

Latest Insights into Past Carbon Cycle Changes from CO₂ and δ¹³C_{atm}

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With 2 Figures

CO₂ represents the most important greenhouse gas released into the atmosphere as a result of human activity. The majority of our knowledge on the increase in CO₂ since the start of the industrialization comes from ice cores, which complement the direct atmospheric CO₂ measurements obtained at Mauna Loa since the 1950s. The combined CO₂ record shows an unambiguous anthropogenic CO₂ increase over the last 150 years from 280 to about 400 ppm in 2014. Values above 300 ppm are unprecedented in the long-term ice core record covering the last 800,000 years, with natural CO₂ concentrations varying between interglacial and glacial bounds of about 280 and 180 ppm, respectively (LÜTHI et al. 2008, PETIT et al. 1999). Moreover, the increase in CO₂ concentrations during the last termination shows significant fine structure (MARCOTT et al. 2014, MONNIN et al. 2001), indicating a sequence of events of CO₂ release to the atmosphere involving different processes acting at different points in time.

Although past atmospheric CO₂ concentrations are known with high precision, the causes of the observed deglacial CO₂ changes cannot be easily attributed quantitatively to individual processes and the cause of the glacial/interglacial 80–100 ppm increase of atmospheric CO₂ remains a hot topic of paleoclimate research. Several processes have been implied (BROVKIN et al. 2012, CIAIS et al. 2012, FISCHER et al. 2010, JACCARD et al. 2013, KÖHLER and FISCHER 2006, MARTÍNEZ-GARCÍA et al. 2009, MENVIEL et al. 2012, STEPHENS and KEELING 2000, TOGGWEILER et al. 2006, TSCHUMI et al. 2011, WATSON and GARABATO 2006). These include:

- Southern Ocean ventilation by wind or buoyancy feedbacks,
- Iron fertilization of the marine biosphere in the Southern Ocean,
- Changes in the re-mineralization depth of organic carbon,
- Release of permafrost carbon during the deglaciation,
- Decreased solubility due to ocean warming,
- Changes in air/sea gas exchange due to changing sea ice cover,
- Marine carbonate feedbacks.

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However, none of these processes alone is able to explain the glacial/interglacial CO₂ change. Substantial progress could come from better estimates of past changes in the carbon stored by the biosphere or from using stable carbon isotopes to constrain sources and sinks of carbon and exchange processes with the atmosphere. The vast majority of the carbon cycling in the Earth system on multi-millennial timescales resides in the ocean. Accordingly, the global $\delta^{13}\text{C}$ of inorganic carbon dissolved in seawater ($\delta^{13}\text{C}_{\text{DIC}}$) may provide the best constraint on past carbon cycle changes (GOODWIN et al. 2011). However, a global compilation of $\delta^{13}\text{C}_{\text{DIC}}$ from marine sediment records is hampered by insufficient spatial representation of vast ocean regions, the limited temporal resolution of many sediment records, and substantial chronological uncertainties. The alternative, to reconstruct the mean $\delta^{13}\text{C}$ record of the well-mixed atmosphere ($\delta^{13}\text{C}_{\text{atm}}$) from the fossil air contained in Antarctic ice cores has been a long-standing

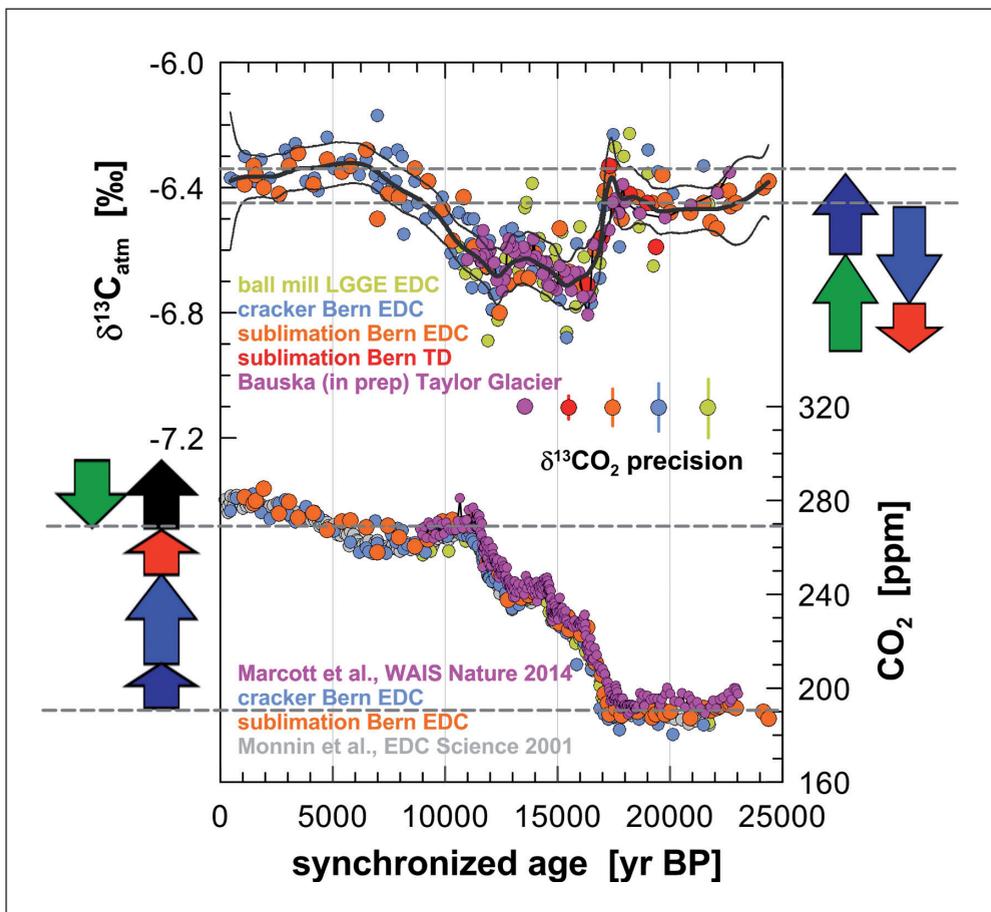


Fig. 1 Deglacial record of atmospheric changes in CO₂ (MARCOTT et al. 2014, MONNIN et al. 2001) and $\delta^{13}\text{C}_{\text{atm}}$ (SCHMITT et al. 2012) and BAUSKA et al. (in preparation). The arrows indicate the approximate glacial/interglacial changes expected from individual carbon cycle processes according to KÖHLER et al. 2005: Changes in sea surface temperature (*dark blue*), Southern Ocean ventilation (*blue*), iron fertilization (*red*), terrestrial biosphere regrowth (*green*) and carbonate compensation (*black*).

quest, and only latest analytical progress was able to improve the measurement error while at the same time cutting down sample size by an order of magnitude.

The new $\delta^{13}\text{C}_{\text{atm}}$ data from the air trapped in Antarctic ice cores, provides improved constraints to revisit the enigma of deglacial CO_2 increase (Fig. 1). Mean $\delta^{13}\text{C}_{\text{atm}}$ levels during the Last Glacial Maximum and the Holocene (as well as for MIS6 and MIS5.5) are surprisingly similar, despite different CO_2 concentrations and the substantially altered climate system. This supports again the notion that the $\delta^{13}\text{C}_{\text{atm}}$ record is the sum of several factors that balance each other to a large extent as shown in Figure 1. The $\delta^{13}\text{C}_{\text{atm}}$ data (LOURANTOU et al. 2010a, b, SCHMITT et al. 2012, SCHNEIDER et al. 2013) from the last two deglaciations suggest a sequence of processes that drove atmospheric CO_2 changes during different stages of the transition from glacial conditions into a milder interglacial world. At the start of the transitions, upwelling of old ^{13}C -depleted waters in the Southern Ocean increased the release of CO_2 to the atmosphere. This process was synchronous with a demise in iron-stimulated bioproductivity in the Southern Ocean, when atmospheric dust concentrations declined rapidly. This carbon release from the ocean was followed by the gradual growth of terrestrial carbon storage in vegetation, soil, and peatlands as evidenced by the slow $\delta^{13}\text{C}_{\text{atm}}$ increase. This process reached well into the subsequent interglacials.

While the well-studied glacial terminations indicate a release of old, isotopically depleted carbon from the deep ocean, it is not yet known unambiguously, when this carbon has been transferred to the deep ocean and where this old carbon has been stored. Again $\delta^{13}\text{C}_{\text{atm}}$ data

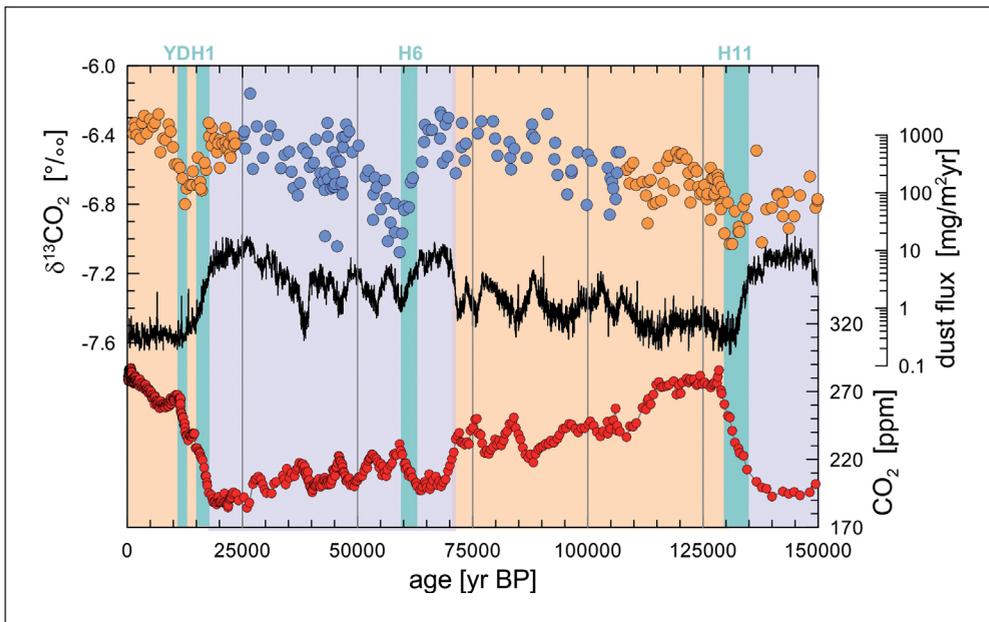


Fig. 2 Record of atmospheric CO_2 (BEREITER et al. 2012) and $\delta^{13}\text{C}_{\text{atm}}$ (SCHMITT et al. 2012, SCHNEIDER et al. 2013) (orange) and EGGLESTON et al. (blue, in preparation). $\delta^{13}\text{C}_{\text{atm}}$ data points from brittle ice show negative outliers due to drill fluid contamination. The background indicates the two mode carbon cycle changes in the Southern Ocean (reduced ventilation in the Antarctic Zone [orange] vs. increased iron fertilization in the Subantarctic Zone [light blue]) as defined by JACCARD et al. 2005).

covering the entire last glacial cycle can answer the first of these questions. Latest results from Antarctic ice cores show a gradual increase in $\delta^{13}\text{C}_{\text{atm}}$ over the entire MIS5 and 4, which culminated during an upwelling event (ANDERSON et al. 2009) observed at the MIS4/3 transition, similar to the one encountered during the last termination. Interestingly, during the MIS5/4 transition, when iron fertilization was most likely to set in, as indicated by the strong increase in iron bearing eolian mineral dust aerosol (LAMBERT et al. 2012, MARTÍNEZ-GARCÍA et al. 2009, WOLFF et al. 2006), no clear increase in $\delta^{13}\text{C}_{\text{atm}}$ is found. This provides an experimental upper bound on the amount of CO_2 reduction by iron fertilization at this time. Again over MIS3 a similar long-term enrichment in $\delta^{13}\text{C}_{\text{atm}}$ is observed which ends with the upwelling event at the beginning of termination I (ANDERSON et al. 2009).

Superimposed on these changes in carbon storage in the abyss, a long-term trend in $\delta^{13}\text{C}_{\text{atm}}$ can also be discerned leading to 0.4 ‰ lighter values in MIS6 compared to the Last Glacial Maximum as well as in MIS5.5 compared to the Holocene. Similar offsets are also seen in marine $\delta^{13}\text{C}_{\text{DIC}}$ records suggesting long-term changes in the isotopic composition of the entire ocean/atmosphere carbon pool (SCHNEIDER et al. 2013).

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