Use and abuse of Keeling plots in paleoatmospheric research: What can we learn from $\delta^{13}CO_2$ in polar ice cores?

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The alternation of ice and warm ages is connected to glacial/interglacial CO_2 concentration changes of approximately 80-100 ppmv with significant fine structure during Termination I (Monnin et al. 2001). Changes in the carbon isotopic signature of CO_2 during that time are expected to add to our understanding what processes were responsible for the observed CO_2 changes. First measurements revealed a glacial/interglacial change in $\delta^{13}CO_2$ of 0.2-0.3‰ (Leuenberger et al. 1992) but significantly higher variations during the termination (Smith et al. 1999). Using the so called Keeling plot approach ($\delta^{13}C = a/CO_2 + b$, where b is taken as representative of the isotopic signature of carbon added or extracted from the atmosphere) it was concluded that the terrestrial biosphere was of major importance for CO_2 changes in the glacial and the Holocene (Smith et al. 1999; Fischer et al. 2003). However, this approach known from terrestrial carbon cycle research represents essentially a carbon isotopic mass balance of a two reservoir system and its application on paleoclimatic CO_2 changes is not straightforward. Here we revisit the Keeling plot approach on paleoclimatic time scales using ice core observations, theoretical considerations and modelling results. Based on output of transient model runs from our global carbon cycle model BICYCLE during the last transition (Köhler et al. 2005) we constrain the conclusions to be drawn from ice core $\delta^{13}CO_2$ data and Keeling plot analyses (Köhler et al. 2006). The effective isotopic signatures of various processes calculated by either the Keeling plot approach or theoretically differ widely from the known $\delta^{13}C$ of the source and are very often indistinguishable in the light of the uncertainties. A back calculation from well distinct fluctuations in pCO_2 and $\delta^{13}C$ to identify their origin using the Keeling plot approach seems not possible.

Extending the Keeling plot approach to a three reservoir system

Two reservoir system

$$A = A_0 + B \text{ and } A\delta^A = A_0\delta_0^A + B\delta^B \Rightarrow \delta^A = \frac{A_0(\delta_0^A - \delta^B)}{A} + \delta^B$$

Three reservoir system

$$A + O = A_0 + O_0 + B \text{ and } A\delta^A + O\delta^O = A_0\delta_0^A + O_0\delta_0^O + B\delta^B$$

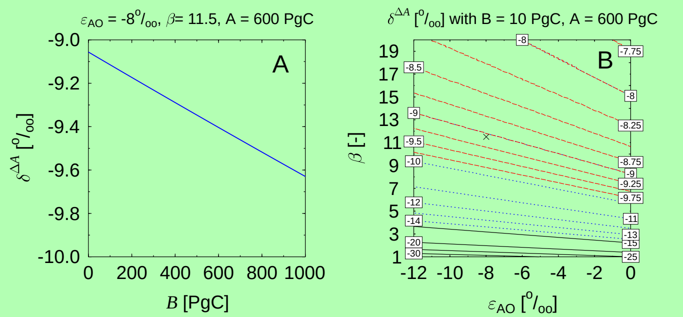
$$A_0 = 600 \text{ PgC and } O_0 = 38,000 \text{ PgC } \delta_0^A = -6.5‰,\ \delta_0^O = +1.5‰\ \delta^B = -25‰$$

$$\varepsilon_{AO} \approx \delta_0^A - \delta_0^O \approx \delta^A - \delta^O \approx -8‰$$

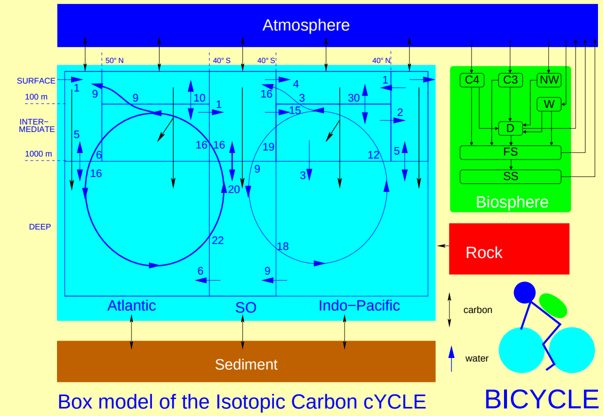
Revelle or buffer factor $\beta = f(\text{temperature, alkalinity, DIC})$: $\beta := \left(\frac{d[CO_2]/[CO_2]}{dDIC/DIC}\right)$.

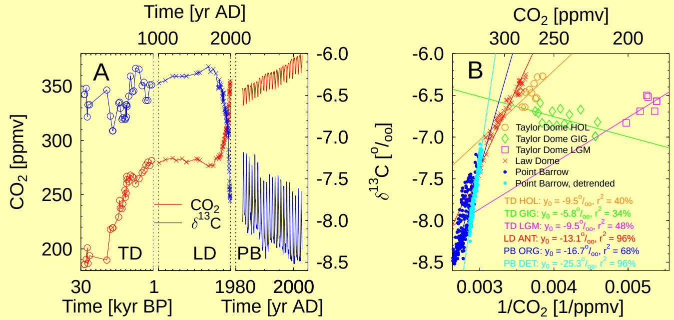
β in recent surface waters varies between 8 and 16 (Sabine et al. 2004). Preindustrial: β (surface ocean boxes): 11.5, with 9 in equatorial waters and 12 in the high latitudes.

$$\text{Finally: } \delta^{\Delta A} = \frac{\frac{A_0+O_0+B-O}{A_0+O_0+B}(A_0\delta_0^A + O_0\delta_0^O + B\delta^B + \varepsilon_{AO}O) - A_0\delta_0^A}{O_0+B-O}.$$



Results of the three reservoirs approach. Effective isotopic signature of the atmosphere $\delta^{\Delta A}$ as function of (A) the size of the terrestrial release and (B) the Revelle Factor β and the fractionation during gas exchange ε_{AO}. The cross in B marks the preindustrial state ($\beta = 11.5$, $\varepsilon_{AO} = -8.0‰$).





A: Data sets of measured CO_2 and $\delta^{13}C$. B: Keeling plot. Point Barrow monthly resolved (1982 – 2002) (Keeling & Whorf 2005; Keeling et al. 2005); original data (PB ORG); detrended (PB DET). Law Dome (1 kyr) (Francey et al. 1999; Trudinger et al. 1999) (LD ANT). Taylor Dome (30 kyr) (Smith et al. 1999); Holocene (TD HOL), glacial/interglacial transition (TD GIG), LGM (TD LGM).

Summary of y-axis intercept y_0 of the steady state Keeling plot analysis for processes changing over Termination I.

Process	y_0 (‰)	Comment
Linear rise in terrestrial carbon storage	−8.6	increase non-linear, steepest slope −25‰
Decrease in marine export production	−8.6	steeper slope during first 50 yr ($y_0 = -9.7‰$)
Rise in NADW formation	−7.8	varies with time; mixture with changes in marine export production during Heinrich 1 event; during Younger Dryas and resumption in the Holocene $y_0 = -7.15 \pm 0.05‰$, steep slope during first 50 yr ($y_0 = -9.5‰$)
Rise in Southern Ocean vertical mixing	−8.2	steep slope during first 50 yr ($y_0 = -11.0‰$)
Decline in sea ice cover	−0.7	regression over whole data set: −3.8‰; different in North (−4.8‰) and South (−77.2‰)
Rise in sea level	−6.4	
Rise in temperature	−3.6	
Sediment/ocean interaction	−5.8	

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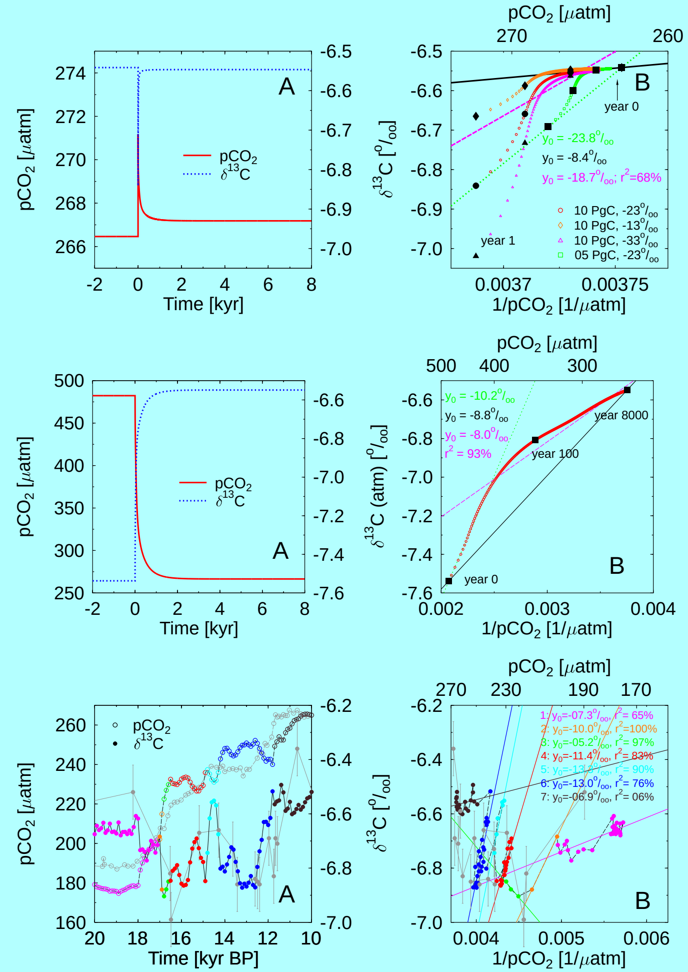

Examples for Keeling plots out of simulation results: Top: Fast terrestrial carbon release. Middle: Switching from abiotic to biotic ocean. Different regression models in Top and Middle: first year only in green; prior/after (steady states) in black; equilibration time in magenta. Bottom: Identifying events with different $\delta^{13}C$ signal during Termination I.

References:

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