

# UC Irvine

## UC Irvine Previously Published Works

### Title

Climate Change During the Last Deglaciation in Antarctica

### Permalink

<https://escholarship.org/uc/item/58c367fm>

### Journal

Science, 272(5268)

### ISSN

0036-8075

### Authors

Mayewski, PA  
Twickler, MS  
Whitlow, SI  
[et al.](#)

### Publication Date

1996-06-14

### DOI

10.1126/science.272.5268.1636

### Copyright Information

This work is made available under the terms of a Creative Commons Attribution License, available at <https://creativecommons.org/licenses/by/4.0/>

Peer reviewed

Our measurements agree with theoretical data based on the revised HKF equation of state, with the possible exception of the lower pH range (Fig. 4). The slight offset may be caused either by improper assumptions in the calculation (21) or by an association constant for  $\text{HCl}^\circ$  that is weaker than predicted (18). This needs to be confirmed, however, by additional experiments.

The YSZ membrane electrode provides a highly accurate means of measuring the pH of compositionally complex aqueous fluids at elevated temperatures and pressures. This is particularly relevant to the study of mid-ocean vent fluids (Fig. 4), where the sensor could be used to measure  $\text{pH}_{T,P}$  directly, providing an unparalleled constraint on sub-sea-floor hydrothermal processes. Results of this study, however, are not limited to the field of geochemistry but are applicable to any study in which accurate pH values of aqueous fluids at supercritical conditions are needed.

#### REFERENCES AND NOTES

1. The critical temperature ( $T_c$ ) of  $\text{H}_2\text{O}$  is 373.917°C [L. Sengers et al., *J. Phys. Chem. Ref. Data* **12**, 1 (1983)].
2. W. L. Bourcier, G. C. Gene, H. L. Barnes, in *Hydrothermal Experimental Techniques*, G. C. Uimer and H. L. Barnes, Eds. (Wiley-Interscience, New York, 1987), pp. 157–188.
3. K. Ding, M. E. Berndt, J. E. Seewald, W. E. Seyfried Jr., *Eos* **69** (fall suppl.), 1488 (1988).
4. W. E. Seyfried Jr. and K. Ding, in *Seafloor Hydrothermal Systems: Physical, Chemical, Biological, and Geological Interactions*, S. E. Humphris, R. A. Zierenberg, L. S. Mullineaux, R. E. Thomson, Eds. (American Geophysical Union, Washington, DC, 1995), pp. 248–272.
5. R. E. Mesmer, C. F. Baes Jr., F. H. Sweeton, *J. Phys. Chem.* **74**, 1937 (1970); D. A. Palmer and K. E. Hyde, *Geochim. Cosmochim. Acta* **57**, 1393 (1993).
6. D. D. Macdonald and D. Owen, *Can. J. Chem.* **51**, 2747 (1973).
7. L. W. Niedrach, *J. Electrochem. Soc.* **127**, 2122 (1980); *Science* **207**, 1200 (1980); D. D. Macdonald, S. Hettiarachchi, S. J. Lenhart, *J. Solution Chem.* **17**, 719 (1988).
8. S. Hettiarachchi, K. Makela, H. Song, D. D. Macdonald, *J. Electrochem. Soc.* **139**, L3 (1992).
9. K. Ding and W. E. Seyfried Jr., *Geochim. Cosmochim. Acta* **59**, 4769 (1995).
10. ———, *J. Solution Chem.*, in press.
11. R. O. Fournier, *Geochim. Cosmochim. Acta* **47**, 579 (1983).
12. P. C. Dell'Orco, E. F. Gloyna, S. Buelow, *Supercritical Fluid Engineering Science: Fundamentals and Applications*, E. Kiran and J. F. Brennecke, Eds. (ACS Symp. Ser. 514, American Chemical Society, Washington, DC, 1993), pp. 248–272.
13. K. L. Von Damm, in (4), pp. 222–247.
14. Temperature was maintained at  $400^\circ \pm 0.5^\circ\text{C}$  by time-proportioning solid-state controllers, and pressure was held at  $40 \pm 0.1$  MPa by a transducer within a Shimadzu 7A HPLC pump, which served as the fluid delivery system.
15. The reference electrode (Ag/AgCl) was installed by a method similar to that described in (10).
16. The sensing electrodes were installed next to the reactor outlet, which helped ensure correspondence between sensor response and fluid samples.
17. J. W. Johnson, E. H. Oelkers, H. C. Helgeson, *Comput. Geosci.* **18**, 899 (1992); J. C. Tanger IV and H. C. Helgeson, *Am. J. Sci.* **288**, 19 (1988); E. L. Shock, E. H. Oelkers, J. W. Johnson, D. A. Sverjensky, H. C. Helgeson, *J. Chem. Soc. Faraday Trans.* **88**, 803 (1992).

18. The association constant of  $\text{HCl}^\circ$  was obtained from the revised HKF equation of state (17) and associated parameters [D. A. Sverjensky, J. J. Hemley, W. M. D'Angelo, *Geochim. Cosmochim. Acta* **55**, 988 (1991)].
19. The association constant of  $\text{NaOH}^\circ$  was from K. Ding and W. E. Seyfried Jr., *Geochim. Cosmochim. Acta* **56**, 3681 (1992).
20. The standard potential for Hg/HgO was calculated from G. B. Naumov, B. N. Ryzhenko, I. L. Khodakovskiy, *Handbook of Thermodynamic Data*, I. Barnes and V. Speltz, Eds., G. J. Soleimani, Transl. (U.S. Geological Survey, Menlo Park, CA, 1974).
21. Trace components, which may have resulted from

corrosion of the experimental system, were very low in comparison with total dissolved NaCl and thus were not considered in speciation calculation. The activity coefficient for all neutral species were assumed to be similar to that for  $\text{H}_2\text{S}$  (19).

22. We thank D. D. Macdonald and J. Pang for their assistance with constructing the YSZ electrode. We are also grateful to M. E. Berndt, D. A. Sverjensky, and two anonymous reviewers for critical comments. This research was supported by NSF grant OCE-9300119.

3 January 1996; accepted 20 March 1996

## Climate Change During the Last Deglaciation in Antarctica

P. A. Mayewski,\* M. S. Twickler, S. I. Whitlow, L. D. Meeker, Q. Yang, J. Thomas, K. Kreutz, P. M. Grootes,† D. L. Morse, E. J. Steig, E. D. Waddington, E. S. Saltzman, P.-Y. Whung, K. C. Taylor

Greenland ice core records provide clear evidence of rapid changes in climate in a variety of climate indicators. In this work, rapid climate change events in the Northern and Southern hemispheres are compared on the basis of an examination of changes in atmospheric circulation developed from two ice cores. High-resolution glaciochemical series, covering the period 10,000 to 16,000 years ago, from a central Greenland ice core and a new site in east Antarctica display similar variability. These findings suggest that rapid climate change events occur more frequently in Antarctica than previously demonstrated.

Among the rapid climate change events, the Younger Dryas (YD, a return to near glacial conditions during the last deglaciation) has received considerable attention because it is the most dramatic of the climate events that have occurred since the end of the last glacial period. It is well documented in the Northern Hemisphere by a variety of paleoclimate records (1).

However, characterization of the YD in the Southern Hemisphere suggests that there may have been regional differences. In New Zealand, glacier advances occurred during this time (2), but along the Pacific rim of the Americas this period is characterized by glacier retreat (3). Stable isotope records developed from several Antarctic ice cores suggest that the most likely analog for the YD in Antarctica is a slight cooling [an Antarctic cold reversal (ACR)] that interrupts a two-step deglaciation comprising two warming trends (4, 5). To further investigate the ACR-YD association and additional complexities of interhemispheric climate change during the last deglaciation, we examined glaciochemical records for the period 10,000 to 16,000 years ago derived from a newly recovered east Antarctic record, the Taylor Dome ice core (Fig. 1).

Taylor Dome ( $77^\circ 47.7'S$ ,  $158^\circ 43.1'E$ , elevation of  $2400 \pm 20$  m) is a local ice accumulation area that supplies ice to major valley glaciers in Southern Victoria Land, Antarctica. It has been dated through a combination of ice flow modeling, marker horizons (radioactive bomb layers and volcanic events), and the correlation of  $^{10}\text{Be}$ ,  $\delta^{18}\text{O}$  of  $\text{O}_2$ , and stable isotopic measurements with other Antarctic ice cores, yielding a  $2\sigma$  precision of dating of  $\sim 350$  years for the period under study (6, 7). Comparison of the stable isotope records from Tay-

P. A. Mayewski, M. S. Twickler, S. I. Whitlow, Q. Yang, J. Thomas, K. Kreutz, Climate Change Research Center, Institute for the Study of Earth, Oceans, and Space, and Department of Earth Sciences, University of New Hampshire, Durham, NH 03824, USA.

L. D. Meeker, Climate Change Research Center, Institute for the Study of Earth, Oceans, and Space, and Department of Mathematics, University of New Hampshire, Durham, NH 03824, USA.

P. M. Grootes and E. J. Steig, Quaternary Research Center AK-60, University of Washington, Seattle, WA 98195, USA.

D. L. Morse and E. D. Waddington, Geophysics Program, University of Washington, Seattle, WA 98195, USA.

E. S. Saltzman, Rosenstiel School of Marine and Atmospheric Sciences, University of Miami, Miami, FL 33149, USA.

P.-Y. Whung, National Oceanic and Atmospheric Administration, Atlantic Oceanographic and Meteorological Laboratory, Ocean Chemistry Division, and Rosenstiel School of Marine and Atmospheric Sciences, University of Miami, Miami, FL 33149, USA.

K. C. Taylor, Water Resources Center, Desert Research Institute, University and Community College System of Nevada, Reno, NV 89506, USA.

\*To whom correspondence should be addressed.

†Present address: Leibniz Labor für Altersbestimmung und Isotopenforschung Christian-Albrechts-Universität Kiel, 24118 Kiel, Germany.

lor Dome and Vostok indicates that dating of the Taylor Dome record is consistent with other Antarctic ice core records and that it displays an ACR event (6). Taylor Dome glaciochemical series that represent continental sources (for example, calcium) have a pattern similar to the Dome B dust record (5); however, Taylor Dome glaciochemical series derived from marine sources (for example, chloride) provide a significantly different signature from that in the stable isotope and dust series.

The high-resolution chemical records from Taylor Dome and the Greenland Ice Sheet Project Two (GISP2, Fig. 1) provide a basis for interhemispheric comparison. GISP2 ice core chronology is based on annual layer counting (8, 9). Both the GISP2 stable isotope record (10) and the GISP2 chemical series display classic North Atlantic climate sequences, including Oldest Dryas, Bølling, Older Dryas, Allerød, Intra-Allerød cold period (IACP), and the YD (Fig. 2).

The GISP2 calcium series differs markedly from that of the Taylor Dome ice core (Fig. 2). Higher concentrations of calcium

in the GISP2 record document the greater influence of continental sources in the Northern Hemisphere. Although both series drop to near-Holocene values at ~14,600 years ago, the Taylor Dome calcium series is marked by a gradual decline in concentration from ~15,600 to 14,600 years ago (Fig. 2). GISP2 calcium concentrations, on the other hand, display a prominent drop at ~14,600 years ago (Fig. 2). The maintenance of near-glacial atmospheric circulation patterns and consequent high amounts of calcium transported to GISP2 resulted because North Atlantic Ocean ice cover was sustained through the early stages of Northern Hemisphere ice sheet decay (11). Because the primary sources for late glacial Antarctic ice core dust are African, Australian, and South American arid regions (12), the stronger meridional and zonal circulation that carried these dusts to Antarctica during the late glacial period (13) apparently gradually

ceased by ~14,600 years ago.

The chloride and calcium series from GISP2 are closely parallel (Fig. 2). The similar behavior of these two dissimilar source species is a product of their incorporation and long-range transport to Greenland in large-scale atmospheric circulation systems such as the westerlies (14, 15). Both seasalt and dust are incorporated into this circulation in regions of strong cyclogenesis that form along marine and atmospheric thermal gradients. In the Southern Hemisphere, fluctuations in the size of polar atmospheric circulation have been documented by examination of recent trends in the Antarctic snow accumulation rate (16) and in Tasmanian tree ring records (17). As of yet, associations between the histories of northern and southern polar atmospheric circulation systems have not been investigated.

Unlike the comparison between the GISP2 and Taylor Dome calcium series, the chloride series do display notable similari-

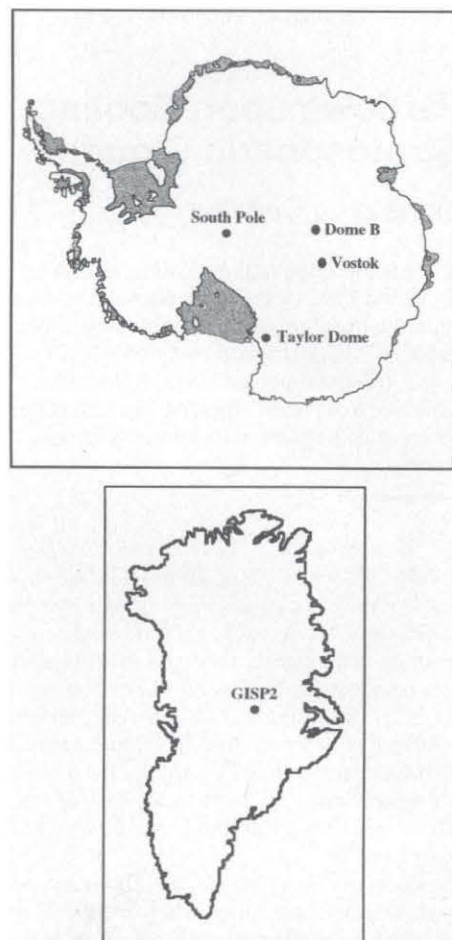


Fig. 1. Location maps for Taylor Dome in Antarctica and GISP2 in Greenland.

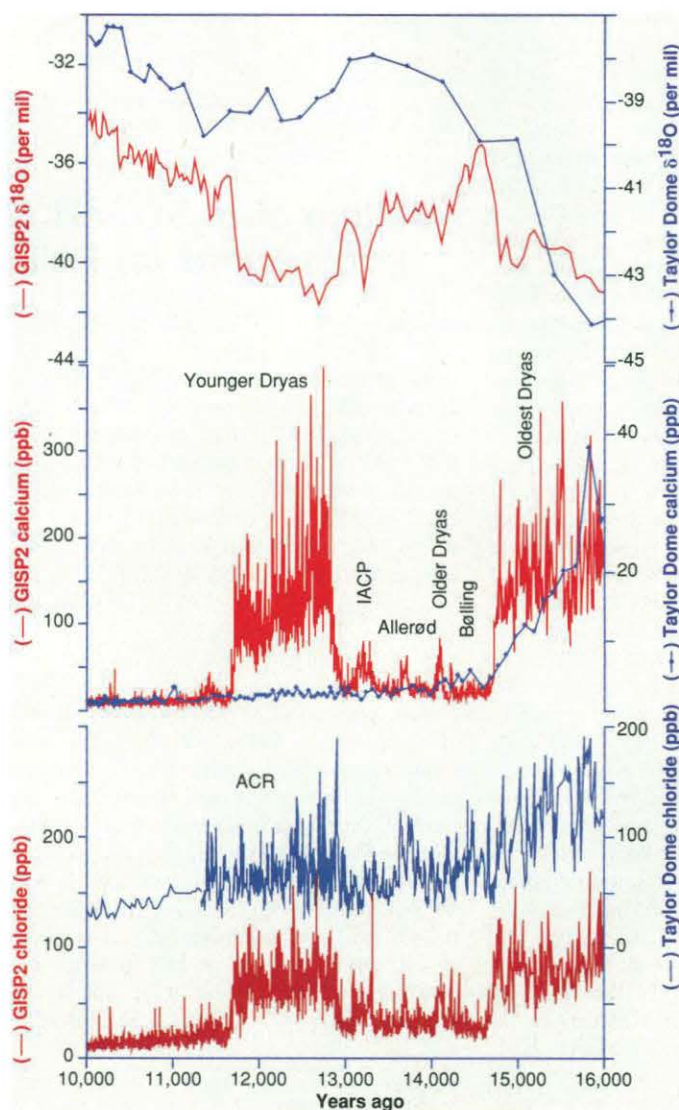


Fig. 2. The  $\delta^{18}\text{O}$  (per mil), calcium [parts per billion (ppb)], and chloride (ppb) series covering the period 10,000 to 16,000 years ago from Taylor Dome and GISP2. The sample interval for GISP2 (red)  $\delta^{18}\text{O}$  is 20 cm, and for GISP2 calcium, 3.5 years. The sample interval for Taylor Dome (blue; dots mark the mid-point of samples)  $\delta^{18}\text{O}$  is 1 m and for calcium, 45 years. The sample intervals for GISP2 chloride (red) versus Taylor Dome (blue) are as follows: for 10,000 to 11,328 years ago, 2.1 versus 228 years per sample; for 11,328 to 13,000 years ago, 3.2 versus 4.5 years per sample; and for 13,000 to 16,000 years ago, 5.1 versus 8.7 years per sample. The classic North Atlantic climate sequence is as follows: Oldest Dryas, Bølling, Older Dryas, Allerød, intra-Allerød cold period (IACP), and Younger Dryas (YD) (21). Age of the YD is with respect to the GISP2 ice core (10).

ties (Fig. 2). To investigate these in greater detail, we resampled a portion of the Taylor Dome record at higher resolution for chloride and compared it with the GISP2 chloride series. Their variability is equivalent (within a factor of 2), and both display similar style abrupt change events. The onset of the YD in the GISP2 record occurs in less than 20 years (8, 18), and although not as well dated, the onset of the ACR in the Taylor Dome record also appears to be rapid (Fig. 2). Mean chloride concentration during the YD in Greenland is 75% of the maximum late glacial value, whereas the ACR at Taylor Dome (Fig. 2) is 54% of the last glacial maximum value, consistent with results from Dome B (5). Although it is tempting to correlate specific, decade-to-century-scale, rapid change events, the control of dating on the Taylor Dome is not equivalent to that of the GISP2 series.

From <10,000 to 14,600 years ago, Southern Hemisphere polar atmospheric circulation was not extensive enough to incorporate significant amounts of dust from ice-free continents of the Southern Hemisphere despite arid conditions during at least portions of the YD-ACR periods in regions such as Africa (19). However, atmospheric circulation was vigorous enough to increase the transport of sea salt to Antarctica. Fluctuations in the size of this atmospheric circulation system are recorded in the Taylor Dome chloride series. This series displays variability and a general sequence of events (a YD equivalent or an ACR plus several other rapid change events) that are very similar to events characterizing the deglaciation record in Greenland ice cores. The diversity of events displayed in the Taylor Dome chloride series may not have been observed in previous Antarctic stable isotope or dust series because of the resolution of these records or because these events were largely restricted to change over the Antarctic Ocean. Because modern sea-salt concentrations decline markedly with distance inland from the coast, sites such as Taylor Dome would be expected to contain a more complete record of fluctuations in sea salt. Glaciochemical series provide a measure of atmospheric circulation (14, 15) and not of regional surface temperature, as do stable isotopes (20). Thus, glaciochemical series provide a compatible view of climate change, recording migrations of atmospheric circulation over continents and oceans.

We conclude, on the basis of our comparison of Taylor Dome and GISP2 ice core records, that similar-scale fluctuations of atmospheric circulation occurred over both northern and southern polar marine areas during at least the deglaciation. Fluctua-

tions in temperature over Antarctica and Greenland may not have been as similar, perhaps because of the dramatically different degree of change in ice cover over these two regions. The origin and detailed phasing of the events compared in this study are still unknown, leaving open the question of a forcing mechanism. However, we now have a demonstration that events similar in variability to those seen in Greenland ice cores do exist in Antarctic ice core records.

#### REFERENCES AND NOTES

1. F. Gasse et al., *Quat. Res.* **32**, 229 (1989); J. T. Overpeck et al., *Nature* **338**, 553 (1989).
2. G. H. Denton and C. H. Henty, *Science* **264**, 1434 (1994).
3. J. T. Heine, *Quat. Sci. Rev.* **12**, 769 (1993).
4. J. Jouzel et al., in *The Last Deglaciation: Absolute and Radiocarbon Chronologies* vol. 2 of NATO ASI Series I, E. Bard and W. S. Broecker, Eds. (Springer-Verlag, Berlin, Heidelberg, 1992), pp. 230-266.
5. J. Jouzel et al., *Clim. Dyn.* **11**, 151 (1995).
6. P. M. Grootes et al., *Eos* **75**, (no. 44), 225 (1994); P. M. Grootes, E. J. Steig, M. Stuiver, E. D. Waddington, D. L. Morse, in preparation.
7. E. D. Waddington, D. L. Morse, P. M. Grootes, E. J. Steig, in *Ice in the Climate System* vol. 12 of NATO ASI Series I, W. R. Peltier, Ed. (Springer-Verlag, Berlin, Heidelberg, 1993), pp. 499-516; B. Malaize et al., *Eos* **75** (no. 44), 226 (1994); E. J. Steig et al., in preparation.
8. R. B. Alley et al., *Nature* **362**, 527 (1993).
9. D. A. Meese et al., *Preliminary Depth-Age Scale of*

*the GISP2 Ice Core* (Cold Regions Research and Engineering Laboratory Technical Report number 94-01, Hanover, NH, 1994).

10. M. Stuiver, P. M. Grootes, T. F. Braziunas, *Quat. Res.* **44**, 341 (1995).
11. A. Ruddiman and A. McIntyre, *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **35**, 145 (1981); E. Bard et al., *Quat. Res.* **31**, 309 (1989); L. D. Keigwin, G. A. Jones, S. J. Lehman, *J. Geophys. Res.* **96**, 16811 (1991).
12. M. DeAngelis, N. I. Barkov, V. N. Petrov, *J. Atmos. Chem.* **14**, 233 (1992).
13. J. R. Petit, M. Briat, A. Royer, *Nature* **293**, 391 (1981).
14. P. A. Mayewski et al., *Science* **261**, 195 (1993).
15. P. A. Mayewski et al., *ibid.* **263**, 1747 (1994).
16. H. Enomoto, *Clim. Change* **18**, 67 (1991).
17. E. Cook et al., *Science* **253**, 1266 (1991).
18. K. C. Taylor et al., *Nature* **361**, 432 (1992).
19. F. Gasse, *ibid.* **265**, 42 (1977); J. C. Stager, *Quat. Res.* **29**, 54 (1988).
20. C. Lorius and L. Merlivat, *IAHS Publication no. 118*, 125 (1977).
21. T. Nilsson, *The Pleistocene Geology and Life in the Quaternary Ice Age* (D. Reidel, Dordrecht, Netherlands, 1983).
22. We thank the NSF for financial support of the GISP2 and Taylor Dome ice core projects. We also thank the drillers from the Polar Ice Coring Office University of Alaska, notably D. Giles and M. Wumkes; the Antarctic Support Associates personnel for camp support and logistics; Squadron VXE6 and the New York Air National Guard (TAG 109) for air support; the GISP2 Science Management Office (University of New Hampshire); and field party members for their able assistance.

5 October 1995; accepted 4 April 1996

## Melting of $\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$ Particles upon Cooling: Implications for Polar Stratospheric Clouds

Thomas Koop and Kenneth S. Carslaw

Polar stratospheric clouds (PSCs) are important for the chemical activation of chlorine compounds and subsequent ozone depletion. Solid PSCs can form on sulfuric acid tetrahydrate (SAT) ( $\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$ ) nuclei, but recent laboratory experiments have shown that PSC nucleation on SAT is strongly hindered. A PSC formation mechanism is proposed in which SAT particles melt upon cooling in the presence of  $\text{HNO}_3$  to form liquid  $\text{HNO}_3 \cdot \text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$  droplets 2 to 3 kelvin above the ice frost point. This mechanism offers a PSC formation temperature that is defined by the ambient conditions and sets a temperature limit below which PSCs should form.

Nitric acid-containing polar stratospheric clouds (type 1 PSCs) are typically observed at temperatures below 196 K (1). Their formation leads to a considerable increase in aerosol surface area and therefore in the rates of important heterogeneous reactions. Despite their importance, the composition and formation mechanisms of type 1 PSCs are not completely understood (2). It is now recognized that background liquid aerosols absorb large amounts of  $\text{HNO}_3$  with decreasing temperature and grow into liquid  $\text{HNO}_3 \cdot \text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$  PSCs (3-5). Alterna-

tively, all, or at least a fraction, of the background nuclei for PSC growth can be solid, most likely SAT. Sulfuric acid tetrahydrate is frequently observed in laboratory experiments (3, 6-8), and the existence of  $\text{H}_2\text{SO}_4$ -containing solids in the stratosphere has been inferred from observations (9). Once formed, SAT particles can persist to temperatures as high as 210 to 215 K, above which they melt to form  $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$  droplets (6).

Because SAT particles are stable over a wide temperature range, they are likely to persist for long periods. Therefore, it is essential to understand how PSCs form when they act as the condensation nuclei. The

Max Planck Institute for Chemistry, Postfach 3060, 55020 Mainz, Germany.