References and notes

1. Gordon, D.C. Jr., Boudreau, P.R., Mann, K.H., Ong, J-E., Silvert, W.L., Smith, S.V., Wattayakorn, G., Wulff, F. and Yanagi, T. (1996). *LOICZ Biogeochemical Modelling Guidelines.* LOICZ Reports & Studies No. 5. Second Edition, vi+96 pp. LOICZ, Texel, The Netherlands
2. Holligan, P.M. and Reiners, W.A. (1991). Predicting the responses of the coastal zone to global change. *Advances in Ecological Research* **22**: 211-255
3. Pernetta, J.C. and Milliman, J. (1995). *Land-Ocean Interactions in the Coastal Zone Implementation Plan.* IGBP Report No. 33, Stockholm, 215pp.
4. Garrels and Mackenzie, F.C. (1972). A quantitative model for the sedimentary rock cycle. *Marine Chemistry* **1**: 22-41
5. Smith, S.V. and Mackenzie, F.C. (1987). The ocean as a net heterotrophic system: implication for the carbon biogeochemical cycle. *Global Biogeochemical Cycles* **1**: 187-198
6. Sarmiento, J.L. and Sundquist, E. (1992). Revised budget for the oceanic uptake of anthropogenic carbon dioxide. *Nature* **356**: 589-593
7. Smith, S.V. and Hollibaugh. 1993. Coastal metabolism and the oceanic organic carbon balance. *Reviews in Geophysics* **31**: 75-89

Long-term variations of the concentration of atmospheric CO_2

by Andreas Indermühle

The concentration of atmospheric CO_2 (the most important greenhouse gas after water vapour) is increasing since the beginning of industrialization from its pre-industrial value of about 280 ppmv to its present value of 365 ppmv (1, 2). In order to understand the impact of this strong perturbation on the carbon cycle and on climate it is important to investigate the global carbon cycle on all time scales. Direct measurements of atmospheric CO_2 exist since 1958. A reliable reconstruction of the concentration of atmospheric CO_2 in the past, a prerequisite for the understanding of the long-term variations, is only possible by measurements on air which is enclosed in bubbles of polar ice.

Such measurements have been done for 20 years in different laboratories with different methods. In all laboratories a sample of ice (mainly from Antarctic drill sites) of 6 to 1500 g is crushed or ground under vacuum without melting. The extracted air is then measured by infrared laser absorption spectroscopy, gas chromatography or volumetry. The analytical uncertainty is 1.2 to 5 ppmv, depending on sample size, extraction method and analytical procedure.

Mechanisms of the global carbon cycle

The main preindustrial sources and sinks of atmospheric CO_2 on a millennial time scale are the land biosphere and the ocean. In addition, ocean-sediment interactions are important processes on longer time scales.

Growth or decay of terrestrial biomass can cause a decrease or an increase, respectively, of the concentration of atmospheric CO_2. At present, the net terrestrial carbon uptake due to CO_2 and nitrogen fertilization is an important sink of anthropogenic CO_2.

The CO_2 partial pressure in sea water is mainly a function of the temperature (solubility of CO_2), salinity, concentration of dissolved inorganic carbon (DIC) and alkalinity (ALK). Changes of these properties in the ocean's surface, which is in contact with the atmosphere, translate into changes of the concentration of atmospheric CO_2 via the air-sea gas exchange. The sea surface temperature (SST) is influenced by changes of the ocean circulation or by large-scale climate transitions such as glacial-to-interglacial transitions. Sea surface salinity, DIC and ALK can be altered by dilution of the ocean surface water (by meltwater input or increased precipitation) and by changes of the ocean circulation. Furthermore, DIC and ALK can be depleted in the surface water by increased biological activity of the marine biosphere (cycling of calcite and organic matter). The biological activity depends, among other things, on the available amount of

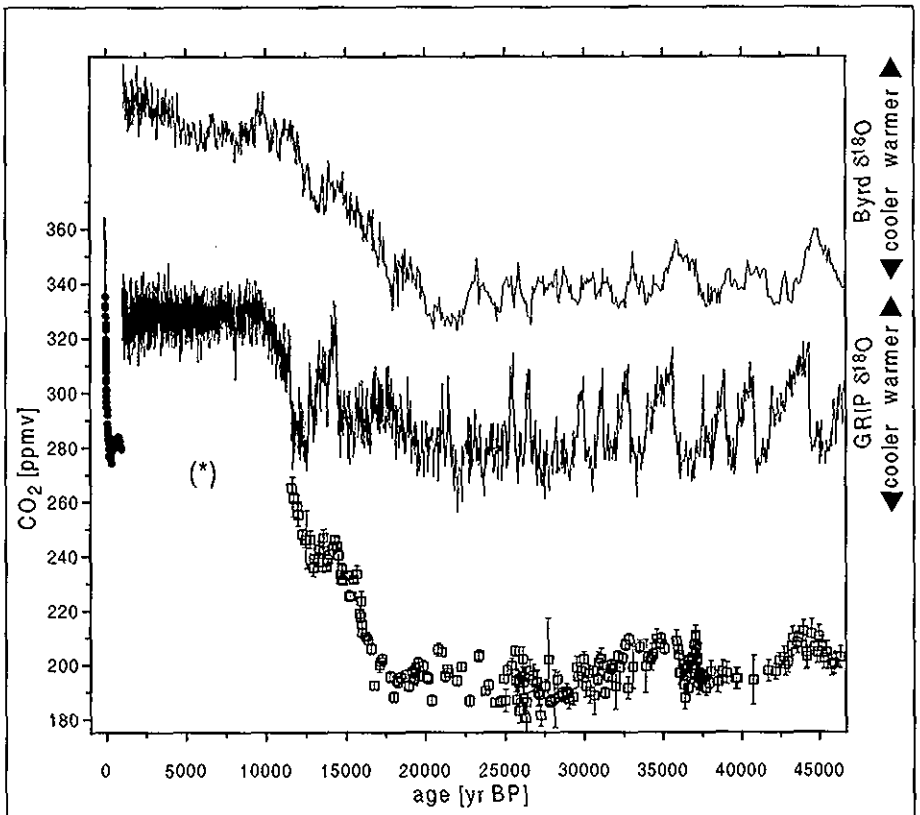

Figure 1. Top curve: Air temperature over West Antarctica as indicated by the Byrd $\delta^{18}O$ (9). Centre curve: Air temperature over central Greenland as indicated by the GRIP $\delta^{18}O$ (8). Bottom curve: CO_2 records from Byrd Station (squares) (10), Law Dome (dots) (11) and Mauna Loa (solid line) (2). (*): A high resolution CO_2 record over the entire Holocene will shortly be published (12).

nutrients, which can be varied by changes of the upwelling of nutrient-rich deep water (3).

High-resolution CO_2 records from ice cores

Figure 1 (bottom) shows high-resolution CO_2 measurements from different Antarctic ice cores, which represent with good accuracy the atmospheric CO_2 concentration. The direct atmospheric measurements from Mauna Loa are also shown. The discussion of the ice core records is divided in three parts. i) During the last glacial (until 18 kyr BP), only small fluctuations of the atmospheric CO_2 concentration of the order of 20 ppmv occur on a millennial time scale; ii) Over the transition from the last glacial maximum to the Holocene (18 - 11 kyr BP) the CO_2 concentration increases from 195 to 267 ppmv; iii) During the Younger Dryas (12.7 - 11.6 kyr BP), a cold period during the last deglaciation, CO_2 rises steadily.

Last glacial

During the last glacial, rapid changes of the air temperature in central Greenland occurred as indicated by the $\delta^{18}O$ record of the GRIP ice core (Figure 1, center). During the so-called Dansgaard-Oeschger (D-O) events, temperature increased by up to 15°C in less than 50 years and then gradually decreased and returned to full glacial conditions. The air temperature over Greenland is strongly influenced by the SST of the North Atlantic. A probable explanation of these oscillations is that the strength of the thermohaline circulation (the "conveyor belt"), which transports heat from the tropics to the North Atlantic, changed. The thermohaline circulation can be disturbed by a freshwater input resulting from iceberg discharge or melting of ice sheets. According to this hypothesis, strong perturbations of the surface water properties could develop, at least in the North Atlantic, during the D-O events, and these could influence the concentration of atmospheric CO_2.

The comparison between CO_2 and $\delta^{18}O$ (GRIP) records suggests a link between atmospheric CO_2 and the most prominent D-O events (45 and 35 kyr BP): Slightly before or during these events the CO_2 concentration increases by about 20 ppmv followed by a gradual decrease over the next 10 kyr. The exact mechanism between the hypothesized fast changes of the thermohaline circulation and the observed CO_2 variations is still not clear. Although sparse, the $\delta^{13}C$ record of CO_2 carries some information about the origin of the CO_2 variations. This record suggests that changes in the activity of the biological pump in the ocean rather than variations in SST are the main reasons for the observed CO_2 trends.

Transition

The ~70 ppmv increase of the atmospheric CO_2 concentration between the last glacial and the Holocene has been the focus of many studies since it was first measured in Antarctic ice cores (for a summary see (4)). But each of the formulated hypotheses is in contradiction to or lacks corroboration by palaeodata. Our present knowledge is as follows:

- It is certain that the beginning of the CO_2 increase (~18 kyr BP) is before the rapid increase of the air temperature over central Greenland and elsewhere (Bølling/Allerød transition, 14.8 kyr BP).
- As indicated by the $\delta^{18}O$ data from Byrd (Figure 1, top) and the CO_2 record, it is most likely that the increase of CO_2 parallels the warming of the Southern Ocean with a lag of less than 1 kyr.

Younger Dryas

The Younger Dryas is a prominent cold period in the North Atlantic region during the last deglaciation. Similar to the D-O events, changes in the thermohaline circulation are a probable explanation for the fast cooling and warming. The atmospheric CO_2 concentration and the temperature in the high northern and southern latitudes during a YD-like event can be simulated in a circulation-biogeochemistry model and compared with climate proxies (5). In this model, ocean-sediment interactions which could have contributed to the long-term glacial-interglacial increase are not simulated. Therefore, this long-term increase is subtracted from the ice core data and then the resulting residual CO_2 is compared with the model (Figure 2,

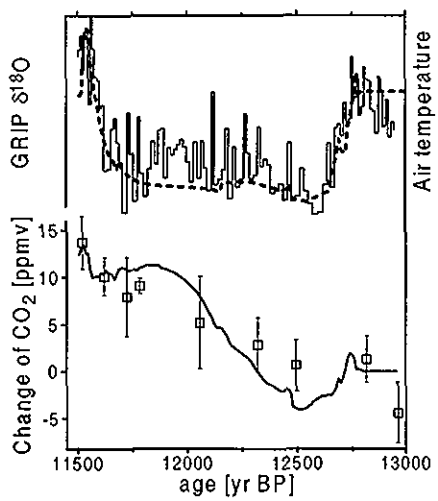

Figure 2. Younger Dryas. Top curve: GRIP $\delta^{18}O$ (8) (solid line) and modelled air temperature (dashed line). Bottom curve: Comparison of modelled changes in the concentration of atmospheric CO_2 (solid line) and residual CO_2 values from Byrd Station (squares) (5).

bottom). The residual CO_2 exhibits an increase of about 20 ppmv during the YD - in good agreement with the model. The main conclusion is that a cooling in the North Atlantic region has only a small effect on the concentration of atmospheric CO_2 because it is spatially limited and compensated by a warming in the Southern Ocean, operating much like a bipolar seesaw (6, 7).

Determination of the relation between the long-term variations of climate and concentration of atmospheric CO_2 remains a challenge. In order to quantify the contribution of the individual mechanisms to observed changes in the concentration of atmospheric CO_2, palaeoclimatic observations with sufficient temporal and spatial resolution and with an accurate chronology are necessary.

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References and notes

1. Neftel, A., Moor, E., Oeschger, H. and Stauffer, B. (1985). Evidence from polar ice cores for the increase in atmospheric CO_2 in the past two centuries. *Nature* **315**, 45-47.
2. Keeling, C.D. and Whorf, T.P. (1999). Atmospheric CO_2 concentrations (ppmv) derived from in situ air samples collected at Mauna Loa Observatory, Hawaii. http://cdiac.esd.ornl.gov/ndps/ndp001.html
3. Volk, T. and Hoffert, M.I. (1985). Ocean Carbon pumps: Analysis of relative strengths and efficiencies in ocean-driven atmospheric CO_2 changes, in *The Carbon Cycle and atmospheric CO_2: Natural variations archean to present* (eds. Sundquist, E.T. and Broecker, W.S.) (American Geophysical Union, Washington, 1985).
4. Broecker, W.S. and Henderson, G. (1998). The sequence of events surrounding Termination II and their implications for the cause of glacial-interglacial CO_2 changes. *Paleoceanography* **13**, 352-364.
5. Marchal, O., Stocker, T.F., Joos, F., Indermühle, A., Blunier, T., and Tschumi, J. (1999). Modelling the concentration of atmospheric CO_2 during the Younger Dryas climate event. *Clim. Dyn.*, in press
6. Broecker, W.S. (1998). Paleocean circulation during the last deglaciation: A bipolar seesaw? *Paleoceanography* **13**, 119-121
7. Stocker, T.F. (1998). The seesaw effect. *Science* **282**, 61-62.
8. Dansgaard, W. *et al.* (1993). Evidence for general instability of past climate from a 250-kyr ice-core record. *Nature* **364**, 218-220.
9. Johnsen, S.J., Dansgaard, W., Clausen, H.B. & Langway, C.C., Jr. (1972). Oxygen isotope profiles through the Antarctic and Greenland ice sheets. *Nature* **235**, 429-434.
10. Neftel, A., Oeschger, H., Staffelbach, T. & Stauffer, B. (1988). CO_2 record in the Byrd ice core 50,000-5,000 years BP. *Nature* **331**, 609-611.
11. Etheridge, D.M. *et al.* (1996). Natural and anthropogenic changes in atmospheric CO_2 over the last 1000 years from air in Antarctic ice and firn. *J. Geophys. Res.* **101**, 4115-4128.
12. Indermühle, A. *et al.* (1999). Holocene carbon-cycle dynamics based on CO_2 trapped in ice at Taylor Dome, Antarctica. *Nature*
13. I appreciate comments by B. Stauffer and T.F. Stocker.