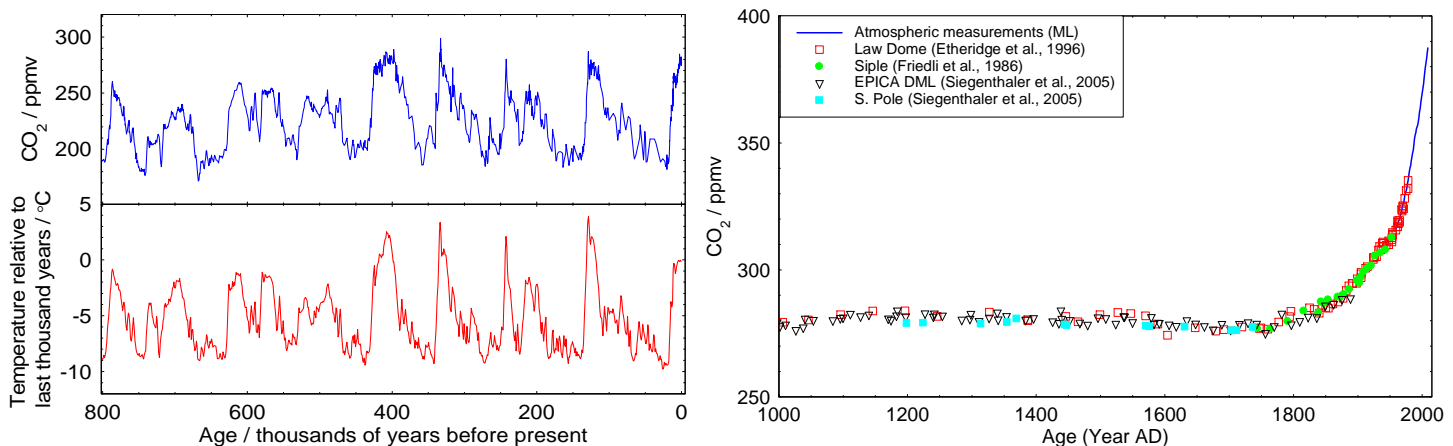


Ice core measurements of trace gases (prepared by Eric Wolff, 30/04/13)

At a CCfCS seminar on 22nd April 2013, Professor Murry Salby of Maquarie University made an unexpected “attack” on the integrity of ice core records of carbon dioxide (and probably methane, although he did not spell this out). I hesitate to summarise what he claimed for fear of misrepresenting him, but as far as I could tell, he used the recent (last few decades) measurements to deduce aspects of a relationship between CO₂ change and temperature, and then stated that what the ice cores show is inconsistent with this relationship. His deduction from that was that the ice core records must be wrong. He characterised it as ice core CO₂ not being conservative, and at one point as the CO₂ being smeared to produce the records we see over the last 800,000 years. He did not propose a mechanism by which either loss or production of CO₂ might have occurred, although he offered some hints when questioned. In this piece, I present the main evidence that the ice core record of CO₂ is a good representation of the past atmospheric concentration, and that the record is not consistent with the changes I think he believes must have occurred. I will also comment on the possible mechanisms he hinted at.

What the ice core record shows



The two most important data slides are here. On the right is CO₂ over the last 1000 years. The blue line is real atmospheric measurements (from Mauna Loa). The other data are from a range of Antarctic ice cores. This slide shows that CO₂ rose out of what had been a very small variability in about 1830. On the left is CO₂ over 800,000 years (Lüthi et al 2008) from the EPICA Dome C and Vostok ice cores. It can be seen that CO₂ varies closely with Antarctic temperature (based on measurements of the D/H ratio in Antarctic ice) across several glacial cycles. It always remained in the range 170-300 ppmv (compare the graph on the right and values in 2013 of about 395 ppmv).

How does the CO₂ record get trapped in ice?

As snow falls each year, layers of unconsolidated ice crystals build up to form the so-called “firn” column. At some depth (typically 60-100 m depending on site) metamorphosis and the weight of overlying snow sinter all the ice grains together to form an impermeable matrix. At this point bubbles of air are sealed off from the atmosphere in tiny (each bubble a few tenths of a mm across) ice containers. These bubbles should contain all stable components of air (N₂, O₂, Ar, CO₂, CH₄, etc.). Deeper down (typically 500-1000 m) the air molecules reach a pressure and temperature regime at

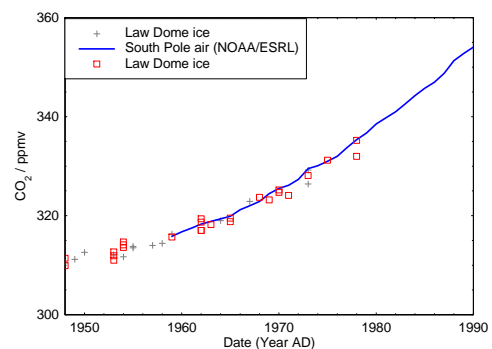
which air hydrates become stable. That means that below that depth, bubbles change to form clathrate hydrate crystals (gas molecules in a cage of water). The air can still be extracted from the clathrates although care must be taken, especially in the transition zone, as there can be fractionation between bubbles and clathrates (some molecules become clathrates at lower pressure than others). Note that CO₂ is always extracted from ice with dry extraction methods (cracking the bubbles open or sublimation), whereas some other gases can be measured with wet freeze/melt techniques.

The enclosure process does impose a natural temporal resolution on measurements: firstly because the firn air at the close-off depth is a diffusive mixture of air that was last at the surface up to a few decades earlier, and secondly because bubbles close over a range of depths (typically a 10 m range). That means that at sites with the highest snowfall rates (e.g. Law Dome, Antarctica), there is a natural resolution of order 10 years, while at sites with very low snowfall (e.g. Dome C), the natural resolution is several hundred years. We choose the former for studies of the recent past, the latter for studies of long time periods where high resolution is not critical.

It is worth mentioning that when the bubbles are broken open to analyse the air, one is actually measuring the concentration of CO₂ in the air sample just as if it was from a flask collected from air today. The air in the clathrates can also be analysed in the same way. Professor Salby incorrectly described the measurement as a “proxy”, but a proxy is when you measure one thing (for example water isotopes in ice) to determine another (temperature above Antarctica). He may believe there is an artefact in the conservation of CO₂ in ice but he is wrong to describe it as a proxy. This makes CO₂ almost unique among palaeo-measurements and gives the huge advantage that a process based model to understand the meaning of the measurements is not required as it is with most measurements.

What is the evidence that CO₂ in ice is a good representation of CO₂ in the air when the bubbles closed?

1. It is possible, by pumping firn air, to measure the concentration of CO₂ in the air/firn column before it is enclosed in the ice. Etheridge et al (1996) measured the concentration of CO₂ in the open firn air and in closed ice core bubbles from the same depth (see their figure 2), and found the same concentration (actually a random 1.3 ppmv difference, similar to the measurement uncertainty), showing that the enclosure process does not affect the concentration. This is a really direct and elegant measurement which shows that, at least at Law Dome, there is no fractionation of CO₂ on enclosure.
2. The same paper by Etheridge et al (1996) also showed that the concentrations in air bubbles dated to the 1960s onwards track perfectly onto those measured in air at South Pole. The figure to the right shows this, including more recent data from MacFarling Meure et al (2006). This confirms that the enclosure process is conservative, and shows that the ice can preserve the magnitude of changes.



3. The plot above of the last 1000 years shows data from 4 different Antarctic sites, that all have very different ice temperatures, snow accumulation rates, and content of other chemistry. If there was an artefact over 1000 years, it would have to be identical at each site, even though the physical and chemical characteristics that would determine that artefact were completely different. The simplest solution is that there is no artefact. The same conclusion can be drawn over a much longer time period by comparing the record of CO₂ across the last glacial termination at sites in West and East Antarctica: exactly the same pattern and magnitude of change is seen, suggesting that there is no “smoothing” artefact over this time period.
4. The timing and amplitude of glacial-interglacial CO₂ change relative to that of changes in Antarctic temperature, is similar in the glacial termination that occurred about 780000 years ago as it is in the one that occurred 20000 years ago. If there was a phase shift or amplitude reduction that was time-dependent, as Professor Salby suggested, this would not be the case.
5. Although the results require much more interpretation, and are less well-resolved, the amplitude, shape and timing of glacial-interglacial CO₂ change found in ice cores is confirmed by boron isotope data from marine sediment cores (Hönisch et al, 2009).

So are there no problems or corrections to ice core CO₂?

A correction does have to be made for what happens in the firn column. This is a diffusive column of air, and a small gravitational fractionation of gases occurs in that column. This imposes an enrichment of about 0.5% for CO₂ (molecular weight 44) compared to N₂ (molecular weight 28). This can be corrected for, either using theory (based on the height of the diffusive column), or using the relative fractionation of ¹⁵N-N relative to ¹⁴N-N to scale the fractionation. Such a correction (amounting to 1-2 ppmv for CO₂) is normally applied to ice core data.

An artefact is observed at some sites, in which unfeasibly large interhemispheric differences (Greenland – Antarctica) or unfeasibly fast changes in CO₂ between samples, are observed in Greenland cores with high contents of other impurities. This may result from production of CO₂ from carbonates or oxidation of organic material in the ice. It is avoided by using only Antarctic cores in which impurity concentrations are always low. Accurate analyses cannot be done with wet extraction methods for the same reason.

When the bubbles convert to air hydrates, there can be a fractionation of different molecules between the phases. In the transition zone it is therefore particularly important to use an extraction method that extracts all the gas, or that extracts equally from clathrates and bubbles. Sublimation techniques have been used to show that no significant artefact is induced.

A small offset (of up to 2% or 6 ppmv) has been observed (Ahn et al 2012) between concentrations measured in the West Antarctic WAIS Divide core and those from East Antarctica. It is not yet clear if this is an analytical/calibration problem or a genuine artefact. The shape of changes observed remains unchanged suggesting that it is a simple offset.

In summary, accurate CO₂ data require careful measurement techniques, and any issues that have arisen have been thoroughly investigated over the last 20 years or more to ensure that the data can be considered accurate to within 1-2% at worst.

Are there any mechanisms for CO₂ in ice to be non-conservative?

CO₂ is a chemical. In order for concentrations to change in a given volume of ice, CO₂ must either be chemically produced or consumed, physically removed or emitted from “sites” where they are not amenable to measurement, or physically moved out of the measurement volume.

Professor Salby mentioned various ways problems could occur:

1. He cited cracks in the ice. Of course ice core scientists have been well aware of this issue for 3 decades. They avoid measurements in heavily cracked areas, but actually a crack simply releases the trapped air, and with proper techniques should not alter the concentrations in bubbles that the crack does not cross. Cracking is generally a big problem only in the transition zone between air bubbles and clathrates where the greatest pressure relaxation of bubbles occurs. Finally cracks would cause random errors not the systematic change in concentrations that Professor Salby suggested must have occurred.
2. He also cited the clathrate formation as a problem. He incorrectly stated that clathrates form at about 100 m depth (10 bars): it is closer to 1000 m (100 bars), depending on temperature. Clathrate formation does not affect the CO₂ in the ice, but there can be fractionation of gases between clathrates and bubbles. Experiments using sublimation to release all the gas quantitatively avoid any danger from clathrate formation.
3. He mentioned melt layers in ice. Melt layers could indeed be a problem as CO₂ could be dissolved in the water freezing to ice. There are never melt layers in ice from the high plateau of East Antarctica, where the mean annual temperature is <-50°C, and summer temperatures are generally <-20°C. We avoid melt layers for CO₂ measurements at other sites.
4. At some point I believe he also cited diffusion of gases. Diffusion of gases does occur in ice but (apart from the very small molecule, helium), it is of order centimetres even over 800,000 years. This can be seen most clearly for methane for which the very sharp jumps that occur at the start of Dansgaard-Oeschger events (typically 40% jumps in <50 years) are preserved at similar amplitude over 800,000 years.

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