

SHORT CONTRIBUTION

A natural artefact in Greenland ice-core CO₂ measurements

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ABSTRACT

Paleoatmospheric concentrations of CO₂ over the last ice ages have been revealed by ice-core analysis. According to the time period (ice age or interglacial) and the hemisphere considered, the ice containing the analysed air bubbles can be either alkaline or acid. It is shown that the interaction between acid and alkaline impurities, when they co-exist naturally in ice, could lead to the production of excess CO₂ in ice samples, and therefore to erroneously-high CO₂ values of no paleoatmospheric significance. The phenomenon is thought to occur only in Greenland ice during climatic transitions. It does not question the low CO₂ levels found in Greenland and Antarctic ice cores for glacial ages.

1. Introduction

Ice-core measurements have revealed large environmental changes for the Last Glacial Maximum (LGM), with respect to present (Holocene) conditions, and in particular a great enhancement of atmospheric dust concentrations in both hemispheres (Cragin et al., 1977; Petit et al., 1981) and a marked CO₂ depletion (Neftel et al., 1982; Barnola et al., 1987).

Numerous cross checks, disregarded by some (Jaworowski et al., 1992), have been done to validate the information recovered from the ice in terms of atmospheric CO₂ concentrations (Raynaud et al., 1982; Barnola et al., 1983). Their results have been mostly successful and it is now accepted that experimental methods presently used for analysing greenhouse gases in ice cores are reliable. Nevertheless, we have revisited the records, in particular because some CO₂ data obtained only from Greenland ice cores seem to be unexplained or doubtful with respect to what can be expected and modelled about past climatic and environmental conditions (Stauffer et al., 1984; Oeschger et al., 1988). This paper indicates a

possible natural alteration of well-delimited parts (the sections corresponding to the climatic transitions) of the atmospheric Greenland archives contained in the ice, without questioning, however, most published data, in particular the low CO₂ values (180–200 ppmv) obtained for ice-age ice.

We will focus the discussion in the first instance on continental dust and gas-derived aerosol. It is known that atmospheric acid species (mainly H₂SO₄ and HNO₃) may react in cloud droplets with primary aerosol particles (sea-salt, continental dust). This acid-base reaction is presently globally in favour of acid species, taking as a reference what is obtained in very remote places, like Antarctica and Greenland: polar precipitation is, in present climatic conditions, weakly acidic (Neftel et al., 1985; Hammer et al., 1985; Legrand et al., 1988). Background rain water is also, on a global scale, naturally acidic (Charlson and Rodhe, 1982), anthropogenic pollution still tending to increase this characteristic. Ice-core records tell us that this situation was rather different during the ice ages, and with some important differences between the Hemispheres. In the South, the

acidity of the ice was strongly reduced, but not entirely neutralized, during the LGM (Legrand et al., 1988). Moreover, at that time, there was in the ice a high concentration of salts ("terrestrial salts"), assumed to be formed by in-cloud reactions (en route to Antarctica) of continental dust (which contains calcium carbonates) with atmospheric acid species (Legrand et al., 1988). No carbonate has been found in ice samples corresponding to the climax of the last glaciation (Legrand, 1987).

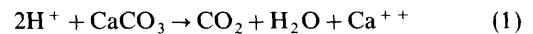
In the North, the natural alkalinity-acidity atmospheric balance appears at that time to have shifted to alkalinity. During the ice age, Greenland precipitation was clearly alkaline (Hammer et al., 1985). We can assume, due to the large excess of the alkalinity of the ice (probably greatly higher than $10 \mu\text{Eq l}^{-1}$, if we refer to conductivity values), that the ice contains essentially unneutralized carbonates and probably also "terrestrial salts" (formed by a similar in-cloud reaction as in the Antarctic). The presence of a residual acidity seems extremely unlikely according to the very low solid conductivity of the ice (Neftel et al., 1985; Hammer et al., 1985), except during special periods which will be commented upon below. Now, regarding CO_2 measurements, the comparison between Antarctic and Greenland ice-core data is generally satisfactory, i.e., the levels are similar in both hemispheres (Staffelbach et al., 1991). However a major discrepancy is found in the Dye 3 core for the rapid CO_2 variation at 1814 m depth, Fig. 1h, associated with the rapid climate change marking the transition Oldest Dryas/Bölling Allerød and also with sudden climatological fluctuations (abrupt climatic changes, ACC) occurring in less than 100 years (Stauffer and Oeschger, 1985; Dansgaard, 1987). These ACC, having a duration of about one millennium, are found only in Greenland ice during the ice age some 30,000–70,000 years B.P. (short/warm interstadials), and are characterized by high isotopic temperatures and high CO_2 concentrations (both similar to interglacial conditions), medium range ($0.2\text{--}0.4 \text{ mg l}^{-1}$), dust concentrations and generally low ionic contents similar to Holocene levels (Finkel and Langway, 1985; Dansgaard, 1987; Dansgaard et al., 1989). Note that for these warm events, the ice is nearly neutral (Hammer et al., 1985). The exact climatic cause of these variations is still a matter of discussion. They will not be debated here

but the rapid CO_2 variations associated with these events are totally concomitant with the climatic changes, something which cannot be easily interpreted glaciologically. The formation of air bubbles in the firn is indeed a long-lasting process which buffers any sudden change of the atmospheric CO_2 concentrations. It occurs with a certain time lag (of the order of several centuries at the Greenland study sites for ice age conditions (Schwander, 1989) after snow deposition.

2. Proposed mechanism

We propose to examine this phenomenon of rapid CO_2 changes with the aid of existing data, assuming that it could be linked with an ice-chemistry artefact. Our assumption is the following: when a sudden temperature increase occurs, the emissions of alkaline dust in the Northern Hemisphere are strongly reduced, but the inputs to Greenland are not totally cancelled. The atmospheric gas-derived acid species (HNO_3 , H_2SO_4) are then no more (or at least much less) neutralized during their transport to high latitudes, and some amounts of nitrate and sulfate may be deposited in Greenland snow in their acid form. Some snow (ice) layers can then be acidic, others alkaline, depending probably on meteorological conditions, wind direction or the season of deposition. This could occur typically at the beginning and during the Bölling-Allerød transition, where the ice is acidic and for which dust levels are observed intermediary between LGM and Holocene levels (Stauffer et al., 1984; Dansgaard, 1987). However, nearly similar conditions are also observed for the rapid events (ACC) and the very end of the Younger-Dryas (Fig. 1).

If, in the ice, this acidity could react with carbonates, it would liberate a certain amount of CO_2 according to (1):



Stoichiometrically, $1.0 \mu\text{Eq}$ of acid produces $0.5 \mu\text{mol}$ of CO_2 ($11 \mu\text{l}$), provided enough carbonate is available.

The amount of CO_2 naturally present in the bubbles can be calculated to about $16 \mu\text{Eq kg}^{-1}$ (equivalent to $0.7 \mu\text{mol kg}^{-1}$ or $16 \mu\text{l kg}^{-1}$) for LGM conditions. If we refer to the pre-industrial

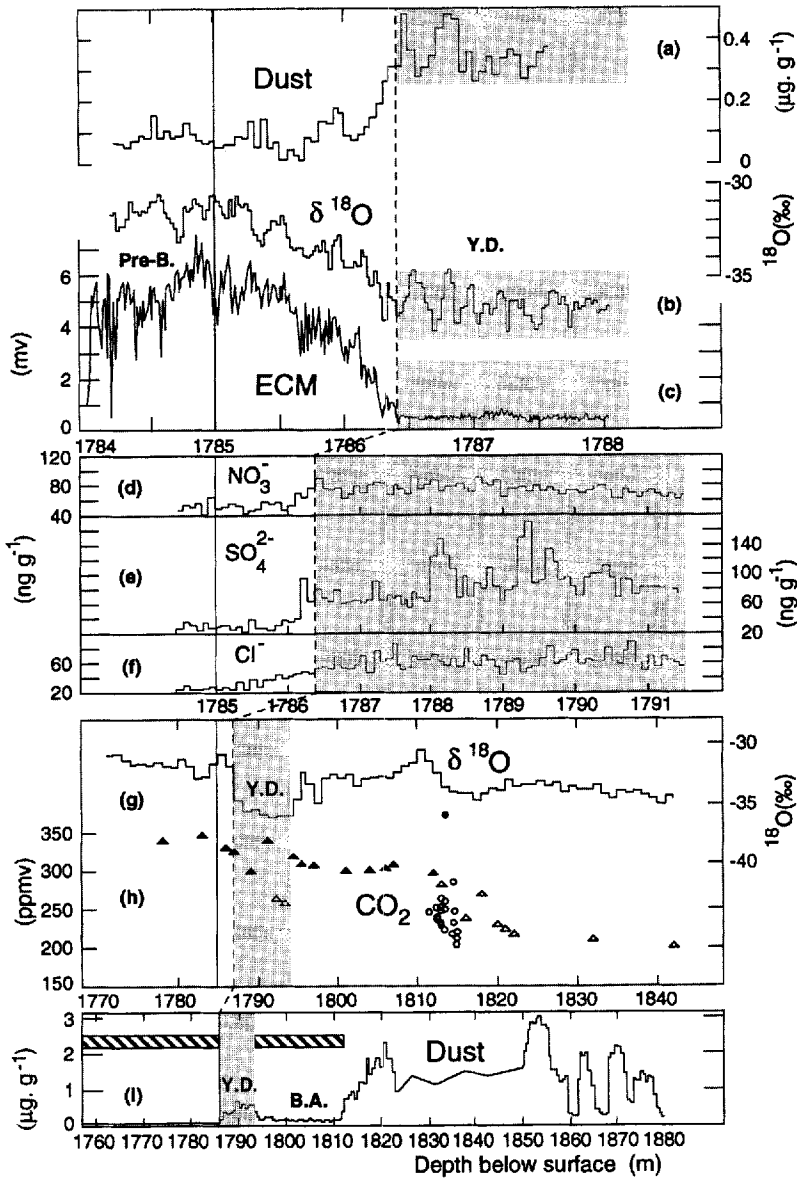


Fig. 1. The end of the Wisconsin time period and the Wisconsin/Holocene transition, as they are recorded in the Dye 3 ice core. The profiles reported here are: (a): dust; (b): $\delta^{18}\text{O}$ (‰): (a) and (b) from Dansgaard et al. (1989); (c): electroconductivity (ECM) from Neftel et al. (1985); (d-f): nitrate, sulfate and chloride concentrations, from Herron and Langway (1985); (g): $\delta^{18}\text{O}$ (‰) and (h): CO_2 (Staufelbach et al., 1991). Filled triangles and circles are suspect CO_2 levels, open circles and triangles are probably correct. For comparison, the highest preindustrial CO_2 level measured in the Byrd core, Antarctica, is 290 ppmv; (i), dust concentration; the striped horizontal bar gives the "acid" parts, deduced from the Hammer et al. (1985) ECM measurements. The beginning of the Pre-Boreal (Pre-B.) is fixed at 1785 m (vertical continuous line) and the end of the Younger Dryas (Y.D.) is estimated at 1786.4 m, vertical steeped line (Dansgaard et al., 1989). The Younger Dryas period has been shadowed. B.A. is for Bölling-Alleröd.

levels of HNO_3 and H_2SO_4 in ice, 1.0 and $0.5 \mu\text{Eq l}^{-1}$, respectively, the mean background acidity is probably always lower than $1.5 \mu\text{Eq l}^{-1}$. The amount of excess- CO_2 ($0.75 \mu\text{mol}$) which can eventually be produced by $1.5 \mu\text{Eq}$ of acid is comparable to the amount already present in the bubbles in the gaseous form. If, for any reason, the acidity present in the ice is able to be in contact with the carbonates, then CO_2 is formed according to (1). A very similar process, but occurring in the liquid phase, has already been invoked by Delmas et al. (1980) for the production of excess- CO_2 by contamination carbonates. The amount formed is limited by the reactant having the lowest concentration. Natural carbonates vary in a large concentration range up to more than $10 \mu\text{Eq l}^{-1}$, whereas the mean acidity seems never to exceed $1.5 \mu\text{Eq l}^{-1}$, which suggests that excess CO_2 could hardly be higher than $17 \mu\text{l}$, increasing ice-age CO_2 concentrations by about 100% and warm period concentrations (280 ppmv) by less than 75% (but carbonates themselves could be the limiting species there). This amount of excess CO_2 lies in the range of the unexplained excess observed in Greenland ice for the time period considered in this paper. This process therefore appears to be a plausible explanation for the high CO_2 contents measured in the Greenland ice layers corresponding to the abrupt climatic changes mentioned earlier.

3. Discussions of data

The data of Dye 3 for the LGM and the transition to the Holocene suggest that this process actually occurs. The various profiles obtained on this deep Greenland ice core have been collated on the same diagram (Fig. 1) for the time period (26 kyr–10 kyr BP) involving the last major climate change and two ACCs. The Younger Dryas/Pre-Boreal transition is located in the Dye 3 core between 1786.4 and 1785.3 m with a duration estimated to be about 50 years (Dansgaard et al., 1989). Environmental changes recorded in the ice at this time are an increase of temperature by $\sim 7^\circ\text{C}$ and of ECM (electroconductometric measurements of the ice, as first used by Hammer (1980)) from 0.5 to 5.5 mV (linked to a corre-

sponding acidity increase) and a decrease of dust concentrations (from 0.3 to 0.1mg l^{-1}), and of nitrate, sulfate and chloride concentrations (by a factor of about 2.4).

Most likely, the acidity increase is due to a lowering of the fraction of SO_4 and NO_3 which is deposited in a neutralized form (CaSO_4 , $\text{Ca}(\text{NO}_3)_2$) with respect to their acid forms, as suggested by the fact that the dust concentration decreases very rapidly (in only 20 years, Dansgaard et al. (1989)) whereas ECM (acidity) increases progressively over 50 years (Nefel et al., 1985). Therefore, the acidity changes at this time reflect atmospheric rather than ice-phase processes.

At 1785.3 m, the sulfate concentration is $\sim 30 \text{ng g}^{-1}$, nitrate $\sim 50 \text{ng g}^{-1}$ and ECM $\sim 5.5 \text{mV}$, all typical Holocene values, whereas dust is still $2\times$ higher than its mean Holocene values. At that time, the ice contains about $1.5 \mu\text{Eq l}^{-1}$ of acidity (H_2SO_4 and HNO_3) and simultaneously an excess of carbonated dust.

As observed and reported by Nefel et al. (1985), chemical reactions are strongly suspected to occur in the ice during storage, in connection with the pressure relaxation. In any case, it was also mentioned by the same authors that impurities are able to diffuse in the ice structure, lowering the amplitude of the seasonal ECM patterns. These observations support our proposition.

We conclude, therefore, that, in this ice which contains both acids and alkaline dust, some acid-base reaction occurs, either in the ice sheet itself or during the ice-core storage, with the formation of CO_2 , according to (1).

The reaction could be favoured by the considerable thinning of the ice layers at great depths, a phenomenon which brings closer the acid and the alkaline sites of the ice. In contrast, in the upper layers, the reaction would be insignificant. The temperature of the ice could also play a rôle, the displacement of the H^+ ions being more rapid when ice temperature comes closer to 0°C .

Such a phenomenon may occur each time that acidity (or even just neutrality) is measured in ice containing relatively high concentrations of dust. Belonging to this case are the ice layers corresponding to the Bölling-Alleröd (1812–1794 m depth in the Dye 3 core), where suspect CO_2 levels are indeed measured, and the ACC around 1860, 1867, etc., m, for which high, unexplained CO_2 levels are also observed.

4. Conclusion

The consequence of this carbonate decomposition is that the rapid CO₂ fluctuations associated with climate changes could well not be an atmospheric reality, at least not as they are now reconstructed from Greenland ice-core measurements. If they really happened, the transitions of CO₂ concentrations from low (full glacial age) to high (warm periods) values recorded in ice, probably occurred differently in the atmosphere: they were most likely less abrupt than is presently thought from Greenland ice measurements. Unfortunately, it appears impossible to reconstruct the true CO₂ atmospheric concentrations corresponding to these specific time periods from only Northern Hemisphere ice cores.

On the other hand, the conundrum of the lack of depth lag between stable isotope and CO₂

profiles is completely solved, without appealing to rheological irregularities (Staffelbach et al., 1988), if our mechanism is accepted.

Fortunately, our proposition casts no doubt on the CO₂ data obtained from Antarctic ice cores not on the data concerning most of the ice-age conditions in both polar regions. For Holocene ice in Greenland, additional measurements are still needed to evaluate the significance of the possible errors in the presently published values.

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