Ice core evidence for the extent of past atmospheric CO_2 change due to iron fertilisation

R. Röthlisberger,[1,2] M. Bigler,[3] E. W. Wolff,[1] F. Joos,[3] E. Monnin,[3] and M. A. Hutterli[3]

Received 23 April 2004; accepted 12 July 2004; published 21 August 2004.

[1] An extended high-resolution ice core record of dust deposition over the past 60 ka from Dome C, Antarctica, is presented. The data are in conflict with the idea that changes in aeolian iron input into the Southern Ocean were the major cause for the 80 ppm glacial-interglacial CO_2 increase. During the deglaciation, the CO_2 increase shows a linear relationship with the fall of the logarithm of the nss-Ca^{2+} flux, a proxy for dust deposition. However, the very large variations in the nss-Ca^{2+} flux related to the glacial Antarctic warm events A1 to A4 were accompanied by small CO_2 variations only. Our data-based analysis suggests that decreased Southern Ocean dust deposition caused at most a 20 ppm increase in CO_2 at the last glacial-interglacial transition. Rapid decreases in dust deposition to the northern Pacific could have been responsible for a maximum of 8 ppm in addition. *INDEX TERMS:* 1615 Global Change: Biogeochemical processes (4805); 4806 Oceanography: Biological and Chemical: Carbon cycling; 4801 Oceanography: Biological and Chemical: Aerosols (0305); 9310 Information Related to Geographic Region: Antarctica. **Citation:** Röthlisberger, R., M. Bigler, E. W. Wolff, F. Joos, E. Monnin, and M. A. Hutterli (2004), Ice core evidence for the extent of past atmospheric CO_2 change due to iron fertilisation, *Geophys. Res. Lett.*, *31*, L16207, doi:10.1029/2004GL020338.

1. Introduction

[2] The concentration of CO_2 in the atmosphere over the last 420 kyr has alternated between about 180 ppm in glacial maxima and 280 ppm in interglacials [*Petit et al.*, 1999]. These changes act as a major amplifier in the climate system, contributing to the strong glacial-interglacial contrast that is observed. Determining the causes of the CO_2 increase at glacial terminations, such as the $\sim$80 ppm increase at the last one (Figure 1), is one of the major challenges in understanding the Earth system. Here we use high-resolution chemical data from an Antarctic ice core to set limits on one of the most pervasive mechanisms that has been proposed, iron fertilisation of the oceans.

[3] The ocean is the most important control on atmospheric CO_2 concentrations on glacial-interglacial timescales [*Sigman and Boyle*, 2000; *Archer et al.*, 2000]. The equilibrium partial pressure of CO_2 in seawater depends on the concentration of dissolved inorganic carbon (DIC) amongst other factors. In high-latitude surface waters, particularly in the Southern Ocean and in the North Pacific, the concentrations of nutrients and DIC remain high and chlorophyll levels low throughout the year. Iron concentrations in these high-nutrient low-chlorophyll (HNLC) regions are very low, and it has been suggested that enhanced aeolian iron deposition into the Southern Ocean was the primary cause for the observed low glacial CO_2 values [*Martin*, 1990]. Several field experiments have demonstrated that addition of iron indeed stimulates biological productivity and reduces surface water pCO_2 in the Southern Ocean and other HNLC regions [*Boyd et al.*, 2000; *Tsuda et al.*, 2003].

[4] Different model analyses focusing on a range of iron-related marine biogeochemical processes, including ocean-sediment interactions [e.g., *Matsumoto et al.*, 2002] yield conflicting results, explaining little [*Bopp et al.*, 2003] up to all of the observed 80 ppm CO_2 increase during past deglaciations depending on the specific parameterisation and interactions included in the model [*Parekh et al.*, 2004; *Ridgwell*, 2003]. Several processes other than iron fertilisation may be responsible for the low glacial CO_2 concentrations [*Sigman and Boyle*, 2000; *Archer et al.*, 2000; *Broecker and Henderson*, 1998].

[5] Here we analyse changes in atmospheric CO_2 concentrations [*Indermühle et al.*, 2000] and aeolian dust deposition as recorded in Antarctic ice cores (Figure 1). The strategy is to estimate data-based bounds for the contribution of iron fertilisation to atmospheric CO_2 variations during periods where variations in aeolian dust supply are large, but changes in other parameters affecting atmospheric CO_2 remained modest. For the first time, chemical data are available at a resolution capable of assessing the role of dust on CO_2 over the past 60 ka, i.e., covering the period of the last four glacial Antarctic warm events and the last deglaciation.

2. Data

[6] The chemical ice core records from Dome C have been obtained by a Continuous Flow Analysis (CFA) system, as described by *Röthlisberger et al.* [2000]. Back to 45 kyr B.P. the data originate from the EDC96 ice core, mainly analysed during the 97/98 and 98/99 field seasons [*Röthlisberger et al.*, 2002]. Data reaching further back in time were obtained from EDC99 during the 01/02 field season. The Dome C EDC96 records are displayed on the EDC1 timescale [*Schwander et al.*, 2001], EDC99 records on the EDC2 timescale (Jakob Schwander, University of Bern, personal communication). Temporal resolution of the chemical records is of the order of at most a few years. Presented here are 50-year averages of the high-resolution data. For comparison, the widely-cited dust record from

[1]British Antarctic Survey, Natural Environment Research Council, Cambridge, UK.
[2]Now at NCCR Climate, University of Bern, Bern, Switzerland.
[3]Climate and Environmental Physics, University of Bern, Bern, Switzerland.

0094-8276/04/2004GL020338$05.00

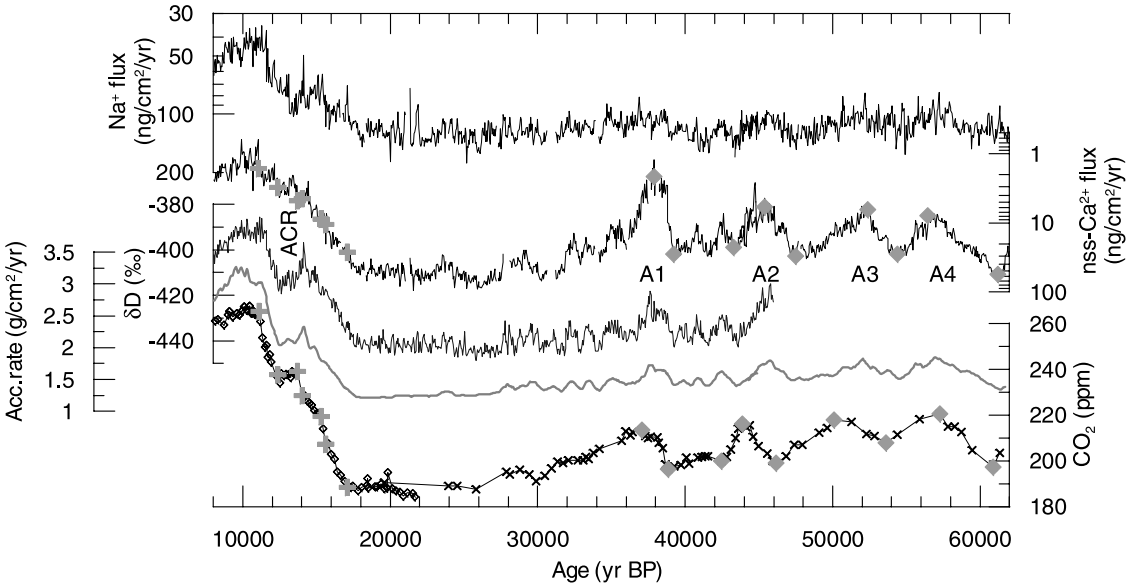

Figure 1. Dome C ice core records covering 10 to 60 kyr B.P. CO_2 concentrations were measured in the Dome C ice core (diamonds) and in the Taylor Dome ice core (crosses). Note that the y-axes of Na^+ and nss-Ca^{2+} are reversed. ACR marks the Antarctic Cold Reversal, A1 to A4 the last four warm events of the last glacial period in Antarctica. Red and blue symbols refer to the bold symbols used in Figure 3. See color version of this figure in the HTML.

Vostok, Antarctica [*Petit et al.*, 1999] includes only approximately 80 data points over the past 60 kyr.

[7] The CO_2 data covering 8 to 22 kyr B.P. were measured in the air bubbles of the EPICA Dome C ice core [*Monnin et al.*, 2001] (EDC96), whilst from 20 to 60 kyr B.P. they originate from the Taylor Dome ice core [*Indermühle et al.*, 2000]. The Dome C deuterium record [*Stenni et al.*, 2003], an indicator of local Antarctic temperature, is so far only published back to 45 kyr B.P., but a comparison of Vostok isotopic records with the Taylor Dome CO_2 data [*Indermühle et al.*, 2000] has shown that the variation over events A2 to A4 were similar in amplitude and timing to event A1. The data from Taylor Dome are transferred to the EDC2 timescale using CH_4 to synchronise the records [*Brook et al.*, 2000] (J. Flückiger, University of Bern, unpublished data). Due to the uncertainty of Δage and of the CH_4 synchronisation, the exact timing of the CO_2 variation relative to the changes in Antarctic temperature, nss-Ca^{2+} and Na^+ remains elusive.

[8] We use the non-sea-salt calcium flux (nss-Ca^{2+}) as a proxy for dust; assuming that the soluble iron content of the dust has remained close to constant, we can treat it as a proxy for iron. Given the long transport route over the respective oceans, we treat ice core dust flux as a proxy for iron input to the relevant ocean. The sodium (Na^+) flux is used as a first-order estimate of sea ice coverage [*Wolff et al.*, 2003]. Changes in transport efficiency could alter the measured nss-Ca^{2+} flux at Dome C. However, it has been shown that changes at the source were the dominant cause for the observed nss-Ca^{2+} variations [*Röthlisberger et al.*, 2002].

3. Glacial Period

[9] During events A2 to A4 the nss-Ca^{2+} flux was reduced from high glacial values to levels similar to those of the Antarctic Cold Reversal (ACR), i.e., only approximately twice the Holocene level (Figure 1). At event A1, nss-Ca^{2+} flux was reduced even further. These strong changes in dust deposition were accompanied by changes in atmospheric CO_2 of up to 20 ppm [*Indermühle et al.*, 2000]. Changes in other parameters potentially affecting atmospheric CO_2 were much smaller during this time interval than during the transition. This suggests that changes in aeolian iron deposition to the Southern Ocean of glacial-interglacial magnitude have a limited effect on atmospheric CO_2.

[10] Potentially, other factors could have masked an impact of iron fertilisation on atmospheric CO_2 during the A1 to A4 events. Changes in the North Atlantic thermohaline circulation and related variations in sea surface temperature, in the marine cycle of organic matter and calcite, and in the terrestrial carbon cycle have likely added to the observed CO_2 variations, suggesting that the net impact of aeolian iron deposition to the Southern Ocean is even smaller than the observed CO_2 variations. For example, model results suggest that a potential collapse of the North Atlantic deep water formation at the onset of the Antarctic warm events led to a release of carbon both from the ocean [*Marchal et al.*, 1999] and the land [*Scholze et al.*, 2003].

[11] Turning to sea ice, there is no evidence from the Na^+ flux for significant changes in sea ice production over A1 to A4 [*Wolff et al.*, 2003]. This suggests a small contribution from changing sea ice coverage of the Southern Ocean to the glacial CO_2 variations. On the other hand, extended sea ice coverage during the glacial period may have reduced the area sensitive to iron fertilisation, limiting the net effect of iron fertilisation on atmospheric CO_2, provided that the iron-limited region of the ocean did not change its location further north during the glacial period.

[12] The periods of low nss-Ca^{2+} were shorter during A1 to A4 than during the transition and atmospheric CO_2 might

not have reached a new equilibrium. Processes such as nutrient supply from sub-surface waters, export of biogenic material to the abyss, coupling between high- and low-latitude ocean processes and ocean-atmosphere exchange adjust over time scales of decades to centuries [*Joos et al.*, 1991; *Matsumoto et al.*, 2002], so that their effect should be fully developed over the events A1 to A4. However, a potential readjustment of the ocean's alkalinity budget and the calcite lysocline [*Archer et al.*, 2000] or changes in the ocean's nitrate inventory, for example, in response to iron-stimulated changes in the calcite to organic matter rain ratio or changes in nitrate fixation [*Broecker and Henderson*, 1998], would accrue on a multi-millenia time scale only. However, observed changes in the lysocline depth [*Broecker and Henderson*, 1998] and co-limitation of biological production by phosphate suggest a limited role for these slow-response scenarios.

[13] In conclusion, the observed change of 20 ppm CO_2 during the Antarctic warm events A1 to A4 likely represents an upper boundary for the effect of reduced iron fertilisation due to a reduction in dust input into the Southern Ocean.

4. Transition

[14] Transferring this insight to the situation during the transition implies that reduced iron fertilisation of the Southern Ocean led to at most a 20 ppm increase in CO_2 over the first half of the transition (from 18 to 14 kyr B.P.), corresponding to the period of largest reduction in dust (interval I and II in Figure 2). Over the same period, CO_2 increased by 40 ppm, i.e., other factors, including their interplay with iron fertilisation, must have accounted for at least 20 ppm. Since the dust flux changed little during interval IV, and since dust in event A1 already reached (albeit temporarily) Holocene levels, it is unlikely that much of the CO_2 increase in interval IV was connected to changing iron fertilisation.

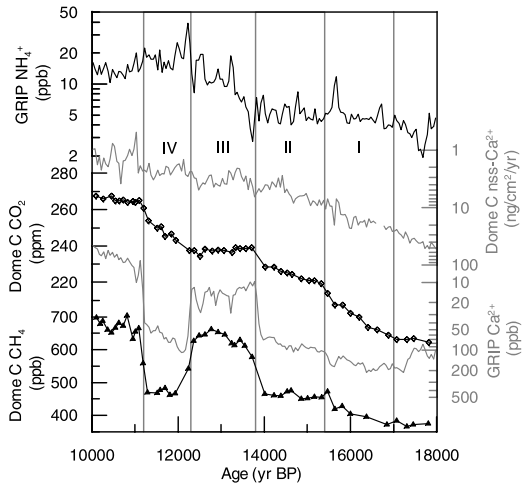

Figure 2. Comparison of Dome C CO_2 and CH_4 records with Greenland and Antarctic aerosol records over the transition from the last glacial period into the Holocene. The intervals I to IV correspond to the periods of different rates of change in CO_2 concentrations as indicated by [*Monnin et al.*, 2001]. Note that the y-axes of the two Ca^{2+} records are reversed.

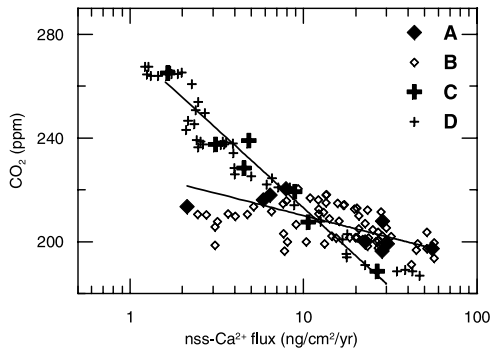

Figure 3. Empirical relationships between CO_2 and nss-Ca^{2+} flux at Dome C for different climatic periods. A: concentration minima and maxima over A1 to A4 (blue symbols in Figure 1). B: CO_2 and corresponding nss-Ca^{2+} flux (250 yr averages) over the period from 30 to 60 kyr B.P. C: concentrations at the boundaries of intervals I to IV (red symbols in Figure 1). D: CO_2 and corresponding nss-Ca^{2+} flux over the period 10 to 18 kyr B.P. The linear fits were calculated based on A and C, with r^2 = 0.66 and r^2 = 0.96, respectively. See color version of this figure in the HTML.

[15] The different relationship between CO_2 and dust over A1 to A4 compared to the transition is shown in Figure 3. As an estimate of a maximum effect and in order to avoid a large scatter due to the uncertainty in the synchronisation of the two ice core records, we compare the maxima of the CO_2 concentration with the minima of the nss-Ca^{2+} flux and vice versa. For the transition, we selected data at the boundaries of the intervals indicated in Figure 2; these CO_2 and nss-Ca^{2+} data originate from the same ice core, therefore the uncertainty in matching the corresponding data points is small. The slope during the glacial period, being itself an upper limit of the effect of dust on atmospheric CO_2, is much smaller than during the transition. The difference between the glacial relationship and the one derived from the data of the transition reflects the amount of CO_2 changes that needs to be caused by other factors.

[16] At the end of interval II and again at the end of interval IV of the transition, CO_2 concentrations increased by 6–8 ppm within less than a few centuries [*Monnin et al.*, 2001], coeval with the large changes in CH_4 that occurred at the warming into the Bølling (corresponding to the end of interval II) and the warming after the Younger Dryas (end of interval IV). This implies that these two increases are due to a northern hemisphere, rather than a Southern Ocean, process. By matching the methane records from Dome C and Greenland, we can precisely align these two periods with data sets from Greenland ice cores (Figure 2). The two warming events were accompanied by large and rapid decreases in the dust input to Greenland. The dust found in Greenland ice cores originates from Asia [*Biscaye et al.*, 1997] and is transported by the westerlies over the northern Pacific and North America to Greenland. The rapid decrease by an order of magnitude suggests that also dust fallout en route was reduced significantly. This could have had a considerable effect on the northern Pacific productivity. While glacial dust supply prevented iron limitation, the

decrease in dust at the end of interval II and IV led to conditions similar to today, i.e., a significant iron deficit [*Tsuda et al.*, 2003]. The suddenly decreased iron supply would be a relatively fast mechanism influencing the carbon cycle and raises the possibility that changes in dust deposition to the northern Pacific were the factor leading to these observed 8 ppm increases in CO_2. However, other large-scale changes such as the reorganisation of the thermohaline circulation occurred at the same time, potentially also affecting atmospheric CO_2 concentrations. Furthermore, the increase in dust at the onset of the Younger Dryas did not leave a reverse imprint on the CO_2 concentrations. One possibility is that the increased dust did have a reverse effect, acting on a longer timescale, and that this was masked by the overlying process that led to the observed increase at a rate of 20 ppm/kyr during interval IV. Based on the ammonium record from the Greenland GRIP ice core [*Fuhrer et al.*, 1996], the North American biosphere evolved rapidly during interval III. If other regions showed a similar development during this period, this could have contributed to the observed temporary stabilisation of the CO_2 concentrations during this interval.

5. Conclusions

[17] Data from Greenland and Antarctic ice cores suggest that the overall effect of aeolian iron deposition to the Southern Ocean on glacial-interglacial CO_2 changes is limited in extent and time. Assuming that a reduction in Southern Ocean iron deposition had a similar impact during glacial times as during the transition, changes of iron supply to the Southern Ocean contributed at most 20 ppm to the CO_2 increase between 18 and 14 kyr B.P. and were negligible thereafter. Reduction of the dust input into the northern Pacific was much faster, but has a smaller effect on CO_2 of up to 8 ppm only. The remaining 50 ppm of increase must thus be ascribed to other processes, possibly acting in concert with iron fertilisation.

[18] **Acknowledgments.** This work is contribution 108 to the "European Project for Ice Coring in Antarctica" (EPICA), a joint ESF (European Science Foundation)/EC scientific programme, funded by the European Commission and by national contributions from Belgium, Denmark, France, Germany, Italy, the Netherlands, Norway, Sweden, Switzerland and the United Kingdom. Thanks to Thomas Stocker and Katsumi Matsumoto for valuable comments and Jakob Schwander for his support with the Dome C chronology. Jacqueline Flückiger and Renato Spahni are acknowledged for providing unpublished methane data. M. H. was supported by the EC project PACLIVA(EVR1-2002-000413).

References

Archer, D. E., A. Winguth, D. Lea, and N. Mahowald (2000), What caused the glacial/interglacial atmospheric pCO_2 cycles?, *Rev. Geophys.*, *38*(2), 159–189.

Biscaye, P. E., F. E. Grousset, M. Revel, S. Van der Gaast, G. Zielinski, A. Vaars, and G. Kukla (1997), Asian provenance of glacial dust (stage 2) in the Greenland Ice Sheet Project 2 Ice Core, Summit, Greenland, *J. Geophys. Res.*, *102*(C12), 26,765–26,781.

Bopp, L., K. E. Kohfeld, C. Le Quéré, and O. Aumont (2003), Dust impact on marine biota and atmospheric CO_2 during glacial periods, *Paleoceanography*, *18*(2), 1046, doi:10.1029/2002PA000810.

Broecker, W. S., and G. M. Henderson (1998), The sequence of events surrounding Termination II and their implications for the cause of glacial-interglacial CO_2 changes, *Paleoceanography*, *13*(4), 352–364.

Brook, E. J., S. Harder, J. P. Severinghaus, E. J. Steig, and C. M. Sucher (2000), On the origin and timing of rapid changes in atmospheric methane during the last glacial period, *Global Biogeochem. Cycles*, *14*(2), 559–572.

Fuhrer, K., A. Neftel, M. Anklin, T. Staffelbach, and M. Legrand (1996), High-resolution ammonium ice core record covering a complete glacial-interglacial cycle, *J. Geophys. Res.*, *101*(D2), 4147–4164.

Indermühle, A., E. Monnin, B. Stauffer, T. F. Stocker, and M. Wahlen (2000), Atmospheric CO_2 concentration from 60 to 20 kyr BP from the Taylor Dome ice core, Antarctica, *Geophys. Res. Lett.*, *27*(5), 735–738.

Joos, F., J. L. Sarmiento, and U. Siegenthaler (1991), Estimates of the effect of Southern Ocean iron fertilization on atmospheric CO_2 concentrations, *Nature*, *349*, 772–774.

Marchal, O., T. F. Stocker, F. Joos, A. Indermühle, T. Blunier, and J. Tschumi (1999), Modelling the concentration of atmospheric CO_2 during the Younger Dryas climate event, *Clim. Dyn.*, *15*, 341–354.

Martin, J. H. (1990), Glacial-interglacial CO_2 change: The iron hypothesis, *Paleoceanography*, *5*(1), 1–13.

Matsumoto, K., J. L. Sarmiento, and M. A. Brzezinski (2002), Silicic acid leakage from the Southern Ocean: A possible explanation for glacial atmospheric pCO_2, *Global Biogeochem. Cycles*, *16*(3), 1031, doi:10.1029/2001GB001442.

Monnin, E., A. Indermühle, A. Dällenbach, J. Flückiger, B. Stauffer, T. F. Stocker, D. Raynaud, and J.-M. Barnola (2001), Atmospheric CO_2 concentrations over the last glacial termination, *Science*, *291*, 112–114.

Parekh, P., M. Follows, and E. Boyle (2004), Modeling the global ocean iron cycle, *Global Biogeochem. Cycles*, *18*, GB1002, doi:10.1029/2003GB002061.

Petit, J. R., et al. (1999), Climate and atmospheric history of the past 420,000 years from the Vostok ice core, Antarctica, *Nature*, *399*, 429–436.

Ridgwell, A. J. (2003), Implications of the glacial CO_2 "iron hypothesis" for Quaternary climate change, *Geochem. Geophys. Geosyst.*, *4*(9), 1076, doi:10.1029/2003GC000563.

Röthlisberger, R., M. Bigler, M. Hutterli, S. Sommer, B. Stauffer, H. G. Junghans, and D. Wagenbach (2000), Technique for continuous high-resolution analysis of trace substances in firn and ice cores, *Environ. Sci. Technol.*, *34*, 338–342.

Röthlisberger, R., R. Mulvaney, E. W. Wolff, M. A. Hutterli, M. Bigler, S. Sommer, and J. Jouzel (2002), Dust and sea-salt variability in central East Antarctica (Dome C) over the last 45 kyrs and its implications for southern high-latitude climate, *Geophys. Res. Lett.*, *29*(20), 1963, doi:10.1029/2002GL015186.

Scholze, M., W. Knorr, and M. Heimann (2003), Modelling terrestrial vegetation dynamics and carbon cycling for an abrupt climate change event, *Holocene*, *13*(3), 327–333.

Schwander, J., J. Jouzel, C. U. Hammer, J. R. Petit, R. Udisti, and E. Wolff (2001), A tentative chronology for the EPICA Dome Concordia ice core, *Geophys. Res. Lett.*, *28*(22), 4243–4246.

Sigman, D. M., and E. A. Boyle (2000), Glacial/interglacial variations in atmospheric carbon dioxide, *Nature*, *407*, 859–869.

Stenni, B., et al. (2003), A late-glacial high resolution site and source temperature record derived from the EPICA Dome C isotope records (East Antarctica), *Earth Planet. Sci. Lett.*, *217*(1-2), 183–195.

Tsuda, A., et al. (2003), A mesoscale iron enrichment in the western subarctic Pacific induces a large centric diatom bloom, *Science*, *300*, 958–961.

Wolff, E. W., A. M. Rankin, and R. Röthlisberger (2003), An ice core index of Antarctic sea ice production?, *Geophys. Res. Lett.*, *30*(22), 2158, doi:10.1029/2003GL018454.

M. Bigler, M. A. Hutterli, F. Joos, and E. Monnin, Climate and Environmental Physics, University of Bern, Sidlerstrasse 5, 3012 Bern, Switzerland.

R. Röthlisberger, NCCR Climate, University of Bern, Erlachstrasse 9a, 3012 Bern, Switzerland. (regine@giub.unibe.ch)

E. W. Wolff, British Antarctic Survey, Natural Environment Research Council, Madingley Road, Cambridge CB3 0ET, UK.