

Interactive comment on “Surface circulation patterns and the pathways of sea surface carbon dioxide (CO₂) off northern Chile (~27.5° S) between 30 and 10 kyr BP: global and/or local forcing?” by J. A. Placencia et al.

Anonymous Referee #1

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This manuscript suffers from at least two major flaws and therefore should not be published.

The authors attempt to reconstruct the partial pressure of carbon dioxide (pCO₂) in surface waters near Chile by comparing the carbon isotopic composition (δ¹³C) of alkenones against the δ¹³C of planktonic foraminifera. In doing so, it is assumed that the δ¹³C of the foraminifera records the δ¹³C of dissolved inorganic carbon without any fractionation. It is further assumed that the δ¹³C of alkenones is offset from the δ¹³C of DIC by an amount that is related in a simple linear way to the pCO₂ of surface

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water (actually, to the aqueous CO₂ concentration, but I use pCO₂ here because the authors convert aqueous CO₂ to pCO₂ in presenting their results). Hence, the authors imply that pCO₂ can be calculated by comparing δ¹³C of alkenones against δ¹³C of foraminifera.

The first failure of this approach is that the δ¹³C of alkenones is not offset from the δ¹³C of DIC by a simple linear relationship that is a function only of pCO₂. As has been pointed out by Bidigare et al. (1997) and by Popp et al. (1998), both cited in this paper, the carbon isotope fractionation between haptophytes (producers of alkenones) and DIC depends also on cell size and on cell growth rate. Growth rate, in turn, depends on many factors, including light, macronutrients (e.g., phosphate) and micronutrients (e.g., iron). The authors note that iron supply varied over the course of their record, and they also note that this may have influenced the growth rates of organisms. If so, then this would have also impacted the fractionation of carbon isotopes between alkenones and DIC. Without a mechanism to correct for changes in growth rate, it is impossible to derive meaningful estimates of pCO₂.

Second, the δ¹³C of planktonic foraminifera is not representative of the δ¹³C of DIC, nor is the δ¹³C of planktonic foraminifera related to the δ¹³C of DIC by a constant factor. In particular, the carbon isotope fractionation between foraminifera shells and DIC is strongly dependent of the concentration of carbonate ion. This sensitivity to carbonate ion concentration is described in many papers by Howie Spero, Jelle Bijma, and their coworkers (e.g., Spero et al., *Nature*, 390 (1997) 497-500; Russell and Spero, *Paleoceanography*, 15 (2000) 43-52). The carbonate ion of the surface ocean worldwide changed appreciably over the course of deglaciation associated with the rise in atmospheric CO₂. More important here, changes in upwelling and in the biological consumption of CO₂ in the region offshore of Chile would have imposed changes in the ambient carbonate ion concentration even larger than those experienced in less dynamic regimes. It is not possible to constrain the carbonate ion concentration from the available data. Consequently, it is not possible to constrain the changes through

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time in the carbonate ion effect on fractionation of $\delta^{13}\text{C}$ between foraminifera and DIC. For these reasons, meaningful reconstruction of surface ocean pCO_2 by the methods employed here are not possible. Therefore, this paper should not be published.

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