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

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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. Fluctuations 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.

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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 VXE8 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.

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Melting of H2SO4·4H2O Particles upon Cooling: Implications for Polar Stratospheric Clouds

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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) (H2SO4·4H2O) 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 HNO3 to form liquid HNO3·H2SO4·H2O 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.

Nitrile–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 HNO3 with decreasing temperature and grow into liquid HNO3·H2SO4·H2O PSCs (3–5). Alternatively, 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 H2SO4-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 H2SO4·H2O 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

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PSC formation mechanism in included in most models involves nucleation of nitric acid trihydrate (NAT) (HNO$_3$·3H$_2$O) on SAT (1). However, recent laboratory experiments (8) and calculations (10) under stratospheric conditions have suggested that the nucleation of NAT on SAT is very strongly inhibited, requiring supercooling by up to 8 K (8). This constraint would imply that once SAT particles have formed, the frequency with which type 1 PSCs occur would be reduced significantly (8), thus affecting polar ozone depletion. However, with a thermodynamic model, it can be shown that SAT particles become unstable and transform into much larger ternary liquid HNO$_3$·H$_2$SO$_4$·H$_2$O droplets upon cooling, thus providing a pathway for type 1 PSC formation at a defined temperature.

The conditions under which H$_2$SO$_4$ solid phases form and persist can be determined by examining the composition of stratospheric H$_2$SO$_4$·H$_2$O droplets and the melting points of the different solid phases (11) (Fig. 1A). For temperatures lower than the melting point, liquid aerosols are supersaturated (supercooled) with respect to the solid. A useful measure of the supersaturation is the saturation ratio S (12) (Fig. 1B). Solid particles are stable with respect to liquids when S > 1 but are unstable when S < 1. For example, a stratospheric sulfuric acid monohydrate (SAM) (H$_2$SO$_4$·H$_2$O) particle is stable in air (with a water partial pressure of 2.5 x 10$^{-4}$ mbar) between about 266 and 216 K (Fig. 1), and SAT is stable between 213 and 188 K. Laboratory experiments have shown that SAT can transform into liquid H$_2$SO$_4$·H$_2$O (with composition at point a in Fig. 1) by warming above about 210 to 215 K (6), and SAT can melt or deliquesce upon cooling below about 220 K (13) (point b) (deliquescence is a solid-to-liquid transformation involving the vapor of the gas phase). Cooling of SAT below about 188 K (point c) would lead to ice formation instead of deliquescence because SAT becomes unstable only below the ice frost point (point d) under stratospheric conditions.

However, liquid stratospheric aerosols absorb considerable amounts of HNO$_3$ at low temperatures (3–5), which can completely change the behavior of SAT particles upon cooling. The saturation ratio with respect to SAT in ternary liquid HNO$_3$·H$_2$SO$_4$·H$_2$O droplets under typical stratospheric conditions was calculated as a function of temperature (Fig. 2A). The presence of HNO$_3$ in the droplets (Fig. 2B) significantly reduces SAT stability. In air containing H$_2$O and HNO$_3$, SAT is stable with respect to the ternary liquid for temperatures higher than point 1 (and therefore remains "dry") but is unstable at lower temperatures. At point 1, SAT can coexist in equilibrium with a ternary liquid (S = 1), so cooling of an initially dry SAT particle to point 1 leads to deliquescence (14). At the initial point of deliquescence (point 1), all of the HNO$_3$ is in the gas phase, so the liquid film that begins to form on SAT has the composition of a pure liquid droplet in equilibrium with a gas phase depleted in HNO$_3$ (in this case, 47 weight % HNO$_3$ and 3 weight % H$_2$SO$_4$) (Fig. 2B). Upon further cooling, SAT continues to dissolve (thick solid line) in pure HNO$_3$ and H$_2$O is partitioned from the gas phase into the liquid. The SAT completely dissolves at point 2, and with further cooling, the composition of the pure liquid droplets continues to follow the thick dashed line (Fig. 2B).

Deliquescence simply arises as a result of the thermodynamic instability of SAT with respect to the ternary solution. One proposed type 1 PSC formation mechanism involves nucleation of a binary HNO$_3$·H$_2$O solution on SAT (5, 10) followed by heterogeneous NAT nucleation. Although amorphous HNO$_3$·H$_2$O phases have been observed to nucleate on glass or silicon surfaces in laboratory studies (15), SAT is not an inert substrate and cannot coexist at thermodynamic equilibrium with a binary liquid HNO$_3$·H$_2$O layer. This restriction excludes the nucleation of a liquid because at the moment of formation a critical embryo is required to be in equilibrium with the supporting nucleus.

Without HNO$_3$ in the gas phase, SAT becomes unstable only below the ice frost point (point d in Figs. 1 and 2). The change in water partial pressure associated with ice growth (even on a fraction of the particles) prevents the remaining SAT particles from deliquescing. The transformation of SAT to a liquid at these low temperatures is therefore only possible in the presence of HNO$_3$. Although SAT is usually the stable H$_2$SO$_4$ solid phase in the stratosphere, sulfuric acid hemihydrate (SAH) (H$_2$SO$_4$·0.5H$_2$O)
might also form. However, SAH would also deliquece upon cooling at approximately the same temperature as SAT.

An important constraint is that deliquescence must occur before the nucleation of any HNO₃ solid phases. For example, at the deliquescence point, SAT is supercooled to about 4 K below its equilibrium temperature, equivalent to a saturation ratio of 20 to 25. However, laboratory experiments have demonstrated SAT deliquescence occurring rather than NAT nucleation: Iraci et al. (8) showed that SAT films cooled in the presence of HNO₃ and H₂O vapor developed a noncrystalline layer containing HNO₃ and H₂O (H₂SO₄ was not detected in the layer at their experimental sensitivity). The noncrystalline films could be held under these conditions for several hours without NAT nucleation, even with NAT saturation ratios as high as 127. We believe that these observations are attributable to the slow transformation of SAT into a ternary HNO₃·H₂SO₄·H₂O liquid (16). In 7 experiments (from a total of 12), the experimental observations agree with our prediction of deliquescence (either a noncrystalline film was observed below the deliquescence temperature T_d or no film was observed above T_d), and in the remaining 5 experiments, the measured temperature differed from T_d by only 0.3 to 1.3 K, which is within the combined ± 1.5 K uncertainty in their experimental conditions and our model calculations. In earlier experiments, Hanson (17) studied the uptake of HNO₃ onto SAT and found that enough HNO₃ was adsorbed by the surface at 191.5 K to form the equivalent of about 30 monolayers of HNO₃. The HNO₃ vapor pressure over this growing layer was 10 to 20 times as great as that over NAT, suggesting the growth of a metastable HNO₃ phase (17). However, we have calculated that SAT deliquescence would have started below 192.5 K, indicating that this observation was probably the result of formation of a ternary solution on the SAT. The calculated HNO₃ vapor pressure of the resulting ternary solution in equilibrium with SAT is approximately half of that observed experimentally, which again is well within the experimental uncertainties (18).

These laboratory observations under stratospheric conditions support our theoretical prediction of SAT deliquescence upon cooling. They also suggest that SAT deliquescence is the preferred phase transition, rather than nitric acid hydrate nucleation from the gas phase, even at high saturation ratios. Therefore, care must be taken in the interpretation of experiments designed to investigate nitric acid hydrate nucleation on SAT or SAH from the gas phase; at temperatures lower than the deliquescence point, nucleation in the ternary liquid is likely to be the controlling mechanism. To assist in the interpretation of laboratory experiments and theoretical calculations, we have calculated the SAT deliquescence temperature and the corresponding NAT saturation ratio as a function of HNO₃ and H₂O partial pressures (Fig. 3).

At present, the best indicator of SAT deliquescence in the stratosphere is probably the change in aerosol size with changes in temperature. Deliquescence leads to significant uptake of HNO₃ and H₂O from the gas phase and a consequent steep increase in aerosol volume (Fig. 4). This change in volume of up to a factor of 10 within a temperature interval of only 1 K should be observable in existing and future field measurements.

As a further possibility, we note that rather than the droplets remaining liquid, their growth after deliquescence could initiate nitric acid hydrate nucleation. Although nitric acid hydrate formation in droplets with equilibrium compositions seems unlikely (7), rapid growth of the deliquescing SAT particles to form large HNO₃·H₂SO₄·H₂O droplets would lead to strong departures from equilibrium (19). In particular, the composition of the smallest particles could approach pure HNO₃·H₂O and cause them to freeze as a nitric acid hydrate (19). In contrast to the Meilinger et al. (19) study, rapid temperature fluctuations would not be needed in our mechanism to induce a strong departure from equilibrium; instead, temperatures would simply have to fall below the deliquescence point. Further laboratory experiments and time-dependent droplet growth calculations are required to answer this question.

Deliquescence of SAT is important not only because it occurs before nitric acid hydrate nucleation but also because it occurs at a well-defined temperature for given abundances of HNO₃ and H₂O (Fig. 3). Moreover, deliquescence sets a temperature limit below which the formation of type 1 PSCs must occur, independent of whether the initial particles are liquid or frozen as known H₂SO₄ hydrates. Even if the background aerosol consists of a mixed population of liquid and solid H₂SO₄ particles, PSC growth must occur at a temperature between the dashed line and the heavy solid line in Fig. 4.

Accurate predictions of PSC formation in the Arctic, where temperatures are often marginal for PSC formation, are a major challenge. One of the greatest obstacles is the uncertainty in the formation temperature of type 1 PSCs in atmospheric models, which is usually assumed to be anywhere between 0 and 4 K below the NAT condensation temperature. Calculations (4, 5) have shown that when the initial background aerosols are liquid, they grow at a well-defined temperature without nucleation. We have shown that when the background aerosols are frozen as known H₂SO₄ hydrates, deliquescence upon cooling also leads to type 1 PSC formation at a defined temperature. This improves considerably our ability to predict the development of PSCs and subsequent ozone depletion.
Compensatory ahpC Gene Expression in Isoniazid-Resistant Mycobacterium tuberculosis

David R. Sherman, Khisimuzi Mdulu, Mark J. Hickey, Taraq M. Arain, Sheldon L. Morris, Clifton E. Barry III,* C. Kendall Stover*†

Mutations that eliminate KatG catalase-peroxidase activity prevent activation of isoniazid and are a major mechanism of resistance to this principal drug for the treatment of Mycobacterium tuberculosis infections. However, the loss of KatG activity in clinical isolates seemed paradoxical because KatG is considered an important factor for the survival of the organism. Expression of either KatG or the recently identified alkyl hydroperoxide AhpC was sufficient to protect bacilli against the toxic effects of organic peroxides. To survive during infection, isoniazid-resistant KatG mutants have apparently compensated for the loss of KatG catalase–peroxidase activity by a second mutation, resulting in hyperexpression of AhpC.

As an intracellular pathogen residing within macrophages, Mycobacterium tuberculosis (MTB) is well equipped to resist toxic oxygen species. However, a principal drug used to treat tuberculosis, isoniazid (isonicotinic acid hydrazide, or INH) interacts with components of the mycobacterial defense against oxidative stress in complex ways. INH is a produg that requires activation to an unstable electrophilic species by the catalase-peroxidase KatG, with hydrogen peroxide (H₂O₂) acting as an electron sink for the reaction (1–3). Once activated, INH inhibits the biosynthesis of cell wall mycolic acids (4), ultimately compromising the inert and largely impermeable barrier that protects mycobacteria against reactive oxygen species and other environmental insults (5). KatG is the only MTB enzyme capable of activating this drug. As a result, KatG-mutant MTB strains are INH resistant.

Tuberculosis bacteria appear to rely on the constitutive defense afforded by their cyclopropenated cell wall mycolic acids, having virtually eliminated an inducible oxidative stress response from their genetic repertoire (6). In other bacteria, a peroxide-inducible genetic response mediated by the transcription factor OxyR is the primary defense against oxidative stress (7, 8). However, the recently identified oxyR gene of MTB is vestigial, containing numerous frameshifts and deletions (6, 9). Without OxyR, the only MTB protein whose expression is peroxide-inducible is KatG, and this induction is insufficient to protect against H₂O₂ challenge (6). It therefore seems paradoxical that loss of KatG function is the major means by which the tubercle bacilli acquire resistance to isoniazid (10, 11). It is unclear how these bacteria adapt to loss of KatG, their only catalase-peroxidase and their only peroxide-responsive gene product, when this activity is considered an important component of intracellular survival (12).

To evaluate the interaction of INH and H₂O₂ in MTB-complex bacilli, we simultaneously administered subinhibitory concentrations of both H₂O₂ and isoniazid to Mycobacterium bovis BCG (an avirulent member of the TB complex). As in Gram-negative bacteria and the soil saprophyte Mycobacterium smegmatis (13), synergy was readily apparent. A reduction in cell viability by a factor of 100 was noted after 72 hours exposure to concentrations of H₂O₂ and INH that separately had no effect in this assay (Fig. 1). When subinhibitory concentrations of both agents were supplied to a katG-deleted BCG strain, no synergy was observed (14). The observed synergy is consistent

![Fig. 1. Synergistic interaction of H₂O₂ and isoniazid.](image-url)

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