Supplement to Alkenone isotopes show evidence of active carbon concentrating mechanisms in coccolithophores as aqueous carbon dioxide concentrations fall below 7 $\mu mol L^{-1}$

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Abstract. Coccolithophores and other haptophyte algae acquire the carbon required for metabolic processes from the water in which they live. Whether carbon is actively moved across the cell membrane via a carbon concentrating mechanism, or passively through diffusion, is important for haptophyte biochemistry. The possible utilisation of carbon concentrating mechanisms also has the potential to over-print one proxy method by which ancient atmospheric CO_2 is reconstructed using alkenone isotopes. Here I show that carbon concentrating mechanisms are likely used when aqueous carbon dioxide concentrations are below 7 $\mu mol L^{-1}$. I use published alkenone based CO_2 reconstructions from multiple sites over the Pleistocene, which allows comparison to be made with ice core CO_2 records. Interrogating these records reveal that the relationship between proxy- and ice core- CO_2 breaks down when local aqueous CO_2 concentration falls below 7 $\mu mol L^{-1}$. The recognition of this threshold explains why many alkenone based CO_2 records fail to accurately replicate ice core CO_2 records, and suggests the alkenone proxy is likely robust for much of the Cenozoic when this threshold was unlikely to be reached in much of the global ocean.

1 Introduction

This supplement, which consists of a pdf (which you are probably reading), an R Markdown file (which when knitted produces the pdf), and three datafiles, provides a literate programming (Knuth, 1984) supplement to "Alkenone isotopes show evidence of active carbon concentrating mechanisms in coccolithophores as aqueous carbon dioxide concentrations fall below 7 $\mu mol L^{-1}$". Together these files allow replication of the analysis required to produce figures 3, 6, 7, 8 and 10 of the paper. The analyses were performed in R (R Core Team, 2020) version 4.0.2 "Taking Off Again" in the RStudio (RStudio Team, 2020) environment, version 1.3.1073 "Giant Goldenrod" under Windows 10.

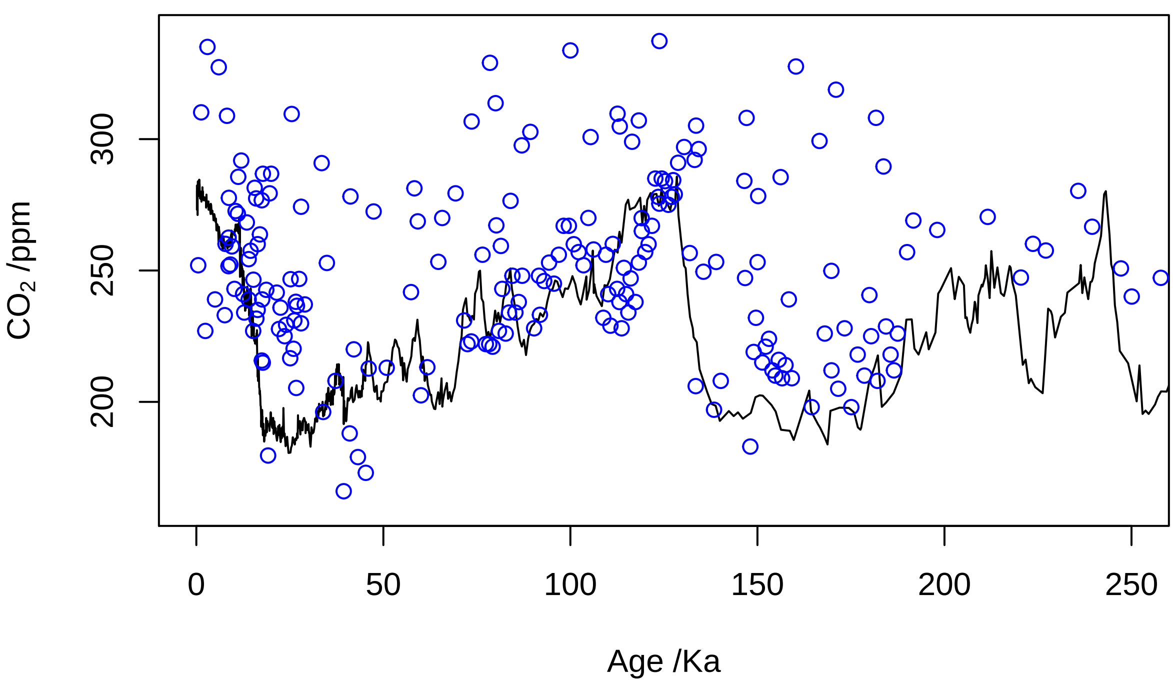
2 Datafiles

Provided as part of this supplement are three datafiles needed to perform all analyses, these are the composite ice core record of (Bereiter et al., 2015) "Bereiter_ice_core_composite.txt", "Compiled G_IG alkenone data.csv" which contains compiled and recalculated $CO_{2(\varepsilon_p - \mathrm{alk})}$ data from the published records used throughout (Badger et al., 2019; Zhang et al., 2013; Jasper and Hayes, 1990; Palmer et al., 2010; Andersen et al., 1999; Bae et al., 2015), and "CO2_uncertainties.tx which contains an internally consistent set of Monte Carlo estimates of uncertainties for the $CO_{2(\varepsilon_p - \mathrm{alk})}$ records. For full citations of the sources for the Bereiter et al. (2015) compilation please see Table 2 in the main paper text.

The $CO_{2(\varepsilon_p - \mathrm{alk})}$ records in the "Compiled G_IG alkenone data.csv" file were recalculated from the original published data to produce one self-consistent dataset, with appropriate values for SST, S, and "b" appropriate for each record. Where the original publication noted a disequilibrium between atmosphere and surface ocean, this was also adjusted for.

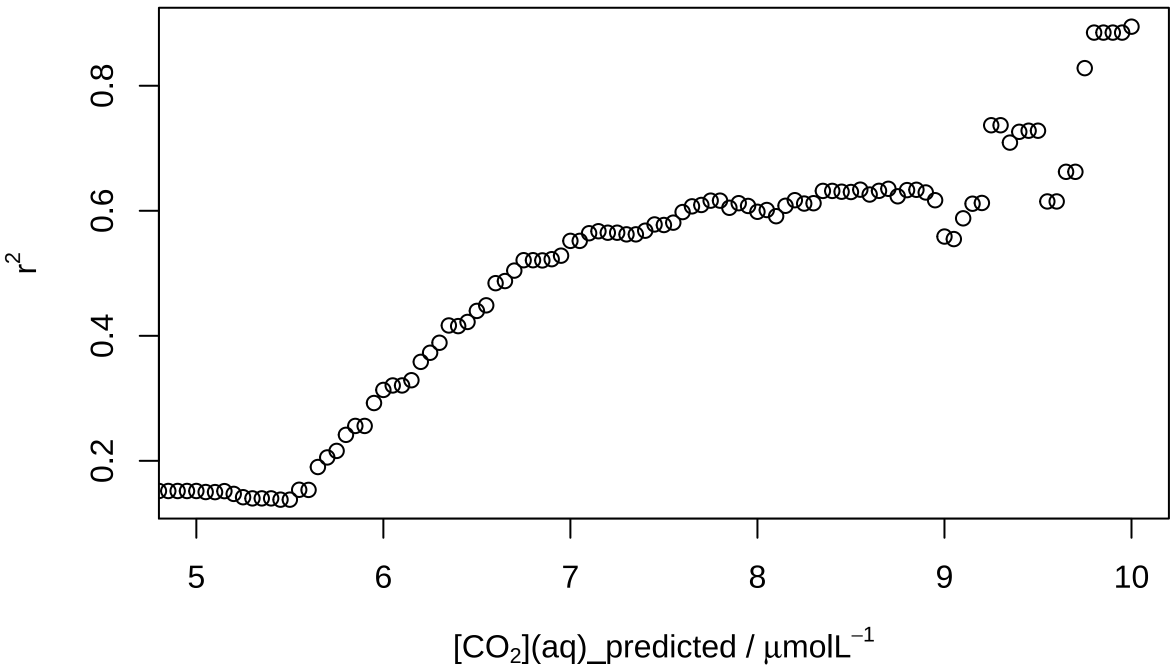
3 Figures

3.1 Figure 3



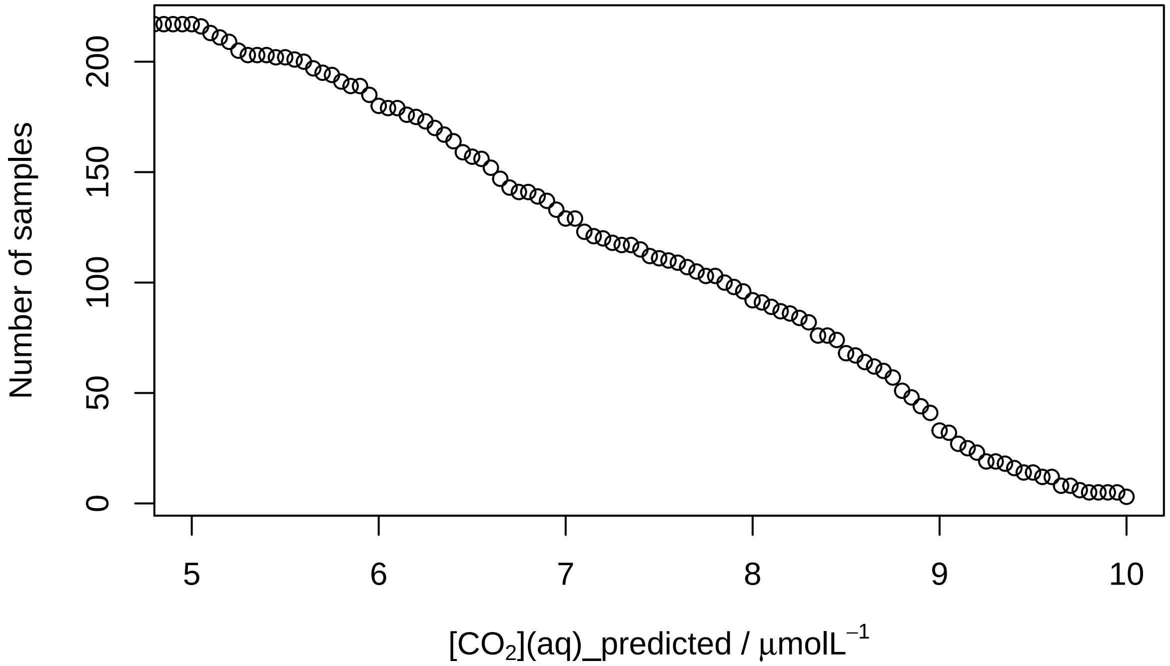
Compiled $CO_{2(\varepsilon_p - \mathrm{alk})}$ -based estimates of atmospheric CO_2 over the past 260 Ka (blue circles) with the ice core compilation of Bereiter et al. (2015) shown as the solid black line. Full sources for the ice core and $CO_{2(\varepsilon_p - \mathrm{alk})}$ records are in Tables 1 and 2 in the main paper.

3.2 Figure 6a



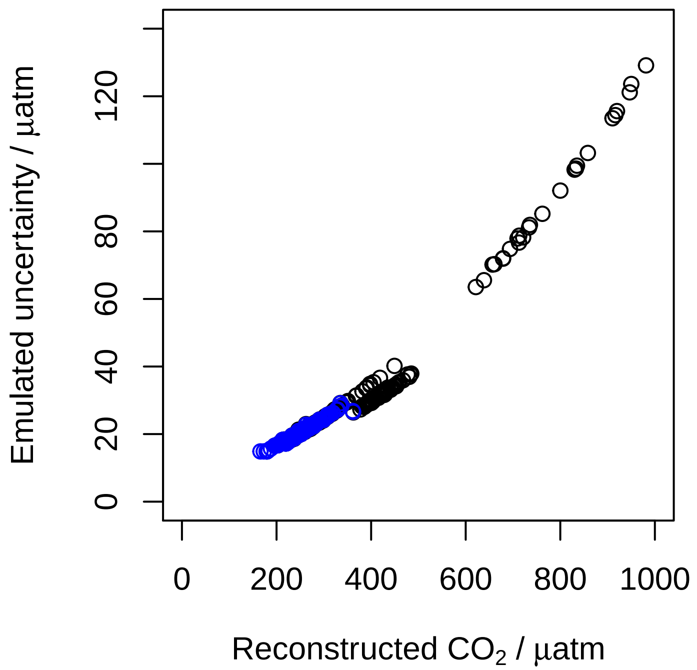
Pearson correlation coefficient of a reducing sample of all compiled $CO_{2(\varepsilon_p - \mathrm{alk})}$ vs the time-equivalent estimate from ice core records (Bereiter et al. (2015)).The sample reduces stepwise by 0.05 $\mu\mathrm{molL}^{-1}$.

3.3 Figure 6b



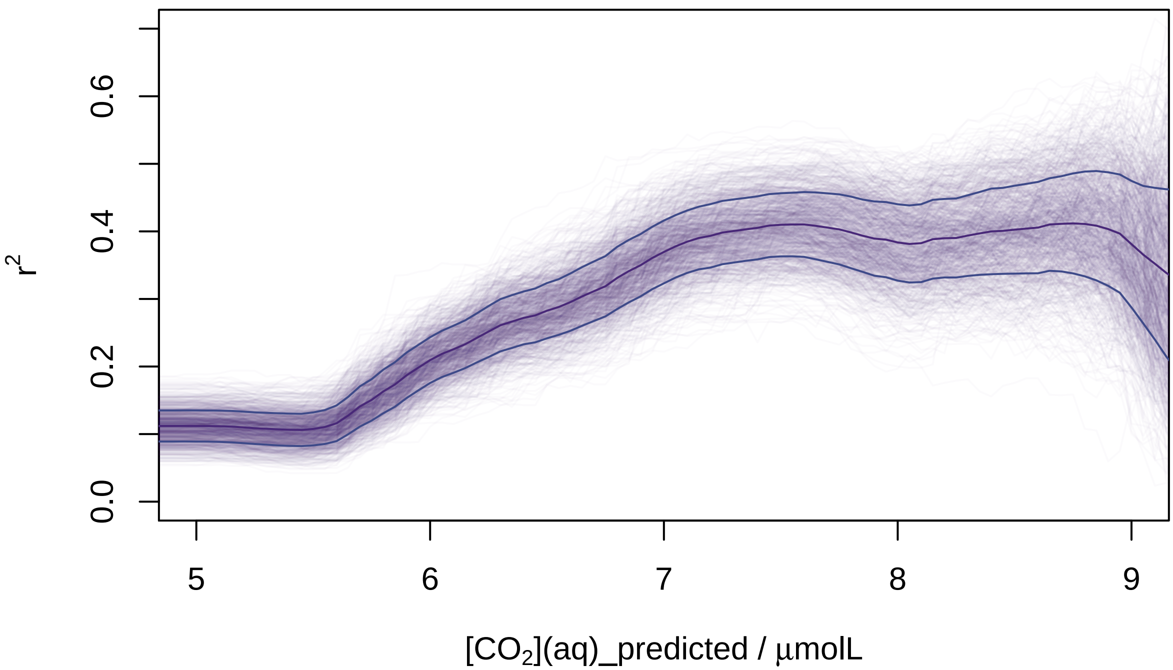
Number of records in each subsample in Figure 6a.

3.4 Figure 7



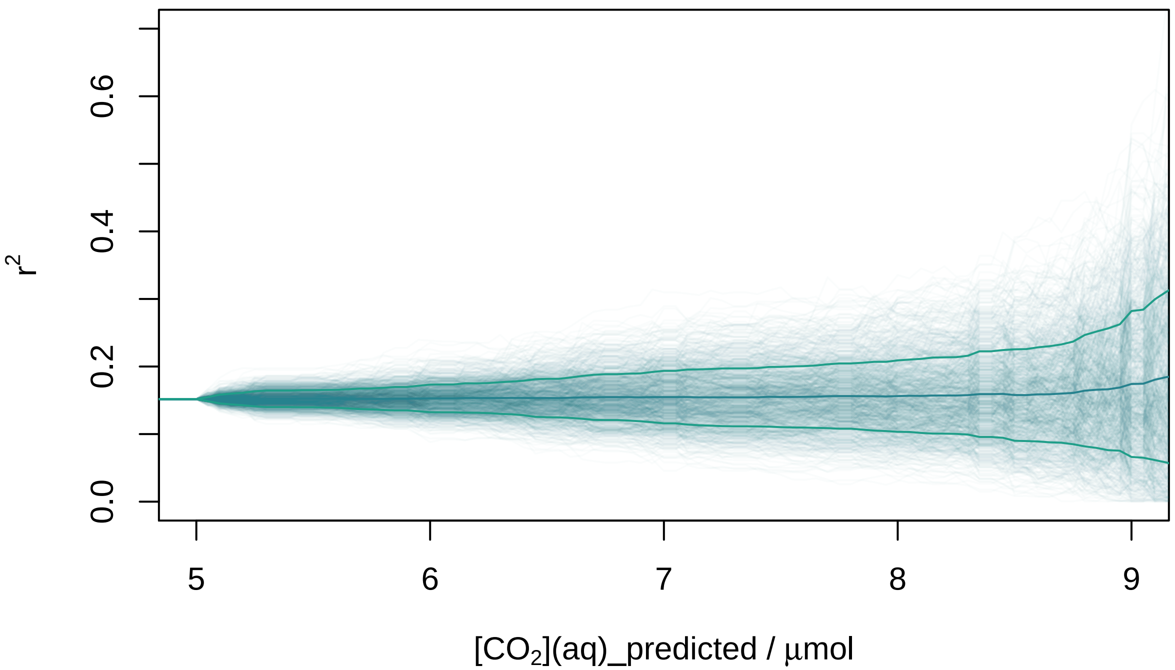
Emulated uncertainty in $CO_{2(\varepsilon_p-alk)}$, generated by running Monte Carlo uncertainty models for all sites in Table 2 applying the same approach to uncertainty as Badger et al. (2013a), Badger et al. (2013b). Estimates used in this study are highlighted in blue.

3.5 Figure 8a



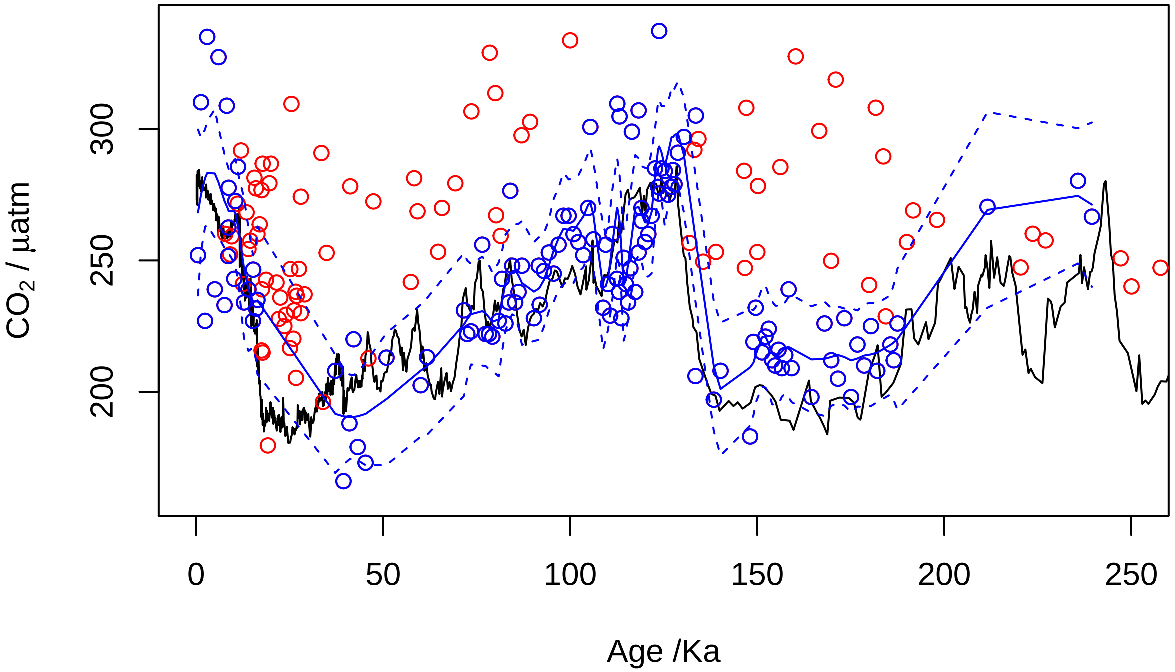
Pearson correlation coefficient of a reducing sample of all compiled $\mathrm{CO}_{2(\varepsilon_\mathrm{p}-\mathrm{alk})}$ vs the time-equivalent estimate from ice core records (Bereiter et al., 2015). As in Figure 6 the sample reduces stepwise by 0.05 $\mu\mathrm{molL}^{-1}$. Panel a shows a 1000 member Monte Carlo analysis, whereby uncertainty in $\mathrm{CO}_{2(\varepsilon_\mathrm{p}-\mathrm{alk})}$ and age is considered, as detailed in the text.

3.6 Figure 8b



Panel b shows a similar 1000 member Monte Carlo analysis, but with random sampling of the whole $\mathrm{CO}_{2(\varepsilon_{\mathrm{p}}-\mathrm{alk})}$ population so that the number of samples is equivalent to the dataset shown in panel a, ie the size of the sample follows that shown in Figure 6b. Means and one σ uncertainties are shown as the bold lines.

3.7 Figure 10



Revised compilation of Pleistocene $CO_{2(\varepsilon_p-\mathrm{alk})}$ vs ice core records. The compiled published records are shown as circles, coloured red where $[CO_2]_{\mathrm{(aq)-predicted}}$ is below a threshold of 7~$\mu mol L^{-1}$, and blue where $[CO_2]_{\mathrm{(aq)-predicted}} > 7$~$\mu mol L^{-1}$. The solid blue line is a loess filter (span 0.1) through the $[CO_2]_{\mathrm{(aq)-predicted}} > 7$~$\mu mol L^{-1}$ values, with 95 % confidence intervals (dashed blue line). The black line is the ice core compilation of Bereiter et al. (2015).

Author contributions. MPSB conceived the study, designed the methodology, analysed the data, prepared the figures and wrote the manuscript (conceptualization, formal analysis, investigation, methodology, vizualization, writing - original draft, review and editing)

Competing interests. MPSB declares that he has no conflict of interest

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