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Determination of gas diffusivity in polar firn: comparison between experimental measurements and inverse modeling

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Abstract. To study air diffusion in polar firns, and thus evaluate the mean age of air constituents as a function of depth, it is necessary to know the effective diffusivity profile for the studied gas and firn. In this work we compare effective diffusivity profiles obtained by two methods: first, by experimental measurements on firn samples, second, using an inverse gas diffusion model. Results are obtained for three gases, CO_2, CH_4 and SF_6, in firns exposed to different climatic conditions. While measurements give similar results for the different sites, the inverse model shows variations depending on the climatic conditions. We therefore conclude that diffusivities measured on small firn samples cannot be directly used to determine the tortuosity profile of real firn and that diffusion models have to be used.

1. Introduction

Polar firn contains air in contact with the atmosphere which diffuses slowly through the open pores, down to the firn-ice transition zone, where the pores close to form air bubbles. As a consequence, large amounts of air dating back several decades can be recovered by pumping interstitial firn air, and used to reconstruct recent trends for atmospheric trace gases.

[*Schwander et al.*, 1993; *Trudinger et al.*, 1997; *Rommelaere et al.*, 1997] have developed models to assess the time needed for each gas to move down from the surface to the close-off. Taking into account diffusion and gravitation in the pores still connected to the surface, they compute a firn mixing ratio profile for the studied gas, given an atmospheric scenario at the surface and a firn diffusivity profile. However, to date this air, the effective diffusivity of the gas must be known. We present here, two approaches to determine this parameter, one based on laboratory experiments and the other on inverse modelling, and compare the results.

2. Experimental measurements

2.1. Experimental procedure

Measurements of effective diffusivities D_{eff} were made on firn samples, with a technique similar to the one used by [*Schwander et al.*, 1988]. It consists in analyzing the shape of the elution peak of a given gas pushed through the sample by a carrier gas (N_2). The Fick's first law links the flux of gas *J(z,t)* to the diffusion coefficient D and to the superficial gas velocity u (with u=s×v, where s is the open porosity and v the flow velocity of the carrier gas) by :

$$J(z,t) = -D\ \partial c(z,t)/\partial z + c(z,t)u \qquad (1)$$

where *z, t, c* are respectively the corresponding depth, time and mixing ratio. The equation of conservation of the solution, derived from Fick's first law, enables calculation of the gas mixing ratio *c(z,t)* in the sample as function of D and u, and thus modeling of the shape of the elution peak. The values for D and u are chosen in order to fit the modeled peak to the observed peak. As D generally depends on u, several measurements are made at different carrier gas velocities. This dependency can be expressed by the theory of gas chromatography [*Van Deemter et al.*, 1956]. Introducing the diffusion coefficient *D(u)* in their equation leads to:

$$D(u) = \gamma D_{ij} + Eu + Cu^2 \ and\ D_{eff} = \gamma D_{ij} \qquad (2)$$

$1/\gamma$ is the tortuosity (linked to the ratio between the distance covered by a gas and the length of the sample), Eu the eddy diffusivity and Cu^2 the mass exchange between the stationary and gas phases. The effective diffusion coefficient D_{eff}, which depends only on the firn structure and molecular diffusivity D_{ij}, is the extrapolation of *D(u)* at zero velocity. [*Arnaud*, 1997] gives a more complete description of the method. The molecular diffusion coefficient, D_{ij}, is computed following [*Bzowski et al.*, 1990], from the interactions between molecules of a binary mixture, at 253 K and 1 atm. We use diffusion coefficients in N_2 (values in air are slightly higher, but the difference is not significant given the scatter of the available data [*Marrero et Mason*, 1972]). D_{ij} values for CO_2, CH_4 and SF_6 in N_2 are 379.38, 536.74 and 235.57 m^2/year.

D_{eff} is then corrected for temperature and pressure effects, following [*Schwander et al.*, 1988]:

$$D_{(T,P)} = D_{T_0,P_0} \times \alpha = D_{T_0,P_0} \times\ P_0/P \times (T/T_0)^{1.85} \qquad (3)$$

where T and P are the temperature ($^\circ$K) and atmospheric pressure (mbar), T_0=253.16 K and P_0=1013.25 mbar, for the experiment or for the site of interest. Due to this pressure and temperature influence on diffusitivity, cold and low altitude sites are the best suited to get old firn air (see table 1).

2.2. Results

Measurements were made on samples from two different sites (Table 1): Vostok, a cold Antarctic site with low accumulation rate, and Col du Dome, a "warm" alpine site with high accumulation and summer melting. The effective diffusivities were measured for SF_6 on Vostok samples, in

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Table 1. Surface temperature T ($^\circ$C), accumulation Acc (kg/m^2/an), altitude Alt (m), atmospheric pressure P (mbar) and correction factor of D_{ij} (see eq. 3) α

	T	Acc	Alt	P	α
De08	-19	1200	1250	845	1.2065
Vostok	-56	22	3471	632	1.2055
Dronning Maud Land	-38	60	2300	730	1.2094
Dome C	-53	30	3240	655	1.1930
Devon Island	-23	300	1800	795	1.2824
Siple	-24	500	1054	860	1.1426
Col du Dome	-11	3000	4300	625	1.7271

the field [*Arnaud*, 1997], to avoid structural modifications during the transport. Col du Dome samples were easily transfered to the LGGE and measurements were made in the laboratory on SF_6 and CO_2. We also include γ data based on O_2 and CO_2 from Siple [*Schwander et al.*, 1988], a "mild" Antarctic site. The γ values versus open porosity are presented on figure 1.

The γ values are not significantly different from one site to another. For porosities lower than 0.4, γ increases linearly with porosity. For higher values, γ seems to stabilize, but these results should be taken with caution, since the samples geometry may have been modified in the experiment [*Arnaud*, 1997]. For very low porosities (less than 0.15), the superficial velocity of the carrier gas becomes high and the linear extrapolation of D at zero velocity (see eq. 2) is no longer valid. The linear regression for porosity lower than .4 is:

$$D_{eff}/D_{ij} = 1.92 \times s - 0.23 \quad (4)$$

with a correlation coefficient of 0.957. This relationship is very close to the one found by [*Schwander et al.*, 1988] on Siple data only.

The spreading of the firn pore network depends on climatic conditions: cold sites have fewer but bigger pores than warm sites [*Arnaud et al.*, 1998]. Apparently, this structural variation does not modify diffusivity. This result confirms one assumption of our model, which neglects interactions between the pore walls and the gas molecules. The ratio of effective to molecular diffusivities, γ, would therefore appear to be governed only by firn porosity.

3. Inverse modelling

3.1. Methodology

In previous modeling studies, effective diffusivities have been determined in different ways: [*Schwander et al.*, 1993] assume that γ profiles are identical in firn exposed to similar climatic conditions and use linear regression based on Siple results. [*Trudinger et al.*, 1997] compute the effective diffusivity profile in DE08 firn with a direct diffusion model. Knowing the CO_2 atmospheric scenario and mixing ratios in the firn, they use a trail-and-error method to compute a γ profile that best fits modeled and observed results. [*Rommelaere et al.*, 1997] use an inverse model to compute the γ profile from CO_2 measurements and atmospheric scenario.

This model, based on a forward diffusion model of gases in firn, has been applied to the sites of table 1. The diffusivity profile (the free parameter of the model) is obtained using a control method, to force the model to reproduce firn measurements, with a given atmospheric scenario as the input [*Rommelaere et al.*, 1997].

Here, γ profiles are reconstructed by inverse modeling for five firns (De08, Vostok, Dronning Maud Land, Dome C in Antarctica and Devon Island in Northern Canada) and for three gases (CO_2, CH_4 and SF_6).

Atmospheric scenarios were built using NOAA data (http://www.esdim.noaa.gov). For Antarctica, CO_2 and CH_4 scenarios are based on the South Pole atmospheric records and from De08 ice results before 1957 for CO_2 [*Etheridge et al.*, 1996] and before 1983 for CH_4 [*Etheridge et al.*, 1998]. For Devon Island, the scenarios come from measurements at Alert back to 1984, and from our Antarctic scenarios before, corrected for the present-day CO_2 and CH_4 gradients between South Pole and Alert. The SF_6 history comes from the quadratic equation given by [*Maiss et al.*, 1996].

3.2. Results

On figure 2 we present the γ profiles obtained with CO_2, CH_4 and SF_6 in Dronning Maud Land firn. To estimate the uncertainty of the method, we have plotted the envelope resulting from 30 runs of the model with CO_2 data perturbed by a gaussian noise (with a standard deviation corresponding to the measurement errors). The three gases (with different histories) give very similar profiles, within or very close to the CO_2 envelope. This indicates that the envelope shown is a good approximation of the uncertainties of the method and that the reconstruction is not sensitive to the input scenario. It is thus possible to use one of the γ profiles to calculate, with the direct model, the firn mixing ratio profiles of other gases. The three reconstructed profiles are especially close near the firn-ice transition zone, which is a crucial zone for diffusion mechanisms. Results on other sites, not shown here, present the same homogeneity for the different gases.

γ profiles based on CH_4 for the five sites are plotted in figure 3. Unlike the experimental results, the profiles are different and three groups can be distinguished :

(1) The warm site, Devon Island, shows very low effective diffusivity even near the surface. This can be due to

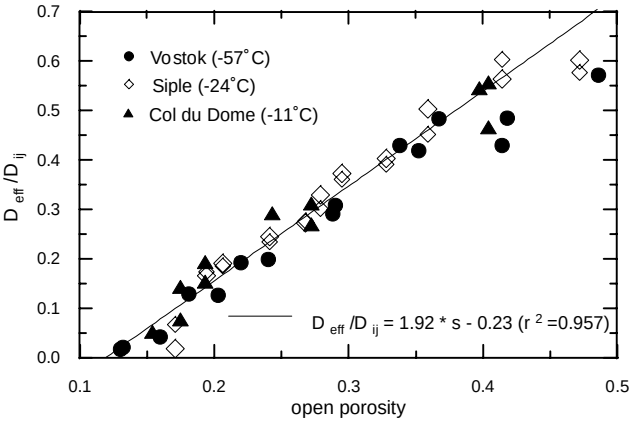

Figure 1. $\gamma = D_{eff}/D_{ij}$ measured on Vostok, Col du Dome and Siple *Schwander et al.* [1988] samples, versus open porosity.

the presence of melt layers which form insulating layers and reduce considerably the effective diffusivity.

(2) The mild sites, Dronning Maud Land and De08. Note that the De08 profile is very similar to the one determined by [*Trudinger et al.*, 1997].

(3) The cold sites, Dome C and Vostok, which also have small density fluctuations. Their D_{eff}/D_{ij} profiles show values above 1 near the firn surface. This can be due to a "well-mixed layer", where air is homogenized by atmospheric fluctuations (winds, thermal gradients...). Mixing by winds can lead to higher diffusivities than in calm air. Such a zone is in agreement with [*Bender et al.*, 1994], who conclude, on the basis of measurements of $\delta^{15}N$ of N_2 and $\delta^{18}O$ of O_2, that a 13 m thick mixed layer is present at Vostok. Our results suggest that a mixed-layer also exists at Dome C.

4. Comparison between experimental and model results

In figure 3 we can compare the experimental linear regression to the modeled profiles. Excluding the Devon Island profile which is very different from the others for the reasons already mentioned, the modeled tortuosity profiles are similar in order of magnitude to the experimental regression. However the shape of the modeled profiles is far from a linear relationship. The slope is lower near the surface and steeper near the firn-ice transition.

The difference between the experimental and modeling approaches gives information about what kind of perturbation influences gas diffusion in the firn. The similarity between the results from small samples of different firns indicates that the effective diffusivity is not affected by the firn micro-structure (pore spreading, size and shape.) Model results show that this parameter is in fact sensitive to the firn macro-structure (at least when larger than the sample size, 4 cm), i.e. density fluctuations. These fluctuations are implicitly included in the model, leading to different modeled diffusivity profiles.

In order to test the influence of these density (or porosity) fluctuations, we have calculated for the De08 firn, the depth profile of the cumulative tortuosity, divided by the considered depth z:

$$\Gamma(z) = \frac{1}{z}\int_0^z \frac{D_{eff}}{D_{ij}}dz \qquad (5)$$

Γ is linked to the relative distance effectively covered by a gas molecule from the surface to the depth z.

Figure 4 shows profiles of Γ versus z, obtained in three different ways: (1) computed by inverse modelling; (2) calculated with the experimental linear regression between D_{eff}/D_{ij} and open porosity (eq. 4), with the mean porosity values used in the model (averaged every 20 cm); and (3) calculated also with the experimental relationship, but with porosity values perturbed with a noise, in order to reflect the seasonnal variations observed on fine density measurements at De08. The curves show that Γ computed with the "noisy" porosity is closer to the modeled cumulative tortuosity, especially near the firn-ice transition, than when computed with the mean porosity. This test shows that tortuosity is very sensitive to porosity variations near the close-off. It is thus necessary, in order to use the linear regression, to know precisely these variations. However in reality, these variations are often poorly known and the use of an inverse model to determine the real tortuosity profile avoids this constraint.

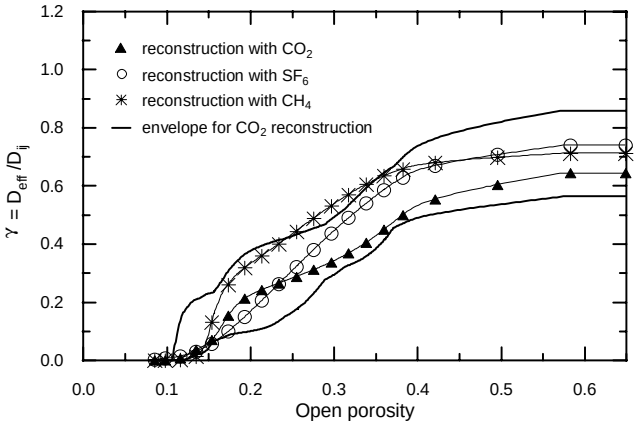

Figure 2. Modelled γ profiles versus open porosity, for CO_2, CH_4 and SF_6 at Dronning Maud Land.

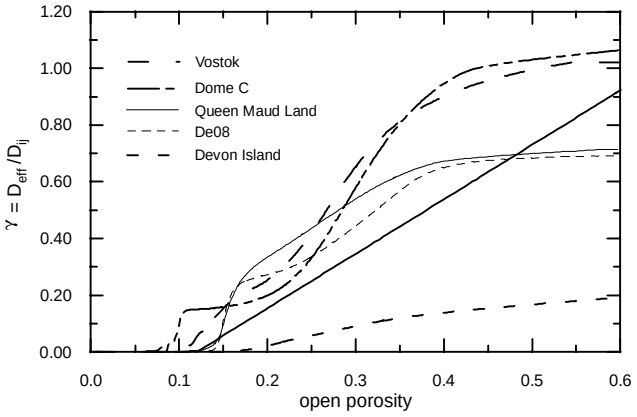

Figure 3. Modelled γ profiles versus open porosity, for CH_4 at Dronning Maud Land, Devon Island, De08, Vostok and Dome C.

5. Conclusion

The two approaches used in this paper show that in order to use experimental results to determine firn tortuosity profiles, it is necessary to know continuously and precisely porosity variations in the firn. If these variations are not known, firn tortuosity profiles can be determined by inverse methods either "manually" as done by [*Trudinger et al.*, 1997], or by using a control method such as the one from [*Rommelaere et al.*, 1997] used in this study. This study also highlights the climatic conditions required to get a firn air history as long as possible. Cold and low altitudes sites have low diffusivities and high accumulation rates sites have deep close-off depths and high density fluctuations, and thus high tortuosity. Thus cold sites at low altitudes and with high accumulation rates are best suited to the recovery of old firn air.

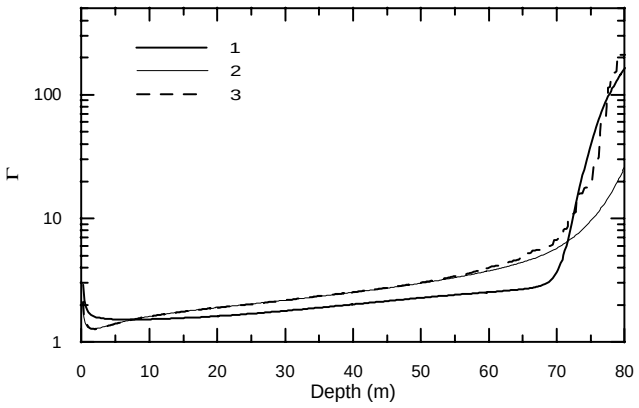

Figure 4. Ratio of effective distance covered by the gas molecules to depth versus z. *Curve 1*: inverse modelling result; *curve 2*: Ratio based on the effective diffusivity given by the regression (4) and mean porosity values; *curve 3*: as for the curve 2, but with randomly perturbed porosity values.

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