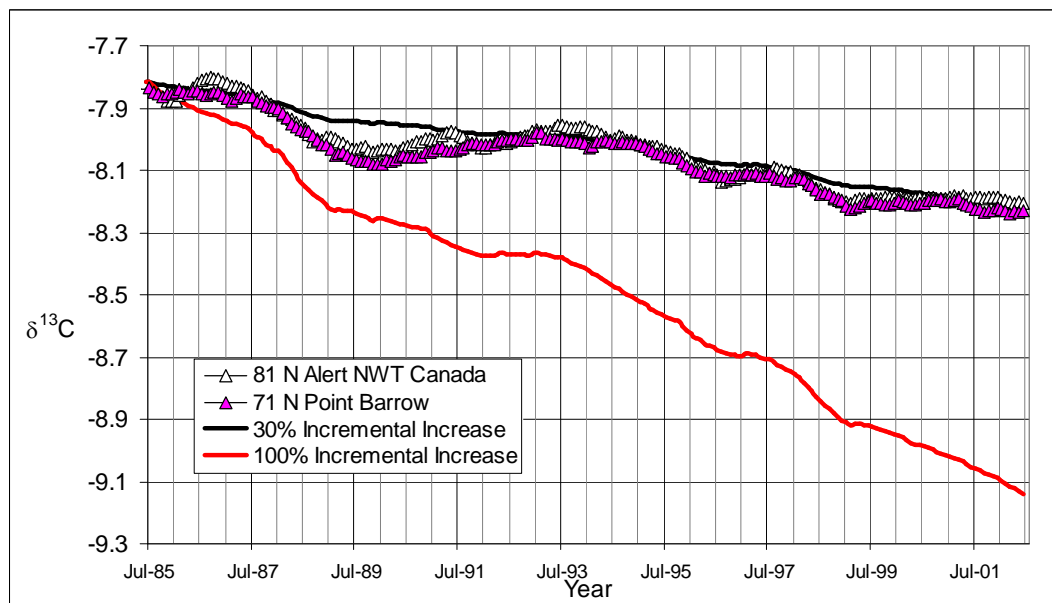
$$\text{CO}_2(i+1) = \text{CO}_2(i) + d\text{CO}_2(i)$$

$$\delta^{13}\text{C}(i+1) = [\delta^{13}\text{C}(i) \cdot \text{CO}_2(i) + \{(1-Y) \cdot \delta^{13}\text{C}(i) + Y \cdot \delta^{\text{ff}}\} \cdot d\text{CO}_2(i)] / \text{CO}_2(i+1)$$

where  $Y$  is the fraction of the monthly increment that comes from fossil fuels,  $\delta^{\text{ff}}$  is the value for  $\delta^{13}\text{C}$  from fossil fuels and  $d\text{CO}_2$  is the monthly increment in  $\text{CO}_2$ . If  $Y < 1$  the  $\delta^{13}\text{C}$  for the balance of  $d\text{CO}_2$  is assumed to be  $\delta^{13}\text{C}(i)$ .

As an example if  $Y = 1$  so all the incremental contribution is from fossil fuels then starting in June 1985 with  $\delta^{13}\text{C} = -7.815$  and  $\text{CO}_2 = 347.8$  ppm at the series end in June 2002  $\delta^{13}\text{C} = -9.138$  while the measured  $\delta^{13}\text{C} = -8.223$  with  $\text{CO}_2 = 375$  ppm. There is no agreement with  $\delta^{13}\text{C}$  measurements for the calculation as illustrated below

However if  $Y = 0.30$  then the time series final value matches the measured final  $\delta^{13}\text{C}$  as can be seen below..



This is the basis with assumptions for the calculation. The incremental additions are proportional to the incremental increases in  $\text{CO}_2$  as **high lighted** in the formula.

The calculation is intended to be an illustration that the derived values do not follow the measurements even after the best match to the data.