

Flow-induced mixing in the GRIP basal ice deduced from the CO₂ and CH₄ records

R. Souchez and M. Lemmens

Département des Sciences de la Terre et de l'Environnement, Faculté des Sciences, Université de Bruxelles, Bruxelles, Belgium

J. Chappellaz

Laboratoire de Glaciologie et de Géophysique de l'Environnement, Domaine Universitaire, Saint-Martin d'Hères, France

Abstract. This paper documents a larger degree of mixing in ice near the bottom of an ice sheet than described, or suspected, previously. It shows, thanks to favourable circumstances due to CO₂ and CH₄ production underneath the ice, that flow-induced mixing within the basal ice has taken place at the scale of a few centimeters in the GRIP core. Such a mechanism must be considered when interpreting the ice properties in the bottom part of ice sheets and must be taken into account as a potential process of layer disruption in the low levels of the Central Greenland ice cores.

The gas composition of basal ice

The silty ice recovered at the base of the 3028.8 m long ice-core of the Greenland Ice Core Project (GRIP) was described in Souchez et al. (1994). By a co-isotopic study, it was shown that local ice formed at the ground surface in the absence of the ice sheet significantly contributes to the formation of the basal silty ice. Wind-drift ice or ice formed at the surface of a frozen ground are the most probable candidates. No significant melting occurred during this process.

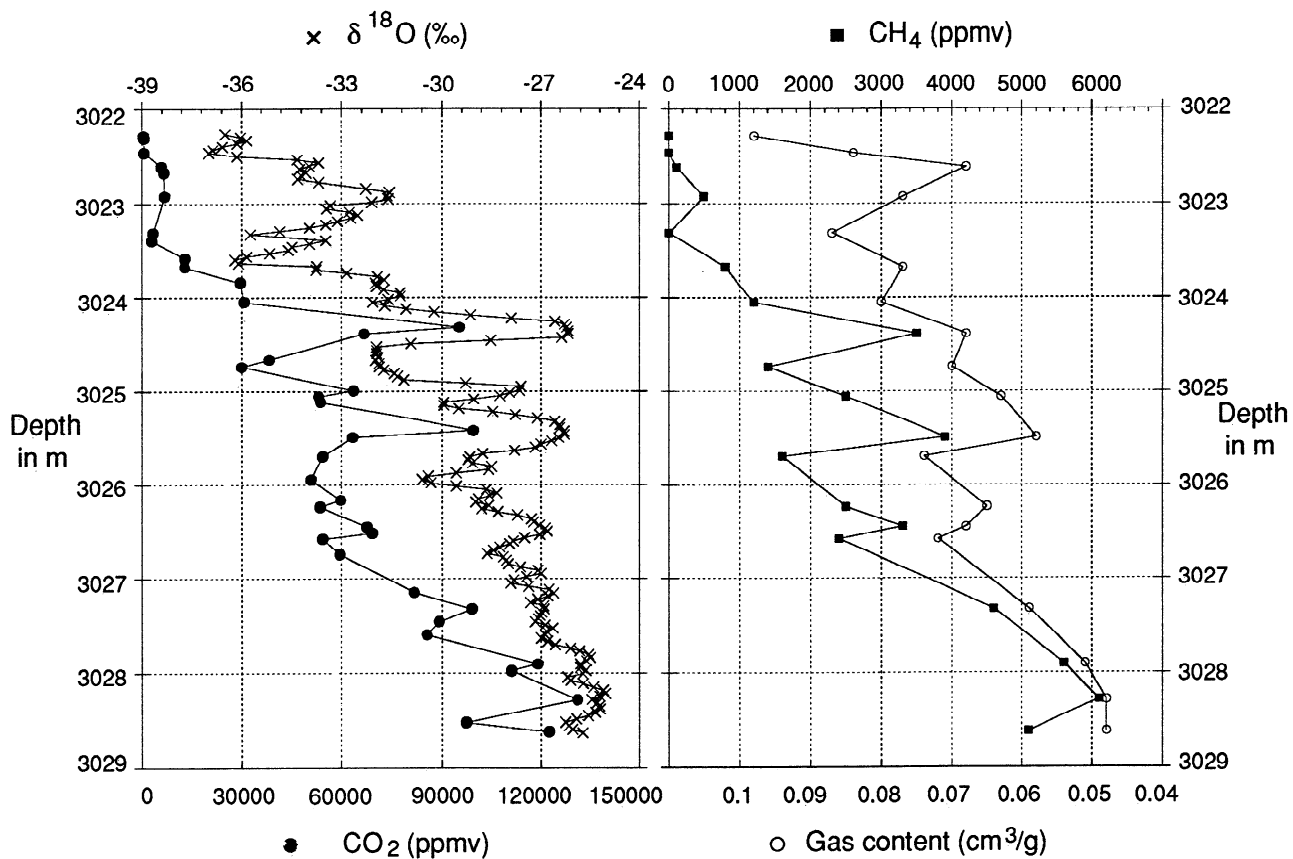


Figure 1. CO₂, CH₄, $\delta^{18}\text{O}$ and total gas content in the basal silty ice from the GRIP core.

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Now, a new approach emerges from gas analyses of this silty ice. Gas analyses have been performed by gas chromatography both in Grenoble [for CH₄, CO₂ and total gas content by a melting-refreezing method (Raynaud et al., 1988 ; Blunier et al., 1993)] and in Brussels [for CO₂ by a dry extraction technique (Souchez et al., 1993)]. The CO₂ values

agree fairly well between the two laboratories : the maximal difference between neighbouring samples is less than 2%. Because of the concentration levels reached, special standards have been used. Residual standard deviations for the samples are 3% for CH₄ and 2% for CO₂, and the relative precision of the total gas content measurements is better than 5% (Martinerie et al., 1994).

The gas composition is far from that of the atmosphere. Concentrations up to 130000 ppmv for CO₂ and 6000 ppmv for CH₄ are reached at the base (Fig. 1). Such extreme values have never been reported in the literature dealing with gas composition analyses in ice sheets.

A general decrease in CO₂ and CH₄ concentrations is observed from the bottom of the profile towards the top of the silty ice. It is accompanied by a general increase in total gas content. If the total gas content is plotted on a reverse scale, then there is a great similarity between the three profiles with peaks and troughs at the same level. Furthermore, a striking similarity exists between these gas profiles and the δ¹⁸O profile of the ice itself. Higher δ-values are related to higher CO₂ or CH₄ concentrations and lower total gas content. This striking similarity is expressed in Table 1 as a correlation matrix showing high correlation coefficients. The CO₂ and CH₄ peaks in the profile are still present if the concentrations are calculated, not in ppm per volume of the gas phase, but per gram of ice, taking into account the total gas content of the ice.

Discussion

The level of CO₂ and CH₄ concentrations in the profile precludes a direct atmospheric origin. Also the unusually low total gas content cannot result from a normal process of atmospheric air trapping in the ice. In-situ production of CO₂ and CH₄ in the snow or in the ice cannot explain as well the concentrations reported here. The anaerobic process needed for CH₄ production would be strongly inhibited by the presence of oxygen and, in any case, the substrate required for microbiological activity would be extremely rare. Very few bacteria have been observed so far in snow of polar regions and/or in ice cores (Abyzov, 1993). Moreover, a dissolved organic content of 0.1 μg/g has been reported for today's Greenland snow (Twickler et al., 1986), which is comparable to the maximum CH₄ level observed in the basal ice, while one would expect much lower CH₄ levels. Also the CO₂ level is much too high to be explained by oxidation of such a low

organic content. Actually, methane and carbon dioxide concentration values of the same order than the ones reported here are known from the permafrost regions of Alaska (Rasmussen et al., 1993 ; Kvenvolden and Lorenson, 1993 ; Kvenvolden et al., 1993) in frozen peat or in fine-grained soils. The origin of the CO₂ and CH₄ present in the basal silty ice of the GRIP core is thus to be found underneath the ice.

Although diffusion from the ground into the ice or into the original sintering wind-drift snow has certainly occurred if we consider the concentration levels reached, diffusion within the solid ice is not the factor which controls the general decreasing trend in concentration upwards. The CO₂ distribution into the ice after 2.4 10⁶ years can be calculated, starting from an initial concentration C₀ at the distance x = 0 by using the second Fick's law. With the most commonly accepted values for the diffusion coefficient of CO₂ in the ice (from 3 10⁻¹⁵ m²s⁻¹ to 3 10⁻¹⁶ m²s⁻¹) (Neftel et al., 1983 ; Hemmingsen, 1959), diffusion will only take place over less than 2 m. A time interval of 2.4 10⁶ years is chosen here since the silty ice can possibly date from the original build up of the Greenland Ice Sheet (Souchez et al., 1994). A shorter time interval will of course reduce the distance over which the diffusion could have been active. Note that a polycrystalline structure of the ice at relatively high temperature (~ -10°C) may have favoured higher gas diffusion coefficients, but as soon as the ice thickness reached about 1000 m, the gases became trapped in gas hydrate structures, precluding any further noticeable gas diffusion in the solid ice (Shoji and Langway, 1982). Changes can to some extent occur after enclathratization since Uchida et al. (1994) have shown that larger air-hydrate crystals grew slowly in compensation for the disappearance of smaller crystals in the Vostok core. This does not however affect the conclusions.

Probably the best argument against an explanation based only on diffusion for the gas profiles remains the similarity between gas and ice parameters. A mixing process between two end-members has to be invoked to explain the covariations of gas composition, total gas content, and δ¹⁸O of the ice, shown by the high correlation coefficients in Table 1. In such a process, ice formed locally at the ground surface in the absence of the ice sheet with high δ-values, low total gas content and high concentrations in CO₂ and CH₄ is mixed with glacier ice from a growing ice sheet having lower δ-values, normal total gas content for polar ice and nearly atmospheric gas composition (the uppermost values of the profile). The local component enriched in CO₂ and CH₄ cannot however be ice from permafrost soil because of the too low dirt content of the silty ice (less than 0.3 in weight percent). Such a mixing process is consistent with the general decreasing trends upwards of δ-values and of CO₂ or CH₄ concentrations since the probability of incorporating some local ice formed at the ground surface into the ice sheet diminishes with the distance from the bed.

Now, it is possible to estimate the δ¹⁸O, [CO₂] and total gas content of the local ice component in the mixing process. As shown in fig.2, a good linear relationship exists between δ¹⁸O and the CO₂ content per g of ice ([CO₂] x total gas content). Using this relationship and the equation of the best fit line between [CO₂] and total gas content, it is possible to deduce from each fixed [CO₂] value of the local component, its total gas content and its δ¹⁸O value. Then, theoretical [CO₂] and δ¹⁸O values with the same various

Table 1. Correlation matrix between the studied variables

	δ ¹⁸ O	[CO ₂]	[CH ₄]	total gas content
δ ¹⁸ O	---	0.918	0.915	-0.850
[CO ₂]	0.918	---	0.982	-0.883
[CH ₄]	0.915	0.982	---	-0.893
total gas content	-0.850	-0.883	-0.893	---

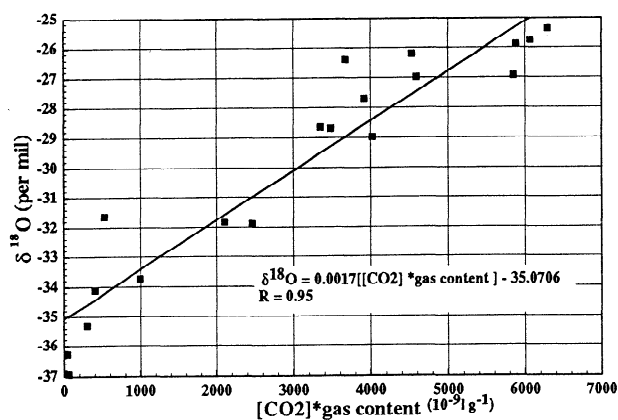


Figure 2. $\delta^{18}\text{O}$ - CO_2 content per g of ice relationship in the basal silty ice from the GRIP core.

mixing proportions can be calculated and the mixing curve obtained can be compared, in a $\delta^{18}\text{O}$ - $[\text{CO}_2]$ diagram, to the distribution of the points representing the ice samples (Fig. 3). The mixing curves are calculated in the following way. Let C be the theoretical $[\text{CO}_2]$ in ppmv for a given mixing ratio M .

$$C = \frac{[M \cdot (C_1 \cdot T_1)] + [(1-M) \cdot (C_2 \cdot T_2)]}{M \cdot T_1 + (1-M) \cdot T_2} \quad (1)$$

C_1 and C_2 are the $[\text{CO}_2]$ in ppmv of the two end-members; T_1

and T_2 their respective total gas content (in cm^3/g). Different values of C are obtained for different mixing ratios M . Independently, $\delta^{18}\text{O}$ values are calculated with the same mixing ratios from the $\delta^{18}\text{O}$ values of the two end-members. The best match exists between theory and measurements if the following end-member values are chosen: $C_1 = 410$ ppmv, $T_1 = 0.098 \text{ cm}^3/\text{g}$, $\delta^{18}\text{O}_{(1)} = -36.99\text{‰}$ for the glacier ice component (these values are those from just above the basal sequence) and $C_2 = 135000$ ppmv, $T_2 = 0.046 \text{ cm}^3/\text{g}$, $\delta^{18}\text{O}_{(2)} = -24.7\text{‰}$ for the local component. These last values are very close to the ones measured at the base of the GRIP core. Any other combination of values for the local component will lead to a less good match.

Mixing at the base of an ice sheet has to some extent been considered theoretically. Weertman (1968) derived a diffusion law for the dispersion of hard particles in an ice matrix that undergoes simple shear deformation. Alley and Mac Ayeal (1994) develop a probabilistic debris entrainment model based on an upward diffusion process. There is indeed some chance that the basal ice will move up from the bed into the ice whenever basal ice encounters an obstacle. These models have however not been substantiated either experimentally or by ice composition studies.

Distortion due to ice flow was considered by Taylor et al. (1993) in both the GISP 2 and the GRIP cores. In the simple shear regime associated with depth-dependent lateral extension that is currently occurring in the basal part of the Greenland Ice Sheet at the GISP 2 site, overturned folding can occur and was documented by Taylor et al. (1993). In the pure

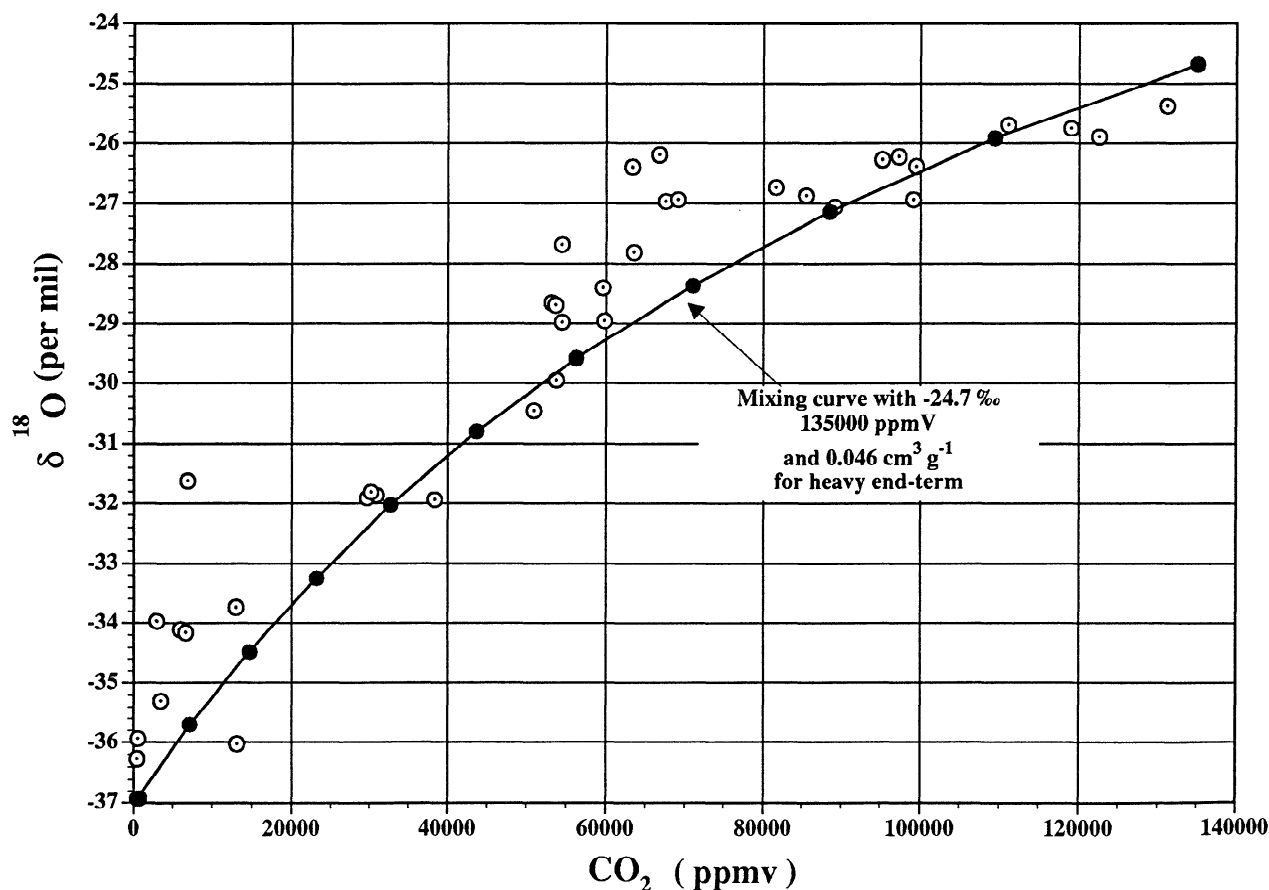


Figure 3. Mixing curve and ice samples from the basal silty ice of the GRIP core in a $\delta^{18}\text{O}$ - $[\text{CO}_2]$ diagram. The different points on the mixing curve represent 10 percent mixing ratio increments.

shear regime associated with vertical compression and thinning that is currently occurring in the basal part of the Greenland Ice Sheet at the GRIP site, boudins can occur. The ice sheet geometry and the position of the ice divide has most likely changed in the past and this will affect deformation at both sites. In the case of basal silty ice at the GRIP site, it was shown that it is a remnant of a growing stage of the ice sheet, probably the original build-up (Souchez et al., 1994), presently under a pure shear regime (Tison et al., 1994). Since the isotopic composition of the local component implies an origin in the absence of an ice sheet (Souchez et al., 1994), the mixing process invoked here possibly occurred in the marginal part of the growing ice sheet.

Conclusion

For the first time, flow-induced mixing at the scale of a few centimeters is shown to occur at the base of an ice sheet. This process can be identified at the GRIP site because of substantial production of CO₂ and CH₄ underneath the ice. Mechanical mixing to a much greater extent than ever documented previously seems to be the only viable mechanism for explaining the observed ice chemistry. It is perhaps not limited to a few meters above bedrock and could commonly occur elsewhere, where it is less easily detectable.

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- R. Souchez, M. Lemmens, Département des Sciences de la Terre et de l'Environnement, Faculté des Sciences CP 160/03, Université de Bruxelles, B-1050 Bruxelles, Belgium. (email: glaciol@is1.ulb.ac.be)
- J. Chappellaz, Laboratoire de Glaciologie et de Géophysique de l'Environnement, BP 96, F-38402 Saint Martin d'Hères, France

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