17. Measurements of OH and H$_2$SO$_4$ were recorded on a selected-ion chemical-ionization mass spectrometer [F. Essel and D. Tanner, J. Geophys. Res. 96, 9205 (1991); ibid. 98, 9001 (1993)]. Two sigma uncertainties on individual 1-s measurements of H$_2$SO$_4$ are ±42% (precision is 20%) but are much reduced for the 1-s averages used here [R. L. Mauldin, et al., 16713 (1998)]. SO$_2$ and DMS measurements were measured with an isotopic-dilution gas-chromatography mass spectrometer [A. Bandy et al., ibid. 98, 23423 (1993)]. The photochemical related parameters CO, H$_2$O, NO, O$_3$, NMHCs, and UV irradiance were continuously recorded as were the meteorological parameters RH and T; for details see {J. Hoel et al., ibid., in press}. The above species and parameters were typically measured and averaged over times ranging from 15 to 5 min. A subset of these (for example, vertical and horizontal winds, dew point, and temperature) was high-resolution 20-Hz data.

18. The time-dependent photochemical box model for diel trends in OH is similar to that described by D. Davis et al. [J. Geophys. Res. 101, 211 (1996)] and J. Crawford et al. [ibid. 102, 28447 (1997)]. The chemical model assumed all calculated species to be in photochemical equilibrium and included 50 standard HOx-NOx-CH$_4$ reactions, 118 NMHC reactions, 15 photolytic reactions, and heterogeneous removal of soluble species. It was constrained by input values for O$_3$, CO, CH$_4$, NMHCs, NO, H$_2$O, temperature, pressure, and, when available, measurements of the longer-lived species H$_2$O$_2$, CH$_2$O, OH, NO$_2$, and peroxyacetyl nitrate. Photolysis rates were calculated with the National Center for Atmospheric Research community radiative transfer code configured for four-stream, SORT calculations. Calculated J-values were scaled for cloud effects based on a comparison of the observed OH and model estimated values (typically 10%).


20. D. Davis et al., ibid., in press.

21. The DMS flux was estimated by using a mass conservation equation with measured DMS and OH values and model-generated diel profiles for NO$_2$ and OH (DMS)/dt = Fdms/EMD - (kOH[OH] + kNO$_3$[NO$_2$]/[OH]) DMS. The first term on the right-hand side is the NO$_2$ source (sea-to-air flux), which depends on the oxidation rate of DMS and the equivalent mixing depth (EMD) [19, 20]. The latter can be viewed as the height of an atmospheric column that contains all DMS mass (both buffer and background) at a constant BL concentration. The DMS oceanic flux is balanced by a comparable loss by reaction with OH and NO$_2$ calculated from the 24-hour profiles for DMS, OH, and NO$_2$. For flight 19 the OH profile was generated independently from an O$_3$/HOx/NOx/CH$_4$ photochemical box model, constrained both by the measured photochemical controlling parameters O$_3$, CO, H$_2$O, NO, NMHCs, CO, and by the limited in situ BL OH measurements [18]. Evaluation of the EMD (1.3 km for flight 19) was based on the vertical concentration data for DMS and CH$_4$ [17, 31]. Using an estimated BL height of 0.6 km, about half the DMS released had been transported into the overlying cloud layer and lower free troposphere.


26. This work was funded by the National Science Foundation. This study is similar to that previously described [17, 19, 31] and is based on 14 sulfur reaction processes, five having two or more branches. Coupled sets of time-dependent continuity equations (with photoxenized transport terms) are integrated to yield time-dependent concentration profiles of sulfur species. The general form of this equation is: 

\[ \frac{d[S]}{dt} = -S_{\text{fai}} + M_{\text{h}} \times [S]_{\text{bulk}} - \]

27. Objective correlation of isotope paleotemperature records from polar ice cores has shown that some climate variations once thought to be synchronous in both hemispheres are in fact out of phase. For example, E. J. Steig, J. W. C. White, S. J. Lehman, D. L. Morse, E. D. Waddington, and G. D. Clow.

Central Greenland ice cores provide evidence of abrupt climate changes in climate over the past 100,000 years. Many of these changes have also been identified in sedimentary and geochemical signatures in deep-sea sediment cores from the North Atlantic, confirming the link between millennial-scale climate variability and ocean thermohaline circulation. It is shown here that two of the most prominent North Atlantic events—the rapid warming that marks the end of the last glacial period and the Bølling/Allerød—Younger Dryas oscillation—are also recorded in an ice core from Taylor Dome, in the western Ross Sea sector of Antarctica. This result contrasts with evidence from ice cores in other regions of Antarctica, which show an asynchronous response between the Northern and Southern Hemispheres.
conclusions regarding the timing of rapid climate change events. Here we present a new stable isotope ($\delta D$) record (Fig. 2) and a new chronology for the last glacial-interglacial transition in the Taylor Dome core. We use both atmospheric methane ($CH_4$) and the isotopic ratio of molecular oxygen ($\delta^{18}O_{atm}$) to tie Taylor Dome to the layer-counted chronology of the Greenland Ice Sheet Project 2 (GISP2) (Summit, Greenland) ice core (7). This approach requires calculation of the age difference ($\Delta$age) between the ice and the younger gas it encloses. For GISP2, we use the gas-age time scale and $\Delta$age values of Brook et al. (8). For Taylor Dome, we obtain a gas chronology by visually matching changes in $CH_4$ and $\delta^{18}O_{atm}$ concentrations with those at GISP2 (Fig. 3). The rapid increases in $CH_4$ before and after the YD provide precise correlation points at 14.6 and 11.6 thousand years before the present (kyr B.P.) (9). The precision of the correlation between 20 and 15 kyr B.P., during which both $CH_4$ and $\delta^{18}O_{atm}$ change relatively slowly, is between 500 and 1500 years.

We calculate $\Delta$age for Taylor Dome as a function of the effective bubble close-off depth (COD), surface temperature ($T$) and accumulation rate ($b$), using the empirical Herron-Langway model to describe the firm densification process (10). We assume that the COD occurs at a density $p_{COD} = 800 \pm 10$ kg m$^{-3}$, as determined from nitrogen isotope ($\delta^{15}N$) measurements in firm air (11). Measured $\delta^{15}N$ in Taylor Dome ice samples independently constrains $\Delta$age by giving a measure of the thickness of the diffusive zone through which gravitational fractionation is manifested. Diffusive layer thicknesses calculated from measured $\delta^{15}N$ provide a minimum estimate of the COD and therefore of $\Delta$age for given $T$ and $b$ (12).

Values for $T$ and $b$ are taken as averages over an interval approximating the original thickness of the firm column (13). We assume that $T$ is a linear function of $\delta D$, where the slope $\alpha = 4.0 \pm 1.5$‰ °C$^{-1}$ (14). We calculate $b$ from the $^{10}Be$ concentration (Fig. 2), where we assume that the dry deposition flux is constant and include a term for wet deposition (15). The $^{10}Be$ method is supported by several observations. First, $^{10}Be$ concentration and $b$ show a strong spatial inverse correlation both locally at Taylor Dome and broadly across the Antarctic continent (16). Second, both empirical and theoretical considerations indicate that the dry deposition flux of $^{10}Be$ at polar latitudes varied little over the last glacial cycle, for averages over time intervals greater than a few decades (17). Third, comparison of $^{10}Be$ with major ion concentrations in the Taylor Dome core shows a high degree of correlation; variation in accumulation rate produces strong covariance among chemical species, including $^{10}Be$ and sulfate, which have very different source functions (18). Finally, flow model calculations, based on high-resolution radar profiles and vertical and surface velocity data, provide independent validation of $^{10}Be$-based estimates of accumulation rates (19). For comparison, we also determine $b$ using calculated values for $T$ (from measured $\delta D$) by assuming that $b$ varies as a linear function of the saturation vapor pressure of water over ice (20). This more commonly used approach, although probably valid for continental sites such as Vostok, is difficult to justify at Taylor Dome, where precipitation is strongly influenced by cyclonic activity (21); relative to the $^{10}Be$ method, it generally overestimates accumulation rates (and therefore underestimates $\Delta$age) during cold periods. Values of $\Delta$age calculated by the different methods vary by up to $\pm$750 years (Fig. 3). The variance in $\Delta$age is greatest in the oldest part of the record (20 to 15 kyr B.P.) but is <300 years during the crucial YD time period and early Holocene and <600 years at 14.6 kyr B.P., at the time of the rapid deglacial warming in the Northern Hemisphere.

We obtain a time scale for Taylor Dome by adding $\Delta$age to the gas ages from correlation with GISP2, using the maximum of the estimates shown in Fig. 3. As will become apparent, this approach is the most conservative for comparing Taylor Dome with other ice core records, because it gives the oldest age for a given depth. We estimate the precision of this time scale by propagating uncertainties in $p_{COD}$, $T$, and $b$ (11, 14, 15) and adding estimated uncertainties arising from the GISP2 age calculation and the curve-matching technique (22). The resulting $\delta D$ time series, from 20 to 10 kyr B.P., is compared in Fig. 4 with $\delta D$ at GISP2. Also shown are $\delta^{18}O$ at Byrd and $\delta D$ at Vostok, both on the Sowers and Bender (3) time scales tied to GISP2 through $\delta^{18}O_{atm}$. For Byrd, where uncertainties in $\Delta$age are small, the time scales of both Sowers and Bender (3) and Blunier et al. (4) are in excellent agreement. For Vostok, uncertainties in $\Delta$age are considerably larger; ages from (3) are up to 1200 years greater than those from (4) over the interval from 20 to 10 kyr B.P.

Figure 4 illustrates three particularly important findings. First, prominent features of the GISP2 record that are absent at Byrd and Vostok appear at Taylor Dome, including...
Differences between the isotope-temperature history from Taylor Dome and those from other Antarctic sites are too large to be attributed to dating errors. Rather, the results indicate that the circum-Antarctic climate response to changes in NADW formation and export may not be uniform. We propose that the North Atlantic character of the isotopic record at Taylor Dome, in particular, reflects the relative proximity of this site to the western Ross Sea, an area of active wind-driven convection and ocean-atmosphere heat exchange in today’s climate (26). We note that a similarly heterogeneous response to transient reduction of NADW formation and export has been observed in some numerical models (27). For example, in the coupled atmosphere-ocean general circulation model simulations of Schiller et al. (28), near-Antarctic waters of the Southern Ocean (areas of vigorous oceanic convection in control simulations) cool in response to reduced formation and export of NADW, whereas other areas of the Southern Ocean warm as a result of changing patterns of atmospheric circulation and increased ocean heat convergence. Taylor Dome may thus record the direct but localized influence of NADW-borne heat on Antarctic climate (29). Given the substantial difficulty of realistically simulating ocean-atmosphere interactions in general, and the dynamics of the Southern Ocean in particular, it may be some time before the role of NADW in shaping Antarctic climate can be rigorously evaluated. In the meantime, our observations can and should be tested by collection and analysis of additional Antarctic ice cores, especially from near-coastal sites.

References and Notes

11. 815N rises through most of the firn column as a result of gravitational fractionation [H. Craig, Y. Horibe, T.
14. The equation of 4% C/13C (equivalent to 0.5% 10Be/9Be) agrees with borehole temperature analyses at Taylor Dome showing a \( \sim 1.5^\circ \) cooling at Taylor Dome since about 4 kyr B.P., during which time dD dropped by \(-6\%\). [E. D. Waddington and G. D. Clow, Earth Planet. Sci. Lett. 78, 260 (1989)].

15. Uncertainty in the curve match is taken as \( \pm 0.5^\circ \text{C} \) [E. D. Waddington, D. L. Morse, thesis, University of Washington, Seattle (1997)].


18. R. B. Alley et al., J. Glaciol. 41, 303 (1995). In the Taylor Dome core, no correlation coefficient between \( ^{10}\text{Be} \) and SO \(_4 \) is \( >0.75 \).


22. The uncertainty in GISP2 \( \Delta T \) is taken from comparison of results from two independent calculations, which are in agreement within \( \pm 100 \) years [8] and J. Schwarcz et al., J. Geophys. Res. 102, 2803 (1997). Uncertainty in the curve model is taken as one-half the range of the calculated results, generally 500 years for the period from 20 to 15 kyr B.P. and 150 years for the period from 15 to 10 kyr B.P.


26. S. S. Jacobs, R. G. Fairbanks, and Y. Horibe [Antarct. Res. Ser. 43, 203 (1985)] estimate that southward oceanic heat transport provides a net flux of heat to the atmosphere of \(-3 \) W/m\(^2\) along the Antarctic coastal margin. Local heat fluxes from leads and polynyas in the western Ross Sea, kept open by the strong westerly wind, produce a mixture of cold and warm water (D. D. Kurtz and D. Bromwich, ibid., p. 177; H. J. Zwally and J. C. Comiso, ibid., p. 203), may be orders of magnitude higher [D. J. Cavalieri and S. Martin, ibid., p. 227].


29. The sensitivity of Taylor Dome to local oceanographic conditions may depend on ice sheet configuration, especially in the position of the Ross Ice Sheet/Ice Shelf margin. Although the Ross Ice Sheet may not have reached all the way to the continental shelf break during the last glacial maximum [K. J. Licht, A. E. Jennings, J. T. Andrews, K. M. Williams, Geology 24, 223 (1996)], the distance between Taylor Dome and seasonally open water would have been greater, and local atmospheric circulation patterns may have been altered [D. L. Morse, E. D. Waddington, E. J. Steig, Geophys. Res. Lett. 25, 3383 (1998)]. We do not therefore expect a simple linear relation between proxies of ocean circulation and Taylor Dome dD even if, as we suggest, changes in ocean circulation are the primary forcing mechanism.

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**Solution Properties of Single-Walled Carbon Nanotubes**

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Naked metallic and semiconducting single-walled carbon nanotubes (SWNTs) were dissolved in organic solutions by derivatization with thionychloride and octadecylamine. Both ionic (charge transfer) and covalent solution-phase chemistry with concomitant modulation of the SWNT band structure were demonstrated. Solution-phase near-infrared spectroscopy was used to study the effects of chemical modifications on the band gaps of the SWNTs. Reaction of soluble SWNTs with dichlorocarbene led to functionalization of the nanotube walls.

With novel structural, electronic, and mechanical properties, SWNTs constitute an important new form of carbon that may find applications in many fields ([1]). The function-alization chemistry of the open ends, the exterior walls (convex face), and the interior cavity (concave face) of the SWNTs is expected to play a vital role in tailoring the properties of these materials and the engineering of nanotube devices. However, all of the currently known forms of SWNT material are insoluble in organic solvents ([2, 3]), making it difficult to explore and understand the chemistry of SWNTs ([4]) at the molecular level. We report here an approach to the dissolution of shortened SWNTs ([5]) in common organic solvents. Various solution spectroscopies were applied to characterize the dissolved SWNTs. We found that the band gaps of some types of SWNTs can be measured directly by solution-phase near-infrared (IR) spectroscopy, which allows the study of the effects of chemical modifications on the band gaps of SWNTs, the key to the molecular design of new SWNT-based materials.

Solution-phase wall chemistry was demonstrated by reaction of the soluble SWNTs (s-SWNTs) with dichlorocarbene. The s-SWNTs will have a rich solution chemistry, perhaps rivaling that of the fullerenes. They are versatile precursors to nanotube-based co-polymers, composites, and metal ligands.

The SWNT-containing raw soot (40 to 60% purity, obtained from CarboLex Inc.) was prepared by the modified electric-arc technique ([3]). Purified SWNTs (>90%) and shortened SWNTs (100 to 300 nm in length) were obtained by the method of Smalley and co-workers ([5]). In the final step of purification, we added HCl to the aqueous suspension of SWNTs before collecting the sample, so that the opened ends of the purified SWNTs were terminated with carboxylic acid groups ([–COOH, IR frequency \( \nu_C = 1719 \text{ cm}^{-1} \)] rather than carboxylate groups ([–COO\(^-\), \( \nu_C = 1620 \text{ cm}^{-1} \)] (Fig. 1). The shortened SWNTs have similar IR features. The Raman spectrum of the shortened SWNTs collected with 1064-nm excitation (\( \omega_0 = 161 \text{ cm}^{-1}, \omega_0 = 1595 \text{ cm}^{-1} \)), where \( \omega_0 \) and \( \omega_0 \) are the Raman-active radial mode and tangential mode frequencies of SWNTs, respectively) is close to that of raw soot (\( \omega_0 = 162 \text{ cm}^{-1}, \omega_0 = 1592 \text{ cm}^{-1} \)).