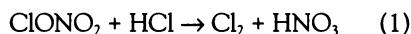


# Sulfate Aerosols and Polar Stratospheric Cloud Formation

Margaret A. Tolbert

Before the discovery of the Antarctic ozone hole, it was generally assumed that gas-phase chemical reactions controlled the abundance of stratospheric ozone. However, the massive springtime ozone losses over Antarctica first reported by Farman *et al.* (1) in 1985 could not be explained on the basis of gas-phase chemistry alone. In 1986, Solomon *et al.* (2) suggested that chemical reactions occurring on the surfaces of polar stratospheric clouds (PSCs) (Fig. 1) could be important for the observed ozone losses. Since that time, an explosion of laboratory, field, and theoretical research in heterogeneous atmospheric chemistry has occurred.

Recent work has indicated that the most important heterogeneous reaction on PSCs is



This reaction converts inert chlorine ( $\text{ClONO}_2$ ,  $\text{HCl}$ ) into photochemically active  $\text{Cl}_2$ . Photolysis of  $\text{Cl}_2$  then leads to chlorine radicals capable of destroying ozone through very efficient catalytic chain reactions. New observations during the second Airborne Arctic Stratospheric Expedition (AASE II) (3) found stoichiometric loss of  $\text{ClONO}_2$  and  $\text{HCl}$  in air processed by PSCs in accordance with reaction 1. As we begin to have an appreciation for the potential role of heterogeneous reactions in the stratosphere, attention is turning toward understanding what kinds of aerosols form in the stratosphere, their formation mechanism, surface area, and specific chemical reactivity. Some of the latest findings, which underline the importance of aerosols, were presented at a recent National Aeronautics and Space Administration (NASA) workshop in Boulder, Colorado (4).

Stratospheric aerosols fall into two main categories: PSCs and stratospheric sulfate aerosols (SSAs). Because PSCs form only at temperatures below 195 K, they are found predominantly in the polar winters. They are subclassified as type I or type II, depending on their formation temperature. Type II PSCs are composed of crystalline water ice and form only when stratospheric

temperatures drop below 188 K, a condition normally met only in the Antarctic winter. Type I PSCs form at temperatures several degrees warmer than the ice frost point and are therefore much more abundant than type II PSCs. Although the exact composition and phase of type I PSCs have not been established, theory, field, and laboratory work has shown that they are composed of mixtures of  $\text{HNO}_3$  and



**Fig. 1.** Photograph of polar stratospheric clouds over McMurdo Station, Antarctica. [Courtesy of D. Hofmann, NOAA Climate Monitoring and Diagnostics Laboratory, Boulder, Colorado]

$\text{H}_2\text{O}$ . These highly acidic  $\text{HNO}_3$ - $\text{H}_2\text{O}$  clouds form in both polar winters, and thus, chemistry on their surfaces could lead to ozone loss in the Arctic as well as Antarctic stratosphere. The exact composition of these clouds is important in determining the ultimate surface area available for heterogeneous chemistry. Thus, a full understanding of the chemical impact of type I PSCs in the Arctic requires identification of the cloud composition, phase, and formation mechanism.

Theoretical work in 1986 first predicted that nitric acid trihydrate (NAT) was the likely composition of type I PSCs (5). Subsequent field observations indicated that  $\text{HNO}_3$  was indeed a key component in type I PSCs (6). The first laboratory studies of these clouds found that under stratospheric conditions, NAT should condense at 5 to 7 K warmer temperatures than ice and thus predicted that type I PSCs were composed of NAT (7). However, field observations in the Arctic (8) have found that type I PSCs often do not form until temperatures drop substantially below the NAT threshold temperature. It has recently been suggested that metastable nitric acid dihydrate

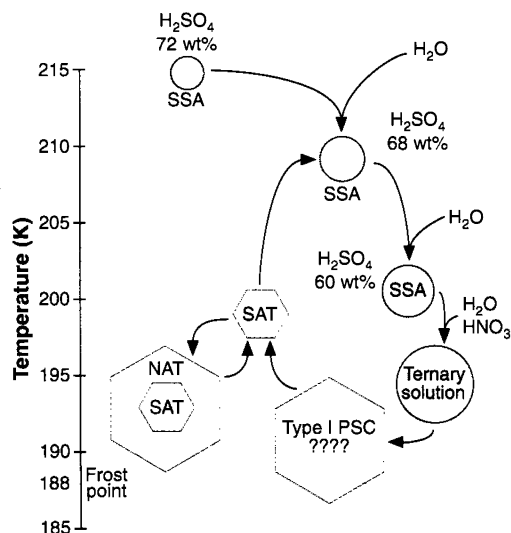
(NAD) may form in the stratosphere because of a nucleation barrier for NAT (9). Other current laboratory work suggests a role for a higher nitric acid hydrate such as the pentahydrate (10).

Most of the uncertainty in the chemical composition of type I PSCs results from a lack of understanding of the nucleation mechanism for these clouds. It is thought that PSCs nucleate and subsequently grow on preexisting SSAs. These globally distributed aerosols are composed of liquid sulfuric acid and water. "Background" levels of sulfuric acid are thought to arise from the oxidation of carbonyl sulfide transported from the troposphere (11). The background aerosols are augmented by volcanic eruptions that inject  $\text{SO}_2$  directly into the stratosphere. This  $\text{SO}_2$  is rapidly oxidized to sulfuric acid and then forms aerosols through homogeneous or heterogeneous nucleation. Over the past two decades, multiple volcanic injections of sulfur into the stratosphere have likely been the dominant source of SSAs, preventing true background levels from ever being achieved.

The increase in aerosol loading attributable to massive volcanic eruptions can be quite substantial. For example, the eruptions of El Chichón (1982) and Mount Pinatubo (1991) caused increases in the abundance of stratospheric sulfuric acid by factors of 30 to 50. Similar to the chemistry that occurs on PSCs, heterogeneous reactions can also take place on and in the liquid sulfuric acid droplets. Heterogeneous chemistry on volcanically enhanced SSAs may in fact be responsible for the low ozone levels observed after these volcanic eruptions, including the record low ozone observed for 1992–1993 (12).

In addition to promoting heterogeneous chemistry, SSAs are thought to serve as the substrates on which PSCs nucleate. However, the exact nucleation mechanism is a topic of considerable debate. At the Boulder workshop, several mechanisms were discussed for type I PSC nucleation. One possible scenario combines several ideas for PSC nucleation (Fig. 2). Under typical mid-latitude stratospheric conditions, the only particles present are the small supercooled sulfate aerosols. Steele and Hamill (13) determined that the acid concentration of these aerosols should be 60 to 80%  $\text{H}_2\text{SO}_4$  by weight for temperatures between 205 and 240 K. As the temperature is lowered, the sulfuric acid aerosols absorb water to maintain equilibrium with the ambient gas and thus become more dilute.

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**Fig. 2.** Life cycle of a polar stratospheric cloud. In one scenario, falling temperatures cause sulfate aerosols to take up water and nitric acid to form droplets of a ternary solution of  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ , and  $\text{H}_2\text{O}$ . Nitric acid trihydrate might then nucleate out of solution, forming a type I PSC. As the temperature rises, the PSC evaporates, leaving behind a frozen SAT aerosol. This frozen aerosol may then serve as an effective nuclei for further PSC condensation at low temperature or may melt to reform a liquid aerosol if the temperature rises above 210 K.

The main controversy centers on what happens next. As the temperature continues to drop, it had generally been believed that the supercooled sulfuric acid aerosols would eventually freeze as sulfuric acid tetrahydrate (SAT). However, laboratory and theoretical studies have shown that sulfuric acid droplets supercool quite readily, and that the freezing point for these aerosols is difficult to predict because of the stochastic nature of freezing. Once frozen, the aerosols were thought to serve as good nuclei for the formation of PSCs. In 1991, Dye and co-workers (8) used this theory to explain why PSCs were often not observed in the Arctic until well below the NAT threshold temperature. They proposed that under slow cooling conditions, only a fraction of the sulfate aerosols would freeze by 192 K. Although this fraction could then serve as effective NAT nuclei, the remaining liquid aerosols would not develop into PSCs. Our group has shown that the SAT aerosols, once frozen, are likely to remain frozen until a temperature of at least 210 K (14). Thus, after the PSCs evaporate, it is thought that a frozen sulfate seed will be available for further nucleation of PSCs.

An alternative theory for PSC nucleation was proposed recently by Molina and co-workers (15). Through laboratory experiments at low temperatures, these authors showed that dilute sulfuric acid will take up significant amounts of  $\text{HNO}_3$ , and they proposed that the SSAs could be ternary solutions of  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ , and  $\text{H}_2\text{O}$  with

up to 10%  $\text{HNO}_3$  by weight under polar conditions. The Molina group found evidence that the increased  $\text{HNO}_3$  in solution caused NAT to crystallize out of the ternary mixture. They proposed that compositional changes in the droplet resulting from NAT crystallization would cause the entire droplet to freeze. The NAT would then grow by additional condensation of  $\text{HNO}_3$  and  $\text{H}_2\text{O}$  onto the seed crystal.

A third theory for PSC formation was presented at the Boulder workshop by T. Peter (Max-Planck-Institut für Chemie). He and his co-workers have proposed that it may not be necessary for the sulfuric acid aerosols to freeze at all for PSC nucleation. In their model, the supercooled sulfuric acid droplets remain liquid as they cool and continue to absorb  $\text{HNO}_3$  and  $\text{H}_2\text{O}$ . As the temperature drops to 190 K, the droplets contain 40%  $\text{HNO}_3$  by weight, and have sequestered much of the atmospheric  $\text{HNO}_3$ . These authors propose that the droplets will remain liquid until the ice frost point is reached. In this model, the type I PSCs at 190 K are thus a supercooled solution of 4%  $\text{H}_2\text{SO}_4$ , 40%  $\text{HNO}_3$ , and 56%  $\text{H}_2\text{O}$ .

Future laboratory and field experiments may yield insight into which, if any, of the above mechanisms for PSC formation dominate in the stratosphere. Researchers are currently performing laboratory experiments with actual aerosol samples to measure parameters such as the freezing nucleation rate for sulfuric acid, the uptake of  $\text{HNO}_3$  by liquid sulfuric acid, and the growth of nitric acid hydrates on liquid and frozen sulfuric acid. The final answer about

the PSC composition and nucleation may, however, have to await field observations. There are several projects in progress to aid in the identification of actual stratospheric aerosols. Infrared extinction data from satellites and aircraft are already being used to identify the average properties of collections of particles. In situ methods are also under development for the characterization of single aerosol particles. As we learn more about the chemical composition of the stratospheric clouds, we may be able to improve our predictions of when and where they might form. This, in turn, will help us understand when heterogeneous chemistry will be important in controlling the abundance of stratospheric ozone.

## References and Notes

1. J. C. Farman *et al.*, *Nature* **315**, 207 (1985).
2. S. Solomon *et al.*, *ibid.* **321**, 755 (1986).
3. C. R. Webster *et al.*, *Science* **261**, 1130 (1993). This issue of *Science* presented results from AASE II (pp. 1130–1158).
4. Heterogeneous Chemistry Workshop, A. R. Ravishankara, chair, Boulder, CO, 8 to 10 November 1993.
5. O. B. Toon *et al.*, *Geophys. Res. Lett.* **13**, 1284 (1986); P. J. Crutzen and F. Arnold, *Nature* **324**, 651 (1986).
6. D. W. Fahey *et al.*, *J. Geophys. Res.* **94**, 11299 (1989).
7. D. Hanson and K. Mauersberger, *Geophys. Res. Lett.* **15**, 855 (1988).
8. J. E. Dye *et al.*, *J. Geophys. Res.* **97**, 8015 (1992).
9. D. R. Worsnop *et al.*, *Science* **259**, 71 (1993).
10. J. Marti and K. Mauersberger, *Geophys. Res. Lett.* **20**, 359 (1993).
11. P. J. Crutzen, *ibid.* **3**, 73 (1976).
12. J. F. Gleason *et al.*, *Science* **260**, 523 (1993); D. J. Hofmann *et al.*, *Geophys. Res. Lett.* **21**, 65 (1994); J. M. Rodriguez *et al.*, *ibid.*, p. 209; D. R. Hanson *et al.*, *J. Geophys. Res.* **99**, 3615 (1994).
13. H. M. Steele and P. Hamill, *J. Aerosol Sci.* **12**, 517 (1981).
14. A. M. Middlebrook *et al.*, *J. Geophys. Res.* **98**, 20473 (1993).
15. M. J. Molina *et al.*, *Science* **261**, 1418 (1993).

# The Prion Connection: Now in Yeast?

Charles Weissmann

Phenomena discovered in higher eukaryotes acquire additional respectability if they are also found in yeast. This is now true for the prion, the agent responsible for a group of transmissible diseases of the central nervous system—Creutzfeldt-Jakob disease in humans, scrapie in sheep, and “mad cow” disease. The propagation of prions has been attributed to a conformational rearrangement of a normal host protein into a pathological form, a rearrangement that is catalyzed by the pathological form itself (see accompanying Perspective). In a report in

this issue of *Science*, R. Wickner suggests that the pathogenesis of an obscure mutational phenotype in yeast is based on the same principle.

Prion diseases are unusual because they can arise spontaneously in the population at large without any apparent cause—so-called sporadic forms—or they can be familial and tightly linked to certain mutations of the *Prn<sup>p</sup>* (prion protein) gene; in either case, the disease can usually be transmitted by inoculation. The peculiar properties of the transmissible agent, the prion, has given rise to speculations that it might be devoid of nucleic acid and consist of protein only (1, 2). Currently, the most

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