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Lee-wave clouds and denitrification of the polar stratosphere

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[1] We present a hypothesis that the known formation of nitric acid hydrates in lee-wave ice clouds produces a "standing crop" of nitric acid trihydrate (NAT) particles, and that growth and sedimentation of these particles efficiently denitrifies the polar stratosphere. Simulations using a simple two-dimensional model illustrate that the large NAT number concentrations produced in lee waves (>0.1 cm^{-3}) lead to low gas-phase HNO_3 concentration in the cloud layer, limiting subsequent particle growth. Provided the NAT existence temperature is not exceeded, these particles slowly sediment out of the cloud layer, at which point further growth is initiated. As a result of the long residence time and vertical wind shear, NAT particles produced in geographically selective regions over a short duration can cause extensive denitrification throughout the lower stratosphere. Our model illustrates that a single hypothetical lee-wave nucleation event [10 hours, 1000 km width (along a longitude) × 100 m altitude] is sufficient to produce significant denitrification (~25%) vortex-wide. *INDEX TERMS:* 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0320 Atmospheric Composition and Structure: Cloud physics and chemistry

1. Introduction

[2] Polar stratospheric clouds (PSCs) play a principal role in destruction of ozone in the wintertime polar stratosphere by providing enhanced surface area for heterogeneous reactions that activate chlorine and by removing HNO_3 from the gas phase [*Solomon et al.*, 1986; *World Meteorological Organization (WMO)*, 1998]. PSCs exist in both liquid and solid phases [*Toon et al.*, 2000]. As temperature decreases, the liquid sulfate aerosol swell with uptake of HNO_3 and water resulting in super-cooled ternary solutions (STS). To form solid particles such as NAT and nitric acid dihydrate (NAD), however, a nucleation barrier must be overcome. The mechanisms and rates of the nucleation process are poorly understood.

[3] Sedimentation of PSC particles irreversibly redistributes HNO_3 from higher to lower altitudes. This process, referred to as denitrification [*Toon et al.*, 1986; *Salawitch et al.*, 1989], increases O_3 loss by reducing the formation rate of NO_2 from HNO_3, thereby slowing the sequestration of the radical chlorine pool into $ClONO_2$ [*WMO*, 1998; *Waibel et al.*, 1999; *Gao et al.*, 2001]. Denitrification is possible only if a small number of particles preferentially grow at the expense of the STS droplets. To grow, these particles must have vapor pressures lower than that of the STS and are thought to be NAD or NAT [*Salawitch et al.*, 1989; *Toon et al.*, 1990].

[4] During the SOLVE campaign (winter 1999–2000) [*Newman and Harris*, submitted to *J. Geophys. Res.*, 2001], several instruments on the NASA ER-2 aircraft observed low concentrations (~10^{-4} cm^{-3}) of large particles (~8–20 μm diameter). These particles contain HNO_3 and are thought to be primarily NAT [*Fahey et al.*, 2001]. Simple growth and sedimentation calculations have shown that the particles likely crystallized at altitudes between 22 and 26 km [*Fahey et al.*, 2001]. Observations from this campaign show that, by mid-January, the Arctic stratosphere was quite denitrified over much of the vortex below 20 km [*Popp et al.*, 2001].

[5] "Selective" nucleation of NAT/NAD (via homogeneous or heterogeneous freezing) has typically been invoked to explain the small concentration of solid particles required to effect vortex-wide denitrification [*WMO*, 1998; *Tolbert and Toon*, 2001]. Consistent with this view, back trajectory calculations by *Fahey et al.* [2001] suggest no preferred freezing location. In a recent modeling study, *Tabazadeh et al.* [2001] using NAD nucleation rates near the high end of existing laboratory data, proposed homogeneous nucleation was responsible for the production of these particles. In this letter, we illustrate how formation of NAT nuclei in lee-wave clouds can generate a flux of large particles in the lower stratosphere and effect vortex-wide denitrification (a similar mechanism is suggested by *Fueglistaler et al.*, submitted to *ACP Discussions*, 2002).

[6] PSC formation in lee waves is well known [*Peter et al.*, 1992; *Tsias et al.*, 1997; *Voigt et al.*, 2000]. In lee waves, adiabatic lofting of air passing over mountain ranges can result in strong cooling at high rates [*Gary*, 1989]. The cooling increases with altitude and, between 22 and 25 km, ice clouds can be formed by the freezing of nearly all background particles (around 10 cm^{-3}) [*Deshler et al.*, 1994; *Carslaw et al.*, 1998]. The subsequent compressional warming of the airmass evaporates ice. It is speculated that HNO_3 taken up on the ice leads to NAT nucleation during the warming phase [*Zondlo et al.*, 2000]. LIDAR observations suggest that NAT may nucleate on a small fraction (e.g., around 2%) of the ice particles [*Carslaw et al.*, 1998]. Observations by *Voigt et al.* [2000] confirm the presence of NAT particles (~0.1–0.5 cm^{-3}) downstream of lee waves. Here, we model the growth and sedimentation of the NAT nuclei formed in these cloud layers to study their potential for vortex-wide denitrification.

2. Theory and Model

[7] The vortex in our model is represented by a cylindrical domain and nucleation events are simulated by seeding 0.2 cm^{-3} NAT nuclei in a nucleation layer at proscribed altitudes, Z_{nuc} (Figure 1). Monodisperse particles of 0.1 μm diameter are chosen to represent NAT nuclei in the nucleation layer. The volume of the nucleation layer is calculated from the air flux through a rectangular cross-section (see hatched region in Figure 1) with vertical thickness, h, and width, b, for a processing time, t_p, of 10 hours. The NAT nuclei in the layer grow with uptake of HNO_3 and water and the resultant particle sizes are calculated.[1]

[8] Based on the Goddard DAO analyses for winter of 1999–2000, we have assumed that angular velocity increases linearly with increasing altitude in the vortex (as listed in Figure 1). The particle size evolution and displacement in the vertical and azimuthal (along the latitude) dimensions are

[1] Growth and sedimentation equations listed in supplementary material. Supporting material is available via Web browser or via Anonymous FTP from ftp://kosmos.agu.org, directory "apend" (Username = "anonymous", Password = "guest"); subdirectories in the ftp site are arranged by paper number. Information on searching and submitting electronic supplements is found at http://www.agu.org/pubs/esupp_about.html.

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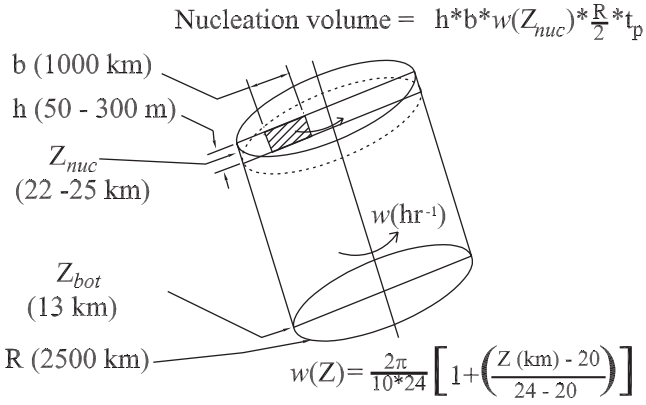

Figure 1. Schematic diagram of the domain used to simulate the polar vortex region (expressions for angular velocity and nucleation volume are also listed). Particles are seeded in a nucleation layer at Z_{nuc} and tracked as they sediment to Z_{bot}. Angular velocity is chosen such that a 2π revolution takes 5 days at 24 km altitude and 10 days at 20 km altitude.

tracked by solving the growth and sedimentation equations.[1] As processes affecting radial motion within the vortex have been neglected, calculations are restricted to two-dimensions.

[9] NAT particle growth is dependent on ambient gas-phase HNO_3 concentrations, which in our model are influenced by the presence of the STS droplets [*Carslaw et al.*, 1995]. In the absence of freezing, the STS droplets dominate the aerosol surface area throughout the lower stratosphere. These droplets exist over the entire temperature continuum but significant HNO_3 (and H_2O) uptake occurs only at temperatures $\lesssim$193 K. For the STS surface area ($\geq$0.5 μm^2 cm^{-3}), equilibrium between the gas and condensed phases will occur in a few hours. At equilibrium, the HNO_3 content of the STS is dependent on the total amount of HNO_3 in the gas and liquid (but not solid) phases. In our model, changes to gas-phase HNO_3 due to growth or evaporation of NAT results in adjustments of the STS composition to maintain this equilibrium.

3. Simulation Results

[10] Simulations were performed for a range of nucleation layer properties as listed in Figure 1. The initial HNO_3 (combined vapor and condensed phase) profile was set to a constant value of 13 ppb at higher altitudes (19.5–25 km), linearly decreasing to 4.5 ppb at 13 km, A constant temperature (191 K, except as noted in Figure 3)

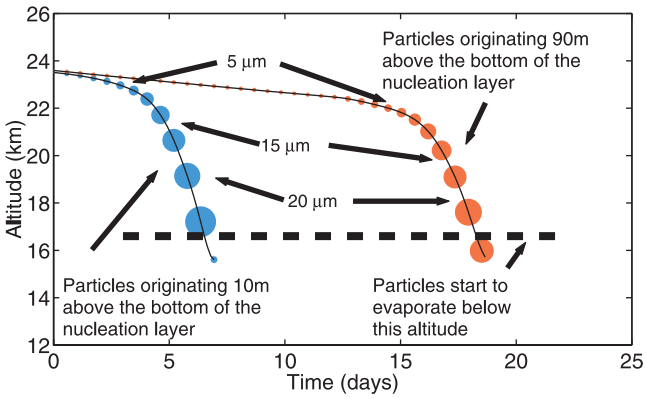

Figure 2. Size evolution and sedimentation of particles originating at varying heights in a 100 m nucleation layer. Model parameters used are as shown in Figure 1 (Z_{nuc} = 23.5 km).

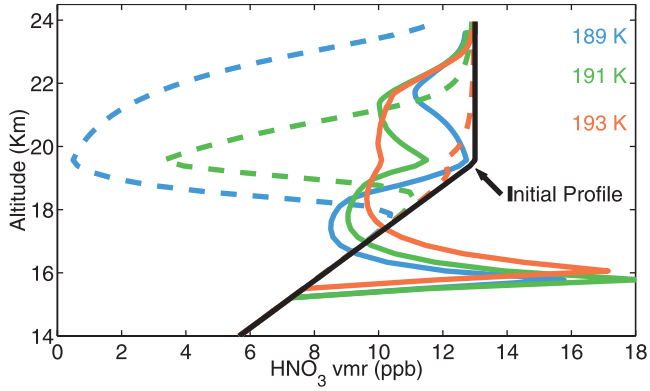

Figure 3. Initial gas-phase and total HNO_3 as a function of ambient temperature. The quantities plotted are: (1) Vortex-averaged total HNO_3 mixing ratios at start (black line) and end (colored solid lines) of simulations; (2) gas-phase HNO_3 mixing ratios (corresponding to STS vapor pressure) at start of simulations (dashed lines). The temperatures are assumed constant (189, 191 or 193 K) at altitudes above 19.5 km and linearly increasing to 210 at 13 km. The other model parameters are as shown in Figure 1 (Z_{nuc} = 23.5 km).

is assumed between 19.5 and 25 km altitudes, linearly increasing to 210 K at 13 km, broadly consistent with remote observations obtained from the NASA ER-2 and DC-8 aircraft (M.J. Mahoney, *per. comm.*). A constant mixing ratio of H_2O (5 ppm) and H_2SO_4 (0.5 ppb) is assumed at all altitudes.

[11] Evolution over time of the particle size and vertical displacement is plotted in Figure 2. In the nucleation layer, particles grow in ~3 hours to ~2 μm diameter before the gas-phase HNO_3 concentrations in the layer reach the NAT vapor pressure. The particles experience no further growth in the nucleation layer and sediment slowly (~80 m/day). Particles originating from the lower altitudes of the nucleation layer sediment to the region of higher HNO_3 concentrations in a short time and then experience rapid growth. The particles formed at higher altitudes within the layer remain near the nucleation altitude for many days as they fall slowly, without experiencing significant growth, through the air denitrified by the earlier sedimenting particles. One implication of this result is that, because particles nucleated at a single location are advected around the vortex for a number of days before they sediment significantly, simple back trajectory calculations that do not resolve the sub-mesoscale dynamics (e.g *Fahey et al.* [2001]) cannot be used to trace the origin of individual particles produced by this mechanism.

[12] In Figure 3, initial gas-phase HNO_3 profiles (dashed lines) are shown for three different temperature profiles. NAT particle growth rates are dependent on the gas-phase HNO_3 concentrations at equilibrium with the STS. This results in non-monotonic growth (and therefore denitrification) with temperature, with the peak growth rate at around 191 K at 50 mbar. At the coldest temperatures, gas-phase HNO_3 concentrations at lower altitudes (below ~21 km) are sufficiently small that the rapidly sedimenting particles are not efficient at removing HNO_3. When temperatures warm above T_{NAT} [*Hanson and Mauersberger*, 1988] (at ~17 km altitude), the particles start to evaporate and release their HNO_3.

[13] The simulation results show that sedimentation of NAT particles nucleated in a single geographic location results in a vortex-wide redistribution of HNO_3. The slow fall rate out of the nucleation layer, coupled with vertical shear in the vortex, result in sedimentation of particles through different vortex airmasses, denitrifying an increasing volume of the vortex at lower altitudes. At and just below the nucleation layer (above ~22 km), the small net shear limits the loss of HNO_3 at all temperatures. While the

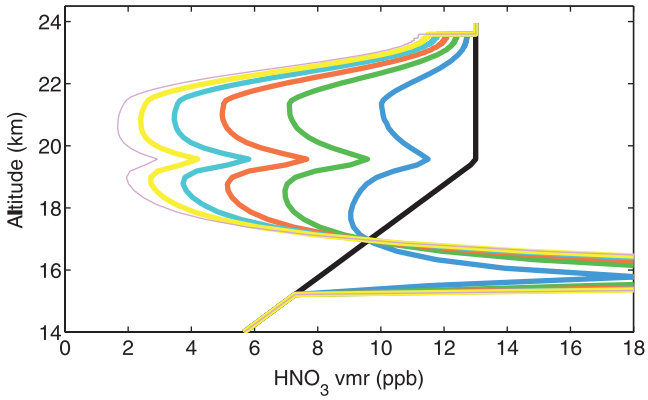

Figure 4. Vortex-averaged total HNO_3 profiles for repeated nucleation events. Each event culminates when all particles have evaporated or sedimented below 14 km. The denitrified vortex-averaged total HNO_3 profile obtained from one nucleation event is used as the input for the next event. A constant temperature of 191 K is assumed at altitudes above 19.5 km and linearly increasing to 210 at 13 km. The other model parameters used are as shown in Figure 1 (Z_{nuc} = 23.5 km).

shear causes particles from different altitudes in the nucleation layer to sediment through different vortex airmasses, there are no mechanisms in our model to disperse particles originating at a single altitude within the nucleation layer. At any time, therefore, particle flux at lower altitudes occurs only over a small range of azimuths (~10%).[2]

[14] The particle flux from a single lee-wave event [10 hours, 1000 km wide (along a longitude) × 100 m altitude] can result in up to ~25% denitrification vortex-wide. If vortex temperatures remain below T_{NAT}, the simulation of this single thin lee-wave-nucleation event produces a flux of large particles at 20 km that lasts longer than 3 weeks (Figure 2)!

[15] With repeated nucleation events, progressive denitrification occurs (Figure 4). Only a handful of such events can produce nearly complete, vortex-wide denitrification between 18 and 22 km. The assumed altitude and thickness of the nucleation layer also control the final distribution and degree of denitrification.[3] Particles originating at higher altitudes denitrify over a larger vertical extent. Thicker nucleation layers, with more NAT particles formed, cause a greater degree of denitrification per event.

4. The Real Atmosphere

[16] Obviously the multi-dimensional nature of polar vortex denitrification is not represented in our simple model. The largest uncertainties are the spatial and temporal distribution of lee-wave clouds and the number of NAT nuclei formed. Sub-mesoscale temperature fields are required to determine these properties. In addition, wind and HNO_3 fields are needed to accurately simulate the subsequent fate of the nuclei and their role in denitrification. Nevertheless, it is useful to make broad comparisons of our simulation results with the relevant observations.

[17] A flux of large particles (10–20 μm) was observed at 20 km by the MASP, CIMS HNO_3, and NO_y instruments during the 1999–2000 SOLVE campaign. During this period, temperatures within the vortex were mostly at or below T_{NAT} and lee-wave ice clouds were often seen (as illustrated in the cover photo of GRL, August 1, 2001). The vortex-averaged particle fluxes, obtained by averaging the calculated particle flux from the CIMS HNO_3 measurements for flight times when $T < T_{NAT}$, between mid-January and early-February ranged from 0.5 to 1 $m^{-2}s^{-1}$. Peak local flux values were sometimes an order of magnitude higher. The simulations described above produce particle fluxes consistent with these peak values. In addition, the simulated particle size distribution (not shown) is quite consistent with the observations [*Fahey et al.*, 2001]. On the other hand, during early March many fewer large particles were observed (Northway et al., submitted to JGR (2001)). A minor warming occurred in mid-February and, in our simulations, this prevents the persistence of the lee-wave-generated particles. While synoptic-scale particle formation can result in vortex-wide denitrification in a relatively short period (few days) for a cold ($T < T_{NAT}$) vortex, comparable vortex-wide denitrification by the lee-wave mechanism requires temperatures below T_{NAT} for a much longer duration (few weeks). If the lee-wave mechanism is correct and exclusive, the prediction is that denitrification would only be observed if cold vortex temperatures persist for several weeks.

[18] During SOLVE, particle flux at 20 km was observed over a vast spatial extent of the polar vortex. In our simulations, however, a single lee wave event produces particle flux only through a small vortex area at any instant of time. During the long residence time of particles in and near the nucleation layer (weeks), a significant portion of the vortex will experience ice lee-wave conditions if the synoptic scale temperatures are cold (e.g., *Carslaw et al.* [1999]). The formation of multiple nucleation layers by these clouds will produce a much more geographically and temporally uniform flux of large particles in the lower stratosphere (as observed during SOLVE) than is simulated for a single event.

[19] Finally, we note that it is possible that a similar process may effect dehydration below the tropical tropopause. For example, propagation of gravity waves to the tropopause may nucleate small ice particles [*Jensen et al.*, 1996]. The subsequent growth of these particles as they sediment through super-saturated air below would result in the redistribution of water to lower altitudes. We suggest that this could result in a very low number density of large ice particles in super-saturated regions of the upper troposphere.

5. Conclusion

[20] Clearly, there may be several nucleation mechanisms at work in producing particles that denitrify the polar vortex. Lee-wave cloud nucleation, however, has been dismissed previously (e.g., *Tabazadeh et al.* [2000] and *Tolbert and Toon* [2001]) because the high number density of small particles formed in these events (and therefore small sedimentation velocity of the particles) was thought to be incapable of producing significant denitrification. As we illustrate here, however, the inhomogeneity in growth rate in and below the nucleation layer results in the temporal (and therefore geographic) redistribution of these particles. The lee-wave layer acts like a "salt shaker" at high altitude slowly circling the vortex producing a moving hailstorm in the lower stratosphere. This study suggests, therefore, that before concluding that unknown nucleation mechanisms are at work [*Tolbert and Toon*, 2001], a much more sophisticated analysis should be performed to test the null hypothesis, i.e. that the known heterogeneous nucleation of nitric acid hydrates in lee-waves could explain the observed denitrification and particle flux.

[2] Details of shear interaction with particle sedimentation is listed in the supplementary material.

[3] Sensitivity test results included in supplementary material.

[21] **Acknowledgments.** The authors thank Leslie Lait, Paul Newman, and Mark Schoeberl for access to trajectory calculations via the NASA Goddard Automailer. We are grateful to Stefan Fueglistaler, Beiping Luo, David Fahey and Ross Salawitch for helpful comments that improved this manuscript. Finally, we thank Thomas Peter and an anonymous reviewer for their insightful comments.

References

Carslaw, K., B. Luo, and T. Peter, An analytic-expression for the composition of aqueous HNO3-H2SO4 stratospheric aerosols including gas-phase removal of HNO3, *Geophys. Res. Lett.*, *22*, 1877–1880, 1995.

Carslaw, K., T. Peter, J. Bacmeister, and S. Eckermann, Widespread solid particle formation by mountain waves in the Arctic stratosphere, *J. Geophys. Res.*, *104*, 1827–1836, 1999.

Carslaw, K. S., et al., Particle microphysics and chemistry in remotely observed mountain polar stratospheric clouds, *J. Geophys. Res.*, *103*, 5785–5796, 1998.

Deshler, T., T. Peter, R. Muller, and P. Crutzen, The lifetime of leewave-induced ice particles in the Arctic stratosphere: 1. Balloonborne observations, *Geophys. Res. Lett.* , *21*, 1327–1330, 1994.

Fahey, D. W., et al., The detection of large HNO3-containing particles in the winter Arctic stratosphere, *Science*, *291*, 1026–1031, 2001.

Gao, R., et al., Observational evidence for the role of denitrification in Arctic stratospheric ozone loss, *Geophys. Res. Lett.*, *28*, 2879–2882, 2001.

Gary, B., Observational results using the microwave temperature profiler during the airborne Antarctic ozone experiment, *J. Geophys. Res.*, *94*, 11,223–11,231, 1989.

Hanson, D., and K. Mauersberger, Laboratory studies of the nitric acid trihydrate: Implications for the south polar stratosphere, *Geophys. Res. Lett.*, *15*, 855–858, 1988.

Jensen, E., O. Toon, D. Westphal, S. Kinne, and A. Heymsfield, Microphysical modeling of cirrus part I: Comparison with 1986 FIRE IFO measurements, *Geophys. Res. Lett.*, *23*, 825–828, 1996.

Peter, T., R. Muller, K. Drdla, K. Petzoldt, and E. Reimer, A microphysical box model for EASOE: Preliminary results for the January/February 1990 PSC event over Kiruna, *Ber. Bunsenges. Phys. Chem.*, *96*, 362–367, 1992.

Popp, P., et al., Severe and extensive denitrification in the 1999–2000 Arctic winter stratosphere, *Geophys. Res. Lett.*, *28*, 2875–2878, 2001.

Salawitch, R., G. Gobbi, S. Wofsy, and M. McElroy, Denitrification in the Antarctic stratosphere, *Nature*, *339*, 525–527, 1989.

Solomon, S., R. Garcia, F. Rowland, and D. Wuebbles, On the depletion of Antarctic ozone, *Nature*, *321*, 755–758, 1986.

Tabazadeh, A., M. Santee, M. Danilin, H. Pumphrey, P. Newman, P. Hamill, and J. Mergenthaler, Quantifying denitrification and its effect on ozone recovery, *Science*, *288*, 1407–1411, 2000.

Tabazadeh, A., E. J. Jensen, O. B. Toon, K. Drdla, and M. R. Schoeberl, Role of the stratospheric polar freezing belt in denitrification, *Science*, *291*, 2591–2594, 2001.

Tolbert, M., and O. Toon, Atmospheric science—solving the PSC mystery, *Science*, *292*, 61–63, 2001.

Toon, O. B., P. Hamill, R. P. Turco, and J. Pinto, Condensation of HNO3 and HCl in the winter polar stratospheres, *Geophys. Res. Lett.*, *13*, 1284–1287, 1986.

Toon, O., A. Tabazadeh, E. Browell, and J. Jordan, Analysis of lidar observations of Arctic polar stratospheric clouds during January 1989, *J. Geophys. Res.*, *105*, 20,589–20,615, 2000.

Toon, O., R. Turco, and P. Hamill, *Denitrification mechanisms in the polar stratospheres*, *17*, 445–448, 1990.

Tsias, A., A. Prenni, K. Carslaw, T. Onasch, L. B. P., M. Tolbert, and T. Peter, Freezing of polar stratospheric clouds in orographically induced strong warming events, *Geophys. Res. Lett.*, *24*, 2303–2306, 1997.

Voigt, C., et al., Nitric acid trihydrate (NAT) in polar stratospheric clouds, *Science*, *290*, 1756–1758, 2000.

Waibel, A., et al., Arctic ozone loss due to denitrification, *Science*, *283*, 2064–2069, 1999.

WMO *Scientific Assessment of Ozone Depletion: 1998* (Rep, 44), World Meteorological Organization, Geneva, Switzerland, 1998.

Zondlo, M., P. Hudson, A. Prenni, and M. Tolbert, Chemistry and microphysics of polar stratospheric clouds and cirrus clouds, *Ann. Rev. Phys. Chem.*, *51*, 473–499, 2000.

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