

When was CO₂ last at 400 ppm? And what was the climate like?

Descent Into the Icehouse Blog post. 13.04.13

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[Note: This is a quick blog post on a specific current media question, not a review paper so I have not attempted to fully reference everything in it.]

Summary

Atmospheric CO₂ is approaching the 400 ppm mark for the first time in human history which begs the question: when was it last that high? A recent high profile suggestion is that CO₂ was that high in the Pliocene epoch (approximately 2.6-5.3 million years ago) and this is now being repeated in the press and around the internet. Here I point out that this claim is based on a few extreme estimates, mostly from sites that systematically overestimate more recent CO₂ levels, while the majority of published Pliocene CO₂ values are in the 250-400 ppm range. The last time we have consistent evidence for pCO₂ over 400 ppm is in the Early Oligocene epoch more than 26 million years ago. This post presents the key graphs and comments on some of the methods used to calculate past pCO₂.

1. Introduction

The famous Keeling curve of atmospheric pCO₂ (partial pressure of CO₂) measurements from Mauna Loa is set to reach 400 ppm (parts per million) for the first time in history, possibly this month, an unwelcome milestone for planet Earth. Some hourly average measurements have already exceeded this value (<http://keelingcurve.ucsd.edu/>). The reason for this is a combination of 1) the relentless rise in pCO₂ due to anthropogenic emissions and 2) the regular small seasonal peak. Annual average atmospheric pCO₂ will exceed 400 ppm within 1-2 years. (Note: some sources claim that a daily average of 400 ppm was reached on May 9th generating global media reports, but this seems to have been subsequently revised: see <http://www.esrl.noaa.gov/gmd/ccgg/trends/weekly.html>).

Even if we were able to hold pCO₂ at around 400 ppm, we are guaranteed further global warming. This is partly because it takes time for the oceans to warm up in response to the atmosphere and partly because of feedbacks involving, for example, water vapour (another greenhouse gas), clouds, methane, ice melt, and changes in the biosphere, all of which take time. These feedbacks and their interactions can be very difficult to model by computer which is one reason why different climate models predict different amounts of warming for the same CO₂ forcing.

Given this, it seems natural to look to the geological record for a time when pCO₂ was as high as it is now. It could be instructive to examine the climate state at a time when all the feedbacks would have had ample time to kick in and respond to each other. We should bear in mind, though, that the past cannot provide a perfect analogue for the future. The further back we go, the more likely it is that other significant factors were different from now (human civilization and land use for a start, and then

the position of the continents, height of mountains, ocean current speeds and directions, and many more).

A more modest aim that drives this kind of research is to provide examples of past climate states that we can use to test the climate models on – the same models we want to use to predict the future. Do the models under- or overestimate the warming produced by CO₂, or do they get it about right? This knowledge is certainly helpful when evaluating uncertainties concerning the future. And it is of course a very interesting scientific question in its own right.

For these reasons it is important to know past atmospheric CO₂ concentrations. Data from bubbles in ice cores extend back almost a million years, but at no point do they show values anything like 400 ppm. In fact they show remarkable consistency, varying rhythmically between about 180 and 280 ppm (reaching a maximum of 300 ppm) in tune with the glacial / interglacial cycles as paced by regular changes in earth's orbit (which affects the distribution of heat that we get from Sun). Clearly we have to go back beyond one million years to find warm climate states and high pCO₂.

Unfortunately we have no unaltered samples of ancient air older than the oldest ice. Air bubbles in amber and other geological materials do not preserve the CO₂ content. This means we have to find something from the past that we can measure in our laboratories that we think was influenced in a predictable way by CO₂ – a gas present in only tiny amounts in air we no longer have access to. Several ingenious CO₂ proxies have been developed but they are all somewhat experimental and involve taking a range of assumptions of varying degrees of confidence. A considerable effort is currently being made by various research groups to develop the proxies because of the extraordinary importance of the question. Several of these research groups are involved in the Descent Into the Icehouse project (<http://descentintotheicehouse.org.uk/>).

According to the Scripps Keeling curve information pages, the last time pCO₂ was over 400 ppm was in the Pliocene epoch (<http://keelingcurve.ucsd.edu/what-does-400-ppm-look-like/>). This claim is already widely reported on the internet. But what is it based on and how reliable is it? The objective of this post is to review some recent literature and see how solid that conclusion is. First we need to briefly review the proxies.

2. The proxies

i. Plant stomatal indices.

The most intuitive proxy is based on the relative frequency of stomata to other cells on fossil leaves (stomatal index). Stomata are little pores that regulate CO₂ uptake into a leaf as well as moisture exchange. It has been shown that for some species of plants, either grown in controlled conditions or from dried specimens in herbaria, that stomatal index correlates well with pCO₂ (the more CO₂ the lower the stomatal index). This seems to make sense because a plant uses its stomata to regulate CO₂ uptake into the leaf to optimize photosynthesis. So all you have to do to estimate past pCO₂ is measure the index on a fossil leaf of known age and apply a modern day statistical calibration. There are however problems and assumptions. Not all species of plants vary their stomata in the predicted way (many seem to show little response or even increase their stomatal index with higher CO₂) and even closely related species in the same genus can respond very differently. Other factors such as humidity /aridity can also affect stomatal index and forest canopies often have local CO₂ levels higher than the atmosphere. Finally there is the question of whether a short-term physiological response seen

in plants in modern greenhouses with high pCO₂ would necessarily be the same if the species was allowed millions of years to evolve and adapt to suit its conditions.

ii Carbon isotopes in alkenones

When organisms photosynthesize they strongly fractionate (discriminate between) the two stable isotopes of carbon (¹²C and ¹³C) and it so happens that the degree of fractionation is itself related to the CO₂ content of the environment that the organism lives in. So if we can measure the carbon isotope ratio (δ¹³C) of organic compounds and we know the carbon isotope ratio of the inorganic carbon in their environment, we can in principle calculate the pCO₂. Early work was done on bulk organic matter but the degree of fractionation varies quite widely between compounds and organisms so a more sophisticated approach is to use a particular class of compounds. The molecule of choice in many palaeo-studies is called an alkenone, a long chain ketone formed by a particular group of marine algae. But like the other proxies, there are complicating factors. We need to assume that the dissolved CO₂ at the study site is in equilibrium with the atmosphere (which means no significant upwelling or downwelling). Temperature has a predictable effect on the carbon isotope fractionation, so this has to be measured (using a temperature proxy) and factored in to the calculation. Physiological effects such as cell size and growth rate also seem to have a large effect on the carbon isotope ratio independent of CO₂ but they can be difficult to estimate for the past and might well have changed through time or with local conditions. Some workers have tried to develop corrections for these. The assumption that ancient extinct species of algae that lived in waters enriched or depleted in CO₂ relative to today fractionated carbon isotopes like the modern ones also has to be made.

iii Boron isotopes in biogenic calcite

Carbon dioxide is an acidic gas that mixes into the ocean where it reacts to yield carbonic acid, bicarbonate and carbonate ions. This changes the acidity of the water (ocean acidification is sometimes known as ‘the other CO₂ problem’). If we can estimate the pH of ancient seawater at a place that was close to equilibrium with the atmosphere, and simultaneously make an assumption of how much carbon was dissolved in it, we can calculate the pCO₂ of the ocean and hence atmosphere. It so happens we can estimate the pH of seawater by exploiting the isotopic composition of the element boron incorporated into fossil calcite (such as the shells of planktonic foraminifera, algae or corals). This is because dissolved boron speciates in seawater (like carbon), in response to pH (forming boric acid and the borate ion). There is a known isotopic exchange between these species and only borate gets incorporated into calcite. So, provided these assumptions hold, to get pH all we need to do is measure the boron isotope ratio (δ¹¹B) of fossil shells and we can calculate the rest. An advantage of this method is that it is based on known physical chemistry that ought to hold good across time, and is not just some modern empirical calibration. Unfortunately it does involve a variety of tricky assumptions, including knowing the seawater temperature and salinity which can also affect the boron isotope equilibrium. If we want to go back millions of years (which we do), we have to estimate the boron isotopic composition of seawater which might well have changed through time. This latter problem becomes the biggest uncertainty for periods greater than a few million years old and it is currently not very well constrained. We also need to assume that whatever organism we study secretes its calcite shell as if it was an inorganic crystal with respect to δ¹¹B or, if it does not, perhaps develop species-specific calibrations.

iv Others

Other proposed proxy methods include analyzing the carbon isotope ratio of soil carbonate, B/Ca ratio of marine calcite, or the phases of evaporate minerals which are CO₂ dependent. This later method probably involves the fewest assumptions of them all but unfortunately can only be applied to very rare geological deposits (so far just 3 in the last 50 million years; Lowenstein and Demicco, 2006). It does, however, confirm the predictions from boron isotopes and alkenones that pCO₂ was much higher than modern in at least some portion of the Paleogene period.

v Cautionary remarks

From the above discussion it can be seen that all the proxy methods are somewhat experimental in their application, especially over millions of years. Various laboratories are working hard to develop them and better constrain the assumptions. This means that the methods themselves are changing as they evolve, often making old pCO₂ estimates non-comparable with newer ones because different assumptions are made and as new knowledge is acquired. All the methods produce 'noise' in the records which arises not just from analytical uncertainty but also from the secondary assumptions (like undetected variations in temperature for example). Potentially more worryingly, the proxies might involve systematic biases of one sort or another. Hence to understand the record in any given publication it is necessary to examine the assumptions carefully. There is no space to do that here - we shall just examine the pCO₂ reconstructions themselves.

The good news is that the three proxies listed all work under controlled experimental conditions and also work fairly well at reconstructing the glacial-interglacial cycles in pCO₂ seen in the ice core records. It so happens that for different reasons, all the methods work less well at higher pCO₂. The stomatal method is the most problematic at levels of CO₂ higher than modern because the calibration data sets are small and variable and non-linear (the effect seems to flatten out at high CO₂). Moreover the biological relations of fossil leaves to their modern counterparts become increasingly distant with geological time. For those reasons I will focus mainly on alkenone and boron estimates.

3. The records

i. Pearson and Palmer (2000)

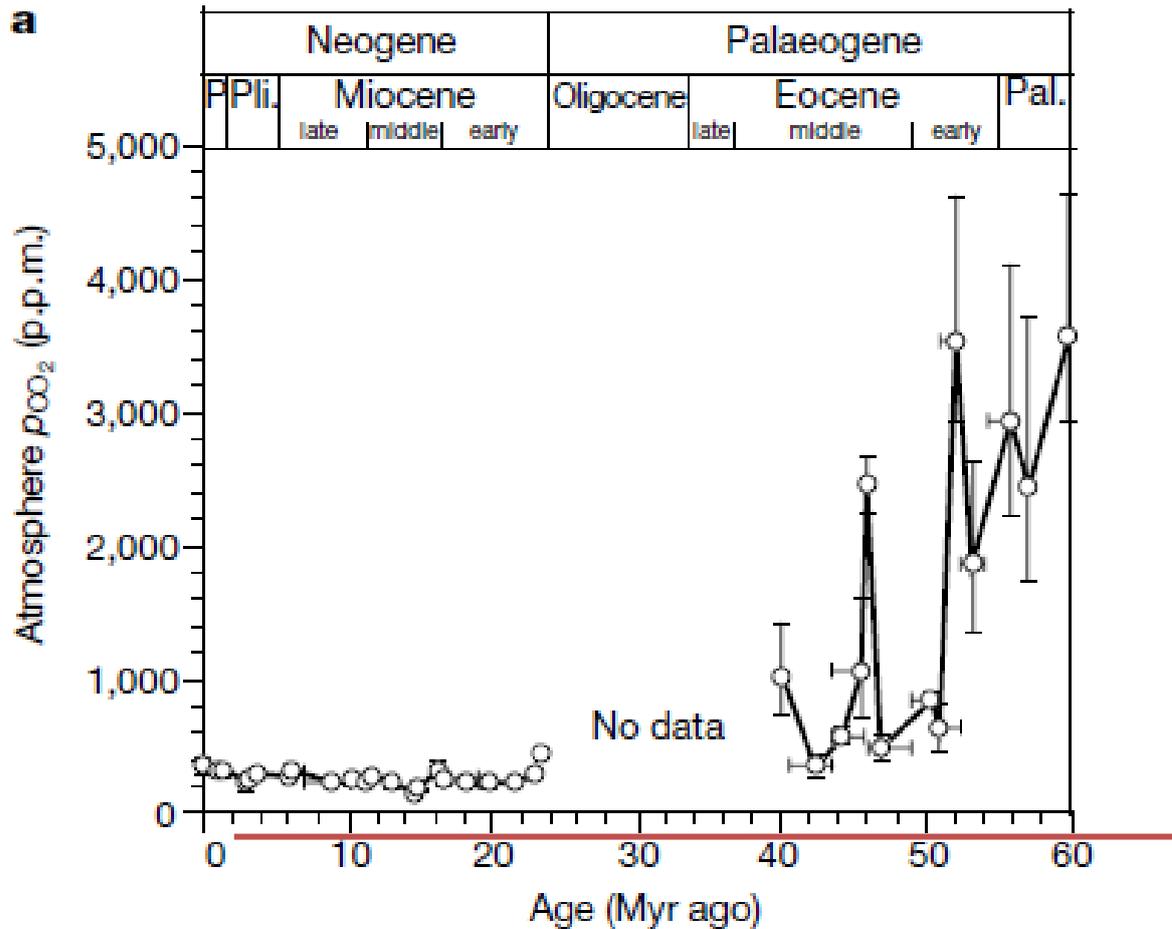


Fig. 1. Cenozoic pCO₂ reconstruction of Pearson and Palmer (2000). Red line added at 400 ppm.

First up we will examine the 60 million year record of Pearson and Palmer (2000) which used boron isotopes on planktonic foraminifera from deep sea cores. Note that in this and all the other plots time runs from right to left. The youngest pCO₂ estimate that is higher than 400 ppm in this record is in the early Miocene about 23 Ma (million years ago). Unfortunately there is a data gap in the Oligocene and upper Eocene. All but one of the estimates for the period 40-60 Ma are higher than 400 ppm, many of them considerably so.

Ongoing research since 2000 has shown that this record suffers from two main problems, both of which make the quantitative estimates problematic. The first is that our understanding of the boron isotope fractionation between the two aqueous species (boric acid and borate) has been substantially revised (Klochko et al., 2006) which would change the calculations. In fact it is impossible to calculate pCO₂ from the raw isotope data if we use the modern fractionation factor! The second is that the measurements were made using Negative Thermal Ionization Mass Spectrometry (N-TIMS) and it has become increasingly clear that this method produces data that is strongly offset from measurements made using Multicollector Inductively Coupled Plasma Mass Spectrometry (MC-ICP-MS). It so happens that these two serious biases work against each other so that if we were to apply a method offset (for example based on Foster et al., 2012), the general pattern and trends shown by the data can be calculated although the absolute values will be somewhat different. This may seem like a desperate argument to make from one of the authors of this old paper (!) but it is backed by the observation that using the same methods and assumptions we were able to produce reasonable and

consistent inter-species offsets and reconstructions of pH versus depth (Pearson and Palmer 1999) which would not have been possible if we were not roughly in the right ballpark, so to speak. We were also able to reconstruct glacial to interglacial changes in $p\text{CO}_2$ with good quantitative accuracy using the same technique (Palmer and Pearson 2003). Clearly, however, the record needs replacing by newer and better data and some contributions toward that are considered below.

ii. Pagani et al. (1999 and 2005)

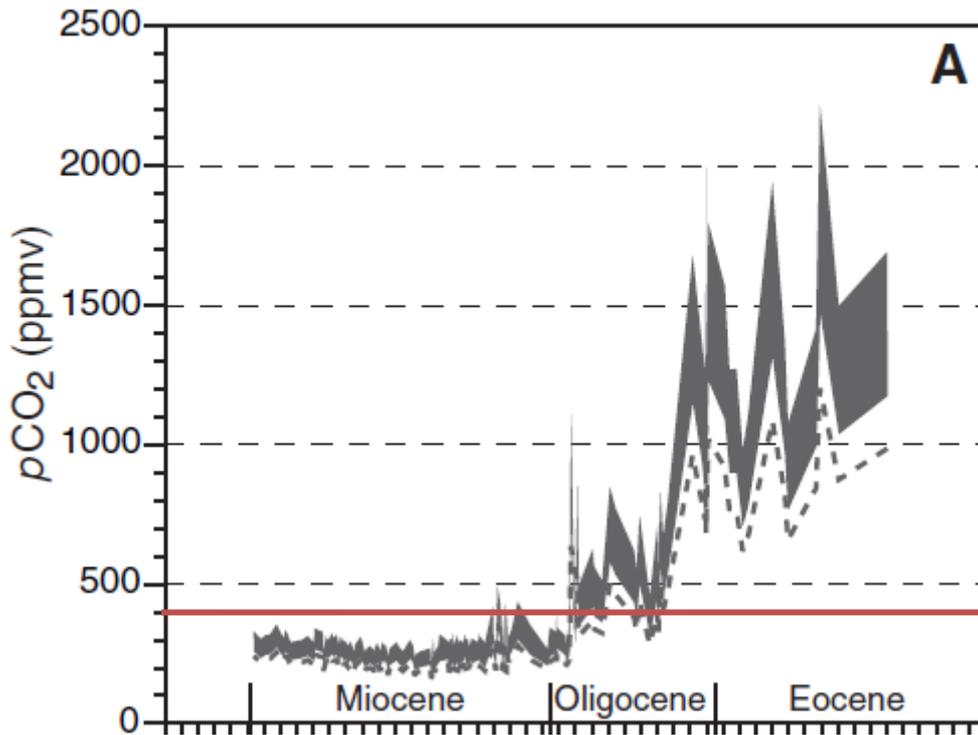


Fig. 2. Record of Pagani et al. (2005) from alkenones from 0-50 Ma. Note there are no data from the last 5 m.yr. Red line added.

The record of Pagani et al. (2005) (the Miocene part of which is from Pagani et al. 1999) utilises the alkenone proxy. It can be seen from this record that the last time there were values > 400 ppm was in the Oligocene epoch (or just maybe in the early Miocene). There have been some recent revisions and additions to this data set since, for example, attempts to account for cell size effects, to deal with areas of high productivity, and to provide better estimates of temperature. However in general the record is similar to Pearson and Palmer (2000) in showing the relatively low $p\text{CO}_2$ values from the Miocene onward (which is, incidentally, something neither research group expected to find when the work started).

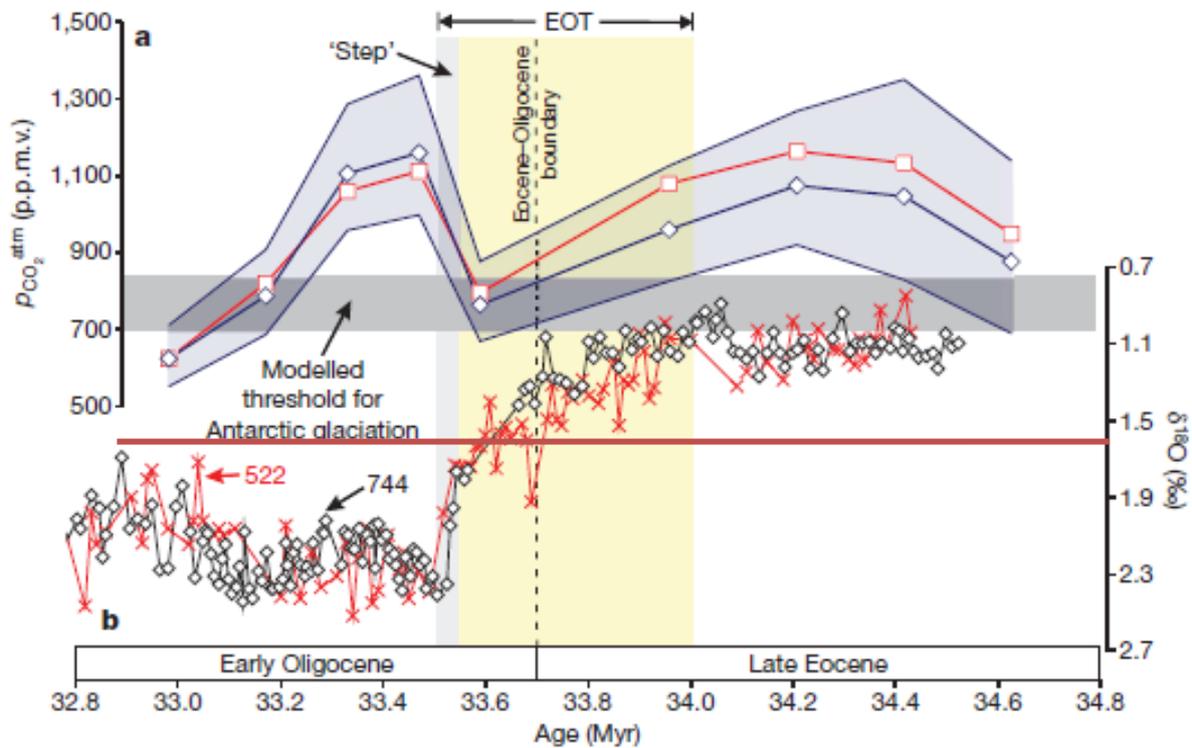


Fig. 3. Boron isotope $p\text{CO}_2$ estimates (red and blue symbols involve different assumptions) and below, oxygen isotopes for the interval 32.8-34.8 Ma from Pearson et al. (2009). Red line added.

This boron isotope study of the late Eocene and early Oligocene employed MC-ICPMS and the fractionation of Klochko et al. (2006) so the results cannot directly be compared with Pearson and Palmer (2000). There is some variability but all the values are well above 400 ppm (red line). The $p\text{CO}_2$ estimates are very sensitive to the assumed boron isotope composition of seawater and could be substantially higher or lower than indicated but are unlikely to be below 400 ppm using any reasonable value.

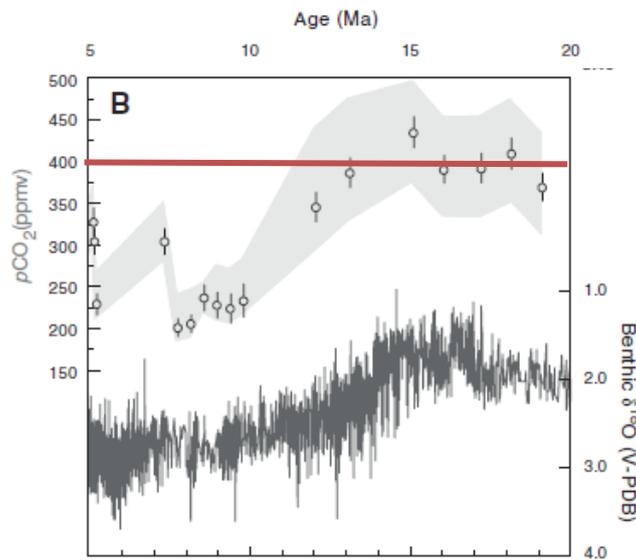


Fig. 4. Boron / Calcium pCO₂ estimates plotted against oxygen isotopes modified from Tripathi et al. (2010). Red line added

This record spans the period 5-20 Ma and is based on measurements of the B/Ca ratio in marine carbonates (as opposed to the boron isotope ratio). It shows two estimates > 400 ppm in the early and middle Miocene (~15 and ~18 Ma). It should be noted however that the method used has been subject to criticism and the understanding of the proxy, as detailed in Tripathi et al. (2010) has been challenged (Allen and Hönisch 2012).

v. *Pagani et al. (2010)*

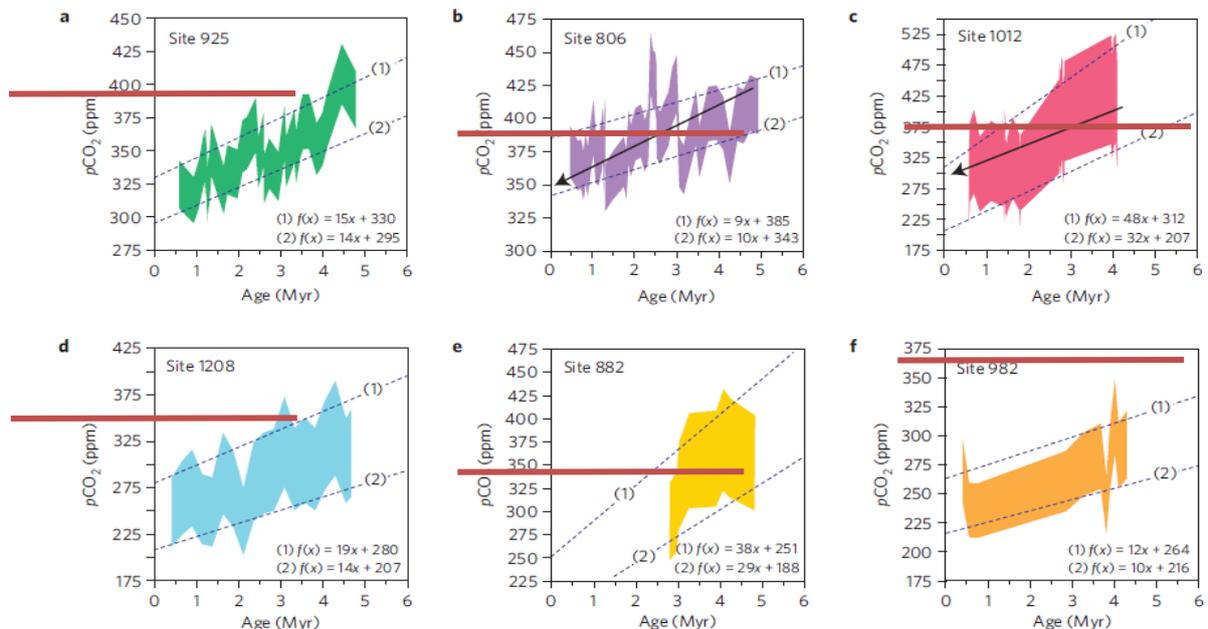


Fig. 5. Alkenone pCO₂ records from Pagani et al. (2010). Red lines added

This paper produced new alkenone records from six different sites extending back to about 5 Ma (covering the Pliocene and Pleistocene epochs). Most of the sites seem to show a trend for declining

pCO₂ over this period although there are large offsets in absolute values and magnitudes of the trends between different sites (note the variable vertical scales on these graphs). A small number of the very highest values at some sites exceed 400 ppm (note colour bands express uncertainty). This was the paper referred to in the Scripps commentary (<http://keelingcurve.ucsd.edu/what-does-400-ppm-look-like/>).

vi Seki et al. (2010)

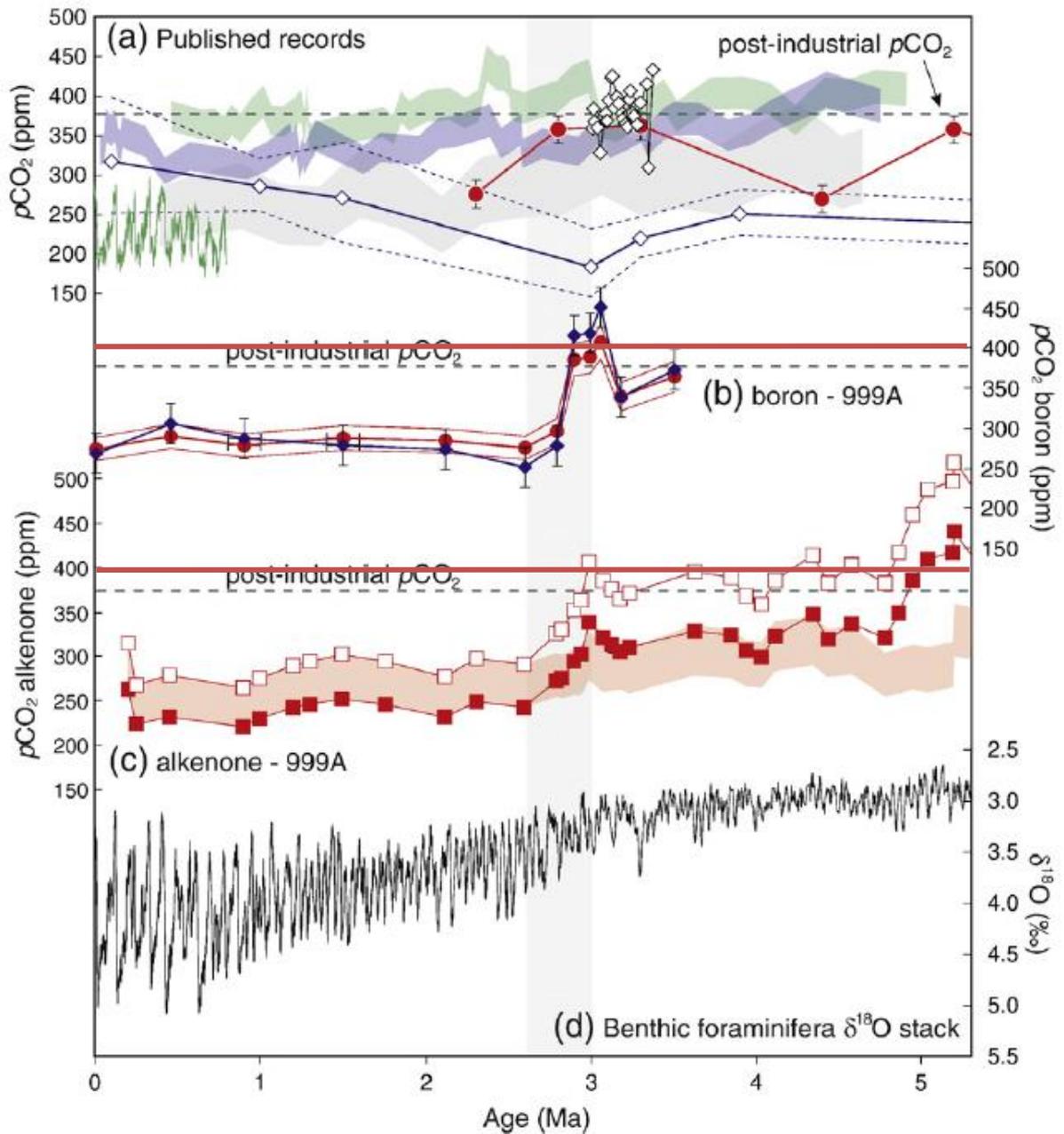


Fig. 6. Previous records (panel a) and new data (panels b and c) for the last 5 million years compared to the oxygen isotope stack from Seki et al. (2010). Red lines added.

Seki et al. (2010) published new $p\text{CO}_2$ estimates from the boron isotope and alkenone proxies from a site not included in the Pagani et al. (2010) study, but the same time range. The top panel shows previous $p\text{CO}_2$ estimates for the period (colour bands are selected sites from Pagani et al. 2010; black diamonds are bulk organic $\delta^{13}\text{C}$ estimates from Raymo et al., 1996; red circles are stomatal estimates from Kurschner et al., 1996; and blue diamonds are the old boron isotope data from Pearson and Palmer, 2000; the green line at the left is the ice core air bubble data from Luthi et al., 2008). Panel b is new boron isotope estimates from the species *G. ruber* with different assumptions about alkalinity (the different symbols) and panel c is the alkenone data both uncorrected (red band) and corrected (between the red squares) for changing cell size effect. It can be seen from this that the Pliocene boron estimates are mostly in the 300-350 ppm range but just exceed 400 ppm around 3 Ma given certain assumptions. The alkenone estimates exceed 400 ppm for a few values around 5 Ma but only if the size correction is taken into account.

vii. Bartoli et al. (2011)

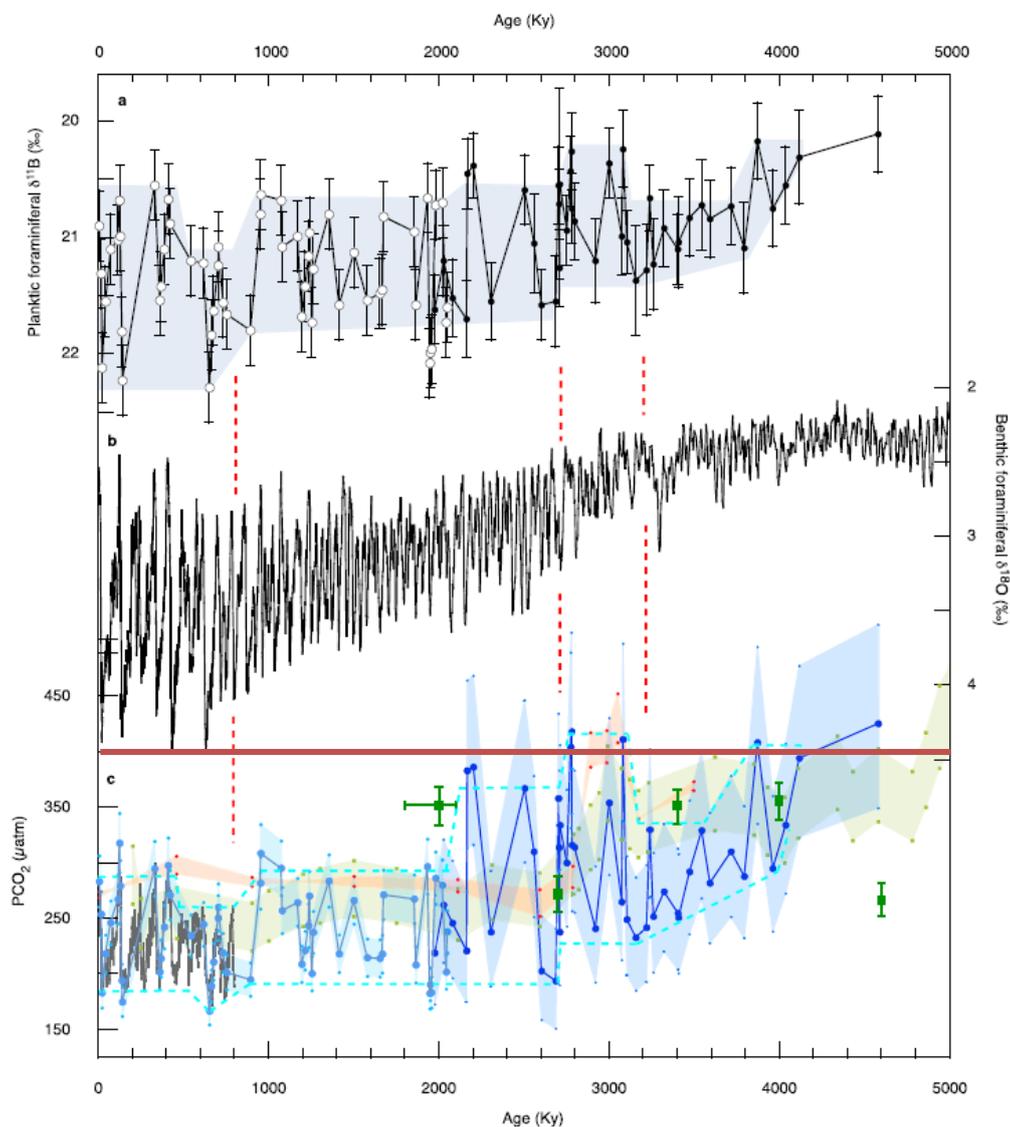


Fig. 7. Boron isotope, $\delta^{18}\text{O}$ and $p\text{CO}_2$ reconstruction by Bartoli et al. (2011). Red line added.

This record is from boron isotopes in the planktonic foraminifer *G. sacculifer*. The estimates are shown on the bottom panel together with some previous (mostly alkenone) records for comparison as

coloured bands in the background. A strength of this record is that it matches well with the glacial-interglacial variability seen in the ice cores (the grey curve confined to the first million years). A small number of data points exceed 400 ppm but most are in the range 200-350 ppm. Like many of the other records, there appears to be a declining trend over the 5 m.yr period. Note that the data were obtained by TIMS and are offset from the values measured in the same species by Seki et al. (2010) so the two data sets are not directly comparable.

viii. Pagani et al. (2011)

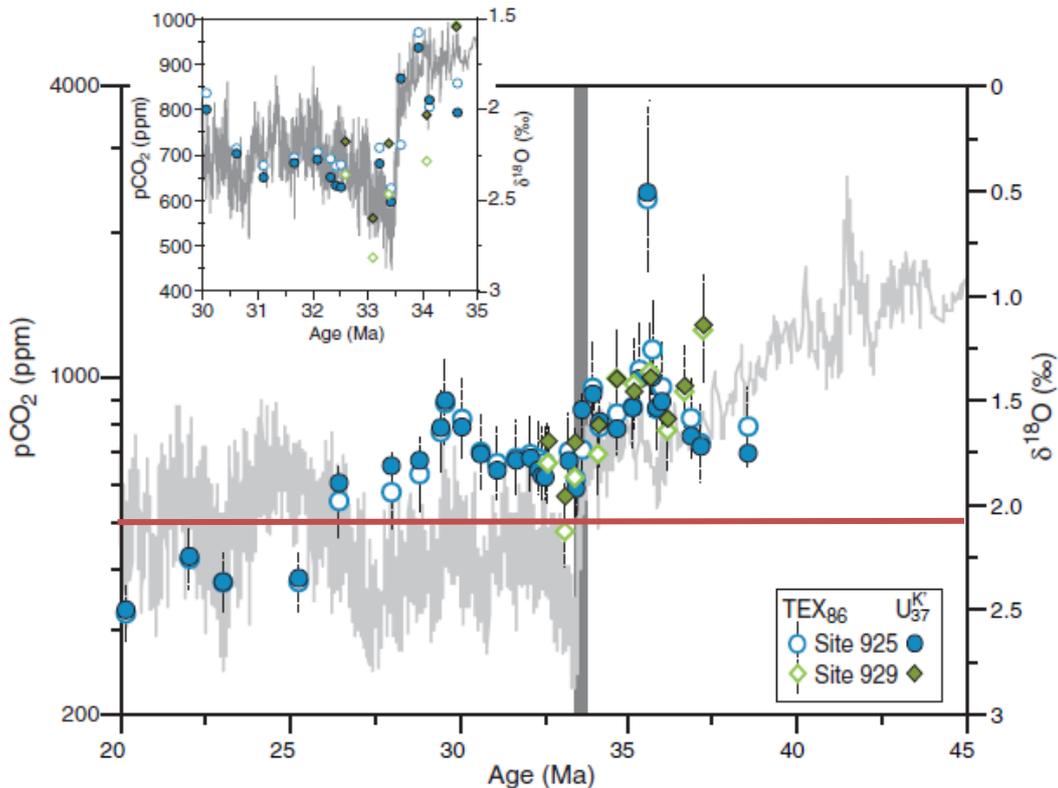


Fig. 8. Alkenone pCO₂ reconstructions (colours) against oxygen isotope stack (grey) from Pagani et al. (2011) for the period 20 – 45 Ma. Red line added.

This study spans the Eocene / Oligocene transition (like Pearson et al. 2009) but covers a much wider range of ages. Various data sets from high latitude settings were excluded for reasons discussed in the paper. All the estimates > 26 Ma are above 400 ppm, only the four points from 20-26 are all below this value.

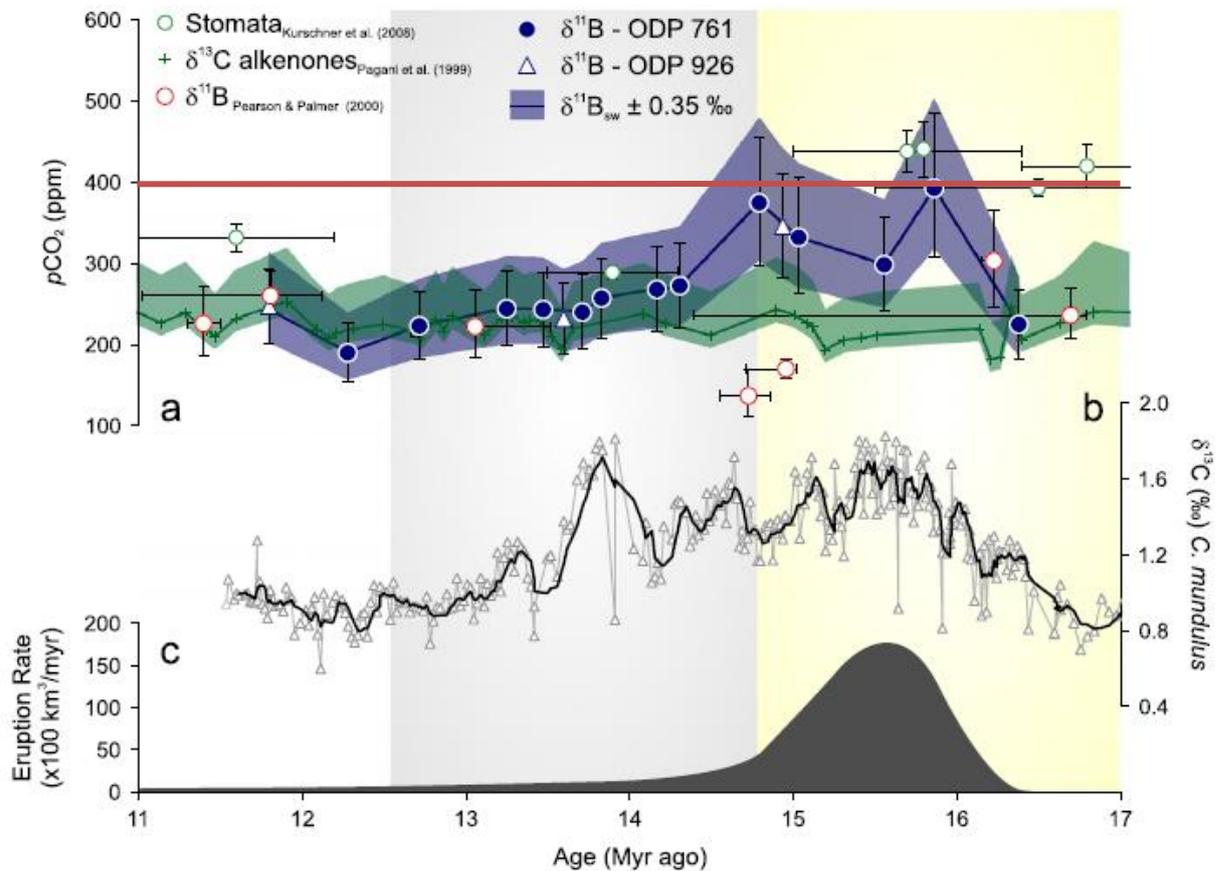


Fig. 9. pCO₂ reconstructions (top panel) versus carbon isotopes and Columbia basalt volcanic eruption rate (bottom panels) from Foster et al. (2012) for the period 11-17 Ma. Red line added.

The new data (dark blue) are from boron isotopes in foraminifera using the same general approach as Pearson et al. (2009) and Seki et al. (2010). The data are shown against some earlier reconstructions of the period (green and red symbols). Note that while there is more structure in this record than older data (alkenone and boron), all the new data points are below the 400 ppm value, even in the warmest part of the Miocene epoch.

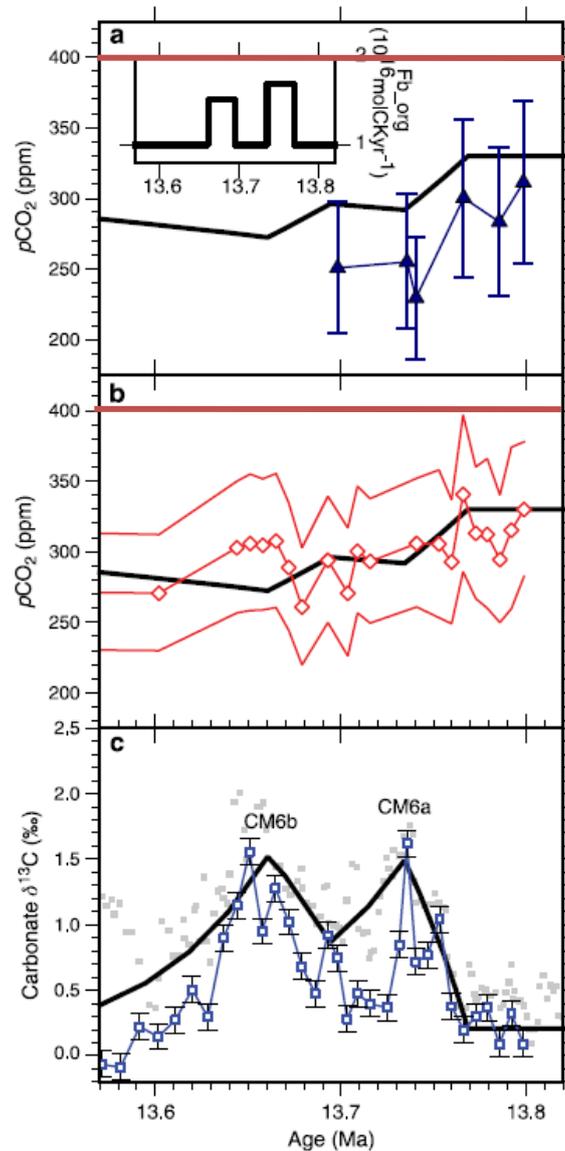


Fig. 10. Boron (panel a, blue points) and alkenone (panel b, red points) pCO₂ reconstructions against carbon isotopes (panel c) from Badger et al. (2013) for the period 13.5-13.8 Ma. Red lines added.

This study employs both boron and alkenone proxies to a Miocene geological section in Malta ranging from 12.5 to 14 Ma. Most of the data are in the 250-350 ppm range, with the boron giving somewhat lower estimates than the alkenones. The data seem to show a declining trend.

4. Synthesis

So let us return to the question: when was atmospheric pCO₂ last higher than 400 ppm? All records agree it was before the Pleistocene (> 2.6 Ma). The bulk of the data from the Pliocene epoch (2.6-5 Ma), using a range of approaches and measurement techniques, are in the range 250-400 ppm and many records seem to indicate a declining trend through that time. We cannot conclude that pCO₂ was > 400 ppm in the Pliocene as a whole – if it was, it was only for short periods. Some of the alkenone

data of Pagani et al. (2010) are slightly higher than 400 ppm (Fig. 4) (hence the Scripps claim that the last time pCO₂ exceeded 400 ppm was in the Pliocene), but note that this is only at sites that seem to give consistently high values compared with other sites and also too high for the last million years when we have the ice core record to guide us. As Pagani et al. (2009) point out, site to site differences in absolute CO₂ estimates may be affected by differences in growth rate, air-sea CO₂ exchange, irradiance, and regional differences in the calibration on the proxy. So it is reasonable to suspect that these higher values may be due to a systematic offset at those sites. A few other values > 400 ppm are found in the boron isotope record of Seki et al. (2010) (Fig. 5b) but this is just for a short interval at ~3 Ma whereas the other data from this record suggest CO₂ during the Pliocene was lower than 400 ppm. The alkenone values > 400 ppm in that paper (Fig 5c) all rely on a cell size correction factor. There are a small number of > 400 ppm estimates from Bartoli et al. (2011) (Fig. 6) but those are mostly very close in the record to much lower estimates, suggestive of variability in the record perhaps as a result of glacial - interglacial fluctuations. The high points in the various records seem to be either around 3 Ma and / or around 5 Ma.

Taken together it seems fair to conclude that the 400 ppm mark *may* have been exceeded for relatively short intervals in the Pliocene (possibly just in interglacial phases) but, given the limitations of the techniques, it is currently difficult to be confident of that conclusion. It seems noteworthy that the Miocene values of Foster et al. (2012) and Badger et al. (2013) are all less than 400 ppm although that mark may have been approached about 15 – 16 Ma in the warmest part of the Miocene. Two measurements reported by Tripathi et al. (2009) exceed 400 ppm in the early Miocene but the method used in that study has been criticised. To find published pCO₂ estimates that are consistently > 400 ppm one has to go back to the Oligocene records of Pagani et al. (2011) and Pearson et al. (2009) (which use the alkenone and boron proxies respectively). So a more conservative conclusion would be that the most recent time that we can be confident pCO₂ was consistently > 400 ppm was in the Early Oligocene epoch, > 26 million years ago, although it may briefly have reached that level for short intervals subsequently.

We must also bear in mind that this field is moving fast and new discoveries for intervals not so far examined in detail may be around the corner, and new and better proxies may yet be discovered.

5. What was the world like when we think pCO₂ last exceeded 400 ppm?

A continental scale ice cap appeared on Antarctica about 33.5 Ma in the earliest Oligocene, possibly triggered by declining pCO₂ crossing a threshold and other environmental factors favourable to ice sheet growth combined (Pearson et al., 2009; Pagani et al., 2011). But the Antarctic ice cap in the Oligocene (and for that matter Miocene and Pliocene) may have been quite dynamic in repeatedly waxing and waning with time, which would have caused sea level to fluctuate sea level up and down, and it was probably centred mainly on East Antarctica. There is little evidence of large scale continental glaciations in the Northern Hemisphere until the last few million years although seasonal sea ice was present since the Eocene. In general, global temperatures were several degrees warmer than modern and sea level was tens of meters higher.

Global temperatures were even more extreme in the Eocene, with no sizable ice cap at either pole and sea levels were consequently 100 m or more above the present level. London was a tropical swamp and the Arctic ocean was fringed with palm trees. Published pCO₂ levels for that epoch are mostly > 500 ppm and generally > 1000 ppm.

All this is not to say that if we sustain 400 ppm in the atmosphere we are destined to have a world like the Oligocene, as other factors may have contributed to global warmth then. Other greenhouse gases especially methane may have contributed to global warmth, as may the very different pattern of ocean and atmospheric circulation. We cannot use the past to generate simplistic links and predictions or try to prove or disprove the greenhouse effect which is the realm of modern atmospheric physics.

But if there is one simple message it is this: The geological record gives us no reassurance that 400 ppm of CO₂ in the atmosphere is a safe level to maintain in the long term (safe, in terms of preserving our continental ice caps). Only climate models with high sensitivity to CO₂ seem to be able to capture the main features of past geological warm climates like the Oligocene and Miocene. And of course halting pCO₂ at 400 ppm is not going to happen.

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