5.5.3. FIRN AIR SAMPLING, 2001

In January 2001, CMDL scientists joined investigators from Bowdoin University, Princeton University, and the University of Wisconsin to collect an archive of 20th century air from the firn (snowpack) at South Pole (Figure 5.42). Samples were collected into separate pairs of 3-L glass flasks for measurements of O_2/N_2 (by Bowdoin and Princeton) and carbon cycle gases (by CMDL/CCGG); individual 3-L stainless-steel and glass flasks for measurements of halocarbons, N_2O, SF_6, and COS; large (33-L) stainless-steel canisters to maintain an archive of air for future analyses; and a few canisters each for measurement of $^{14}CH_4$ (by NIWA and CSIRO) and very low-level analyses of SF_6 (by Scripps Institution of Oceanograpy, SIO) (Table 5.9). All samples were analyzed during 2001, including initial analyses of the archive canisters. Although it was hoped to obtain air dating back to the turn of the century, the analyses suggest that the earliest date was 1921 for CO_2 and just after 1900 for gases that diffuse more slowly, such as methyl bromide and methyl chloride.

CMDL scientists have been participating in the collection and analysis of firn air from Antarctica and Greenland since

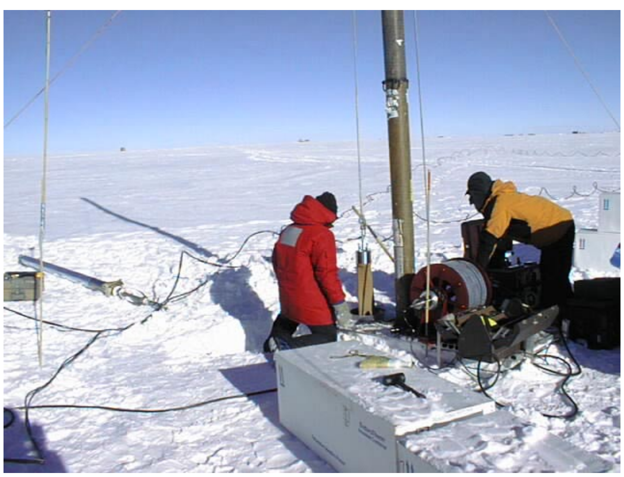

Fig. 5.42. Bladder being sent down into one of the two holes at South Pole for subsequent sampling of firn air. The 10-m-long bladder was pressurized to inhibit airflow from above while firn air was sampled through a 15-cm-high, stainless-steel-lined open chamber situated between the bottom of the bladder and the bottom of the hole. Each of two holes, extending ultimately to the snow-ice transition at 122-m depth, was drilled and sampled at 2- to 10-m increments. The drill lies on the snow to the left.

TABLE 5.9. Gases Measured in South Pole Firn Air, 2001

Institution	Gas
CMDL or Univ. of Colorado	CO_2, CO, CH_4, N_2O, H_2, SF_6, CFCs, HCFCs, HFC-134a, CH_3Br, CH_3Cl, CH_3I, COS, halons, $^{13}CO_2$
Princeton Univ. or SIO	$^{15}N_2O$, $N_2{}^{18}O$, $^{15}N_2$, $^{18}O_2$, $^{17}O_2$, $^{14}CO_2$, Ar, Kr, Xe, Ne, Ar/N_2, O_2/N_2, SF_6
NIWA or CSIRO	$^{14}CH_4$

1995. Samples have been analyzed from Vostok, Taylor Dome, South Pole, and Siple Dome in Antarctica and from Tunu in Greenland. The data have been used to estimate the atmospheric histories of these gases where real-time measurements were not available [*Battle et al.*, 1996; *Butler et al.*, 1999], extending the earliest records of many trace deep sampling conducted at that site; the first was in 1995. Samples from this most recent collection provide a unique opportunity to examine the diffusion of trace gases in the firn (Figures 5.43 and 5.44), which should reduce error in the estimation of the age of the firn air. Also, the oldest firn air ever collected comes from South Pole, which makes the archived samples particularly valuable for future analyses of gases not yet reported.
gases from the late 1970s back to the end of the 19th century. They also have been used to evaluate seasonal biasing of the mean gas mixing ratios [*Severinghaus et al.*, 2001]. The 2001 sampling at South Pole was the second

Preliminary evaluation of the data from the 2001 campaign shows that diffusion rates of gases in the firn are very close to molecular rates, calculated by extrapolation of measurements made at very high temperatures to the temperature of the firn, ~ −50°C. Although often used in models of firn air movement, such extrapolated values are always suspect. Determination of the actual diffusion rates in the firn will remove this uncertainty and allow for the direct calculation of gas diffusion at these temperatures and, subsequently, the mean age of the air at each depth.

Data are being analyzed and evaluated with the objectives to (1) improve estimates of trace gas diffusion at low temperatures and the corresponding effect on mean-age estimates for firn air samples and (2) report 20th century histories of gases, such as COS, previously not analyzed throughout the century. Other laboratories are currently analyzing the archive of air in 33-L canisters in an attempt to obtain reliable records of additional gases. It is anticipated that sufficient air will be available for analysis of even more gases and isotopes as new analytical techniques become available.

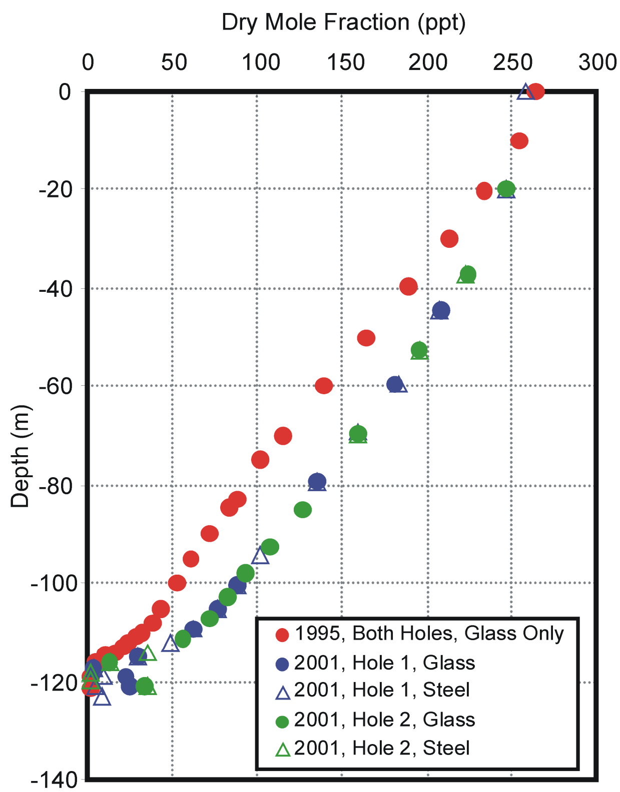

Fig. 5.43. CFC-11 in South Pole firn air in 1995 and 2001. Samples in 1995 were collected from two separate holes, but only into glass flasks. Samples in 2001 also were collected from two separate holes, but both glass and electropolished stainless-steel flasks were used. Note the lower value at the surface in 2001, reflecting the decreased atmospheric burden between 1995 and 2001. Also note the 20-m penetration at mid-depth, where the gradient is steepest and vertical restriction still low.

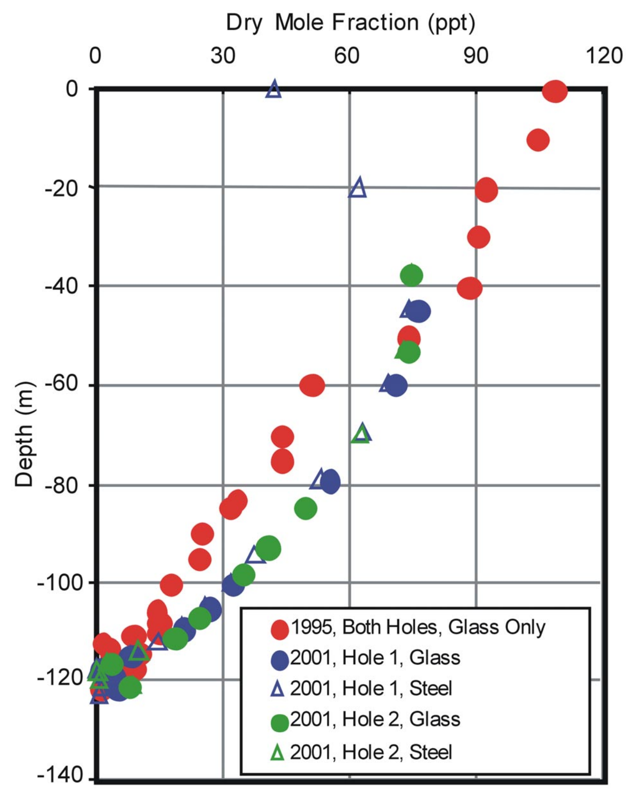

Fig. 5.44. CH_3CCl_3 in South Pole firn air in 1995 and 2001. The 1995 sampling suffered from contamination in the glass flasks, which compromises the interpretation of some of the data points. The 2001 sampling was apparently free of contamination. Note not only the penetration that is similar to that of CFC-11 (Figure 5.43), but also the evidence for the stark turnaround in the CH_3CCl_3 trend in the atmosphere. The turnover occurred in about 1994 in the southern hemisphere, which was an insufficient time lag for this signal to be recorded in the firn in 1995. (The northern hemispheric turnover, in about 1993, was recorded in Greenland firn as early as 1996 [*Butler et al*., 1999].) By 2001, the peak of CH_3CCl_3 had penetrated to 45-m depth.