# Winter Sampling of Shallow Firn Air at the South Pole to Understand Processes Affecting Firn Atmospheric Histories and Ice Core Gas Records

JEFFREY P. SEVERINGHAUS
*Scripps Institution of Oceanography, University of California, San Diego, La Jolla, CA 92093-0244*

In January and July 1998 a cooperative project was carried out at the South Pole CMDL Clean Air Laboratory to sample air from the top 15 m of the snow (firn). The goal was to better understand gas fractionation processes that may affect the atmospheric gas histories obtained from the air in the deep firn column. Previous studies in summer have shown a marked isotopic anomaly in the top 10 m of the firn, driven by thermal fractionation in response to the strong temperature gradient in the top few meters. No samples had been taken in winter, however, so Scripps Institution of Oceanography (SIO) was curious to know (1) if the opposite sign of the temperature gradient produced an opposite isotope anomaly, as expected, (2) if the air in the firn convects spontaneously during winter in response to colder air overlying warmer air, which could bias the ice core record of gas isotopes, and (3) if adsorption and desorption on snow grains could explain anomalies in some halogenated species. For comparison a summer sampling was done first. Both data sets show the expected isotope fractionation because of temperature gradients. The winter data reveal a robust isotope anomaly of opposite sign, as expected, that exceeds a diffusion-only model prediction driven by Automatic Weather Station surface temperature data. No evidence for vigorous gas mixing because of convection was found, although the misfit of the data to the model may suggest slow downward motion or a sampling artifact. It appears unlikely that rectification of seasonality biases the deep firn or ice core record at this site, although this study is just a "snapshot" and may have missed episodic events. No evidence for adsorption or desorption was found.

## INTRODUCTION

The porous and permeable layer of snow on top of polar ice sheets is typically 50-100 m thick and is known as the firn layer. At the base of this layer the firn is continuously transformed into impermeable ice. The air in firn mixes slowly with the atmosphere, primarily by molecular diffusion [*Schwander et al*., 1988]. Consequently, the mean age of the air (defined as the time elapsed since the air crossed the surface) increases downward in the firn and reaches several decades at sites with thick firn [*Schwander et al*., 1993].

A number of recent studies have exploited this fact to reconstruct atmospheric concentration histories of various gases, such as halocarbons [*Butler et al*., 1999], $O_2/N_2$ ratios and $N_2O$ [*Battle et al.*, 1996], and $^{13}C$ of $CO_2$ [*Francey et al*., 1999]. Other recent studies have taken advantage of the fact that temperature gradients in the firn arising from rapid climate variation leave an isotope record of abrupt climate change in trapped air in ice cores [*Severinghaus et al.*, 1998; *Leuenberger et al.*, 1999; *Severinghaus and Brook*, 1999; *Lang et al.*, 1999]. At many polar sites, surface temperature varies by >30ºC seasonally. This creates strong temperature gradients in the top few meters of the firn due to the fact that the firn at ~10 m depth closely maintains the mean annual temperature at all times [*Paterson*, 1969]. Theory predicts that these gradients will lead to a characteristic pattern of thermally fractionated gases in the upper ~15 m of the firn column. A model of heat and gas diffusion in the firn enables a precise numerical prediction of the magnitude and shape of this pattern, when forced with the known surface temperature history. The model has no adjustable parameters and thus serves as a stringent test of our understanding of the physical processes governing gas-isotope ratios in shallow firn:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial z}\left( D(z,T)\left[ \frac{\partial C}{\partial z} - \underbrace{\frac{\Delta m g}{RT}}_{\text{Gravitational settling}} + \underbrace{\Omega \frac{dT}{dz}}_{\text{thermal diffusion}} \right] \right) \qquad (1)$$

where

| | |
|---|---|
| $C$ | isotope delta value (e.g., $\delta^{15}N$) |
| $t$ | time |
| $z$ | depth |
| $D$ | effective molecular diffusivity of gas in porous snow |
| $T$ | temperature, K |
| $\Delta m$ | mass difference between isotopes |
| $g$ | gravitational acceleration |
| $R$ | gas constant |
| $\Omega$ | thermal diffusion sensitivity, ‰ $K^{-1}$ |

A separate model of heat delivers temperatures to the gas model [*Alley and Koci*, 1990]. Comparison of the modeled temperature profiles with several measurements (taken from thermisters buried in the borehole) shows good agreement (Figure 1a).

## SAMPLING AND ANALYSIS

Because of the difficulty of handling samples outdoors in winter, gas sampling was arranged to be done from indoors. Using a hand coring tool, on January 18, 1998, a 15-m deep borehole located 42 m due grid E of the NE corner of the Clean Air Building was drilled. Tubes with stainless steel intake screens on the ends were placed in the hole at desired depths, and

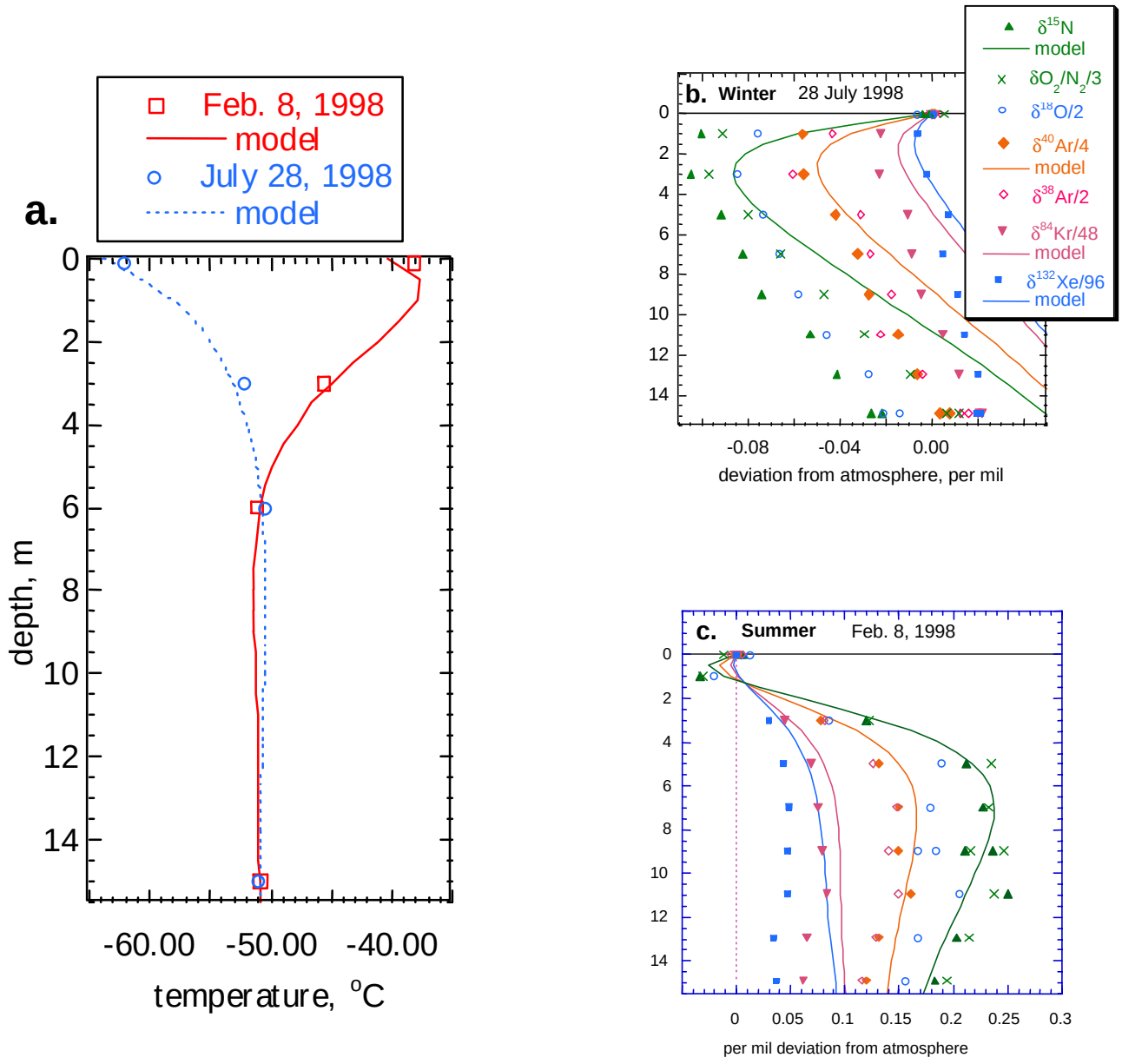


Fig. 1. Depth profiles of measured temperature (a) and gas composition in the shallow firn at the south pole. Winter sampling (b) reveals a large negative isotope excursion due to thermal isotope fractionation caused by the cold temperatures at the surface relative to the temperature at 10 m depth. Summer sampling (c) reveals the opposite pattern, as expected. Model calculations (shown as lines) are based on the measured surface temperature history for this site and the known diffusivities of these gases. Gravitational settling causes a steady linear downward increase that is independent of season and that is additive to the thermal fractionation signal. The strong winter anomaly, even stronger than predicted from the model, argues against any vigorous convective mixing that would have erased the signal by homogenizing it with the atmosphere.

the tubes were extended into the building for samples to be taken indoors. The hole was backfilled with snow and layers of slush to impede downward movement of surface air. After backfilling, the tubes were pumped on to remove as much contamination as possible. Sampling by pumping on the tubes was done on February 8 and again on July 28. This technique is similar to that used to sample air in sand dunes [*Severinghaus et al.*, 1997]. Samples were pumped at 4 L $min^{-1}$ for 16 minutes to flush the lines and the sample flasks. The air was dried by passing it through a column packed with granular phosphorous pentoxide. The air was stored in 2-L flow-through glass flasks as described by *Battle et al.* [1996]. Flasks were analyzed mass

spectrometrically at the University of Rhode Island and SIO for $^{15}N/^{14}N$ and $^{40}Ar/^{36}Ar$ ratios and other gas ratios including $^{40}Ar/^{38}Ar$, $^{18}O/^{16}O$ of $O_2$, $O_2/N_2$, $^{84}Kr/^{36}Ar$, and $^{132}Xe/^{36}Ar$. Results of two aliquots, measured for $\delta^{15}N$, $\delta^{18}O$, and $\delta O_2/N_2$ from 3 m depth at south pole February 8, were rejected on the basis of high $CO_2$ concentrations (22 and 31% above normal) that suggested gross contamination with laboratory air.

## RESULTS

Gravitational settling enriches the heavier molecules at the bottom of a stagnant air column in proportion to the mass difference $\Delta m$, so gravity should affect $\delta^{40}Ar$ four times as much as $\delta^{15}N$ [*Lindemann and Aston*, 1919; *Craig et al*., 1988; *Sowers et al*., 1989; *Schwander*, 1989]. In other words, if gravity were the only process acting on a gas mixture, $\delta^{15}N$ would be equal to $\delta^{40}Ar/4$. To facilitate comparison all results are presented here with the $\delta$ value divided by $\Delta m$.

SIO wanted to know what the shallow firn gas profile did in winter when the temperature gradient was reversed from the more commonly studied summer profile. In winter cold dense air overlies warmer air in the firn and might become unstable and undergo Bernard convection [*Powers et al*., 1985]. If the wintertime thermal diffusion anomaly were not expressed because of convection, the mean annual thermal fractionation signal would be nonzero even when annual mean temperature change was zero. In other words, there would be a rectifier of seasonal temperature change, and this signal would be transmitted to the deep firn and create a bias in the bubble air-based thermal diffusion paleoindicator.

The tendency to undergo Bernard convection in a porous media can be estimated from the dimensionless Rayleigh number [*Powers et al.*, 1985]. Taking the coefficient of thermal expansion of air as 0.0045 $K^{-1}$, the depth of the layer with strong temperature gradient as 5 m, the temperature difference across this layer as 10 K, the permeability of the firn as $4 \times 10^{-9}$ $m^2$, the dynamic viscosity of air as $1.4 \times 10^{-5}$ kg $m^{-1}$ $s^{-1}$, and the thermal diffusivity as 0.22 $m^2$ $s^{-1}$, a Rayleigh number of 4 is obtained. This is sufficiently close to the critical value for the onset of convection (10-30) that natural convection in snow cannot be ruled out by this calculation. Further, this assumes a one-dimensional firn without irregularities (snow dunes or sastrugi) that might get convection started much more easily. If vigorous convective stirring during winter were important, one would expect to see a greatly attenuated thermal fractionation signal. In fact a fully developed negative isotope anomaly, with an amplitude slightly larger than that predicted by a pure diffusion model driven by observed surface air temperature (Figure 1b) was observed. The summer data are shown for comparison (Figure 1c).

The marked deviation of the winter data from the deeper part of the model is not understood. It seems possible that gradual downward flow is advecting the values obtained at shallower depths to deeper levels, as hypothesized at Siple Dome (J. Severinghaus, Thermal fractionation of air in polar firn by seasonal temperature gradients, in preparation, 2000). Alternatively, intermittent turbulent convective mixing may be weak enough that it does not homogenize and erase the isotope fractionation, yet strong enough that it acts to transport the isotope signal downward into the firn faster than would molecular diffusion alone. In other words, mixing by eddy diffusion would double or triple the effective diffusivity over the molecular diffusivity. Adding an arbitrary intermittent eddy diffusion term to our model produces this effect, demonstrating plausibility but not proof.

## CONCLUSIONS

Seasonal effects penetrate no deeper than 40 m in the firn at current measurement precision. Therefore, the firn-ice transition at 114 m is effectively isolated from seasonality and records a time-averaged value of the fluctuations in the shallow firn. Trapped air in ice is, therefore, susceptible to rectification in principle. The gas isotope profile observed in the shallow firn during winter is nearly symmetrical to that observed during summer, suggesting that they should cancel in the annual mean. However, this conclusion assumes that the sampling dates were representative of average conditions and did not miss strong episodes of convection by chance. Deep firn isotopes do fit a pure gravitational model well, though, indicating that seasonal anomalies probably do cancel [*Battle et al.*, 1996]. No sign of thermally driven adsorption or desorption was seen. These conclusions should be regarded as valid for one site at one time, and generalized to other sites with caution.

***Acknowledgments***. I thank Ralph Keeling, Mark Battle, and Michael Bender for discussions; James Butler for inviting me to do a wintertime sampling at the south pole using CMDL resources; Lt. Nathan Hill of CMDL for taking the samples; Julie Palais of NSF-OPP for making the south pole travel possible; Michael Bender for hosting J.P.S. in his laboratory at the University of Rhode Island; Alexi Grachev for making thermal diffusion sensitivity measurements; and Charles R. Stearns at the University of Wisconsin-Madison for surface temperature data from the Automatic Weather Station Project funded by the National Science Foundation (NSF). Support came from NSF grant OPP 9725305.

## REFERENCES

Alley, R.B., and B.R. Koci, Recent warming in central Greenland?, *Ann. Glaciol., 14*, 6-8, 1990.

Battle, M.. et al., Atmospheric gas concentrations over the past century measured in air from firn at the South Pole, *Nature, 383*, 231-235, 1996.

Butler, J.H., M. Battle, M.L. Bender, S.A. Montzka, A.D. Clarke, E.S. Saltzman, C.M. Sucher, J.P. Severinghaus, and J.W. Elkins, A record of atmospheric halocarbons during the twentieth century from polar firn air, *Nature, 399*, 749-755, 1999.

Craig, H., Y. Horibe, and T. Sowers, Gravitational separation of gases and isotopes in polar ice caps, *Science, 242*, 1675-1678, 1988.

Francey, R.J., M.R. Manning, C.E. Allison, S.A. Coram, D.M. Etheridge, R.L. Langenfelds, D.C. Lowe, and L.P. Steele, A history of delta C-13 in atmospheric $CH_4$ from the Cape Grim air archive and antarctic firn air, *J. Geophys. Res., 104*, 23,631-23,643, 1999.

Lang, C., M. Leuenberger, J. Schwander, and S. Johnsen, 16°C Rapid temperature variation in central Greenland 70,000 years ago, *Science, 286*, 934-937, 1999.

Leuenberger, M., J. Schwander, and C. Lang, Delta (15)N measurements as a calibration tool for the paleothermometer and gas-ice age differences: A case study for the 8200 BP event on GRIP ice, *J. Geophys. Res., 104*, 22,163-22,170, 1999.

Lindemann, F.A., and F.W. Aston, The possibility of separating isotopes, *Phil. Mag. Ser. 6, 37*, 523-534, 1919.

Paterson, W.S.B., *The Physics of Glaciers*, 250 pp., Pergamon, 1969.

Powers, D., K. O'Neill, and S.C. Colbec, Theory of natural convection in snow, *J. Geophys. Res., 90*, 10,641-10,649, 1985.

Schwander, J., The transformation of snow to ice and the occlusion of gases, in *The Environmental Record in Glaciers and Ice Sheets*, edited by H. Oeschger and C.C. Langway, Jr., pp. 53-67, John Wiley, New York, 1989.

Schwander, J., B. Stauffer, and A. Sigg, Air mixing in firn and the age of the air at pore close-off, *Ann. Glaciol., 10*, 141-145, 1988.

Schwander, J., J.-M. Barnola, C. Andrie, M. Leuenberger, A. Ludin, D. Raynaud, and B. Stauffer, The age of the air in the firn and the ice at Summit, Greenland, *J. Geophys. Res., 98*, 2831-2838, 1993.

Severinghaus, J.P., and E.J. Brook, Abrupt climate change at the end of the last glacial period inferred from trapped air in polar ice, *Science, 286*, 930-934, 1999.

Severinghaus, J.P., R.F. Keeling, B.R. Miller, R.F. Weiss, B. Deck, and W.S. Broecker, Feasibility of using sand dunes as archives of old air, *J. Geophys. Res., 102*, 16,783-16,792, 1997.

Severinghaus, J.P., T. Sowers, E.J. Brook, R.B. Alley, and M.L. Bender, Timing of abrupt climate change at the end of the Younger Dryas period from thermally fractionated gases in polar ice, *Nature, 391*, 141-146, 1998.

Sowers, T., M.L. Bender, and D. Raynaud, Elemental and isotopic composition of occluded $O_2$ and $N_2$ in polar ice, *J. Geophys. Res., 94*, 5137-5150, 1989.