Microphysical Simulation of Polar Stratospheric Clouds Within the Community Earth System Model

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Microphysical Simulation of Polar Stratospheric Clouds

Within the Community Earth System Model

by

Yunqian Zhu

B.S., Nanjing University, China 2008
M.S., University of Colorado, Boulder 2011

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Microphysical Simulation of Polar Stratospheric Clouds Within the Community Earth System Model written by Yunqian Zhu has been approved for the Department of Atmospheric and Oceanic Sciences

Dr. Owen B. Toon

Dr. Charles G. Bardeen

Date _______________

The final copy of this thesis has been examined by the signatories, and we find that both the content and the form meet acceptable presentation standards of scholarly work in the above mentioned discipline.
Polar stratospheric clouds (PSCs) are critical elements for polar ozone depletion. A new PSC model coupling stratospheric chemistry, microphysics and climate is constructed and the formation of STS (Super-cooled Ternary Solution) and NAT (Nitric-Acid Trihydrate) PSCs are explored.

STS particle properties are dominated by thermodynamics. Simulations of particle volumes and size distributions are generally within the observational error bars. STS particles are not in equilibrium with their environment when the particle surface area is smaller than $4 \mu m^2/cm^3$. A new nucleation rate equation for NAT is derived based on observed denitrification in the 2010-2011 Arctic winter. The homogeneous nucleation scheme leads to supermicron NAT particles as observed. The simulated the lidar backscatter, and denitrification are generally within observational error bars. However, the simulations are very sensitive to temperature.

Using the same STS and NAT schemes, as well as a prognostic treatment for ice PSC formation and dehydration, the PSCs are simulated during the Antarctic winter of 2010. The current model correctly simulates large NAT particles and denitrification, but cannot produce NAT with high backscattering ratio/number density sometimes observed by CALIPSO. However, our simulated ice has similar backscatter and depolarization which is often attributed to NAT by CALIPSO. Possibly the CALIPSO algorithm misclassifies ice as NAT when the stratosphere is denitrified or dehydrated. STS and NAT form near the pole in May and June, but form a ring outside 80’S later in the winter when polar HNO3 is depleted. Ice always forms in the coldest area, but becomes less abundant later in the winter.
The model is missing some processes forming NAT such as gravity waves or evaporating ice. These processes should be added to the model in the future.
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Chapter 1

Introduction

Polar stratospheric clouds (PSCs), also known as nacreous clouds or mother of pearl clouds, form inside the strong polar vortexes in Arctic and Antarctic wintertime. The clouds, which had been observed for more than a century, drew attention after the Antarctic ozone hole was discovered [Farman et al., 1985]. They have been found to be a critical element of Antarctic and Arctic ozone depletion [Solomon et al., 1986]. PSCs provide the surface areas for heterogeneous reactions that convert inert chlorine-containing compounds into photochemically active chlorine, which is the cause of the extensive Arctic and Antarctic ozone loss in the polar springtime. It is also found that the condensation of HNO$_3$ on PSCs and denitrification by the sedimentation of large HNO$_3$-containing particles [Toon et al., 1986, 1990; Waibel et al., 1999; Fahey et al., 2001] reduces NOy and thereby slows the reformation of inert chlorine reservoirs. On the other hand, falling ice particles containing H$_2$O dehydrate the winter polar vortex, which inhibits ozone loss, though it is a small suppression compared with the promotion from denitrification.

Numerous models and laboratory experiments have been constructed to understand PSC microphysics because of their importance to ozone loss. However, many different types of PSCs were discovered during the last century, and their formation processes are complicated. PSCs are classified into three major types: STS (Super-cooled Ternary Solution), NAT (Nitric-Acid Trihydrate) and ice.

STS forms from stratospheric sulfate aerosols. When temperature decreases in the polar night, the sulfuric acid aerosols uptake HNO$_3$ and H$_2$O gradually and grow into STS [Crutzen and Arnold, 1986; Toon et al., 1986]. STS particles have relatively
high vapor pressures, allowing them to come to equilibrium with the local nitric acid vapor, water vapor and temperature within minutes or hours under some conditions. Most current PSC models assume STS is in equilibrium with the temperature and environmental HNO$_3$ and H$_2$O abundance [Carslaw et al., 1995]. However, both observations and models suggest STS not in equilibrium for several hours after a rapid change in environmental conditions [Peter et al., 1994; Lowe et al., 2003]. Those rapid changes in environmental conditions are observed frequently in mountain waves [Lowe et al., 2006]. One interesting topic we explore is non-equilibrium growth of STS and the differences in particle properties between non-equilibrium and equilibrium assumptions in regions where mountain waves are not present.

One type of solid PSC, NAT, can be formed through many processes including: depositional nucleation of nitric acid on ice [Luo et al., 2003] or SAT (sulfuric acid tetrahydrate) particles [Zhang et al., 1996] and subsequent evaporation of the ice [Luo et al., 2003] or SAT; as well as homogeneous [Tabazadeh et al., 2002]or heterogeneous nucleation [Hoyle et al., 2013] of STS particles. Understanding the processes leading to formation of NAT particles is important because the formation process controls the number and size of NAT particles. Large NAT particles, near 5-10 µm in diameter, contain a high abundance of HNO$_3$ and have fall velocities that are great enough to denitrify the stratosphere. Smaller NAT particles, near 1-3 µm, do not fall fast enough to produce significant denitrification, at least in the Arctic where temperatures to not remain cold for long [Toon et al., 1990]. In the Antarctic, on the other hand, the PSC simulations by Höpfner et al. [2006] demonstrate the NAT particles formed from evaporating ice particles generated by mountain waves have radii smaller than 3 µm and particle volumes larger than 0.3 µm$^3$/cm$^3$. Those small NAT particles have the potential to grow larger and then denitrify the lower stratosphere significantly [Dhaniyala et al., 2002; and Fueglistaler et al., 2002].
Not only the amount of solid PSCs, but also the size, number density, shape and density of the particles contribute to the fall velocity of the particles. These variations of microphysical features increases the difficulty of comparing simulations with satellite or in situ observations, because a single instrument usually is not able to provide all the characteristics [Vincent, 2007; Hinds, 2012]. For example, in order to compare simulations with lidar observations at visible wavelengths we need to know the particle sizes and to make assumptions about particle shapes, because the lidar depolarization at visible wavelengths is highly dependent on both size and particle shape [e.g. Toon et al., 2000].

To explore the many questions related to the formation of PSCs and their impact on stratospheric chemistry, we develop a detailed PSC model using the Community Earth System Model (CESM)/Whole Atmosphere Community Climate Model (WACCM), which includes the MOZART (the Model for OZone And Related chemical Tracers) chemical model, coupled with the Community Aerosol and Radiation Model for Atmospheres (CARMA). We evaluate the PSC formation, denitrification and dehydration with an emphasis on microphysical formation of STS and NAT particles. We compare our results with historical data from satellite, balloon and aircraft.

In Chapter 2, we describe the microphysical processes we use for PSC formation. Simulations are compared with historical data mainly from the 2010-2011 Arctic winter. This winter had the largest Northern Hemisphere ozone loss on record. In Chapter 3, we discuss the optical properties of modeled PSCs in comparison with CALIPSO observations in the 2010 Antarctic winter. In Chapter 4, we analyze PSCs simulation in the 2010 Antarctic winter and discuss the necessity to further develop our PSC model.
Chapter 2

Development of a Polar Stratospheric Cloud Model within the Community Earth System Model using constraints on Type I PSCs from the 2010-2011 Arctic winter

2.1 Introduction

Polar stratospheric clouds (PSCs) form in the lower stratosphere during the polar night. Thermal radiation to space combined with a lack of solar heating in wintertime cool the winter polar stratosphere, while the strong winds in the polar vortex isolate the cold polar air from the warm air at lower latitudes. During the winter of 2010-2011, a cold Arctic vortex lasted from December until the end of March [Manney et al., 2011; Sinnhuber et al., 2011]. The unusual length of this cold period resulted in a prolonged presence of PSCs and significant gradual denitrification. The denitrification provides a useful test for modeling Nitric Acid Trihydrate (NAT) formation. Here we develop and test a new 3-D model of PSCs using data from the 2010-2011 Arctic winter. This model could potentially make improved forecasts for PSC formation and ozone depletion, though the sensitivity of the results to temperature may make forecasts challenging in the Arctic.

PSCs are important to understand because heterogeneous reactions on PSCs convert inactive chlorine (ClONO$_2$ and HCl) into photochemically active chlorine [Solomon et al., 1986], which together with related reactions involving Br, causes extensive ozone loss when sunlight is available to drive catalytic cycles [Molina and Molina, 1987]. PSCs also denitrify, reducing NO$_y$, and thereby slowing the reformation of chlorine and bromine reservoirs [Toon et al., 1986]. In addition, falling ice-PSC particles dehydrate the winter polar vortex, mainly over Antarctica [Kelly et al., 1989],
and perhaps a larger part of the southern hemisphere stratosphere [Schoeberl and Dessler, 2011]. Observed cooler Arctic stratospheres in recent years, coupled with more severe ozone depletion, increases the need to improve the modeling of PSCs [Rieder et al., 2014].

The efficiency of chlorine and bromine activation, denitrification, and dehydration varies between the multiple types of PSCs and stratospheric sulfates. Observations show that the microphysics and the heterogeneous chemical influences of PSCs are quite complicated. Recent research indicates that chlorine activation is due more to the presence of super-cooled ternary solution (STS) rather than to nitric-acid trihydrate (NAT) particles [Kühl et al., 2004; Wegner et al., 2012]. Some studies suggest that cold sulfates are also very important because measurements show enhanced ClO and decreased HCl at temperatures below 195 K even in the absence of significant polar stratospheric cloud particle surface area [Hanson et al., 1994; Kawa et al., 1997; Drdla and Müller, 2012; Wegner et al., 2012]. Ice clouds also provide surface area for heterogeneous chemistry, but reactions on other PSC types are fast enough that the chemistry has often gone to completion before it has become cold enough for significant amounts of ice clouds to form [Wegner et al., 2013]. Observations and theories suggest that large NAT particles with small number densities, rather than ice particles, are the predominant cause of denitrification [Toon et al., 1990; Waibel et al., 1999; Fahey et al., 2001; Lambert et al., 2012].

PSCs are classified into two main categories based upon their chemical and physical properties. Type I PSCs are composed primarily of H₂O and HNO₃ in either a crystalline phase, NAT (or type Ia), or a liquid phase, supercooled ternary solutions, STS (or type Ib). Type II PSCs, on the other hand, consist of crystalline water-ice particles (which probably contain small amounts of nitric acid and sulfuric acid) [Toon et al., 1989; Lowe and MacKenzie, 2008].
As the main particles found in the stratosphere outside the polar vortex, liquid H$_2$SO$_4$ aerosols serve as the condensation centers for HNO$_3$ and H$_2$O when STS particles form in the winter season in both hemispheres. NAT particles are solids, and their formation requires a phase change. The processes that form NAT are still not clear, but are likely to be of three main types. One possible type of process is that H$_2$SO$_4$ aerosols freeze to form sulfuric acid tetrahydrate (SAT). Then through nucleation followed by condensation of nitric acid, SAT becomes coated by NAT. However, this process is unlikely, because SAT deliquesces to form STS as nitric acid supersaturations rise due to falling temperatures [Koop and Carslaw, 1996]. A second possible process is heterogeneous freezing of nitric acid to form NAT on ice [Middlebrook et al., 1996; Biermann et al., 1998; Carslaw et al., 1998; Waibel et al., 1999; Wirth et al., 1999]. NAT is likely left behind when the ice sublimes, a process that has been observed directly in wave clouds [Peter et al., 1994; Wirth et al., 1999]. Another possibility is that Type Ib STS particles may freeze, either heterogeneously [Hoyle et al., 2013] or homogeneously [Carslaw et al., 2002; Tabazadeh et al., 2002; Daerden et al., 2007], to form NAT (possibly with nitric acid dihydrate (NAD) as an intermediate phase [Bertram et al., 1996; Disselkamp et al., 1996; Bertram and Sloan, 1998]). The existence of homogeneous nucleation of NAT from STS in the stratosphere is under debate. As we will show the nucleation rates involved are very small, and hence difficult to observe in laboratory settings. Some studies suggested that the NAT could homogeneously nucleate from STS if stratospheric temperature remains near 190 K for more than 1 day [Salcedo et al., 2000]. However, bulk experiments [Koop et al., 1995, 1997, 2000] suggest that liquid stratospheric aerosol droplets exist without freezing for temperatures higher than the ice frost point unless the H$_2$SO$_4$ weight percent is below 0.01%. Some measurements [Curtius et al., 2005; Murphy et al., 2007; Weigel et al., 2014] report non-volatile residuals are found inside the PSC particles, which indicates the possibility of
heterogeneous nucleation of NAT by micrometeorites. While each of these processes may occur in the polar vortex over broad geographic regions, it is also possible that NAT formation is heavily influenced by stratospheric mountain waves. The waves can introduce small spatial scale, but large amplitude, temperature fluctuations which may promote the freezing of STS directly to NAT [Tsias et al., 1997; Zondlo et al., 2000]. At very low temperatures, Type II PSCs composed of ice form by freezing Type Ib PSCs [Toon et al., 1989; Tabazadeh et al., 1994]. Ice particles can also form through heterogeneous nucleation from STS containing insoluble nuclei [Engel et al., 2013] or SAT [Fortin et al., 2003].

The goal of this study is to investigate the formation of Type I PSCs, the dominant PSC clouds in the Arctic region during the winter of 2010-2011. In this work we answer three questions:

1. Can our model properly simulate the particle volume, size distribution, lidar backscatter, PSC composition and other data related to the fundamental properties of the clouds that are important for ozone loss?

2. Can our model properly simulate the denitrification during the Arctic winter 2010-2011?

3. Can our model properly simulate the evolution of ozone and the related chemicals controlling ozone over the 2010-2011 Arctic winter?

Below we first review the data that are available for the Arctic winter of 2010-2011 and for other years that might be relevant. We next discuss the model we use to simulate the PSCs. We then present comparisons of simulations with the data, and address the three questions posed above.
2.2 Observational databases for PSCs

2.2.1 CALIPSO

The CALIOP (Cloud-Aerosol LIDar with Orthogonal Polarization) lidar system onboard the CALIPSO (Cloud-Aerosol Lidar and Infrared Pathfinder Satellite Observations) spacecraft has been operating since June 2006 [Winker et al., 2007]. CALIOP is a two-wavelength, polarization sensitive lidar. It provides both high vertical resolution profiles (60-180 m for lower stratosphere) of backscatter at 532 and 1064 nm and two orthogonal (parallel and perpendicular) polarization components at 532 nm [Winker et al., 2007]. The space based lidar classification scheme was developed from the ratio of the perpendicular to parallel component of aerosol backscatter $\delta_{aerosol}$, called the depolarization ratio, and the inverse scattering ratio ($1/R_{532}$) [Pitts et al., 2009]. The scattering ratio, $R_{532}$, is the ratio of total volume backscatter at 532 nm to the molecular backscatter coefficient at 532 nm. The detailed classifications of compositions based on these quantities are described by Pitts et al. [Pitts et al., 2007, 2011, 2013].

CALIOP not only provides high spatial (smoothed to 5km horizontal resolution and 180m vertical resolution for PSC products) and temporal resolution observations of the distribution of PSCs, but also provides considerable insight into PSC composition and formation mechanisms [Pitts et al., 2007, 2009, 2011]. By using the PSC identification algorithm and composition classification scheme [Pitts et al., 2009], CALIPSO can provide time series of PSC coverage, which together with the altitude profile determines the volume of the winter vortex containing PSCs. The data used in this research are based on version 1 CALIOP Level 2 PSC data products available through the NASA Langley Atmospheric Science Data Center (ASDC) (http://eosweb.larc.nasa.gov/).
2.2.2 Aura MLS

MLS is the Microwave Limb Sounder onboard NASA’s Earth Observing System (EOS) Aura satellite. Aura was launched into a near-polar sun-synchronous orbit in 2004 [Schoeberl, 2007], and continues to collect data as of this writing. MLS observes on a global scale both day and night. Aura MLS, is based on UARS (Upper Atmosphere Research Satellite) MLS [Waters et al., 1999]. MLS measures millimeter and submillimeter wavelength thermal emission, which can avoid the obscuration caused by aerosols or thin clouds in infrared and shorter wavelength observations. Aura MLS is able to measure temperature and many species in the gas phase and we are interested in the following species in this paper: H$_2$O, HCl, HNO$_3$ and O$_3$. The typical vertical resolution of observations at lower stratosphere is 2-3.7 km for H$_2$O, ~3 km for HCl, 3-5 km for HNO$_3$ and 2.5 km for O$_3$. The MLS systematic error (accuracy) for HNO$_3$ is ±0.25-0.5 ppbv for 100-32 hPa and ±0.5-1 ppbv for 22 hPa. The random error (precision) is ±0.7 ppbv for MLS HNO$_3$ data. For the vertical level 20-68 hPa, the MLS accuracy is 4-7% for H$_2$O, 0.05-0.2 ppmv for O$_3$ and 0.1-0.2 ppbv for HCl; the precision is 6-8% for H$_2$O, 0.04-0.1 ppmv for O$_3$ and 0.2 ppbv for HCl [Livesey et al., 2011] (http://mls.jpl.nasa.gov).

2.2.3 MIPAS

MIPAS (Michelson Interferometer for Passive Atmospheric Sounding) operated onboard the sun-synchronous polar orbiting ENVISAT (Europe’s Environmental monitoring satellite) from July 2002 to April 2012. Since 2005, the latitudinal coverage of MIPAS tangent points ranges from 87.5° S to 89.3° N at 3.7° latitude steps, and typically from 6 to 70 km altitude in its nominal observation mode. It is a Fourier transform spectrometer taking limb sounding infrared measurements between 685 cm$^{-1}$ and 2410 cm$^{-1}$ (14.6-4.15 µm). The spectra can be analyzed to measure pressure, temperature, the concentrations of gas phase species, as well as the abundance of PSCs and their composition over a continuous vertical profile [Höpfner et al., 2006b; Fischer et
Since MIPAS mid-infrared spectra are affected by cloud interferences, cloudy sweeps are removed from the analysis so only a partial coverage of the vortex can be obtained at PSC altitude. In this paper, we make use of data from the MIPAS2D database [Dinelli et al., 2010] retrieved with a 2D tomographic approach and will compare the model results with MIPAS observations of HNO$_3$ and ClONO$_2$ [Arnone and Hauchecorne, 2012; Arnone et al., 2012]. The accuracy of HNO$_3$ measured by MIPAS is 7-13% for the area in which we are interested, and the random error is 2-10% [Dinelli et al., 2010; Arnone et al., 2012]. For ClONO$_2$ [Arnone and Hauchecorne, 2012; Arnone et al., 2012] observed by MIPAS, the accuracy is 5 to 20% and the precision is 2-10% (0.05-0.15 ppbv). The adopted data was self-consistently interpolated to potential temperature levels and averaged within the vortex by Arnone et al. [2012].

### 2.2.4 ACE-FTS

The Atmospheric Chemistry Experiment (ACE) measures the concentrations of atmospheric constituents by absorption spectroscopy using the sun as a light source [Bernath, 2006]. Both PSCs and cirrus clouds can be seen clearly by a high-spectral resolution (0.02 cm$^{-1}$) Fourier Transform Spectrometer (FTS) from 2-13 μm (750-4100 cm$^{-1}$) and the visible/near IR imagers at 0.527 and 1.020 μm, with a good vertical and horizontal resolution (1 km), during sunset and sunrise [Dodion et al., 2007]. The PSC size distributions and volume density for different components of particles can be obtained from the ACE data based on the wavelength dependence of aerosol bands in the spectrum. The retrieval technique is based on a least squares retrieval between a measured spectrum and the reference spectra. For example, the reference spectra of liquid droplets (STS) use the Mie approximation [Bohren and Huffman, 1983]; while, the discrete dipole technique [Draine and Flatau, 1994] is used for the solid hydrates and ice particles.
2.2.5 SCIAMACHY

SCIAMACHY (Scanning Imaging Absorption SpectroMeter for Atmospheric CHartography) on-board ESA's Envisat satellite [Burrows et al., 1995; Bovensmann et al., 1999] measures the limb scattered solar radiation. Using the radiation profiles from 750 nm and 1090 nm, von Savigny et al. [2005] define a threshold to detect PSCs, called the color index ratio. In this paper, we will compare the model results with SCIAMACHY limb data retrieved at PSC altitudes in the 2010-2011 [Hommel et al., 2014] Arctic winter.

2.2.6 in-situ observations

Unfortunately, we are not aware of any in-situ data in the Arctic winter of 2010-2011, so we use data from earlier years. Our rationale for using data from other years is that many, but not all, PSC properties are controlled by equilibrium thermodynamics. These properties should be fixed by temperature, as well as the abundances of H2O and HNO3, with little influence from the air mass history. During the Airborne Arctic Stratosphere Experiment (AASE) in January and February 1989, fourteen NASA ER-2 flights took measurements of PSCs and sulfate aerosols at potential temperatures of 440 to 460 K (nominal pressures of 50 to 60 hPa [Dye et al., 1992]) using a forward scattering spectrometer probe (FSSP) model 300 [Dye et al., 1990; Baumgardner et al., 1992]. These studies provide detailed measurements of PSC particle volume.

On December 9th, 2001, a balloon-borne gondola provided detailed in-situ measurements of particle composition, size, number concentration, phase, and backscatter in an Arctic stratospheric cloud between 22 and 26 km [Deshler et al., 2003a]. On this balloon flight, particle compositions of HNO3 and H2O were measured by an aerosol mass spectrometer [Schreiner et al., 2002]. The particle size and number concentrations were measured using four optical particle counters [Deshler and Oltmans, 1998; Deshler et al., 2003b]. Particle phase was derived from depolarization
measurements at 532nm using a laser backscatter sonde described by Adriani et al. [1999]. Water vapor was measured by a frost point hygrometer [Ovarlez and Ovarlez, 1994] and temperature was measured by a Vaisala temperature sensor.

During the SOLVE/THESSEO (the Stratospheric Aerosol and Gas Experiment (SAGE) III Ozone Loss and Validation Experiment and the Third European Stratospheric Experiment on Ozone) campaign between January and March in 2000 Arctic winter, the NASA ER-2 high-altitude aircraft with three instruments onboard flew through the lower stratosphere and identified large nitric acid hydrate particles (diameter more than 10 µm) for the first time inside the polar vortex [Fahey et al., 2001]. The sizes were retrieved from observations by the NOAA NOy instrument, which has a front inlet and rear inlet that allow it to distinguish particle diameters less and greater than 2 µm. Later, this discovery was confirmed by direct observations of size distributions using the Multiangle Aerosol Spectrometer Probe (MASP) [Brooks et al., 2003]. In the 2009-2010 Arctic winter, large NAT particles were observed again during the RECONCILE (Reconciliation of Essential Process Parameters for an Enhanced Predictability of Arctic Stratospheric Ozone Loss and its Climate Interactions) campaign [von Hobe et al., 2013]. Molleker et al. [2014] retrieved the size distribution with sizes between 1 and 40 µm based on the detection of single scattered laser light by the FSSP-100 instrument.

We compare the simulated particle volume with the ER-2 flight observation in 1989. Also, we compare the simulated particle size distribution with the balloon data in 2001, ACE observation, ER-2 flight observation during SOLVE/THESSEO campaign in 2000, and M-55 aircraft observation during RECONCILE campaign in 2009-2010.

2.3 SD-WACCM/CARMA PSC Model Description

The Community Aerosol and Radiation Model for Atmospheres (CARMA) [Toon et al., 1988] has been coupled with the Whole-Atmosphere Community Climate Model
[García et al., 2007] with Specified Dynamics (SD-WACCM-4.0) to simulate the advection, diffusion, sedimentation, deposition, coagulation, nucleation, and condensational growth of atmospheric aerosols [Bardeen et al., 2008]. The NCAR Community Earth System Model (CESM) is the common numerical framework for WACCM [Marsh et al., 2013]. In these simulations a horizontal resolution of 1.9° in latitude and 2.5° in longitude is used. The model is defined on 88 vertical levels ranging from 6x10^{-6} hPa, roughly 140 km, down to the surface. The vertical resolution is about 1km in the lower stratosphere. CARMA-3.0 simulates the main microphysical processes and transport due to sedimentation and Brownian diffusion. SD-WACCM transports the aerosols using resolved winds and eddy motions.

The SD-WACCM model uses the MOZART chemical model (the Model for OZone And Related chemical Tracers) [Brasseur et al., 1998; Hauglustaine et al., 1998; Horowitz et al., 2003; Kinnison et al., 2007; Emmons et al., 2010; Lamarque et al., 2012] to treat the PSC heterogeneous chemical processes. In the current versions of WACCM,
STS and NAT form at a prescribed supersaturation with a prescribed size distribution and number density [Kinnison et al., 2007; Wegner et al., 2013]. In our SD-WACCM/CARMA version, we replace the STS and NAT parameterizations with microphysical processes. The time and space varying surface area density and effective radius of PSCs and sulfates derived from CARMA pass into MOZART for heterogeneous reaction rate calculations. The prognostic H$_2$O routines in WACCM are used to treat ice cloud formation and dehydration [Wegner et al., 2013]. The SD-WACCM/CARMA run is four time slower than a SD-WACCM run because of an additional 7 sulfur chemistry tracers and 80 PSC tracers. The sulfur chemistry includes reactions involving OCS, SO, SO$_2$, S, HSO$_3$, SO$_3$, and H$_2$SO$_4$ [English et al., 2011 and references therein]. The PSC tracers in the model include 20 size bins each for HNO$_3$ and H$_2$SO$_4$ in STS, as well as 20 bins each for H$_2$SO$_4$ (as SAT) and HNO$_3$ in NAT. Particulate water is not treated explicitly in the aerosol, but rather is assumed to stay in equilibrium with the gas phase.

In addition to PSCs, SD-WACCM/CARMA contains a complete package for stratospheric sulfates [English et al., 2011]. The sulfate model treats particles composed of H$_2$SO$_4$ and H$_2$O and has been compared with observations [English et al., 2011]. We do not currently consider micrometeorites, though other versions of the model have included them [Neely et al., 2011]. HNO$_3$ has been added to this sulfate model by including the growth of HNO$_3$ within the sulfate particles for STS and the growth of HNO$_3$ in NAT. The main microphysical processes for PSCs include homogeneous nucleation of sulfuric acid from the gas phase [English et al., 2011], homogeneous nucleation of NAT from STS, as well as condensation and evaporation of sulfuric and nitric acid. Figure 2.1 presents the main aerosol types that are involved in PSC microphysical processes in our model. The detailed descriptions of these microphysical
processes related to PSCs formation are given below. Parameter settings for the base case and for several sensitivity cases are listed in Table 1.

We use the SD-WACCM/CARMA model nudged with Goddard Earth Observing System 5 (GEOS5) [Reinecker et al., 2008] assimilated data every 30 min with a nudging relaxation of time of 50 hours [Brakebusch et al., 2013]. The GEOS5 data have a resolution of 6 hours and are interpolated into 30-minute nudging intervals. From the tests done by Brakebusch et al. [2013] and Brakebush [2013], the mean difference between the simulations and GEOS5 data are -0.16±0.77 K for temperature, -0.08±1.83 m/s for zonal wind, and -0.01±1.9 m/s for meridional wind. The model fields that are nudged are: horizontal winds, temperatures, surface pressure, surface wind stress, and sensible and latent surface heat flux. The nudging scheme is applied below 50 km; the model is fully interactive above 60 km. A linear transition is applied between 50 km to 60 km. The temperature is a significant factor for PSC heterogeneous chemical reaction rates [Brakebusch et al., 2013] and PSC formation, especially the NAT nucleation rate as shown in section 2.3.4. Unfortunately, GEOS5 is not reality and the small temperature differences between GEOS5 and reality can be significant as we discuss below.

![Figure 2.2](image.png) The SD-WACCM temperature minus the MLS temperature at different potential temperatures inside the vortex from December 1, 2010 to March 31, 2011. The blank regions indicate missing values.
Figure 2.2 shows the temperature difference between MLS temperatures and SD-WACCM [Brakebusch, 2013; Brakebusch et al., 2013]. Figure 2.2 shows that model temperatures are about 1.5 degree warmer than MLS temperatures from 450 K to 550 K, which is the main PSC formation area in the northern hemisphere. Below this region, model temperatures are about 0.5-1 degree colder than the MLS temperatures around 400-450 K. The validation of MLS version 3.3 temperature also states that the differences between GEOS5 and MLS are -0.5±0.3 K to +1.5±0.6 K between 100 hPa and 17 hPa at the pole [Schwartz et al., 2008; Livesey et al., 2011]. The temperature accuracy for MLS data is -2 to 0 K for the region from 17 hPa to 52 hPa and 0-1 K for 52 to 100 hPa. The MLS precision is ±0.6 K and ±0.8 K [Livesey et al., 2011]. Although the temperature difference is small, as we will show below changes in the temperature in the model by 1 K can lead to significant differences in nucleation rates, which reflect themselves in significant differences in the simulated denitrification.

We initialize using 5-year SD-WACCM runs to stabilize the stratospheric chemistry and sulfate aerosols. We start the simulations on Oct. 1, 2010 before PSCs formed in the Arctic and run until the end of March 2011 when PSCs had disappeared.
Table 1 The parameter settings in the base case model and other tuning values.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Base Case</th>
<th>Variation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>GEOS5</td>
<td>-1.5 K [Brakebusch, 2013]</td>
</tr>
<tr>
<td>CARMA time step</td>
<td>1.7 sec to 15 min*</td>
<td></td>
</tr>
<tr>
<td>CARMA bins</td>
<td>20 bins for each species</td>
<td></td>
</tr>
<tr>
<td>PSC dry radius range</td>
<td>0.000343-22.26 µm</td>
<td></td>
</tr>
<tr>
<td>Sulfate particle surface area for heterogeneous chemistry</td>
<td>Reduced by 4 at and above 650 K potential temperature</td>
<td></td>
</tr>
<tr>
<td>HNO₃ diffusion coefficient</td>
<td>D_HNO₃ = 0.466D_H₂O (see Appendix A)</td>
<td></td>
</tr>
<tr>
<td>STS particle shape</td>
<td>Sphere</td>
<td></td>
</tr>
<tr>
<td>Growth (liquid) Accommodation coefficient</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>Coagulation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature Accommodation coefficient</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>Growth (solid) Accommodation coefficient</td>
<td>0.93</td>
<td>0.4, 0.2 [Crowley et al., 2010]</td>
</tr>
<tr>
<td>NAT nucleation scheme</td>
<td>STS scheme (no NAT nucleates)</td>
<td></td>
</tr>
<tr>
<td>NAT particle density (g/cm³)</td>
<td>1.62 [Taesler et al., 1975]</td>
<td></td>
</tr>
<tr>
<td>NAT particle shape</td>
<td>Sphere</td>
<td>Flat plate (ratio of length and radius is 0.2)</td>
</tr>
</tbody>
</table>

* We constrain the supersaturation change of the species to limit the time step.

** The definitions of case names are given in paragraph 2.3.4.
2.3.1 Condensation and evaporation

Once nucleation of sulfuric acid particles occurs, H₂SO₄ vapor and water vapor condense on these background sulfate aerosols in the stratosphere [Turco et al., 1979; Hamill et al., 1982]. As the temperature decreases, HNO₃ gas will condense on the sulfate aerosols. This condensation results in STS formation. We do not assume that STS is in equilibrium with nitric acid vapor, as most other PSC models do, but rather follow its growth kinetically. Once NAT nucleates, the NAT particles also grow and evaporate.

The growth and evaporation equation for NAT and STS, discussed in Appendix A, is described in Toon et al. [1989] and is similar to that employed by Barkstrom [1978] and subsequent work [Ramaswamy and Detwiler, 1986]. This equation provides the particle growth/evaporation rate, and hence how much H₂SO₄ and HNO₃ mass should be moved between bins.

The growth equation requires equations for acid concentrations, vapor pressures and surface tensions among others. The acid concentration, or weight percent, is required to calculate vapor pressure, surface tension and ternary solution density. The weight percent of HNO₃, H₂SO₄ and H₂O [Luo et al., 1995] assumes that water vapor is in equilibrium with the particles, and varies with particle size. The HNO₃ vapor pressure uses the Luo et al. equations for STS [Luo et al., 1995] and Hanson’s equations for NAT [Hanson and Mauersberger, 1988]. The surface tension and particle density of ternary solutions is calculated by using empirical polynomial equations [Martin et al., 2000]. The detailed equations are listed in Appendix A.

2.3.2 Coagulation

As the particles move through the atmosphere, coagulation occurs when the particles collide with each other. The coagulation equations for our model are described in Appendix B. The numerical algorithm is based on Jacobson et al. [1994].
Coagulation of PSC particles with each other is not a very important process, because their numbers are small and their lifetimes are short. However, it is essential to consider coagulation for the longer-lived sulfuric acid particles, particularly when active nucleation is occurring. In the stratosphere, once the sulfate particles have grown to sizes near 10 nm or larger, coagulation controls the particle numbers, and the nucleation scheme is of little importance \cite{English2011}.

### 2.3.3 Vertical transport

After the particle forms it will be transported across the spatial grid. WACCM performs the transport by winds and eddy diffusion, and CARMA performs the transport forced by gravity and Brownian diffusion. Brownian diffusion is not important except above 100 km where the atmosphere starts to separate by molecular weight. The fall velocities are computed with the Stokes-Cunningham equation \cite{Fuks1964}, as described in Appendix C.

### 2.3.4 NAT homogeneous nucleation and SAT melting

After STS has formed due to the condensational growth, nitric acid trihydrate (NAT) and nitric acid dihydrate (NAD) can crystalize from it though homogeneous nucleation, or possibly through heterogeneous nucleation. Unfortunately, the nucleation processes are not understood at the present time. We explore several possible homogeneous nucleation pathways as discussed below. To calculate how fast STS nucleates into NAT, we calculate the nucleation probability, which represents the probability that an STS particle will convert into NAT in a certain time period \cite{Koop1997}. Tabazadeh et al. \cite{2002} concluded that surface based nucleation was more consistent than volume based nucleation with all the available laboratory kinetic data. The nucleation probability based on surface nucleation rate is written as \cite{Koop1997}: 
\[ \text{Nu}_{\text{probability}} = 1 - \exp(-J_s \cdot \text{Surface Area} \cdot dt) \] \tag{1}

Where \( dt \) is a CARMA time step. For the Surface Area, we use the surface area of an individual STS particle in each size bin. The NAT surface-based nucleation rate is written as [Tabazadeh et al., 2002]:

\[ J_s = N_s \left( \frac{kT}{h} \right) \exp \left[ \frac{-\Delta G_{\text{act}}^{s}}{RT} \right] \] \tag{2}

In this equation, \( N_s = X_{\text{HNO}_3} n_s \). \( X_{\text{HNO}_3} \) is the mole fraction of \( \text{HNO}_3 \) on the surface of the particle and \( n_s \) is the approximate number density of molecular surface sites, which is about \( 10^{15} \text{ cm}^{-2} \). \( k \) is the Boltzmann constant; \( h \) is the Planck constant; \( R \) is the gas constant; \( T \) is the temperature; and \( \Delta G_{\text{act}}^{s} \) is the nucleus free energy. We use the following empirical equations for the formation free energy for NAT surface based nucleation [Tabazadeh et al., 2002]:

\[ \Delta G_{\text{act}}^{s,NAT} (X_{\text{HNO}_3}, T) = 11.5593 + 0.0804214T - \{71.5133 - 0.256724T\}X_{\text{HNO}_3} \] \tag{3}

\[ \Delta G_{\text{act}}^{s,NAT} (X_{\text{HNO}_3}, T) = (-45.2429 + 0.364844T) \frac{\Delta G_{\text{act}}^{NAD}(X_{\text{HNO}_3}, T)}{\Delta G_{\text{act}}^{NAD}(0.246T)} \] \tag{4}

<table>
<thead>
<tr>
<th>Table 2 Summary of Scenarios</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Short name</strong></td>
</tr>
<tr>
<td>STS-only</td>
</tr>
<tr>
<td>NATscheme</td>
</tr>
<tr>
<td>NATJ/10</td>
</tr>
<tr>
<td>slopeflat</td>
</tr>
<tr>
<td>NADscheme</td>
</tr>
<tr>
<td>NADJ/100</td>
</tr>
</tbody>
</table>
Figure 2.3 illustrates the average HNO$_3$ mole fraction in STS particles as a function of temperature from our model simulation, the nucleus free energy for five test cases and their corresponding nucleation probability. Panel A is the average mole fraction we sample in our model at a pressure of 50 hPa at the beginning of the winter before the onset of denitrification and dehydration. The particles take up HNO$_3$ as the temperature decreases below 200 K and STS starts to form. Eventually a maximum nitric acid mole fraction is reached around 190 K and at lower temperatures the HNO$_3$ mole fraction declines because the particles take up H$_2$O quickly as the temperature approaches the frost point. The mole fractions and temperatures are used to compute the nucleus free energy (shown in Figure 2.3b) and the nucleation probabilities (shown in Figure 2.3c) using the equations described above or with some modification (see Table 2). The curves shown in the example in Figure 2.3c are derived assuming a typical STS particle with 0.25 µm radius and surface area of 0.785 µm$^2$.

Figure 2.3 Panel (a) shows the modeled HNO$_3$ mole fraction; Panel (b) calculates the nucleus free energy based on the equations in this section and the HNO$_3$ mole fraction shown on panel (a); Panel (c) shows the nucleation probability of one typical STS particle in 30 min (one WACCM physics-time step). The names of five cases refer to Table 2.
We conduct several simulations based on variants of the NAT surface nucleation equation from Tabazadeh et al. [2002]. Table 2 shows short names for the various nucleation rate equations used in simulations and the main characteristics of the simulations. Firstly, we use the NAT and NAD surface nucleation equations [Tabazadeh et al., 2002]. Then, we divide the nucleation rate, \( J_s \), by 10 and 100 respectively (shown by dashed lines in Figure 2.3b), which shifts the nucleation probability about 1 and 2 orders of magnitude lower than in the NAT and NAD scheme. Note dividing \( J \) by a factor is equivalent to adding a constant to the free energy terms for the unmodified \( J \). The factors are listed in Table 2. Note that the NAT schemes have a very abrupt onset near 190 K, while the NAD schemes have a less sensitive temperature dependence. The case labeled slopeflat was obtained by dividing the nucleation free energy in NAT scheme equation by 2, and then adding a constant, as noted in Table 2.

![Image of nucleation free energy](image)

Figure 2.4 The nucleation free energy (kcal/mol) as a function of mole fraction of HNO\(_3\) inside an STS particle and the temperature for three test cases: slopeflat, NATscheme and NADscheme.

The nucleation probability of the slopeflat nucleation scheme is less dependent on temperature (and HNO\(_3\) mole fraction) than the other four schemes as shown in Figure 2.3c. The free energy of the slopeflat case is within 10% of the free energy of the NAD and NAT schemes; it is very close to the NADJ/100 case [Knopf et al., 2002; Voigt et al., 2005; Höpfner et al., 2006b] which has been applied in Daerden’s model [Daerden
et al., 2007]. The measurements used to retrieve the equations in Tabazadeh’s paper have an order of magnitude uncertainty in the nucleation rate and an uncertainty of about 2 degrees in temperature. Moreover, Tabazadeh et al. [2002] had to extrapolate the laboratory data over temperature and over mole fraction. The free energies for five cases shown in Figure 2.3 are within about 10% of the values from each other, but the $J$ values vary by six orders of magnitude. Given the small variations in the free energies in Figure 2.3, and the extrapolations made in deriving them by Tabazadeh et al. [2002], we feel we are justified in varying the free energy slightly to obtain better fits with observed denitrification as discussed below.

The nucleation probability in Figure 2.3c increases rapidly as temperature declines from 193 K to 190 K. However, this perceived dependence on temperature is somewhat misleading. Figure 2.4 shows that the nucleation free energy is actually very sensitive to the mole fraction of the STS compared with its sensitivity to the temperature. Falling temperatures, however, generally cause the mole fraction to increase. Eventually the nucleation rate (Figure 2.3) reaches a plateau as the temperature drops because the mole fraction of HNO$_3$ in STS starts to decline at very low temperatures.

As discussed below, the 2010-2011 Arctic winter does not provide extensive data for empirically deriving the nucleation rate. Therefore, the equation for slopeflat case may be improved in the future when further years with Arctic denitrification may be observed. Note, however, in Figure 2.3 that about 1 STS particle in 1 million is converted to a NAT particle in 30 min. The rate, which incidentally makes laboratory measurements very difficult, is consistent with observations. STS particles have a radius that is about 30 times smaller than that of developed NAT particles. Therefore, the mass of 40 NAT particles would be comparable to the mass of the remaining 1 million STS particles (Mass is proportional to the cube of NAT radius). Therefore, large
NAT particles cannot be very numerous or STS/NAT mixtures would contain little STS. Of course, since most optical observations are sensitive to particle area rather than mass, at the same mass small STS particles are more effective than large NAT particles at altering optical properties, as discussed by Toon et al. [2000] and therefore easier to detect.

Our simulations only produce NAT particles with relatively large sizes. However, there may be other mechanisms, not treated here, that would produce small NAT particles. The nucleation rate of NAT from STS might increase substantially in mountain wave clouds or gravity waves if very low temperatures are accompanied by high mole fractions of nitric acid when STS is driven out of equilibrium due rapid the temperature changes [Tsias et al., 1997]. Also, ice particles in mountain wave clouds are known to be numerous and small. Therefore, NAT formed on ice particles in such waves are likely to have small particle sizes [Carslaw et al., 1998; Luo et al., 2003].

When the temperature rises, ice and NAT particles evaporate and leave SAT behind. SAT will melt when the temperature is warmer than 210–215 K [Middlebrook et al., 1993]. However, SAT also deliquesces if the temperature declines and the NAT supersaturation increases [Koop and Carslaw, 1996]. It is also proved by laboratory [Iraci et al., 1995] and calculations [MacKenzie et al., 1995] that the nucleation from SAT to NAT requires supercooling by up to 8 K. Therefore, if NAT evaporates, our model converts all the SAT particles back into STS and NAT is not allowed to recondense on them until nucleation of NAT from STS occurs again.

2.4 SD-WACCM/CARMA Simulations of PSCs

2.4.1 Microphysical features of PSCs in the base case model

Before proceeding to a detailed analysis of the PSCs in the 2010-2011 winter, we first present some microphysical results from the base case STS-only model and the
slopeflat case. There are certain parts of the model, such as weight percent of species in STS particles and STS particle volumes, that are basically related to thermodynamics, and do not depend on the detailed history of the PSCs, assuming only that the total water vapor and total nitric acid are known. Other parameters such as the STS particle size distribution may depend on the PSC history, but also can be roughly compared with data with similar current environmental conditions due to rapid equilibrium times.

In this part, we try to investigate: Can our model properly simulate the particle volume, size distribution, lidar backscatter, PSC composition and other data related to the fundamental properties of the clouds that are important for ozone loss?

### 2.4.1.1 Weight percent of species inside STS particles

![Figure 2.5 Weight percent of each species in STS particles from the model (colored circles) around 52 hPa compared with Carslaw's model with 3.5 ppm H$_2$O (dashed lines) and 5.5 ppm H$_2$O (dotted lines).](image)

The weight percent of STS particles (equivalent to mole fraction) is very important for NAT nucleation, because the NAT nucleation probability is very sensitive to the HNO$_3$ mole fraction as shown in Figure 2.4. Since our model uses non-equilibrium calculations for STS growth, comparing the weight percent computed in the model with equilibrium values indicates how fast STS particles respond to temperature changes. Generally, the weight percent is controlled by thermodynamics, so it is more or less
independent of the details of the atmospheric dynamics and the history of the PSCs given fixed abundances of water and nitric acid. The “average weight percent” is the total mass of each composition in a grid box divided by the total mass of STS, so it is effectively a volume-weighted average.

Figure 2.6 HNO$_3$ supersaturation with respect to STS as a function of surface area density using the same sample points as Figure 2.5. Different colors represent the different temperature range. Negative supersaturation means the particles are evaporating.

Figure 2.5 shows the STS particle weight percent from the model at 52 hPa from one day of the STS-only case compared with the weight percent from Carslaw’s thermodynamic model [Carslaw et al., 1995] at the same pressure level. Each circle in Figure 2.5 represents the average weight percent of different species in one model grid box, with particle sizes about 0.05-0.5µm. Note that in our model the weight percent varies across the size spectrum so that the weight percent of some bins could be different from the weight percent shown in this graph. However, the bins that have the typical STS sizes (0.05-0.25 µm) do not vary significantly from the means in Figure 2.5 because the mass mostly concentrates in those bin sizes. For Carslaw’s model we assume 10 ppbv HNO$_3$ and 0.1 ppbv H$_2$SO$_4$ and present results for two different water vapor mixing ratios, 3.5 ppmv H$_2$O and 5.5 ppmv H$_2$O. These choices for H$_2$O, HNO$_3$ and H$_2$SO$_4$ are close to the values of these species in the model. The HNO$_3$ in the model is about 10 ppbv ± 0.3 ppbv, and H$_2$SO$_4$ about 0.1 ppbv ± 0.1 ppbv. The H$_2$O is within 3.5-
5.5 ppmv. The model results are in the range of Carslaw’s thermodynamic model for temperatures between 188 K and 192 K, which means that the STS generally remains close to equilibrium at these temperatures.

Figure 2.5 and Figure 2.6 show that at some places the weight percents of HNO$_3$ and H$_2$SO$_4$ are outside the range of equilibrium values at temperatures above about 192 K, where the particles contain little nitric acid. This lack of equilibrium occurs because the sulfate aerosols have small surface area density (around 3 µm$^2$/cm$^3$, shown in Figure 2.6), which is not enough surface area to pull the ambient nitric acid vapor to equilibrium quickly. Figure 2.6 indicates that in those regions with surface areas larger than about 4 µm$^2$/cm$^3$ the particles are in equilibrium with the HNO$_3$ vapor. As illustrated in 4.2, surface areas are often lower than 4 µm$^2$/cm$^3$, and therefore the use of an equilibrium model for STS will lead to errors in predictions of STS masses, sizes and acid concentrations.

2.4.1.2 Particle Volume

Figure 2.7 The particle volumes from the STS-only model (colored circles) compared with ER-2 aircraft observations (black dots) in January and February, 1989 at 50-60 hPa [Dye et al., 1992]. The different colors represent different saturation status of HNO$_3$ over the particles.

Particle volume represents the amount of the total reservoir of nitric acid that is condensed. Comparing simulated to observed particle volume as a function of
temperature is an indirect test of the growth scheme in the model, and a direct test of the thermodynamics. Generally the particle volume is controlled by thermodynamics, so it is more or less independent of the details of the atmospheric dynamics and the history of the PSCs, given fixed abundances of water and nitric acid.

Figure 2.7 shows the particle volumes from the STS-only model (colored circles) compared with ER-2 aircraft observations (black dots) [Dye et al., 1992]. The different colors for the model represent the supersaturation of HNO$_3$ over the particles. The blue circles represent the particles with HNO$_3$ supersaturated, these particles tend to absorb more HNO$_3$ into the particles. The red circles represent the particles with HNO$_3$ undersaturated, these particles tend to evaporate HNO$_3$ into gas phase. The green circles represent the particles with HNO$_3$ generally in equilibrium. As the temperature decreases, the sulfate particles take up HNO$_3$ and water to form STS. Once the temperature decreases to 192 K, the particle volume increases rapidly as the HNO$_3$ vapor pressure over the STS particles falls, and nitric acid and water are moved from the gas phase to the condensed phase. Most of those colder particles are in equilibrium. When the temperature is above 196K, the particle volume is not highly dependent on the HNO$_3$ saturation ratio because the main components of the particles are H$_2$SO$_4$ and water. When the temperature is above 200 K, the particle volume from the model is slightly lower than the observations. At temperatures between 192 K and 196 K, the model shows two values of volume, with one value generally representing undersaturated conditions and the other supersaturated conditions. The differences between the volumes are not only caused by the varying HNO$_3$ and H$_2$O spatial distribution in the model, but also occur because the particles with small volumes don’t have enough time to reach equilibrium with the vapor because of their low surface area density. At temperatures below 190 K the model, which only has such low temperatures at relatively low latitudes, has about half the volume observed. However, the gas phase
H$_2$O and HNO$_3$ were not measured. If we assume an STS number density of 10 cm$^{-3}$, in order to have the particle volume of 6 µm$^3$/cm$^3$ when the temperature is lower than 190 K as observed, the STS particle size would be about 0.5 µm. This size is much bigger than a typical STS particle size (0.05-0.3 µm). Therefore, the observed PSCs must have a significant H$_2$O uptake to increase the particle size significantly when the temperature is lower than 190 K.

### 2.4.1.3 Size Distribution

The particle size distribution may reflect the history of the particles. Sizes vary as condensation or evaporation occurs, which is rapid for STS. However, the NAT portion of the size distribution depends on the number of STS particles that nucleated to form NAT, the amount of time the NAT has had to grow, and can also be affected by particle sedimentation removing particles as they fall, or adding them if they descend from higher layers.

Figure 2.8 shows the STS simulated volume size distribution at about 18-19km (52 hPa) averaged over the entire polar vortex on Jan. 24, 2011 in the base case STS-only model, compared with the observations at particular locations in prior years. In the simulation the total nitric acid averaged over the vortex at this location was about 10 ppbv. The size distribution of STS will shift slightly as the total nitric acid varies.

Figure 2.9 illustrates a simulated size distribution using the slopeflat nucleation scheme at 71-75°N and 102-110°E at 61 hPa (~17-18 km) on Jan 02, 2011 compared with NAT observations in previous years. The size distribution of NAT particles is largely dependent on the air mass history, and highly variable in observations and in our model. This comparison is meant to point out that the homogeneous nucleation scheme is able to simulate some of the larger NAT particles that have been observed. The observations are from the FSSP-100 instrument on the M-55 aircraft during the 2009-2010 winter [Molleker et al., 2014] and from the NO$_y$ instrument on ER-2 aircraft
in 1999-2000 described by Fahey et al. [2001] around the same height. The observations here only show NAT particles while the simulations include both STS and NAT. The simulations produce particles in the same general range of sizes, but the total numbers of particles and shapes of the distributions vary significantly. In part these differences can be attributed to different histories of the particles in the model and observations, and of course differences in temperatures, and nitric acid abundance between the years of the observations and simulations. They also likely represent different nucleation rates between the model and nature.

Figure 2.8 Vortex average volume size distributions from the base case STS-only simulation of SD-WACCM/CARMA (blue) at 18-19 km compared with ACE-FTS data (green) [Zasetsky et al., 2007] at 18-23 km in 2005 and balloon observation (red) [Deshler et al., 2003a] at 22-26 km in 2001.
Figure 2.9 Number size distribution of STS and NAT particles from case slopeflat of SD-WACCM/CARMA (blue) at around 18 km compared with the NOy instrument observations in 1999-2000 [Fahey et al., 2001] and FSSP-100 instrument observations in 2009-2010 [Molleker et al., 2014] around the same height.

Figure 2.10 The source and sink terms that influence the HNO₃ abundance in the polar night.
Figure 2.11 Diagram showing the impacts of nucleation rates on particle size, particle fall velocities and on denitrification.

2.4.2 Denitrification features

Denitrification is one of the indicators of whether the NAT nucleation scheme is realistic since NAT is the main contributor to denitrification. Figure 2.10 describes the possible processes that influence the HNO$_3$ concentration during the polar night inside the polar vortex. These processes include chemistry, transport and microphysics. Heterogeneous chemistry is a significant source of HNO$_3$. Reactions on sulfate particles and on PCSs convert ClONO$_2$ and N$_2$O$_5$ to HNO$_3$. Therefore, a proper treatment of sulfate aerosols is very important for HNO$_3$ prediction. STS takes up HNO$_3$ but will not cause permanent denitrification (temporary removal from the gas phase does occur) since the fall velocity of STS is very small, so STS will evaporate back to HNO$_3$ when temperature rises. NAT falling out of the stratosphere is the main sink term for total (gas + particle) HNO$_3$. In addition, the HNO$_3$ abundance is affected by mixing across the
vortex edge during sudden stratospheric warming (SSW) [Matsuno, 1971] and the reformation of ClONO$_2$ in later season [Brakebusch, 2013].

As mentioned previously we find that only a very small number of STS particles nucleate to form NAT and as a consequence the NAT surface area is much smaller than the STS surface area on average (they are often spatially separated, so NAT can dominate locally). As a result NAT is generally unable to reduce the gas phase partial pressure to the NAT vapor pressure unless it is present for a substantial period of time.

In contrast, if NAT particles nucleate quickly and convert a significant number of STS particles to NAT, then they very quickly will reduce gas phase HNO$_3$ below the STS vapor pressure and pull HNO$_3$ from the gas phase and from STS. In this case reducing the nucleation rate will create fewer NAT particles with bigger radii, which likely increases the denitrification as illustrated in the top two panels of Figure 2.11. However, the slow nucleation scheme in our model, shown in bottom two panels of Figure 2.11, does not lead to a sudden dramatic reduction in partial pressure in the gas phase. In this case, decreasing the nucleation rate doesn’t affect the size of the particles very much. Therefore, reducing the nucleation rate decreases the denitrification.

In order to compare the chemistry and PSCs occurring inside the polar vortex with data, we define the vortex using scaled potential vorticity (sPV) [Dunkerton and Delisi, 1986; Manney et al., 1994] values greater than $1.4 \times 10^{-4}$ s$^{-1}$ or $1.7 \times 10^{-4}$ s$^{-1}$. sPV is calculated by using the GEOS5 wind field for both model and MLS observations. The vortex average method for MLS data applies sPV of $1.4 \times 10^{-4}$ s$^{-1}$ [Brakebusch, 2013]. sPV’s calculation for MIPAS observations uses the European Centre for Medium-Range Weather Forecasts (ECMWF) high resolution ERA-interim meteorological products [Arnone et al., 2012]. The vortex average method applies sPV of $1.7 \times 10^{-4}$ s$^{-1}$ for MIPAS data described by Arnone et al. [2012].
Figure 2.12 shows the HNO$_3$ partial column abundance from 400-700 K potential temperature averaged over the polar vortex based on gas-phase HNO$_3$ data from MLS and simulations with the SD-WACCM/CARMA model using several NAT nucleation schemes. It is possible that comparing the column amount of nitric acid in the model and observations might be misleading because of possible compensating errors in different parts of the column. Below we also discuss the vertical profile of the nitric acid to alleviate this problem.

The STS-only simulation of nitric acid in Figure 2.12 (top left panel, green) shows the situation in which no NAT forms. While the gas phase column declines when gas is converted to particles, there is no significant loss of nitric acid from sedimentation over the winter because the STS particles are small (which we have confirmed with a simulation with no fall velocity-not shown). Rather, the difference between the HNO$_3$ column between the start and end of winter for the STS-only case is due to dynamical transport between the vortex and its surroundings. Therefore, the difference between the STS case and the MLS observations (red) at the end of winter, when no PSCs remain, represents an estimate of the permanent denitrification caused by NAT particles. From December to late March, almost 50% of the nitric acid column is lost comparing the STS-only case and the MLS data inside the vortex from 400 K to 700 K potential temperatures.

The simulations with different NAT nucleation schemes in Figure 2.12 show how important the nucleation scheme is to the denitrification. An interesting feature of the data is that very low average temperatures and low minimum temperatures at 475 K occur in late December with little denitrification. However, similarly low temperatures occur in January and February that do lead to denitrification. Comparing the denitrification simulated using the NATscheme, NADscheme and reduced rates (NATJ/10 and NADJ/100), we find that NATscheme is a slow nucleation scheme
(reducing the rate reduces denitrification) and NADscheme is a fast nucleation scheme (reducing the rate increases denitrification). Among the five cases tested, the slopeflat case and NATJ/10 are closer to MLS data than the others. But the nitric acid in the gas phase in NATJ/10 increases in February and March, which indicates insufficient denitrification at that time. The HNO$_3$ line for the NADscheme decreases sharply when PSCs are present. As a fast nucleation scheme, the NADscheme nucleates many NAT particles, which take up HNO$_3$ rapidly from the environment (the NADscheme nucleates NAD particles, but we assume NAD transforms to NAT immediately). Those NAT particles contribute to the temporary denitrification but cannot grow very big due to their large number density. They evaporate back to gas phase when temperature goes up and the HNO$_3$ remains at similar pressure levels to the original one. This explains why the nucleation rate between the NATJ/10 and the NAD schemes differ by 4 orders of magnitude (Figure 2.3), while the denitrification at the end of the season is about the same.

There are several additional factors that can impact the denitrification rate, beyond the number of NAT particles. Using the slopeflat nucleation rate, we vary the temperature, the sticking coefficient, the NAT particle mass density and the NAT particle shape (see Table 1) to see how these parameters affect the denitrification. Figure 2.13 shows the HNO$_3$ column for these three simulations compared with the base slopeflat simulation and MLS observations. The denitrification decreases when we reduce the sticking coefficient for NAT growth. The sticking coefficient reduces the growth rate of NAT, which yields lower-mass particles with reduced fall velocity. When we reduce the NAT particle density or change the shape to flat plates, the denitrification increases. Reducing the density increases the size of particles, which leads to a larger growth rate and more denitrification. The shape of the particle influences the fall velocity [Pruppacher and Klett, 1997]. Generally the non-spherical shape decreases the
fall velocity because of the increased drag force [Cheng et al., 1988]. When we change the NAT particle shape from spherical to a flat plate, the enhanced particle surface area not only decreases the fall velocity, but also the growth rate increases relative to a spherical particle. Hence, for reduced particle density and changed shape, the decrease in fall velocity at a fixed radius is overcome by the increase in radius due to increased growth rate.

The lower right panel in Figure 2.13 shows simulations with reduced temperature as well as reduced temperature and sticking coefficient. When we apply a 1.5 K reduction to the heterogeneous chemistry as described by Brakebusch [2013] and CARMA microphysics processes, the denitrification increases strongly because the area of the vortex with STS particles increases resulting in a higher nucleation rate of NAT. The grey line shows a case with a 1.5 K temperature reduction and with a sticking coefficient for nitric acid on NAT of 0.2 [Crowley et al., 2010]. In this case the nitric acid column is similar to that from the baseline temperature. In summary, the denitrification is very sensitive to the temperature, which limits the ability to use observations to constrain microphysical parameters such as the nucleation rate and the sticking coefficient.

Further information linking the nucleation rate and particle properties can be gained by examining the HNO$_3$ seasonal variation as a function of altitude (potential temperature). Figure 2.14 shows the vortex average gas phase HNO$_3$ volume mixing ratio on different potential temperature surfaces from December to March from MLS data, MIPAS data [Arnone et al., 2012] and a simulation using the slopeflat nucleation rate.

The simulation compares well with MLS and MIPAS data on the 550 K level (about 22-23 km) though there is too much nitric acid in February and March. The model (Figure 2.2) shows a consistent warm bias at this level for February and March.
Also, it denitrifies too much at lower altitudes (475 K and 400 K), especially at 400 K. This difference in nitric acid may again be due to the cold temperature bias in the model at these levels (Figure 2.2). As a result of the cold bias, the NAT particles cannot evaporate fast enough to return the nitric acid back to the gas phase around 400 K. Instead, the NAT particles fall out of the stratosphere. However, the sensitivity tests by Woiwode et al. [2014] indicate that the renitrification at the lower altitude is not very sensitive to ±1 K temperature bias. Instead, the falling velocity of NAT is important for simulating the renitrification of HNO₃. In our test cases, we tune the falling velocity by changing the particle density, the NAT shape and sticking coefficient influence the falling velocity. But in all cases, less denitrification at lower altitudes results in not enough denitrification at higher altitudes. Therefore, the falling velocity cannot resolve the missing renitrification in our model. Another possibility is that our model only simulates large NAT particles, while the real situations may contain both large and small NAT particles. The smaller sizes can evaporate faster and fall slower.

The overestimation of temporary denitrification in January and February at 475 K can be caused both by particles falling from levels above uptaking the HNO₃ and by the nucleation and growth of NAT at 475 K itself. Tests we conducted show that, the denitrification at 475 K is mainly caused by the particles falling down to 475 K and their subsequent further growth at this level. We conducted a test (not shown) in which we did not allow nucleation of NAT at 475 K. The denitrification at this level improves less than 10%. When we reduce the sticking coefficient for NAT to 0.4 or we reduce the nucleation rate by a factor of 3 for levels above 475 K, the HNO₃ mixing ratio can match MLS and MIPAS well at 475 K. However, these tuning methods also influence the 550 K NAT nucleation and growth. Therefore, the underestimate of HNO₃ at 475 K at the end of December might suggest the need for a better nucleation equation or better parameters for growth, or a more accurate temperature history.
At 650 K, our model overestimates HNO$_3$ during the winter and finds that it increases in time (not shown in figures). Since PSCs rarely form at this altitude (near 26-28 km), the increasing HNO$_3$ is due to the heterogeneous chemistry occurring on the surface of sulfate aerosols. In this winter, the STS forms until 26-27 km only at the beginning of January (see Figure 2.19 and Figure 2.21 below). In Figure 2.14 (and in all other simulations in this paper), we divided the sulfate aerosol surface area density (but not STS surface area density) by a factor of four for the heterogeneous chemistry at potential temperatures larger than 650 K. We choose a factor of 4 so that the surface area in our model is similar to that used in the standard WACCM model without CARMA. In that model the surface area density of sulfuric acid aerosols is interpolated to the model grids based on the CCMVal2 recommendations [Eyring et al., 2008]. However, the database has missing data at high latitudes polar regions. These gaps are filled by a liner interpolation method [Eyring et al., 2008]. With this change, the simulations agree well with the MLS and MIPAS data at 650 K. As we discussed in the introduction, cold sulfate aerosols is important for chlorine activation. Unfortunately there are no data on the sulfate surface area at these altitudes, latitudes and times. There are also limited data on the sulfur cycle in the upper stratosphere. These simulations indicate subtle problems with the sulfate cycle in the middle stratosphere in our model that are important to resolve in the future for simulations of the ozone budget.

Considering only homogeneous nucleation, most of the cases considered in Figure 2.12 predict large permanent denitrification in December and January, in contrast to the observations. The slopeflat case is the best in predicting the denitrification for the winter of 2010-2011, and the relative lack of denitrification in December.
Figure 2.12 The top left panel and bottom panels show the gas phase HNO$_3$ concentration in the vortex column from MLS data (red), compared to simulations with different nucleation schemes. The MLS error bars show the vortex column systematic error. The top right panel shows the condensed phase HNO$_3$ (expressed as the vortex column number of HNO$_3$ molecules with units, following the far left axis, of $10^{16}$#/cm$^2$) in STS (green) and NAT (blue) respectively. Note condensed phase nitric acid is less than 10% of the vapor phase. In the top right panel the vortex average temperature at 475 K potential temperature [Brakebusch, 2013] is marked as red dots; the minimum temperature is given as grey dots.
Figure 2.13 The gas phase HNO$_3$ column concentration inside the vortex from MLS (red), and simulations using the slopeflat nucleation and the cases that tune the parameters based on slopeflat case. The MLS error bars show the vortex column systematic error.
Figure 2.14 The vortex average HNO$_3$ gas mixing ratio from MLS, MIPAS [Arnone et al., 2012] and a model case slopeflat at different potential temperatures. The MLS error bar shows the systematic error assuming one standard deviation of 0.5 ppbv for 400-550 K and 1 ppbv standard deviation for 650 K.

Figure 2.15 - Figure 2.18 compare PSC properties from the slopeflat simulation with CALIPSO data on Jan 03 at about 26 hPa (~22 km), Jan 26 at 36 hPa (~20.5 km) and Feb 27 at 36 hPa (~20.5 km). Figure 2.15 shows the CALIPSO composition, the modeled HNO$_3$ mass in STS and NAT, along with the ice mass mixing ratio. The CALIPSO composition marked as STS+NAT1 is STS with little NAT; STS+NAT2 is STS with intermediate NAT; STS+NAT3 is STS mixed with a large amount of NAT [Pitts et al., 2011]. On Jan 03, an STS cloud was located just east of the coast of Greenland,
where temperatures are lowest, while a NAT cloud was observed over Southern Norway and Sweden. The same cloud pairing can be found on Jan 26 and Feb 27 (Figure 2.15): the largest mixing ratios of HNO₃ in STS and NAT are often separated with a small amount of mixed clouds in between. This is a consequence of the slow growth rate of NAT. NAT is nucleated in the location of the STS cloud in the previous days. NAT has a lower vapor pressure and, once formed, exists at higher temperature than STS. However, it takes considerable time for NAT to take nitric acid from the STS cloud. Therefore, for Jan 03 for example, as the temperature increases along the streamlines from Greenland to Norway the mass in the STS cloud slowly fades away, and the STS cloud is replaced by an equally massive, but optically inferior, NAT cloud. At the same time, new STS particles grow at locations with cold temperatures along the Greenland coast. However, CALIPSO often observes mixed clouds (red, green and black dots in Figure 2.15) [Pitts et al., 2009, 2011]. No ice particles are detected on Jan 03 at 26 hPa for both CALIPSO and the model. On Jan 26, CALIPSO observes a little ice cloud near the Russian islands located at about 90E, while the simulations produce a larger range of ice clouds. On Feb 27, both CALIPSO and the simulation show about the same coverage of ice clouds near the Russian islands.

Figure 2.16 shows the STS backscattering ratio, the NAT backscattering ratio assuming spherical particles, and the CALIPSO backscattering ratio at the same time and location as Figure 2.15. It would be better to treat the NAT particles with non-spherical optical models. However, the shape of NAT particles, and its variation in time and space is not known. We plan to explore this issue in future work. To calculate the backscattering ratio for modeled PSCs, we use the number density and particle radius from the model results and apply the Mie code by Bohren and Huffman [1983]. The estimated refractive indecies for STS [Luo et al., 1996] are [1.32, 1.35, 1.38, 1.40, 1.42, 1.435, 1.447, 1.45, 1.45, 1.45, 1.45] for STS from 0% to 100% HNO₃ weight percent in
10% increments for all temperatures. For simplicity, even though NAT is non-spherical, we assume it to be spherical (and therefore cannot derive a depolarization ratio) with a constant refractive index of 1.43. The backscattering ratio is the ratio of the aerosol plus molecular backscattering divided by the molecular backscatter. Figure 2.16 shows that the magnitude of the backscattering ratio of STS and NAT particles in the simulation is consistent with the CALIPSO observations. Both the observations and the modeled STS backscattering ratios show a maximum value of ~ 5.

Figure 2.17 presents the STS and NAT effective radius, and NAT number density for the same conditions as Figure 2.15. The effective radius of STS particles is about 0.2-0.3 µm and NAT effective radius is ~ 5µm for the locations with maximum HNO₃ abundance and number density. Figure 2.18 presents the temperature and wind vectors, the MLS HNO₃ and modeled gas phase HNO₃ for the same conditions as Figure 2.15. The features of areas of reduced gas phase HNO₃ are well simulated compared with MLS observations on the days shown.

Figure 2.19 shows the vortex average volume mixing ratio of HNO₃ from the model compared with SCIAMACHY observations [Hommel et al., 2014] at the altitude of PSCs. The highest altitudes of PSCs from the model are consistent with the observations. Also, the times of formation and disappearance of PSCs agrees with the observations, with the exception of the period after March 15, when the model does not have PSCs. With SCIAMACHY, the highest altitude of PSCs declines from about 28km in early January to near 20 km in mid-March. The model has a similar behavior, though PSCs only reach about 26 km in early January.

The surface area density (SAD) is important for the heterogeneous chemistry occurring on the surface of PSC particles. Figure 2.20 shows the modeled vortex average SAD of STS and the maximum SAD of STS. The average SAD has the peak at an altitude around 400 K over the season. The SAD magnitudes and locations mimic the
patterns in the STS mass mixing ratio shown in Figure 2.15. The surface area of NAT particles (not shown) is nearly zero (about 2 orders of magnitude lower than SAD of STS particles).

Figure 2.21 shows the time dependence of the volume of air that is occupied by PSCs during the winter of 2010-2011. In this case, the model defines a PSC to be continuous over a grid cell at the mean value, and a PSC to be present if the backscattering ratio is greater than 1.32, or NAT is present with more than 5 ppbm HNO₃ inside the particles. This volume is compared with observations from CALIPSO which defines a PSC to be present if the backscattering ratio is higher than 1.32 for horizontal smoothing scales of 135 km [Pitts et al., 2009], which is close to the resolution of our model. CALIPSO uses both backscattering ratio and perpendicular backscatter for PSC identification. The detailed thresholds for different spatial resolution are described by Pitts et al., [2009]. We exclude the areas north of 82°N from our model, because CALIPSO cannot observe those high latitudes. The model shows consistent cloud locations and cloud amounts compared with CALIPSO data. In early March, both the model and CALIPSO indicate spatially limited PSC cloud formation around 15 to 18 km, which forms due to the prolonged cold vortex for this winter. In late January, the model has cloud coverage of 8 million km² while CALIPSO detects about 6 million km². Also, the model misses a spatially limited PSC cloud formation event in mid-February. In Figure 2.19, NAT has large concentrations in these two periods. CALIPSO cannot detect some areas with large NAT particles at low number densities. The temperature bias in the model may be another possible reason resulting in NAT formation that is different from the observations in Figure 2.21.
Figure 2.15 Polar view plots of CALIPSO-retrieved PSC composition (first column), HNO$_3$ inside STS particles (second column), HNO$_3$ inside NAT particles (third column) and ice mass mixing ratio (last column). The data for Jan 03 is at 22 km and model output at 26 hPa (~22 km) at 00:00 GMT, Jan 04, 2011. For Jan 26 and Feb 27, the data is at 20.5 km and the model output is at 36 hPa (~20.5 km) at 00:00 GMT, Jan 26 and Feb 27, 2011. The CALIPSO composition marked as STS+NAT1 is STS with little NAT; STS+NAT2 is STS with intermediate NAT; STS+NAT3 is STS mixed with a large amount of NAT.
Figure 2.16 The CALIPSO backscattering ratio (left), the modeled STS backscattering ratio (middle) and the modeled NAT backscattering ratio assuming spherical NAT particles (right). The altitude and the time is the same as Figure 2.15.
Figure 2.17 The modeled STS effective radius (left column), NAT effective radius (middle column) and NAT number density (right column). The altitude and the time is the same as Figure 2.15.
Figure 2.18 The modeled temperature and wind vector (left column), the MLS HNO$_3$ mixing ratio (middle column) and modeled HNO$_3$ mixing ratio (right column). The altitude and the time is the same as Figure 2.15.
Figure 2.19 HNO$_3$ vortex average volume mixing ratios (contours) in modeled STS (left panel) and modeled NAT (right panel) are not compared with mixing ratio from SCIAMACHY but only PSC occurrence height (red lines) [Hommel et al., 2014]. SCIAMACHY observations are retrieved for the PSC altitude from Jan. 1 2011 to March 2011, and are identical in the left and right panels. The absence of contours at 15-16 km is missing data rather than values near zero of HNO$_3$ mixing ratio due to poor definition of the polar vortex below this level.
Figure 2.20 The simulated surface area density as a function of potential temperature and time. Panel (a) is the vortex average surface area for STS particles; Panel (b) is the maximum surface area for STS particles.
2.4.3 Ozone related chemicals

Ozone and its related chemicals are influenced by heterogeneous chemistry occurring on the surface of PSCs and of sulfate aerosols. These reactions depend both on reaction rates and on the surface area of the PSCs and sulfate aerosols.

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Figure 2.21 Evolution of PSC area coverage during the 2010-2011 Arctic winter from CALIPSO (top) and the model (bottom). The blank parts in the CALIPSO plot represent missing data.

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Figure 2.22 Evolution of vortex average mixing ratios of ozone-related chemicals at 475 K in base case and a case with -1.5 K adjustment in temperature for heterogeneous chemistry and PSC formation. H₂O and O₃ are in ppmv; HCl and ClONO₂ are in ppbv. The criteria for scaled potential vorticity for MLS data and its correspondent model
results is 0.00014; and for MIPAS data [Arnone et al., 2012] and its correspondent model results is 0.00017.

The evolution of the chemicals involved in ozone loss is another indicator that PSCs are properly simulated. Figure 2.22 shows the O$_3$, HCl, H$_2$O and ClONO$_2$ average volume mixing ratios inside the vortex from two slopeflat cases, which differ by the temperature assumed, compared with MLS and MIPAS data. We chose to examine the lower temperature case because [Brakebusch et al., 2013] found that important modeled reaction rates produced more realistic results with the lower temperature. Water vapor in our model is treated by the WACCM hydrological scheme. Water vapor mainly responds to the air temperature, but shows little difference between the two simulations. In the slopeflat case, the H$_2$O mixing ratio (green lines) from WACCM is within 5% of the MLS observations, which is within the uncertainty of the data. The HCl matches the observations at the beginning and the end of the season. However, the simulation is about 50% higher than the observations in January and February. One possible reason for this difference is that HCl is soluble in STS particles, which has not been considered in the growth process in our PSC model. A more likely reason is that the model does not have enough ClONO$_2$ at the beginning of the winter to react with HCl and deplete the HCl mixing ratio down to the observed levels [Brakebusch, 2013]. The model overestimates ozone at 475 K by about 25% at the end of the simulations, probably because of the temperature bias in the model.

Brakebusch et al. [2013] show that the -1.5 K bias can significantly influence the heterogeneous chemistry reaction rates, because the uptake reaction coefficients in liquid sulfuric acid aerosols and STS change rapidly at the STS formation temperatures [Shi et al., 2001; Lowe and MacKenzie, 2008]. The lower temperature case does show better performance on ozone and HCl, though it does more poorly on ClONO$_2$ as shown in Figure 2.22 right panel. As discussed previously, the -1.5 K case produces too much
denitrification (Figure 2.13), but that could be compensated by, for instance, reducing the sticking coefficient of HNO$_3$ on NAT to 0.2 (Figure 2.13).

2.5 Conclusions

STS and NAT particle microphysics have been added to the WACCM/CARMA sulfate model as an initial step towards building a complete PSC model. The model does not currently contain interactions between nitric acid and ice clouds. We posed three questions in the paper:

1. Can our model properly simulate the particle volume, size distribution, lidar backscatter, PSC composition and other data related to the fundamental properties of the clouds that are important for ozone loss?

2. Can our model properly simulate the denitrification during the Arctic winter 2010-2011?

3. Can our model properly simulate the evolution of ozone and the related chemicals controlling ozone over the 2010-2011 Arctic winter?

In order to address question 1, the microphysical characteristics of the simulated STS and NAT particles have been compared with available observations. The total volume of STS particles versus temperature, as well as the STS volume size distributions, closely resemble the observations (Figure 2.7 and Figure 2.8). The simulations often produce NAT particles with a radius bigger than 10 µm (Figure 2.9). Such large particles have been observed. The weight percent of HNO$_3$ in STS particles compares well with Carslaw’s equilibrium model indicating the STS particles respond to the environmental temperature very quickly relative to a WACCM time step of 30 min and generally remains close to equilibrium (Figure 2.5). However, evaporating clouds and other clouds with modest surface areas of a few µm$^2$/cm$^3$ are not able to maintain equilibrium (Figure 2.6).
The simulated height of PSCs is within a few kilometers of the height of PSCs observed by SCIAMACHY. The area of the vortex south of 82N that contains PSCs is similar to CALIPSO retrieved cloud coverage. The simulated cloud coverage shows an overestimate in late January relative to CALIPSO. The overestimation may be caused by different NAT definitions between the model and CALIPSO. Also CALIPSO cannot detect NAT particles with small surface areas.

In order to address question 2, we explored several nucleation rate expressions for NAT particles, which were constrained by the observed denitrification history for winter 2010-2011. The challenge in duplicating this history is that little denitrification occurred in December, but significant denitrification occurred in January, despite both periods having similar low temperatures at the altitude of the 475 K potential temperature surface, which is a common PSC formation altitude for this winter. The nucleation rate equations we considered were based on the NAT and NAD surface nucleation equations [Tabazadeh et al., 2002]. We find the nucleation rate is mainly dependent on the HNO$_3$ weight percent inside the STS particle rather than the temperature (note that HNO$_3$ weight percent is temperature dependent). The five nucleation rate expressions we considered have free energies within 10% of each other, but the nucleation rates vary by several orders of magnitude. The slopeflat case was the best scheme among those considered because the HNO$_3$ evolution in those simulations is the closest to MLS observations. We found that the denitrification is very sensitive to temperature variations at the 1.5 K level (Figure 2.13), which is within the errors of observed temperatures. When we apply a -1.5 K temperature bias in our model for heterogeneous chemistry and CARMA microphysics, the denitrification at all levels increases significantly because the temperature influences both the area of the vortex with STS particles and the NAT nucleation rate. Low temperatures could be somewhat compensated for using an uptake coefficient of 0.2, which slows the growth of the
particles once they have nucleated and reduces the denitrification. Changing the shape of NAT particles to flat plates or lowering density, which should reduce the fall velocity, does not slow down the denitrification as might be expected because the increased particle area leads to larger growth, larger particles, and faster sedimentation.

The slopeflat scheme is a slow nucleation scheme, which means the particles initially nucleated do not have enough surface area to quickly pull nitric acid away from STS. As a consequence, the individual NAT particles do not compete with each other for vapor and grow to roughly the same size independent of the nucleation rate. As a consequence the denitrification goes up when the nucleation rate increases. Another consequence of the low area is that considerable time is needed to transfer HNO$_3$ to the NAT. This slow growth, and even slower evaporation, of NAT results in STS clouds, with freshly nucleated NAT, being separated by large geographic distances from NAT clouds with similar mass mixing ratios as the original STS clouds. We find evidence that such NAT and STS clouds have independent locations in both simulations and in CALIPSO data (Figure 2.15 and Figure 2.16). CALIPSO does indicate more STS and NAT mixed clouds than the model does, but this is difficult to quantify because of lack of information about how to represent the backscatter by non-spherical NAT particles. While the masses of the STS and NAT clouds are similar, the NAT clouds have 10 to 100 times less surface areas making them less chemically reactive, and more difficult to detect optically, than STS clouds.

Our model simulates stratospheric sulfates as well as PSC particles. We find that at altitudes corresponding to 650 K potential temperature that few PSCs form, and the sulfate surface area is large enough to impact heterogeneous chemistry for nitric acid and push the values well above those observed. While there are no data on the sulfate surface areas, we believe our model is not realistic because the high SAD in our model around 650 K results in an excessive production of HNO$_3$ through the
heterogeneous chemistry compared with MLS and MIPAS observations. These results suggest both the potential importance of sulfate particles, and the need for models to do a better job simulating the stratospheric sulfur cycle.

The polar view of temporary and permanent denitrification in the slopeflat case is similar to MLS observations during three typical PSC formation days: Jan 03 at 26 hPa, Jan 26 at 36 hPa and Feb. 27 at 36 hPa (Figure 2.18).

We considered the 3rd question by simulations of ozone in the year 2010-2011. Our model underestimates the ozone depletion in March compared with MLS observation, which is probably due to a high temperature bias in the model. A sensitivity test with -1.5K adjustment [Brakebusch, 2013] improves the modeled O₃, which indicates a small temperature bias can significantly influence the heterogeneous chemistry reaction rates. The model also overestimates the HCl amount during January and February, which is probably because the model does not have enough ClONO₂ to react with HCl during these times. However, HCl is also better predicted with the 1.5 K temperature decrease.

There are a number of factors in our model that require improvement. The NAT nucleation is very sensitive to temperature, which makes it difficult to constrain microphysical parameters such as the nucleation rate and the sticking coefficient. The nucleation rate is so slow at relevant stratospheric temperatures that laboratory experiments to retrieve the nucleation rate are very difficult. Fewer than 1 in one thousand STS particles nucleate to form NAT. Our current model does not produce submicron NAT particles. We are currently ignoring mountain wave clouds as well as gravity waves. Gravity waves will produce thermal oscillations, which may trigger some NAT formation in STS clouds [Tsias et al., 1997]. Mountain waves are very important over the Scandinavian Peninsula [Alexander et al., 2013]. We believe our model picks up the longest wavelength waves, which respond to the entire mountain range, but there
are many smaller, higher amplitude temperature changes. These likely lead to the formation of some smaller NAT particles. We also do not include the interaction of nitric acid with water ice clouds. Submicron-sized NAT particles with large number density may be released as the ice evaporates [Höpfner et al., 2006b]. Heterogeneous nuclei [Hoyle et al., 2013; Grooß et al., 2014] might be required for NAT nucleation, and stratospheric sulfates commonly contain micrometeorites. However, fully evaluating the possible impact of heterogeneous nuclei requires tracking the evolution of the nuclei, which has not yet been done.

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Chapter 3
Comparing simulated PSC optical properties with CALIPSO observations

The CALIPSO satellite is an important source of high-resolution PSC observations. The CALIOP (A-train Cloud-Aerosol Lidar with Orthogonal Polarization) lidar on CALIPSO [Winker et al., 2007, 2009] detects PSCs by measuring backscatter and depolarization. In this paper, we use the CALIPSO Lidar Level 2 Polar Stratospheric Cloud (PSC) data product, which includes perpendicular backscatter coefficient, total backscattering ratio, and particulate depolarization ratio along CALIPSO orbit tracks. These data are used by the CALIPSO team to infer PSC composition.

The visible wavelength backscattering ratio ($R_{532}$) is defined as the total (both polarizations) volume backscattering coefficient ($\beta_{\text{particle}} + \beta_m$) at 532 nm divided by the molecular backscatter coefficient ($\beta_m$) at 532 nm. The particulate depolarization ratio is the ratio of the perpendicular to the parallel polarization components of the particulate backscatter coefficient at 532 nm. The particulate depolarization is calculated by subtracting the molecular influence from the total depolarization ratio [Lambert et al., 2012]:

$$\delta_{532}^{\text{particle}} = \frac{\beta_{\text{TOT},\perp} - \beta_{m,\perp}}{\beta_{\text{TOT},\parallel} - \beta_{m,\parallel}} = \frac{R_{532,\perp} - 1}{R_{532,\parallel} - 1} \delta_m$$

Where $\delta_m$ is the molecular depolarization given by Hostetler et al. [2006] as 0.00366. The total perpendicular backscatter coefficient is the particulate plus the molecular perpendicular backscatter.
Pitts et al. [2009] use the values of backscattering ratio and particulate depolarization to derive a scheme to determine PSC composition. Here, I compare the PSC composition derived from the CALIPSO classification algorithm with the PSC composition in our simulations used to compute the optical properties observed by CALIPSO.

### 3.1 CALIPSO detection and classification of PSCs

Pitts et al. [2009] describe CALIPSO’s PSC composition detection and classification algorithm. The first step in the algorithm is to eliminate measurements that are too close to the noise limits to consider. For the 450–550K potential temperature altitude level, the typical PSC detection threshold of the backscattering ratio is 2.60, 1.82, 1.51, and 1.32 for horizontal smoothing scales of 5, 15, 45, and 135 km. If CALIPSO finds its signal below the noise level for a high spatial resolution, it will average to a larger spatial domain, up to the 135 km limit, to obtain a measurable signal. The typical PSC detection threshold of the perpendicular backscatter coefficient is $3.62 \times 10^{-6}$ km$^{-1}$ sr$^{-1}$, $3.53 \times 10^{-6}$ km$^{-1}$ sr$^{-1}$, and $3.28 \times 10^{-6}$ km$^{-1}$ sr$^{-1}$ for smoothing scales of 15, 45, and 135 km. The detection algorithm doesn’t use the perpendicular backscatter coefficient at 5 km horizontal resolution due to high noise. Noise not only eliminates some data points from consideration, it also spreads the values of the points that are measured as discussed below.

In formulating the CALIPSO classification product, assumptions were made about the abundances of condensable species that are present. 10 ppbv of nitric acid, 5 ppmv of water and 10 cm$^{-3}$ of total PSC number density were assumed at 50 hPa. These choices produce well-defined separations for STS, NAT and ice in theoretical calculations of the lidar properties that are measured. However, in our simulations and in reality, denitrification and dehydration yield a range of values for these abundances, and the actual concentrations vary with altitude even when the mixing ratios are fixed.
We find this variation in the amount of material present, as well as noise, produces a considerable spread in the values of the backscatter and depolarization, which mixes particle compositions across the possible choices.

The CALIPSO PSC classification algorithm devised by Pitts et al. [2009] has 6 regions of the space in inverse backscatter ratio versus depolarization plots. An example is shown in Figure 3.1.

![CALIPSO PSC classification](image)

Figure 3.1 The CALIPSO classification for PSC compositions.

STS, the only liquid PSC, is assumed to have depolarization upper boundary of 0.035 and a backscatter ratio in the range $0.8 > 1/R_{532} > 0.4$ and decrease linearly to 0.03 in the backscatter ratio range of $0.3 > 1/R_{532} > 0.2$, and then in range where depolarization decreases monotonically to a value near 0.005 for backscatter values $0.05 > 1/R_{532} > 0$. This definition follows a probability distribution function approach according to the CALIPSO cloud-aerosol discrimination algorithm [Liu et al., 2004]. It is well known that this definition for STS is not unique, as discussed further below,
because NAT can be present with an undetectable depolarization at the visible wavelengths used by CALIPSO. Pitts et al. [2009] define three classes for NAT/STS mixtures in which the depolarization of the NAT is evident at visible wavelengths. Mix1 is STS mixed with NAT that is not strongly backscattering; Mix2 is STS mixed with NAT that is strongly backscattering; Mix2-enhanced is a subset of Mix2 clouds, in which NAT has sufficient number density (\(n > 0.1 \text{ cm}^{-3}\)), and therefore small size, to be very highly backscattering. The boundary between Mix1 and Mix2 uses an empirical curve assuming a NAT number density of \(10^{-3} \text{ cm}^{-3}\) and effective radius of 7 \(\mu\text{m}\). In addition, Mix1 includes all the particles when \(1/R_{532} > 0.1\). The enhanced NAT region is defined by \(0.5 < 1/R_{532} < 0.2\) and depolarization ratio above 0.1.

Three sources of misclassification have been identified. PSCs are sometimes misclassified due to noise, especially the particles near the boundary between two classes [Pitts et al., 2009, 2013]. We add noise to our computed values of backscatter and depolarization to better compare with the CALIPSO data. Another source of misclassification is that lidars with visible wavelength depolarization are known to misclassify NAT in a large fraction of clouds that contain STS. This detection issue was first reported by Brown et al. [1990], who often were able to detect NAT using near-infrared depolarization measurements, but not visible depolarization measurements. Toon et al. [2000] explained this observational problem by noting that the STS particles have high backscatter per unit mass while the NAT particles have low backscatter per unit mass.
comparable masses of NAT and STS particles can yield a visible depolarization signal that is close enough to zero to be compatible to be STS clouds. However, the strong decline in the backscatter with wavelength for the small STS particles, but not the larger NAT particles allows the NAT to be optically more important at infrared wavelengths. Therefore, it would not be surprising if many of the clouds that CALIPSO identifies as STS, in fact also contain large NAT particles in addition to STS. Pitts et al., [2013] discuss the misclassification of ice particles into the Mix2 category due to denitrification from 10ppbv to 5 ppbv. The denitrification limits the formation of STS and produces a lower backscattering ratio for STS compared with STS growing from a reservoir of 10ppbv. Therefore, the STS/ice mixtures shift to the lower backscattering area where Mix2 is located.

3.2 PSC optical properties retrieved from the model

The simulations are made using the PSC model based on the SD-WACCM model (the Whole-Atmosphere Community Climate Model [Garcia et al., 2007] with Specified Dynamics (SD-WACCM-4.0)) coupled with CARMA (The Community Aerosol and Radiation Model for Atmospheres) [Toon et al., 1988; Bardeen et al., 2013]. The model details are the same as described in [Zhu et al., 2015, Chapter 1]. The simulation discussed here covers the period from May to September 2010.

In order to compare the simulated PSC properties with data from CALIPSO, we calculate the total backscattering ratio, the perpendicular backscatter coefficient and particulate depolarization ratio of STS, NAT and ice particles. Our grids are very large, about 2° in latitude. Our simulations assume that each type of cloud (STS, NAT or ice) is spread uniformly over the grid cell and is mixed with the other types of clouds. In reality there may be ice clouds in part of a grid cell, and STS or NAT clouds in another part. CALIPSO high-resolution data would distinguish the individual clouds.
In the model, we calculate the perpendicular backscatter coefficient \( \beta_{\text{particle}+m,\bot} \), backscattering ratio \( R_{532}^{\text{STS}} \) and particulate depolarization \( \delta_{532} \) of STS, NAT, and ice. We also combine these clouds into Type I (STS+NAT), ice/STS mixture and total PSCs. The total PSCs represent the clouds that CALIPSO data smoothed into 135 km resolution might report in which any individual clouds are homogenized over the larger spatial grid. The other calculations are useful for understanding the components of the observations, and for an alternative method of compiling statistics of cloud types. The definitions we use are:

\[
\beta_{\text{particle}+m,\bot} = \beta_{\text{NAT},\bot} + \beta_{\text{ICE},\bot} + \beta_{m,\bot}
\]

\[
R_{532}^{\text{STS}} = 1 + \frac{\beta_{\text{STS}}}{\beta_m} = \frac{\beta_{\text{STS}} + \beta_m}{\beta_m}
\]

\[
R_{532}^{\text{NAT}} = 1 + \frac{\beta_{\text{NAT}}}{\beta_m} = \frac{\beta_{\text{NAT},\bot} + \beta_{\text{NAT},\|} + \beta_m}{\beta_m}
\]

\[
R_{532}^{\text{ICE}} = 1 + \frac{\beta_{\text{ICE}}}{\beta_m} = \frac{\beta_{\text{ICE},\bot} + \beta_{\text{ICE},\|} + \beta_m}{\beta_m}
\]

\[
R_{532}^{\text{Type}} = 1 + \frac{\beta_{\text{NAT}}}{\beta_m} + \frac{\beta_{\text{STS}}}{\beta_m} = \frac{\beta_{\text{NAT},\bot} + \beta_{\text{NAT},\|} + \beta_{\text{STS}} + \beta_m}{\beta_m}
\]

\[
R_{532}^{\text{ICE/STS}} = 1 + \frac{\beta_{\text{ICE}}}{\beta_m} + \frac{\beta_{\text{STS}}}{\beta_m} = \frac{\beta_{\text{ICE},\bot} + \beta_{\text{ICE},\|} + \beta_{\text{STS}} + \beta_m}{\beta_m}
\]

\[
R_{532}^{\text{TOT}} = 1 + \frac{\beta_{\text{STS}}}{\beta_m} + \frac{\beta_{\text{NAT}}}{\beta_m} + \frac{\beta_{\text{ICE}}}{\beta_m} = \frac{\beta_{\text{STS}} + \beta_{\text{NAT},\bot} + \beta_{\text{NAT},\|} + \beta_{\text{ICE},\bot} + \beta_{\text{ICE},\|} + \beta_m}{\beta_m}
\]

\[
\delta_{532}^{\text{NAT}} = \frac{\beta_{\text{NAT},\bot}}{\beta_{\text{NAT},\|}}
\]

\[
\delta_{532}^{\text{ICE}} = \frac{\beta_{\text{ICE},\bot}}{\beta_{\text{ICE},\|}}
\]

\[
\delta_{532}^{\text{Type}} = \frac{\beta_{\text{NAT},\bot}}{\beta_{\text{STS}} + \beta_{\text{NAT},\|}}
\]

\[
\delta_{532}^{\text{ICE/STS}} = \frac{\beta_{\text{ICE},\bot}}{\beta_{\text{STS}} + \beta_{\text{ICE},\|}}
\]

\[
\delta_{532}^{\text{TOT}} = \frac{\beta_{\text{NAT},\bot} + \beta_{\text{ICE},\bot}}{\beta_{\text{STS}} + \beta_{\text{NAT},\|} + \beta_{\text{ICE},\|}}
\]
Where, the molecular perpendicular backscatter coefficient is:

\[ \beta_{m,\perp} = \beta_m \cdot \delta_m / (1 + \delta_m) \]

We calculate the backscattering coefficient for STS, the perpendicular and parallel backscattering coefficient for ice and NAT using a T-matrix approach [Mishchenko and Travis, 1998]. We use real refractive indices of 1.43 for STS, 1.50 for NAT, and 1.308 for ice with imaginary parts of the refractive index of 0.0. We assume NAT to be spheroids with an aspect ratio of 0.9, ice particles to be spheroids with an aspect ratio of 0.95, and STS to be spherical. From the T matrix code, we are able to obtain the backscatter cross-section (backscatter coefficient over the number density) and depolarization \( \delta_{\perp}^{\text{NAT}} = \frac{\beta_{\text{NAT},\perp}}{\beta_{\text{NAT}}} \) and \( \delta_{\parallel}^{\text{ICE}} = \frac{\beta_{\text{ICE},\parallel}}{\beta_{\text{ICE}}} \) as a function of radius. Note that the backscatter cross-section calculated in Mishchenko and Travis [1998]'s code equals to \( \pi r^2 \) times the backscatter gain [Pinnick et al., 1980]. Therefore, we divide it by \( 4\pi \) to obtain the backscatter cross-section we describe in this paper.

For STS and NAT, the model provides the size distribution information needed for the optical calculations. However, our model only tracks the ice mass. In order to compute the backscatter due to ice clouds we assume that the number of ice particles is equal to 1% or 10% of the number of STS particles in the grid cell. This is equivalent to assuming that 1% or 10% of STS particles nucleated to form an ice particle when an ice cloud forms. For example, if 2 ppmm of water condenses to form ice at 50 hPa, and 10 cm\(^3\) STS particles are present, then the typical size of an ice particle will be 6.8 µm if the number density of ice is equivalent to 1% of STS. Observations of ice particles in wave clouds suggest they are smaller than 3µm [Höpfner et al., 2006a], indicating a larger fraction of the STS particles nucleate to form ice in wave clouds. However, my model cannot resolve wave clouds, so I neglect this possibility in our calculations.
Figure 3.2 Depolarization for NAT and ice particle as a function of particle radius from T matrix code (blue lines) and the model (green dots) in July 2010.

We compare the compositions used in our simulations with those derived from the CALIPSO algorithm below. However, there are several hazards in this comparison. It is helpful to understand how depolarization and 1/R532 depend on cloud mass and cloud particle size to understand these hazards.

Figure 3.2 shows the depolarization as a function of radius for NAT and ice particles with particular choices for particle shape. Depolarization represents one axis of the graphs used to define PSC composition and Figure 3.2 is meant to help understand how the values on this axis depend on particle size. Depolarization is also affected by mixing various types of particles. The blue lines are directly from the T-matrix code. The green dots are the NAT depolarization for the size distribution or ice depolarization retrieved from model output for simulations of PSCs in the Antarctic in July 2010. The equation for NAT depolarization averaging over the size bin is: (Here, I only show the depolarization rather than depolarization ratio. The depolarization ratio is influenced by parallel terms from STS and ice.)

$$\delta_{532,\text{avg}}^{\text{NAT}} = \frac{\sum_{i=0}^{N_{\text{bin}}} \delta_{532,i,\text{bin}}^{\text{NAT}} N_{i,\text{bin}}^{\text{NAT}}}{\sum_{i=0}^{N_{\text{total}}} N_{i,\text{bin}}^{\text{NAT}}} \cdot \frac{\sum_{i=0}^{N_{\text{bin}}} N_{i,\text{bin}}^{\text{NAT}}}{\sum_{i=0}^{N_{\text{total}}} N_{i,\text{bin}}^{\text{NAT}}} \cdot \beta_{\text{NAT},\perp,\text{bin}}$$

Where, $N$ is the number density of NAT.
From the model, the NAT radius is mainly above 1 µm and the NAT depolarization varies from 0 to 0.5. The modeled values for NAT are spread relative to the T-Matrix calculation because there is a size distribution of particles. The effective radius is used as the relevant radius in Figure 3.2. The ice depolarization varies rapidly from 0.3 to 0.8 around 2 µm. The ice is mono-disperse in our simulations, so its depolarization matches that of the T-Matrix calculation.

Figure 3.3 1/R_{532} for each PSC types as a function of particle effective radius. The green dots are from the same data as shown in Figure 3.2. The purple dots are two test cases with 100 times greater nucleation rates than the green dots for NAT (middle panel) and 10 times the ice number density as the green dots (right panel). The blue lines are from the T matrix code assuming 10ppbm for STS and NAT, 1ppmm for ice. The hatched regions represent an estimate of the particles classified in Mix2 (dots, middle panel), Mix2-enhanced (stripe, middle panel) and ice (dots, right panel).

Figure 3.3 shows 1/R_{532} as a function of particle effective radius. 1/R_{532} is the abscissa of the plot used by CALIPSO to determine PSC composition. The hatching areas are estimates of CALIPSO classification ranges: Mix2 (dots, middle panel), Mix2-enhanced (stripe, middle panel) and ice (dots, right panel). These estimates are based on the classification in Figure 3.1 and the depolarization variation as a function of radius in Figure 3.2. The green dots are the results derived from the model in July at 52 hPa. The purple dots are two model test cases in order to get higher backscattering ratio. The one in the middle panel increases the NAT nucleation rate by 100, yielding about 10 times as many particles as the case shown with green dots. The one in the right panel increases the ice number density by 10 (assuming ice number density is equivalent to
10% of STS number density). In the third part of this chapter, we will further discuss how these two test cases influence the classification histogram. The blue lines are the results from T-matrix code, assuming a fixed condensed mass mixing ratio of 10 ppbm for STS, 10 ppbm for NAT, and 2 ppmm for ice. The backscatter varies with radius, because the extinction varies with radius (for fixed mass the extinction drops linearly with radius as the size increases for fixed mass and particles larger than about 1 \( \mu \)m), and the backscatter part of the phase function varies with the radius. The particle density is assumed to be 1.5 g/cm\(^3\) for STS, 1.62 g/cm\(^3\) for NAT and 0.92 g/cm\(^3\) for ice.

Figure 3.3 shows that as the effective radius of STS varies from 0.1 \( \mu \)m to 0.4 \( \mu \)m in the model that the backscatter ratio increases (1/R\(_{532}\) decreases). STS usually has a number density \( \sim 10 \) cm\(^{-3}\), which is fixed by the number of sulfuric acid particles in the stratosphere. As the size of STS particles increases in response to declining temperature and or increasing environmental gas amount the backscatter increases due to the rising mass. In the blue line the condensed mass is fixed, so that as the size increases the number of particles decreases.

In our model, most of the NAT clouds have about the same number density of particles, because the nucleation rate equations do not produce high nucleation rates. Therefore, smaller NAT particles reflect less condensed mass. For this reason, the green points in Figure 3.3 deviate lie above the blue line, for which the number of particles must go down as the size increases to conserve mass. It is possible that in nature, processes not included in our model will produce NAT clouds with larger numbers of small NAT particles. In that case nature may follow the blue line, rather than the green one that our model follows. Most of the NAT particles in Figure 3.3 from the model results have mass mixing ratio less than 10 ppbm (green dots that area above the blue line). When we increase the nucleation ratio by 100 (shown as purple dots), the radius of the particles decreases compared with green dots. We obtain more particles identified in
Mix2 and with higher mass mixing ratio (below the blue line). However, NAT is usually mixed with STS in the real atmosphere. NAT may have a large radius and small number density, but mixed NAT/STS clouds will have a low value of $1/R_{532}$ because STS provides significant backscattering.

The modeled ice in Figure 3.3 also has a constant number density of particles, again causing the green points to deviate from the blue line. Clouds with smaller sized ice crystals simply have less mass, and therefore a $1/R_{532}$ value that is close to 1. When the number density of ice increases by 10 times, more clouds fall into the ice region of the diagram with smaller particle radius but higher backscattering ratio. There are two conclusions we draw from the ice simulations in Figure 3.3. First there are likely many clouds being produced in nature with small radii, but high particle number densities, and significant amounts of mass. Such clouds will have $1/R_{532}$ values in the ice range. However, especially as dehydration proceeds, there will be ice clouds with low masses. These clouds will produce $1/R_{532}$ values that fall into the various Mix states that the CALIPSO algorithm attributes to NAT, as suggested by [Pitts et al., 2013].

An additional complication in using the CALIPSO algorithm to compare PSC composition with our simulations is that the CALIPSO instrument has noise, which the model does not have. Here, we compute the noise following Engel et al. [2013]. The backscatter coefficients (both perpendicular and parallel) with noise are estimated by picking a random number from a normal distribution with a defined expectation and standard deviation. The expectation is the same as the simulated backscatter coefficient without noise. The standard deviation (uncertainty) is estimated using the equations as follows:

$$
\sigma(\beta) = \frac{1}{75} \sqrt{\beta \left(2.39 \times 10^{-8} m^{-1} sr^{-1} \times \frac{1500 km}{\Delta_{horizontal}} \times \frac{5 km}{\Delta_{vertical}}\right)}
$$
Where, $\beta$ is either perpendicular or parallel backscatter coefficient, $\Delta_{\text{horizontal}}$ is the horizontal averaging distance, which we assume is 135 km. $\Delta_{\text{vertical}}$ is the vertical averaging distance which is 180 m in CALIPSO. The noise is calculated for each of the four components of the total backscatter coefficient.

$$\beta_{\text{TOT,\perp}} = \beta_{\text{NAT,\perp}} + \beta_{\text{ICE,\perp}} + \beta_{m,\perp}$$

$$\beta_{\text{TOT,\parallel}} = \beta_{\text{NAT,\parallel}} + \beta_{\text{STS}} + \beta_{\text{ICE,\parallel}} + \beta_{m,\parallel}$$

### 3.3 A comparison of PSC compositions determined from simulations and from CALIPSO data

As mentioned previously, a complication in comparing the CALIPSO data with the simulations is that some of the clouds observed by CALIPSO might be smaller than a model grid cell. Cloud mass does not impact the depolarization, but it does impact the backscatter ratio. If a cloud is smaller than the grid cell, its mass concentration will be higher than the grid cell average, the backscatter will be higher than the grid cell average, and the points on the depolarization ratio versus $1/R_{532}$ plot will move to the right toward lower values of $1/R_{532}$. 
Figure 3.4 The depolarization ratio versus $1/R_{532}$ at 18.7 km (52 hPa) in July 2010. Panel a is the CALIPSO defined STS in red, Mix1 in purple, Mix2 in green, Mix2-enhanced in dark green and ice in blue [Pitts et al., 2009]. Panel b is the modeled PSC types individually with STS in red, NAT in purple and ice in blue. Panel c is panel b with noise. Panel d and e are the modeled Type I and STS/ice mixture. The red color is the particles with $R_{532}>1.32$ and perpendicular backscatter coefficient $<3.28\times10^{-6} \text{ km}^{-1}\text{sr}^{-1}$. The purple color in panel c and the blue color in panel d is the points with perpendicular backscatter coefficient $>3.28\times10^{-6} \text{ km}^{-1}\text{sr}^{-1}$. Panel f shows the total PSCs with noise. The colors represent the same thresholds as defined in panel a.

Figure 3.4 shows the depolarization ratio and $1/R_{532}$ from a simulation at 52 hPa and from CALIPSO data at 18.7 km in July 2010. The simulation assumes that the number density of ice is 1% of STS, and that the aspect ratio is 0.9 for NAT and 0.95 for ice. Panel a shows the CALIPSO observations with STS in red, Mix1 in purple, Mix2 in green, Mix2-enhanced in dark green and ice clouds in blue. Panel b and c display the modeled optical properties for STS (red), NAT (purple) and ice clouds (blue) individually without and with noise. Clearly adding noise spreads the points across the histogram, creating points at higher (and lower) depolarization, as well as creating a wide range of backscatter values.
CALIPSO has much higher resolution along the track than the model. Panel c might be most relevant for comparison to CALIPSO data if the clouds were in fact separated in space within each grid cell. Panel c clearly illustrates where different types of clouds occur on this type of graph. Most notable is that the points CALIPSO attributes to Mix2 and Mix2-enhanced mixtures of STS and NAT are ice clouds in our model. Of course, our model may not be correctly representing the clouds, so that the CALIPSO interpretation may be correct. However, our model shows the CALIPSO interpretation is not unique, and water ice clouds could be responsible for many of the observations that CALIPSO assigns to NAT. From the middle to the end of the season, especially in the Antarctic, the polar stratosphere is often dehydrated from ~5ppmv to ~2ppmv by the ice particles in the coldest regions, which inhibits the formation of STS particles in those dehydrated areas. Also, the ice clouds uptake the H₂O and reduce the amount to water vapor for STS formation. Figure 3.5 (top panel) shows the STS radii changing with temperature under different water vapor assumptions. STS is calculated using 10ppbv of HNO₃ and 5 or 2 ppmv of H₂O at 50 hPa by the equilibrium model [Carslaw et al., 1995] assuming no solid phase formed. With 5 ppmv of water vapor, STS starts to grow significantly at 191 K; while under the dehydrated condition, the STS particles don’t add significant mass until 188K. If the atmosphere is also denitrified, there is even less STS. The bottom panel shows the depolarization ratio versus 1/R₅₃₂ of ice/STS mixtures with different assumptions of ice radii (r =1, 7 µm) and ice number density (nd = 0.01, 0.1, 1 cm⁻³). Here, the STS backscattering coefficient uses the radii in the top panel and the number density of 10 cm⁻³. The red color represents the case with 5ppmv of water vapor; the blue color represents the dehydrated atmosphere with 2ppmv of water vapor. For each case, we calculate the optical properties for 4 different temperatures: 185K, 186K, 187K and 188K. When the water vapor is 5ppmv, most of the points are within the area with 1/R₅₃₂<0.2. However, under the dehydrated condition,
the $1/R_{532}$ is often higher than 0.2, except the case with ice number density of 1 cm$^{-3}$. Also, the depolarization ratio of the dehydrated case is generally higher than the non-dehydrated case.

Figure 3.5 The top panel shows the STS radii variation as a function of temperature under two different water vapor assumption (5ppmv or 2 ppmv) calculated from the equilibrium model [Carslaw et al., 1995]. The HNO$_3$ is assumed to be 10 ppbv. The bottom panel shows the depolarization ratio versus $1/R_{532}$ for STS/ice mixture. The backscatter of STS is calculated using the radius in the first panel. The backscatter of ice is calculated with various radii (1.7 µm) and various number densities (0.01, 0.1, 1 cm$^{-3}$). For each scenario, the optical properties are calculate for 4 different temperatures: 185K, 186K, 187K and 188K.

Figure 3.4d illustrates the optical properties of STS and NAT clouds assuming ice is not present. As can be seen, the STS reduces the mixed cloud depolarization, but
moves the value of $1/R_{532}$ to the right (lower values) compared with Figure 3.4b. Figure 3.4e shows that if STS is mixed with ice clouds, the highest depolarization points are reduced relative to Figure 3.4b, but many points in the STS domain are eliminated relative to panel b.

Figure 3.4f shows the same simulation from which the optical properties are computed in Figure 3.4c, but now assuming all of the types of particles are present over the entire grid cell, and adding experimental noise. In this case one cannot simply identify a composition attached to one point, since several different types of particles are present in each location. Nevertheless, comparison of panel c and f shows that ice dominates much of the regions attributed to ice, Mix2 or Mix2-enhanced by the CALIPSO algorithm.

In Figure 3.4c and f, NAT clouds are mainly located in the Mix1 cloud area. The homogeneous nucleation scheme in our model generates NAT with number densities around $10^{-3} \sim 10^{-4}$ cm$^{-3}$ [Zhu et al., 2015, Chapter 1]. It is possible that additional NAT nucleation mechanisms, such as by evaporation from ice clouds, might produce higher number density NAT clouds with smaller sizes. As illustrated in Figure 3.3 this type of NAT with radius smaller than $\sim 6$ µm might spread some points into the Mix2 region and with radius smaller than $\sim 1$ µm might contribute to Mix2-enhanced region. For STS/NAT mixtures, the NAT radius must be even lower to be in Mix2 or Mix2-enhanced regions. However, in our current simulations, the points in Mix2 region are mainly caused by ice.

Ice clouds dominate the enhanced-NAT and ice areas panel c and f. Also, the presence of ice mixed with STS pulls the mixture to non-zero depolarization leaving less STS in the area with low depolarization ratio. Understanding the properties of Antarctic ice clouds better is critical to improving simulations of the CALIPSO data.
Ice clouds are not as common in the Arctic as in the Antarctic. Figure 3.5 illustrates the CALIPSO optical data from December-February of the 2010-2011 Arctic winter at 18.7 km (~52 hPa). As can be seen there are fewer ice points, and fewer Mix2 or Mix2-enhanced NAT points in the Arctic relative to the Antarctic, especially points with the high depolarization ratio and high backscattering ratio.

Figure 3.6 CALIPSO observation of PSCs in 2010-2011 Arctic winter at 18.7 km. The colors represent the same classification as in Figure 3.4a.

Figure 3.7 and Figure 3.8 show the occurrence of each PSC type in the CALIPSO algorithm in the Arctic 2010-2011 winter and the Antarctic winter from June-August, 2011 at 18.7 km (~52 hPa). The map has been divided into 84 of 4°×30° grid box from latitude 82° to 54° and longitude -180° to 180°. The occurrence represents the times that each type of PSCs appears in a grid box in a month. The locations with the highest occurrences of Mix2-enhanced are also the places with high occurrences of ice clouds. This coincidence suggests ice clouds may be misclassified into the Mix2-enhanced category. However, it is also possible that those Mix2-enhanced particles are released from ice particles due to the evaporation.
Figure 3.7 Arctic 2010-2011 PSC occurrence in each map grid box. The maps are divided into 4°×30° grid box from latitude 82° to 54° and longitude -180° to 180°.

Figure 3.8 Antarctic 2010 PSC occurrence.
In the simulations just described, ice particles have the majority of optical data points in the enhanced Mix2 area, but some points lie in the ice, Mix1 and Mix2 regions of Figure 3.4a. This result can be modified if we assume a different fraction of STS particles nucleate to form ice than the 1% taken in Figure 3.4b. Figure 3.9a illustrates a simulation assuming the ice number density equals to 10% of the STS number density. In this case more ice points lie in the ice domain of Figure 3.9a than in Figure 3.4a. Unfortunately, there are no constraints on the number of ice particles that nucleate, and it is likely to be highly variable because it may depend on the cooling rate as it does for cirrus cloud formation [Jensen and Toon, 1994].

In Figure 3.4b and d, the NAT particles are mainly located in the Mix1 area. Figure 3.9b illustrates a test assuming the nucleation rate of NAT is 100 times larger that assumed in Figure 3.4. In this case more NAT particles are found in the Mix2 area but we still have no NAT appearing in Mix2-enhanced area. Producing more NAT particles results in fewer particles that are identified as STS. One of the reasons for the reduction in STS is that more NAT particles exist within the STS clouds increasing the depolarization for that area. Also, when more NAT particles exist, they pull the HNO$_3$ from the STS particles because the vapor pressure is lower over NAT particles, causing the STS to evaporate.

In order to make a better comparison with the CALIPSO observations, the model needs to include a microphysical model for ice that includes release of NAT from evaporating ice.
Figure 3.9 The depolarization ratio versus $1/R_{532}$ from two model cases with each PSC type plotted individually. Panel a is the simulated PSC types individually when ice number is 10% of STS number density. Panel b is the simulated PSC types individually with nucleation rate of slopeflat*100.

The frequency of occurrence of different types of clouds is another interesting metric for comparing simulations and observations. Table 3 provides a quantitative comparison between CALIPSO observations and modeled PSCs by counting the PSC occurrence along the A-train orbit in 2010 from May to September. The model resolution is 1.9×2.5 degree, which is about 200 km in latitude. This resolution is much coarser than the CALIPSO resolution along the orbit, which can be as high as 5km. CALIPSO may take 40 measurements in a model grid box and show 5 points of STS, 10 points of Mix1 or 2, 15 points of ice, and 10 points with no PSC. The simulated PSCs may have STS, NAT and ice in one grid box. We can either distinguish it as one type of mixed clouds, or distinguish 3 types of clouds in one grid box with each type sharing a third of the grid. CALIPSO only observes PSCs during the dark, so sunlight points are eliminated from the simulations.

We count the number of the total observations and the number of PSC occurrences for each month from May to September 2010 for CALIPSO and the simulation illustrated in Figure 3.4. Table 3 shows the percentage of PSC occurrence in each month and total percentage from CALIPSO and the simulation. We count the
model results in two different ways: count each PSC type individually and if they appear in the same grid, they share half or a third of the grid. In this way, STS, NAT and ice are not mixed together. The identification for each type is not dependent on their backscattering ratio and depolarization ratio because their types are known. To be clear, the STS category is pure STS, the Mix1 category is pure NAT (because the model only sees NAT in Mix1 as we discussed before), and the ice category is pure ice. The thresholds are still applied: the backscattering ratio of 1.32 for STS, the perpendicular backscatter coefficient of $3.28 \times 10^{-6}$ km$^{-1}$sr$^{-1}$ for NAT and ice. This method eliminates some particles that count as PSCs if they mix together. Another way of counting the cloud types is to calculate the total depolarization and backscattering ratio and count the total PSC occurrence. Note that in this case composition refers only to the optical points that appear in region of the depolarization versus inverse backscatter ratio. This way may misclassify the types as we discussed before. The simulations show a somewhat higher percentage of PSCs than CALIPSO, especially in the June and July. The model likely sees a higher frequency of clouds because if cloud is present anywhere in the grid cell it is counted as cloudy, whereas CALIPSO would count PSC free areas.

Figure 3.9 shows the percentage of each PSC composition contributing to the PSC occurrence. The upper left panel is the CALIPSO composition distribution. The upper right panel is the simulation shown in Figure 3.4c that counts each type individually. The bottom left panel is the simulation in Figure 3.4f that counts the total PSC occurrence. The bottom right panel is a test case in which we don’t count the ice particles if the mass mixing ratio of ice is lower than 0.8 ppm.

When the PSC types are counted individually, upper right panel, the ice particles dominate the percentage from June to September and STS dominates in May. When the total PSCs are counted, Mix2+Mix2-enhanced is dominating because ice particles in the model are often classified into Mix2+Mix2-enhanced category as shown in Figure 3.4.
Because of large contribution of ice clouds, we conduct another model case (model case 4), which we don’t count the backscattering ratio and the depolarization if the mass mixing ratio of ice is lower than 0.8 ppmm. For this case, we find a PSC occurrence percentage (in Table 3) and the percentage of each PSC types contributing to PSC occurrence (in Figure 3.9, bottom right panel). As we eliminate some ice particles, the percentage of total PSCs has been reduced to 12%, which agrees better with the CALIPSO PSC frequency in each month except August. Figure 3.9 bottom right panel shows the STS frequency agrees with the observation better than in the other cases. However, Mix1 has a higher percentage than the observation, possibly indicating some of NAT/STS mixture should have smaller NAT particles so that points shift to Mix2 category.

Table 3 The PSC occurrence percentage from the CALIPSO observation in 2010 Antarctic winter and the model case 1 and model case 4 at 52 hPa.

<table>
<thead>
<tr>
<th></th>
<th>May</th>
<th>Jun</th>
<th>Jul</th>
<th>Aug</th>
<th>Sep</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>CALIPSO</td>
<td>4.63%</td>
<td>26.06%</td>
<td>20.89%</td>
<td>13.57%</td>
<td>3.02%</td>
<td>14.51%</td>
</tr>
<tr>
<td>Model Individually</td>
<td>2.83%</td>
<td>27.07%</td>
<td>32.18%</td>
<td>18.10%</td>
<td>2.73%</td>
<td>17.65%</td>
</tr>
<tr>
<td>Model Total</td>
<td>3.49%</td>
<td>33.49%</td>
<td>35.57%</td>
<td>18.91%</td>
<td>3.29%</td>
<td>20.27%</td>
</tr>
<tr>
<td>Model Total eliminate ice</td>
<td>3.46%</td>
<td>25.61%</td>
<td>17.51%</td>
<td>6.4%</td>
<td>1.5%</td>
<td>11.97%</td>
</tr>
</tbody>
</table>
Figure 3.10 The percentage of each PSC types contributing to PSC occurrence at 52 hPa for each month in Antarctic 2010. The top left panel is CALIPSO composition \cite{Pitts et al., 2009}. The other panels are the modeled results with different counting method described in the content.

### 3.4 Conclusions

This work is focused on the comparison of optical properties between simulations and CALIPSO data in the Antarctic winter of 2010. The work suggests several possibilities to improve the microphysics processes in the PSC model and the CALIPSO classification algorithm.

Currently, the PSC model in WACCM/CARMA contains detailed microphysics processes for STS and NAT growth, evaporation and sedimentation, as well as a homogenous nucleation of NAT from STS particles. The model also tracks the size and number information for STS and NAT particles every 30 minutes. However, the prognostic $H_2O$ routines in WACCM only provide the mass of ice particles and the model also lacks interaction between ice and Type I PSCs. The exploration in this work proves the necessity to improve the ice PSC package in the model when we simulate the Antarctic PSCs.
The depolarization ratio versus 1/backscattering ratio figures (Figure 3.4 and Figure 3.9) shows the current NAT homogeneous nucleation scheme only produce Mix1 clouds defined by CALIPSO classification algorithm. In order to create NAT particles in Mix2 and Mix2-enhanced area, the particle radius needs to be smaller than 6 µm and 1µm respectively according to the calculation assuming 10ppbv of NAT in the condensed phase. Simply increasing the homogeneous nucleation rate of NAT increases the number density of NAT and therefore some NAT particles are located in Mix2 area. However, increasing the NAT nucleation rate reduces the clouds in the STS area because increasing NAT increases the depolarization ratio of STS/NAT mixture, and because a higher number density of NAT particles results in more HNO₃ removal from the air and STS so that the STS particles shrink to smaller sizes. A better nucleation scheme from STS to NAT is needed or, more likely a transformation from ice to NAT is necessary [Höpfner et al., 2006a].

The optical properties for ice are based on the mass-mixing ratio from the model output. We assume the ice number density is either 1% or 10% of STS number density. When we assume ice number density equivalent to 1% STS number, most of the ice particles are classified into Mix2-enhanced category. This result might be a hint that Mix2-enhanced particles may contain some ice particles in the CALIPSO classification algorithm, because the ice and enhanced NAT often occur at the same locations in the PSC occurrence analysis for both Arctic 2011 and Antarctic 2010 winters (Figure 3.7 and Figure 3.8). [Pitts et al., 2013] found that the CALIPSO algorithm may misclassify ice into Mix2 area due to moderate or severe denitrification. In this paper, we discuss the possibility to misclassify the ice due to strong dehydration. As shown in Figure 3.5, the dehydrated atmosphere with 2ppmv water vapor produce a lower backscattering ratio and a higher depolarization ratio compared with the situation with 5ppmv gas phase water vapor. This is because the dehydration reduces the formation of STS
particles. The particle sizes of STS under dehydrated condition are smaller than in a STS clouds with 5 ppmv of water. Therefore, STS contributes less to the backscattering ratio and less to the parallel backscatter when the depolarization ratio is calculated in dehydrated conditions.

It is difficult to make a quantitative comparison between CALIPSO and the model, because CALIPSO has a resolution along the orbit that is about 30-40 times higher than the model. The simulations show higher PSC occurrences than the CALIPSO due to the lower resolution of the simulations. The higher resolution of CALIPSO may also produce a different percentage of each type from the model results.

All the analyses indicate that we need a better model of ice number, sizes and cloud fraction when we derive the optical properties, as well as a better ice PSC microphysical treatment in the model.
Chapter 4

PSCs, denitrification and ozone depletion during 2010 Antarctica winter

4.1 Introduction

Polar stratospheric clouds (PSCs), which can have vertical and horizontal dimensions comparable to those of the United States, have been observed from the surface in the Arctic for centuries and Antarctic for at least 100 years [Hesstvedt, 1962; Wilson, 1966]. However, their geographic and temporal distributions were first clearly determined by satellite [McCormick et al., 1982]. After the Antarctic ozone hole was discovered [Farman et al., 1985], PSCs drew attention because of their important roles in polar ozone depletion. Their most significant role is providing the surface area for heterogeneous chemistry [Solomon et al., 1986]. Although the main heterogeneous chemistry processes are similar between Arctic and Antarctic ozone depletion, the wintertime Antarctic polar vortex is generally colder, more stable, and longer lasting than the Arctic one due to the weaker planetary wave activity in the Southern Hemisphere. The colder temperature is associated with stronger denitrification inside the Antarctic vortex and larger ozone depletion in the Antarctic springtime [Solomon et al., 2014]. Denitrification, caused by sedimentation of PSCs, promotes ozone depletion by reducing NOy, which prohibits the deactivation of halogen-based chemicals [Toon et al., 1986]. Dehydration, which is also pronounced in the Antarctic polar vortex, but not the Arctic polar vortex, inhibits ozone depletion by reducing heterogeneous (chlorine-activating) processing rates because of decreased solubility of HCl and HNO3 in STS (supercooled ternary solution) droplets [Wegner et al., 2013] and by depressing the Nitric Acid Trihydrate, NAT, equilibrium formation temperature [Chipperfield and Pyle, 1998].
Although PSCs cover much of the Antarctic polar cap during the austral winter from June to September, it is important to know the vertical and spatial distributions of PSCs because different particle types dominate chlorine activation, denitrification and dehydration [Pitts and Poole, 2014]. Pitts and Poole, [2014] use CALIPSO (Cloud-Aerosol Lidar and Infrared Pathfinder Satellite Observation) observations averaged over 2006 to 2014 to show that STS is the main component of PSCs in the early and late winter; lower number density NAT mixed with STS dominates at the lowest altitudes throughout the winter season; while higher number density NAT mixtures with STS dominates the PSCs above ~20 km from late June to early September. Ice PSCs occur typically on relatively small scales. Observations in 2006 by CALIPSO [Pitts et al., 2007] combined with CloudSat [Wang et al., 2008] show that PSCs have the highest occurrence frequency over the Antarctic Peninsula and over the ice sheets of the East Antarctic.

PSCs formation in Antarctica is not only influenced by the consistent cold temperature over the winter, but also is affected by temperature fluctuations due to inertia-gravity waves [Shibata et al., 2003] and orographic-gravity waves. Alexander et al. [2013] analyze the PSCs during the Antarctic winters from 2007 to 2010 and conclude that 76% of ice clouds and 44% of CALIPSO defined enhanced NAT clouds over the Transantarctic Mountains and Antarctic Peninsula are generated because of orographic gravity waves. However, considering all PSCs over Antarctica, only about 5% are generated by mountain waves. Numerical simulations by Höpfner et al. [2006] and Eckermann et al. [2009] compared with MIPAS (the Michelson Interferometer for Passive Atmospheric Sounding) PSC observations, suggest the Antarctic Peninsula and Ellsworth Mountains trigger ice PSC formation and heterogeneous nucleation of NAT particles on ice particles. As the ice evaporates in warmer regions downstream of the Peninsula, submicron-sized NAT particles with large number density may be released
from the evaporating ice particles. The gravity wave activity derived from models [Noel and Pitts, 2012] and observations [Alexander et al., 2011] both show that orographic waves have an impact on ice cloud occurrences observed by CALIPSO.

Large NAT particles, often called NAT-rocks due to their super-micron particle sizes [Fahey et al., 2001], play an important role in denitrification [Toon et al., 1990; Waibel et al., 1999; Carslaw et al., 2002], though their number densities can be quite small. Zhu et al., [2015] are able to simulate NAT-rock particles using a homogeneous surface nucleation scheme modified from Tabazadeh et al. [2002] for the 2010-2011 Arctic winter. Antarctic PSC simulations by Höpfner et al. [2006] demonstrate the NAT particles formed from evaporating ice particles generated by mountain waves can also denitrify the lower stratosphere significantly [see also Dhaniyala et al., 2002; and Fueglistaler et al., 2002].

As the temperature falls below the frost point ($T_{\text{ICE}}$), the ice PSC particles (Type II PSCs) form. Dehydration, a redistribution of water vapor caused by the sedimentation of ice PSC particles, is more evident in the Antarctic vortex than the Arctic vortex [Kelly et al., 1990]. Dehydration is frequently observed in the Antarctic polar vortex [Kelly et al., 1989; Vömel et al., 1995] with variation in the spatial distribution and timing from year to year [Nedoluha et al., 2000]. The formation of ice particles may provide extra surface area for heterogeneous chemistry but it is more likely the chlorine activation is completed on the surfaces of other types of PSCs before ice clouds form [Wegner et al., 2013].

Here we simulate PSC formation and its impact on ozone chemistry in the 2010 Antarctic winter and compare with observations from MLS, MIPAS and CALIPSO to answer the following questions:

1. What are the different properties of PSCs over time and space during 2010? How long do the PSCs last during the 2010 Antarctic winter?
2. Do 2010 Antarctic winter simulations show the belt of small NAT particles downwind of the Antarctic Peninsula as observations of previous winters do? Can our homogeneous nucleation scheme simulate small NAT particles, or do the numerous small NAT particles form from evaporating ice particles? Can a global model resolve the temperature perturbations over the Antarctic Peninsula well enough to capture the physics of NAT formation there?

3. Do large NAT particles form in the Antarctic winter, and are they properly simulated by model? Are chemical features of the vortex, such as denitrification and ozone loss sensitive to the numbers of large NAT particles formed?

4. What are the denitrification and dehydration features in the 2010 winter and how do simulations compare with MLS observations? Is Antarctic dentrification sensitive to small temperature bias, as shown by SD-WACCM simulations to be a problem in the Artic [Brakebusch et al., 2013; Zhu et al., 2015]?

4.2 Data description

CALIOP (Cloud-Aerosol Lidar with Orthogonal Polarization), onboard the CALIPSO (Cloud-Aerosol Lidar and Infrared Pathfinder Satellite Observations) satellite, is a two-wavelength, polarization sensitive lidar that provides high vertical resolution profiles (60-180 m for lower stratosphere) [Winker et al., 2007] to study PSCs [Pitts et al., 2007, 2009, 2011]. However, the temporal resolution is low at a given location, since the orbit repeats every 16 days. CALIOP measures the backscatter coefficient at 532 and 1064 nm, and two orthogonal (parallel and perpendicular) polarization components at 532 nm [Winker et al., 2007]. Pitts et al. [2009, 2013] developed an algorithm to detect and classify PSCs by defining thresholds for scattering ratio and depolarization ratio for various types of PSCs. However, it is difficult to distinguish PSC types for mixed clouds of NAT and STS. Another limitation for CALIPSO PSC detection is that only nighttime data can be used to detect PSCs due to
the noise contribution from reflected sunlight. Also the satellite orbit limits observations to North of 82° S. Although the algorithm can distinguish NAT-rock particles [Pitts et al., 2009], the author suggests comparing with in-situ data for confirmation.

4.3 Model setup

The model setup in this work is the same as described in Zhu et al. [2015]. The SD-WACCM model (the Whole-Atmosphere Community Climate Model [Garcia et al., 2007] with Specified Dynamics (SD-WACCM-4.0)) is coupled with CARMA (The Community Aerosol and Radiation Model for Atmospheres) [Toon et al., 1988; Bardeen et al., 2013], and nudged with GEOS5 data (Goddard Earth Observing System 5) [Reinecker et al., 2008]. The model initializes with 5-year SD-WACCM stabilized stratospheric chemistry and sulfate aerosols and runs from May 1 through the winter until Oct 1, 2010. The nucleation scheme for NAT formation applies the slopeflat case as described in [Zhu et al., 2015]. This nucleation scheme is modified slightly from the homogeneous surface nucleation scheme of Tabazadeh et al., [2002]. A sensitivity test case called “-1.5 K case” applies a temperature bias of -1.5 K for both PSC microphysics and heterogeneous chemical reactions as described by Zhu et al. [2015]. In another test called “slopeflat100”, we multiply the nucleation rate by 100 for the slopeflat case to evaluate the sensitivity of denitrification to the nucleation rate.

4.4 Results

We calculate the backscattering ratio and depolarization ratio from the simulations to retrieve the cloud coverage and PSC occurrence frequency in section 4.4.1 of this chapter. The method to retrieve the optical properties and the threshold for the classifications are the same as described in Chapter 3. In summary, the refractive index is 1.43 for STS, 1.5 for NAT and 1.308 for ice. The shape of STS is spherical. The shapes of NAT and ice are spheroids, with aspect ratios of 0.9 and 0.95 respectively. The NAT
nucleation scheme uses slopeflat. The ice is assumed to have a number density equivalent to 1% of the STS number density. Noise has been applied to all calculations of optical properties in section 4.4.1, as discussed in Chapter 3. In section 4.4.2, we discuss NAT formation mechanisms in the Antarctic. In section 4.4.3, we discuss the impact of the PSC properties on HNO₃, and ozone.

4.4.1 The temporal and spatial distribution of PSC types

4.4.1.1 PSC cloud coverage for different cloud types

The season length and vertical coverage of Antarctic PSCs is similar from year to year, but with some variations of the PSC altitudes and PSC types [Pitts and Poole, 2014]. The CALIPSO observed patterns for each PSC type in 2010, shown in Figure 4.1, are similar to those in other years in Antarctica [Pitts and Poole, 2014]. We present the PSC cloud coverage throughout the Antarctic winter from simulations and from CALIPSO in Figure 4.1. The date ranges from May 1 to Sep 31, 2010 and the height ranges from 15 km to 30 km. The cloud coverage and the fraction of each PSC type for both model and CALIPSO are the areas north of 82° S. When CALIPSO data are interpolated into a grid box in order to calculate the areas, the cloud coverage is calculated by multiplying the area of the grid box times the frequency of PSC types [Pitts et al., 2007]. We show them in three categories: STS, Mix (including Mix1, Mix2 and Mix2-enhanced) and ice. The fraction is calculated using the area of each PSC type divided by the total area. The fraction of STS, Mix and ice add to one. The left panels in Figure 4.1 are the CALIPSO observations; the middle panels are the modeled coverage; the right panels shows the STS and STS/NAT mixed clouds without counting the backscatter from ice.

As shown in Figure 4.1, for the 2010 Antarctic winter, the PSCs appear in late-May and fade away in late-September. The modeled cloud coverage shows the largest
cloud coverage from mid-Jun to mid-July as CALIPSO does, but the model shows larger cloud coverage. A second peak of large cloud coverage lasts from mid-August to the end of August in both simulations and observations. We suggest that the larger area covered by clouds in the model is a result of the lower spatial resolution of the model than CALIPSO. The modeled clouds cover the whole grid cell when we calculate them, while CALIPSO likely sees regions within a model grid cell that are not cloud covered.

STS in the model dominates the area coverage in May and June in the simulations, which is also seen in the CALIPSO data. If we don’t take the ice backscatter into account, as shown in the right panels, more STS clouds are shown through the winter and fewer clouds are found in the Mixed category. CALIPSO also finds STS dominates in late September in the area lower than 18 km, but most of the cloud in this period in the model are Mixed clouds. But not many clouds exist in late September. CALIPSO observations show that Mixed clouds mainly dominate from mid-Jun to Mid-September. Mix clouds also show 3 peaks: ~15 km in late-May, 18-24 km in late July and 20-23 km from late August to early September. The model Mixed clouds show a similar pattern and peaks but usually with larger areas. As discussed in Chapter 3, Mixed clouds may contain STS, as well as NAT and/or ice. Both simulated and observed ice clouds appear from early-June to mid-September but usually cover only a small fraction of the area containing PSCs (about 20%-40%). But some ice clouds are identified as Mixed clouds in the model as we discuss in Chapter 3.
Figure 4.1 The PSC cloud coverage and each PSC type coverage at different altitudes over 2010 winter. The CALIPSO data are shown in left panels. The modeled total PSC is shown in the middle panels. The modeled Type I PSC is shown in the right panels.

4.4.1.2 PSC occurrence frequency

To have a quantitative comparison between model and data, we compute PSC monthly occurrence frequency at 72 hPa, 52 hPa and 26 hPa as shown in Figure 4.2, Figure 4.3 and Figure 4.4. We split the South Pole into 5 zones (upper left panels in the figures) to analyze the appearance of PSCs in each zone. Zone 1 is the area between 75° S and 82° S (red). Zone 2-5 is the area between 55° S to 75° S in different longitude divisions (blue, green, black and purple). Zone 1 has the highest number of total observation points. However, it is less important when we calculate the PSC coverage due to the smaller area. The 3 markers in the scatter plots represent different PSC types: STS in asterisk, Mixed in square and ice in diamond. The colors of the markers correspond to the colors of the 5 zones. The black lines in the scatter plots represent the 1 to 1 values of the observed and simulated occurrence. The modeled PSCs are
interpolated onto the A-train track in order to calculate the occurrence frequency. The occurrence frequency means the times each PSC type is found divided by the total number of observations in each zone.

For all three pressure levels, zone 1 (the Pole) usually has the highest PSC occurrence frequency, followed by zone 5 (Antarctic Peninsula) and zone 2 (East Antarctic). The CALIPSO and CloudSat observations in 2006 also find the same pattern with the highest frequencies near the Antarctic Peninsula and over the ice sheets of the East Antarctic [Pitts et al., 2007; Wang et al., 2008].

July, August and September are months with the highest cloud occurrence frequency. For 72 hPa (Figure 4.2), the model often underestimates the STS, but overestimates the mixed cloud frequency by about 3 times, especially in zone 1. Also, the ice in zone 1 is often overestimated. For 52 hPa, the model also underestimates the STS, but overestimates the Mixed cloud, especially in June and August. For 26 hPa, the PSC occurrence frequency is much less than for 52 hPa. STS is underestimated and the ice is overestimated in June and July. Generally, ice particles are only a small fraction during the whole season. The ice particles are mainly identified in zone 1 (the Pole) and some in zone 5 (Antarctic Peninsular). The occurrence frequency of modeled ice is higher than the observations in zone 1 but consistent with the observation in zone 5. However, as discussed in Chapter 3, we think a lot of ice clouds are misclassified as Mixed clouds by the CALIPSO algorithm.
Figure 4.2 The monthly PSC occurrence frequency at 72 hPa (17 km) for five different zones shown in the upper right panel. The different marker shapes represent different PSC types: STS as asterisk, Mixed in square and ice in diamond. The different marker colors represent different zones. The top two panels are May and June and the bottom three panels are July, August and September.
Figure 4.3 The monthly PSC occurrence frequency at 52 hPa (18.7 km) for five different zones shown in the upper right panel. The meaning of different markers is the same as Figure 4.2. The order of the panels are the same as Figure 4.2.

Figure 4.4 The monthly PSC occurrence frequency at 26 hPa (22.6 km) for five different zones shown in the upper right panel. The meaning of different markers is the same as Figure 4.2. The order of the panels are the same as Figure 4.2.

4.4.1.3 The spatial distribution of PSCs

Figure 4.5 to Figure 4.9 show the spatial distribution of PSCs and related chemicals at 52 hPa for each month from May to September. The spatial distributions and the evolution of PSCs over the winter provide clues to the mechanisms forming PSCs.

To construct Figure 4.5 to Figure 4.9, the CALIPSO composition data, as well as MLS and MIPAS gas phase chemical data are interpolated into the model grid. Due to the high resolution along the orbit, CALIPSO usually has ~30 observation points in one model grid box. For any given CALIPSO observation only one type of PSC is recorded. This way, some fine scale structures of the PSCs types resolved by CALIPSO are missing from the simulations. The CALIPSO occurrence frequency of PSCs is found by
dividing the number of observations of a given PSC type appearing in one grid box during the month by the total number of measurements that CALIPSO made in a grid box in the month. Due to their orbits, CALIPSO and MLS do not observe all the grid cells in the model, but miss those south of 82° S. The white color in the CALIPSO or MLS data panels indicates missing data. Also, the orbits of CALIPSO, MLS and MIPAS repeat every 16 days and do not observe all longitudes during the month, which contributes to the jagged, or finger-like, pattern at the equatorward edges of the figures for PSCs and gas phase chemical fields. The PSC occurrence frequency we define for the model is the number of PSC types in a grid cell divided by the total number of the model outputs in the same grid cell in the month. The modeled occurrence frequencies are not smooth due to the noise added to the optical properties (see Figure 4.9). It should be noted that the model and CALIPSO frequencies are not identical. The model samples every grid cell with each output, while CALIPSO samples a specific point for a specific time, and may only sample some grid cells a few times during the month. The hatching patterns in the modeled Mixed clouds represent NAT contributes over 30% of the occurrence in those areas. The areas without hatching in the Mixed clouds panel mean at least 70% of the occurrences are due to ice.

According to Figure 4.5 to Figure 4.9, both the model and the observations show a high frequency of PSC occurrence in the inner vortex during May and June, which is consistent with the location of the cold temperature center in May and early June rather than location of the highest mixing ratios of nitric acid which are near the equatorward edge of Antarctica. No ice is found in May in either the model North of 82°S, or CALIPSO observations, but ice clouds do form in June.

In our model, STS and NAT (shown in hatching pattern in modeled Mix plot) start to fade away from the center of the pole and form along with ice clouds near the equatorward edge of Antarctica in July and August. The hatching indicates NAT
contributes to the occurrence in those hatching areas. Figure 4.7 and Figure 4.8 shows that ice is often found from the pole to Antarctic Peninsular and downwind of the Antarctic Peninsula in Jun and July. This location for STS, NAT and ice clouds is preferred because the region with temperatures colder than 195K expands equatorward through July and August, while the cold center of the vortex has been dehydrated and denitrified in previous months. Therefore, the ice, STS and NAT tend to form close to the edge of the vortex where the gas concentration remains high, and temperatures are low.

Ice is not found in a ring or belt around Antarctica in either the model or CALIPSO data. Instead its concentration is asymmetric and no longer pole centered as early as June. Generally ice clouds prefer to form in the longitude sector between 60° W and 30° E. As the winter progresses STS also becomes most abundant in this longitude sector. Starting from June, the STS and ice are more likely to form downwind of the Antarctic Peninsula, and the Ellsworth Mountains, which are the highest in Antarctica. This sector is also where the coldest temperatures occur on the monthly mean at fixed latitude. In contrast, Mixed clouds are more evenly distributed in longitude. From the hatching pattern in the Mixed cloud panels, we can see the NAT clouds form a circle all the way around the pole, rather than concentrating downwind of the Antarctic Peninsula. This distribution of STS and NAT is likely due to the slow movement of nitric acid from STS to NAT due to its lower vapor pressure as the particles move downwind from the Antarctic Peninsula. The NAT then begins to return nitric acid to the air as the air approaches the Antarctic Peninsula from the west and encounters warmer temperatures.

By September, STS, NAT and ice clouds are much less common than earlier in the winter. The model doesn’t predict any ice clouds, but CALIPSO does see them just above the Antarctic Peninsula.
H2O vapor is depleted during the winter. The simulated water vapor is very similar to that observed by MLS. At the end of the season, the difference in water vapor mixing ratio between the depleted pole and the higher latitudes (North of 50° S) is about 3 ppmv. The simulated gas phase HNO3 is often lower than that observed by MLS. But the areas where the model has lower HNO3 are usually outside the vortex where no PSCs form. The HCl in the model is much less depleted than the MLS observations. In July and August, the data shows the lowest HCl values near the pole (close to zero), while the model has a ring shape of HCl with a high value near the pole. This situation could be related to the ClONO2 fields we show in the last 2 panels. The MIPAS observed ClONO2 is much higher near the pole in June, than in the simulations. The higher ClONO2 near the pole can react with HCl and cause the HCl depletion near the pole.
Figure 4.5 The occurrence frequency of PSC types in May at 52 hPa from both CALIPSO and the model. The first column is CALIPSO STS, Mix, ice frequency, H2O from the model and from MLS; the second column is the modeled STS, mix, ice frequency, HCl from the model and from the MLS; the third column is the monthly average temperature, modeled HNO3, MLS HNO3, modeled ClONO2 and MIPAS ClONO2.
Figure 4.6 The occurrence frequency of PSC types in June at 52 hPa from both CALIPSO and the model. The plot orders are the same as Figure 4.5.
Figure 4.7 The occurrence frequency of PSC types in July at 52 hPa from both CALIPSO and the model. The plot orders are the same as Figure 4.5.
Figure 4.8 The occurrence frequency of PSC types in August at 52 hPa from both CALIPSO and the model. The plot orders are the same as Figure 4.5.
Figure 4.9 The occurrence frequency of PSC types in September at 52 hPa from both CALIPSO and the model. The plot orders are the same as Figure 4.5.
4.4.2 Different possible mechanisms for NAT formation

Our model with an empirically derived nucleation rate has been demonstrated to form large NAT particles with small number density. The nucleation rate was empirically derived to explain Arctic denitrification for the winter 2010-2011 [Zhu et al., 2015]. In this section, we want to investigate two questions:

1. Do large NAT particles form in the Antarctic winter, and are they properly simulated by model?

2. Do observations provide clues to the NAT particle size in the Antarctic? If there are small numerous NAT particles downwind the Antarctic Peninsula, how do they form? Our model does not include microphysics process to produce NAT from ice PSCs nor does it have enough resolution to represent temperature fluctuation from mountain waves. Therefore, it is interesting to determine if there are important conflicts between our simulations and data related to these omissions in the formation of NAT.

CALIPSO observations in 2008 [Lambert et al., 2012] conclude that denitrification is associated with low number densities (< 10^{-3} cm^{-3}) of NAT with large effective radius (>5-7 µm) in early Antarctic winter before the temperature drops below the ice frost point. According to this conclusion, we look at the 2010 simulation in our model compared with the observations from May 24 to May 28, which is a period of strong denitrification. Figure 4.10 shows the simulated PSC properties compared with CALIPSO and MLS observations at 52 hPa. Those properties show the total PSC compositions in these 5 days, the maximum backscattering ratio, depolarization ratio, mass mixing ratio, effective radius and number density. The optical properties from the model are plotted without noise in order to see more clearly how they overlap each other. The depolarization for STS, NAT and ice is defined to be the perpendicular backscatter for each type divided by the parallel backscatter for each type. The total depolarization ratio is calculated by the perpendicular backscatter from all the PSCs divided by the
parallel backscatter from all the PSCs. These definitions are discussed further in Chapter 3.

The locations of the simulated STS and NAT generally capture the location of the observed PSCs. The observed backscattering ratio (~4) has the highest value in East Antarctic (around 40° E, 82° S). The simulated STS backscattering ratio is ~2.5. The highest backscatter in the simulations is provided by ice particles near the pole. In CALIPSO observations, the Transantarctic Mountains and Ross Ice Shelf, around 160° E to 160° W and 80° S, show a low backscattering ratio (~1.3) as well as a high depolarization ratio (~0.5), which is consistent with the model results. The model indicates that STS/NAT mixtures provide the backscattering ratio and the depolarization in this area. The simulation has large NAT particles (>10 µm) with number density about 2e-4 cm⁻³.

The CALIPSO composition algorithm suggest few ice clouds, but as discussed in Chapter 3 the algorithm can misidentify ice as an NAT/STS mixture. The simulated ice has a mixing ratio ~0.5 ppm and a backscattering ratio of 4. The ice is present with STS over a large fraction of the geographic area near 82°. CALIPSO identifies Mixed clouds in East Antarctic. However, the simulated NAT doesn’t have strong backscatter signals in this area. Instead, ice particles show strong depolarization and backscatter there.

In summary, during the May 24-28 time period the simulations suggest that NAT is present, but likely not observable by CALIPSO. Instead, the depolarization observed by CALIPSO is likely due to ice. This confusion of ice and NAT makes it difficult to clearly identify the source of denitrification using only CALIPSO data. However, our model is consistent with denitrification at this time due to large NAT particles.
Figure 4.11 presents a comparison of the simulations with CALIPSO and MLS observations from July 18 to Jul 22, 2010 at 52 hPa. The data in Figure 4.11 show high backscattering ratio and depolarization downstream of the Antarctic Peninsula from 60°W to 60°E and a moderate backscattering ratio from 60°E to 180°. In our simulations, the backscattering ratio is high from 60°W to 60°E because of ice particles. The STS increases the backscattering ratio moderately. From 60°E to 180°, the model shows a high backscatter and depolarization south of 80°S due to ice. In the area north of 80°S, the model shows a backscattering ratio ~1.2 and a depolarization ratio ~3 due to STS/NAT mixture. This backscattering ratio value is lower than the CALIPSO observation (~3) in this area, which suggest a higher number density of NAT particles based on the arguments given in Chapter 3.

To explore how NAT forms during this period of time we need to better isolate NAT clouds and ice clouds. We plot the PSC evolution from July 14 to July 20 at 2 days intervals in Figure 4.12. To avoid the influence of falling particles from above, we draw the plots for 26 hPa. On Jul 14 and Jul 18 (the first and third columns), the CALIPSO algorithm suggests both STS and wave ice formation at the Antarctic Peninsula. The simulations suggest NAT particles forms downwind. By July 20 (the fourth column), both STS and ice start to disappear, while NAT exist as a ring covering much of Antarctica. This sequence provides a hint for the formation of numerous NAT particles that could nucleate from STS or ice from previous days and exist downwind at higher temperature when both STS and ice fade away. Figure 4.13 shows the optical properties from CALIPSO and the model on the 20th at 26 hPa. The CALIPSO observations show a ring shape of backscattering ratio with high depolarization ratio. However, the model overestimates the backscatter of ice and underestimates the backscatter from NAT due to the large size and small number density of NAT. Therefore, a ring shape cannot be seen in the modeled backscattering ratio. But the depolarization ratio in the model
shows a moderate depolarization ratio for NAT in a ring shape. The CALIPSO data also show a high depolarization ratio with a low backscattering ratio over 0° to 90° E within 80°S, which they didn't classify into any category. In this area, the model sees ice with high backscattering ratio and depolarization.

Therefore, the answers to the two questions are: 1. According to the simulations and observations on May 24-28, large NAT particles with small number density exist at 52 hPa. Our model suggests they do denitrify. However, CALIPSO is likely seeing ice on these days, and cannot be used to reliably identify the locations of NAT clouds. 2. The current model with empirical nucleation of NAT particles is not able to simulate the numerous small NAT particles observed downwind of the Antarctic Peninsula (in July, for example at 26 hPa). In future work, we will add temperature fluctuations due to the mountain wave to the model to test if empirical nucleation of NAT from STS with large temperature fluctuations leads to the formation of small NAT particles. We will also add the release of NAT from evaporating ice to determine if that process can form small NAT particles in a global model.
Figure 4.10 The modeled PSCs compared with CALIPSO and MLS at 52 hPa on May 24 - May 28, 2010. The first column is the total CALIPSO defined particle composition over five days and the simulated STS and NAT effective radius; The second column is simulated maximum HNO$_3$ mixing ratio for each composition and simulated STS and NAT number density; The third column is the maximum CALIPSO backscattering ratio and the maximum modeled total, ice, STS and NAT backscattering ratio; The fourth column is the maximum CALIPSO depolarization ratio and modeled maximum total, ice, STS and NAT depolarization ratio. The last row shows the minimum gas phase HNO$_3$ from MLS and the model.
Figure 4.11 The modeled PSCs compared with CALIPSO and MLS at 52 hPa from Jul 18 to Jul 22, 2010. The plots orders are the same as Figure 4.10.
Figure 4.12 The modeled PSCs compared with CALIPSO and MLS at 26 hPa from Jul 14 to Jul 20, 2010. The first column is the CALIPSO STS, modeled STS, CALIPSO Mix, modeled NAT, CALIPSO ice and modeled ice in Jul 14. The second column is for Jul 16. The third column is for Jul 18 and the fourth column is for Jul 20.
Figure 4.13 shows the backscattering ratio and depolarization ratio from the model and the CALIPSO at 26 hPa on Jul 20th, 2010.
4.4.3 Sensitivity tests for denitrification, dehydration and ozone depletion

It is difficult to compare simulations of the PSC types in the global model with data, as we discussed in previous sections and in Chapter 3. However, small NAT particles would not lead to denitrification directly due to their small size, and large NAT particles likely add little to heterogeneous chemistry due to their small surface areas. Here, we explore if the current SD-WACCM/CARMA model is able to simulate HNO$_3$ and H$_2$O evolution well compared with the data.

Figure 4.14, to Figure 4.16 shows the simulated temperature, HNO$_3$ and H$_2$O evolution over the 2010 Antarctic winter at different pressure levels averaging the points between 80° S and 82° S. The Figures also show MLS observations [de Laat and van Weele, 2011] from the same area. The plots show the observations in red, the base case in blue, a simulation with model temperatures reduced by 1.5 K in green, and a simulation with 100 times higher nucleation rate for NAT from STS in purple. The error bars represent the systematic errors: for HNO$_3$ the estimated error is 0.5 ppbv for 68 and 32 hPa and 1 ppbv for 21 hPa; for H$_2$O the estimated error is 7% for all three levels. The error bar for MLS temperature represents the differences between GEOS5 and MLS according to the validation of MLS version 3.3 [Schwartz et al., 2008; Livesey et al., 2011].

Figure 4.14 shows that the temperature field from the model is within the error bar but about 1.5 K warmer than the MLS observations as discussed by Brakebusch et al., [2013] for both Arctic and Antarctic. Figure 4.15 and Figure 4.16 show that both the HNO$_3$ and H$_2$O fields are within the error bars of the observations at 68 hPa and generally within the error bar at 32 hPa until the end of August. However, the initial HNO$_3$ in the model is lower than observed at low pressures. At 21 hPa, the observation is higher than the model for both HNO$_3$ and H$_2$O during August. The simulated
denitrification and dehydration is stronger than observed at 32 hPa in September and at 21 hPa in August, though the simulations and the data agree near day 300. The -1.5K sensitivity test suggests that small temperature differences do not matter greatly in the Antarctic, though Zhu et al. [2015] showed they did matter in the Arctic. As discussed in Chapter 3, one could increase the simulated NAT and ice backscatter if the particles were smaller. Figure 4.15 shows the impact of increasing the NAT nucleation rate by 100 (slopeflat100 case). The slopeflat100 case shows the denitrification occurs about two weeks or a month earlier than in the slopeflat case or in observations. But the denitrification at the end of the season doesn’t vary much between the slopeflat and slopeflat*100 cases except at 21 hPa. At this pressure level, the slopeflat100 case shows a stronger denitrification than the other two model cases or observations. We conclude that increasing the homogeneous nucleation rate to achieve smaller NAT particles, which is required to better agree with CALIPSO data in some cases, produces worse agreement with denitrification. Therefore, our homogenous nucleation rate calculation [Zhu et al., 2015] is likely close to what happens in nature, but there are additional processes producing small NAT particles in certain circumstances when denitrification is not occurring rapidly. It is most likely that these other processes include production of NAT from evaporating ice, and/or production of NAT in wave clouds.
Figure 4.14 The temperature evolution over the 2010 Antarctic winter at 3 different pressure levels averaged over the points south of 80° S compared with MLS observations [de Laat and van Weele, 2011]. The red lines are the MLS temperature; the blue lines are the model temperature nudged with GOES5; and the green lines show the model temperature minus 1.5K.
Figure 4.15 The HNO\textsubscript{3} evolution over 2010 Antarctic winter at 3 different pressure levels (top 3 panels) and contours from 100 hPa to 10 hPa (bottom 4 panels) averaging the points south of 80 S compared with MLS observation. The error bars in the top panels represents the systematic error as 0.5 ppbv for 68 and 32 hPa and 1 ppbv for 21 hPa [Livesey et al., 2011]. The colors in the top 3 panels represent MLS data in red, slopeflat case in blue, temperature-1.5K case in green and slopeflat100 case in purple. The contour plots show the HNO\textsubscript{3} volume mixing ratio in ppbv for MLS data and 3 model cases.

Figure 4.16 The H\textsubscript{2}O evolution over 2010 Antarctic winter at 3 different pressure levels (top panels) and and contours from 100 hPa to 10 hPa (bottom panels) averaged over the points south of 80 S compared with MLS observations. The error bar in top 3 panels represents the systematic error of 7%. The colors in the top 3 panels represent MLS data in red, slopeflat case in blue. The contour plots show the H\textsubscript{2}O volume mixing ratio in ppmv for MLS data and 3 model cases.

Figure 4.17 to Figure 4.19 shows the ozone, HCl and ClONO\textsubscript{2} trends for the winter of 2010. The ozone trends figure (4.17) shows three different simulations and MLS data. The HCl, and ClONO\textsubscript{2} trends figures (4.18 and 4.19) show the slopeflat case and MLS or MIPAS data.

O\textsubscript{3} is about 20%-30% low in the model through the winter. At the end of the winter (September and October), the O\textsubscript{3} is depleted at 32 and 68 hPa, but rises at 21
hPa, as observed. Another point to notice is that when we reduce the temperature (increasing the rate of chlorine activation on PSCs) or increasing the NAT nucleation rate (increasing the denitrification and prohibiting the deactivation of halogen-based chemicals), the ozone depletion is stronger compared with slopeflat case.

HCl in Figure 4.18 doesn’t have the depletion features from June to September that are observed, which is probably because the ClONO$_2$ in the model is about 1 ppbv lower than the observations by MIPAS (Figure 4.19).
Figure 4.17 The O$_3$ evolution over 2010 Antarctic winter at 3 different pressure levels (top 3 panels) and and contours from 100 hPa to 10 hPa (bottom 4 panels) averaged the points south of 80 S compared with MLS observation. The 3 cases are the same as Figure 4.15.

Figure 4.18 The HCl evolution over 2010 Antarctic winter at 3 different pressure levels averaged the points south of 80 S compared with MLS observation.
Figure 4.19 The ClONO$_2$ evolution over 2010 Antarctic winter at 3 different pressure levels averaged the points south of 80 S compared with MLS observation.

4.5 Conclusions

We explore the features of PSCs and related chemicals during the Antarctic winter of 2010. We compare simulations of the spatial and temporal distribution of PSCs and related gases with CALIPSO and MLS data. We listed four questions at the beginning of the paper.

Question 1 asked: What are the different properties of PSCs over time and space during 2010? How long do the PSCs last during the 2010 Antarctic winter?

In order to answer question 1, we compute the optical properties of PSCs from the model and classify them using the CALIPSO classification algorithm by Pitts et al. [2009]. We use 3 main categories for the comparison here: STS, Mix (Mix1+Mix2+Mix2-enhanced) and ice. The retrieved PSC cloud coverage (Figure 4.1) shows that the PSCs
for 2010 Antarctic winter last from late May to mid September. CALIPSO indicates the
STS dominates from late-May to mid-June as well as in September; while the Mix
clouds dominate in July and August, especially around 15 km in late May, 22 km in July
and late August. In the model, the temporal distribution shows that STS particles
dominate at the beginning of the season in May and Jun and contribute a small fraction
later in September. The Mix cloud is the main cloud type in June and July in the
simulations, but its frequency is overestimated in the model, likely because of the lower
resolution of the model relative to CALIPSO. Using the CALIPSO composition
algorithm both observations and simulations find ice clouds form in June, July and
August, but usually contribute to a small fraction of PSCs. However Chapter 3 and the
model show that the CALIPSO algorithm often confuses ice clouds with NAT. NAT is
often present in the model, but at levels that CALIPSO cannot observe. Many of the
Mixed clouds in the CALIPSO data may in fact contain ice.

The spatial distribution shows the PSC often form near the pole, the Antarctic
Peninsula and East Antarctica. The quantitative analysis (Figure 4.2 to Figure 4.4)
shows an underestimation of STS and overestimation of Mixed and ice compared with
CALISPO observations at 26 hPa, 52 hPa and 72 hPa. In the polar view figures at 52
hPa (Figure 4.5 to Figure 4.9), STS forms at the cold center in May and June, while
later in the winter, less STS forms near the Pole, and instead it forms as a belt around
the periphery of the Antarctic continent since HNO₃ and H₂O has been depleted in the
previous months nearer the poles. STS shows a high frequency of occurrence downwind
of the Antarctic Peninsula. Ice formation occurs in the coldest regions but becomes
weaker in late winter after strong dehydration. The modeled Mix category of PSC is
located in the same spatial areas as the observed Mixed PSC, but with a higher
occurrence frequency. But both STS/NAT and STS/ice mixtures contribute to the Mix
category. The STS/ice mixture especially has a high contribution to the occurrence near the pole.

Question 2 asks: Do 2010 Antarctic winter simulations show the belt of small NAT particles downwind of the Palmer Peninsula as observations of previous winters do? Can our homogeneous nucleation scheme simulate small NAT particles, or do the numerous small NAT particles form from evaporating ice particles? Can a global model resolve the temperature perturbations over the Antarctic Peninsula well enough to capture the physics of NAT formation there?

The polar view of PSCs during the time from July 14 to July 22 at 26 hPa demonstrates the NAT belt downwind of the Palmer Peninsula (Figure 4.12 and Figure 4.13). On July 20th, the CALIPSO observation shows a belt shape of high backscattering ratio and corresponding high depolarization ratio, which suggest a high number density of small NAT particles. However, the model shows a NAT belt but with low backscattering ratio. The observed formation of STS and wave ice particles indicates the Antarctic Peninsula probably triggers enhanced NAT formation. However, our model only simulates large NAT particles with effective radius above about 5 µm. In the future it may be necessary to include NAT nucleating from ice in the microphysical process. It may also be necessary to parameterize temperature fluctuations over the Antarctic Peninsula due to the mountain wave. As indicated by Fueglistaler et al., [2003], the grid box in our model is too coarse to resolve mountain waves.

Question 3 asks: Do large NAT particles form in the Antarctic winter, and are they properly simulated by model? We analyses the PSC at 52 hPa from May 24 to May 28, 2010 (Figure 4.10). The observations show a low backscattering ratio and a high depolarization ratio at the Transaction Mountain and Ross Ice sheet area. This observation may indicate large NAT particles form in the early season as discussed by a previous research [Lambert et al., 2012]. The modeled NAT appears in the observed
location with low number density ($\sim2\times10^{-4}$#/cm$^3$) and effective radius above 10 µm. However, CALIPSO may be observing ice particles rather than NAT particles, so it is not clear that the simulations can be easily compared with observations. Nevertheless, we find that our simulations correctly simulate the denitrification in the Antarctic winter, and in Chapter 2 we showed we were close to simulating the denitrification in the Arctic winter. We conclude that our nucleation rate is doing a good job predicting the number and size of the NAT particles that are responsible for denitrification. For example, increasing the nucleation rate to produce smaller particles leads to too much denitrification. We suggest that observed smaller NAT particles do not form due to an enhanced homogeneous nucleation rate, but instead form a different process that is not strongly coupled to denitrification. Such a process would include ice cloud evaporation to release NAT, or formation in wave clouds.

Question 4 asks: What are the denitrification and dehydration features in the 2010 winter and how do simulations compare with MLS observations? Is Antarctic denitrification sensitive to small temperature bias, as shown by SD-WACCM simulations to be a problem in the Artic [Brakebusch et al., 2013; Zhu et al., 2015]? We find that the modeled H$_2$O and HNO$_3$ are within the error bars of MLS observations at 68 hPa and generally within the error bar before the end of August at 32 hPa. We also find that the simulated denitrification is not sensitive to the temperature within error bars, though it was sensitive for a simulation conducted in the Arctic [Zhu et al., 2015]. We also find that increasing the NAT nucleation rate by 100 (slopeflat100 case) leads to an earlier denitrification about half a month or a month compared with observations. But at the end of the season, the HNO$_3$ amounts are very close for the model cases, except the 26 hPa, where the slopeflat100 case shows a lower HNO$_3$ amount than observed.

My model has a number of improvements that could be made. Most important is to better simulate ice clouds and the NAT particles that might be generated when they
evaporate. Further simulations of years other than 2010 would also help to identify situations in which greater discrimination between the contributions of ice and NAT to the Mixed type of particle might be possible.
Chapter 5

Conclusions and future plans

This thesis focused on studying the formation of polar stratospheric clouds, due to the complex influences of different types of PSC particles on stratosphere chemicals involved in the ozone lifecycle. A PSC microphysical model has been built on the Community Earth System Model in order to have detailed understanding of three main types of PSCs: STS, NAT and ice. In Chapter 2 to Chapter 4, we bring out several science questions about PSC formation and their related chemicals in both the Arctic and Antarctic.

As the first stage of our study, we built a detailed microphysical model for STS and NAT to explore PSC formation in the 2010-2011 Arctic winter. The climate model has an H_{2}O routine to treat the formation of ice and dehydration. No interactions have been included between ice and other PSCs. First, we compared the microphysical features like size distributions, chemical fractions inside STS particles, and particle volumes at different temperature with historical data. The model is demonstrated to be able to reproduce the microphysical features successfully. One major difference between our model and other current models is that STS is formed kinetically in our model rather than assumed to be in equilibrium. The modeled STS generally remains close to equilibrium unless the surface area is below 4 \mu m^2/cm^3. Another important feature from our model is that the NAT nucleation scheme we use (the homogeneous nucleation scheme based on Tabazadeh et al. [2002]) is able to reproduce the rock-NAT particles (above 10\mu m) that were discovered by several in-situ observations [Fahey et al., 2001; Molleker et al., 2014].
Denitrification is one of the hardest parts to simulate because the formation mechanisms of NAT still remain unknown. To explore the denitrification in 2010-2011 winter, we use the homogeneous nucleation scheme by Tabazadeh et al. [2002] and tune the nucleation rate or nucleation free energy to find the best curves to fit the MLS HNO$_3$ observation. We also tune the NAT number density, NAT sticking coefficient, NAT shape in order to change the fall velocity of NAT particles and explore how these factors influence denitrification. In addition, we apply one test with -1.5K temperature bias for PSC and its chemistry suggested by [Brakebusch, 2013]. Through all these tests, we obtain a new homogeneous nucleation equation that fit the MLS observation the best. This equation is based on the homogeneous surface nucleation scheme [Tabazadeh et al., 2002] but tuned so that the nucleation free energy is less dependent on the temperature. However, the temperature sensitivity of denitrification increases the difficulty to constrain the microphysical parameters for NAT in this winter. The NAT nucleation rate is very sensitive to the temperature because the temperature is one of the factors in the nucleation equation and it controls the other factor, STS composition, in the equation. The homogenous nucleation rate expressions we considered have free energies within 10% of each other, but the nucleation rates vary by several orders of magnitude. A temperature bias of -1.5K increases the denitrification significantly not only through the NAT nucleation but also through changing the area of the vortex. But severe denitification caused by lowering the temperature could be compensated using a lower sticking coefficient of NAT, which slows the growth rate of NAT and reduces the fall velocity.

In Chapter 3 and Chapter 4 we use the same PSC model and explore Antarctic PSCs. First of all, we retrieve the optical properties of 3 main PSC types and compare with CALIPSO PSC products and its classification algorithm [Pitts et al., 2009]. The depolarization and backscatter indicates our current model with homogenous nucleation
of NAT only produces Mix1 clouds in the CALIPSO classification which in the model corresponds with NAT with sizes larger than ~6 µm and with low number density. Increasing the nucleation rate of NAT increases the backscattering ratio from NAT particles, but at the same time, reduce the STS cloud amount. This is because the NAT/STS has a higher depolarization if the NAT number increases. It is also because a higher number of NAT particles absorb more HNO$_3$ from the air and STS and reduce the STS particle sizes. However, our current nucleation rate correctly reproduces denitrification in the Antarctic. We believe that we correctly predict the NAT particles that are responsible for denitrification, but not the NAT particles that are observed to have small particles sizes. Therefore, an additional NAT nucleation scheme is needed, which is likely transformation from evaporating ice to NAT [Höpfner et al., 2006b] or nucleation from STS to NAT due to strong temperature fluctuation due to gravity waves.

The model only tracks the mass of ice particles. In order to obtain its optical properties, we assume the ice number density equivalent to 1% of STS number density. The results show a majority of ice particles are classified in the enhanced NAT category (2<backscattering ratio<5) rather than ice category (backscattering ratio>5). This misclassification can be caused by denitrification as suggested by Pitts et al. [2013]. In our study, we discuss the possibility to misclassify the ice clouds due to the dehydration. The particle size of STS shrinks under dehydrated conditions. The smaller STS sizes decrease the backscattering ratio from STS that contribute to the STS/ice mixture backscatter. But it is very likely the way we retrieve the physical properties for ice is not precise. We need a better model of ice to predict number, sizes and cloud fraction.

Another difficulty to compare CALIPSO data and the model results quantitatively is the coarse resolution of the model. The model often predicts a larger cloud coverage than observed because the modeled clouds cover the whole grid cell with
one type of PSCs or their mixtures, while CALIPSO likely sees a cloud fraction with and without clouds within a model grid cell.

Two different NAT formation mechanisms may dominate at different times in the Antarctic winter. Large NAT particles form early in the season[\textit{Lambert et al.}, 2012]. In our simulation, both the model and the observations have a small backscattering ratio and large depolarization, as well as moderate denitrification occurring in the Transantarctic Mountains and Ross Ice sheet areas from May 24 to May 28, 2010. We conclude that our nucleation scheme is able to simulate the NAT in the early season.

The second situation usually occurs in mid-season when the HNO$_3$ has been depleted near the pole. For the year under consideration, CALIPSO observed a belt shape of high backscattering ratio and high depolarization ratio on July 20$^{th}$ downwind of the Antarctic Peninsula, which indicates a high number density of small NAT particles. However, while our model captures the belt shape if we look at the NAT mass and depolarization ratio, it does not reproduce the backscattering ratio. The observations from previous days indicate that the Antarctic Peninsula probably triggers enhanced NAT formation from STS and wave ice particles. It is necessary to include ice and NAT interactions, as well as the temperature fluctuations due to waves, in future models to simulate the NAT and ice in mid-season of the Antarctic winter.

The denitrification in Antarctic is close to MLS observation, which indicate the current homogeneous nucleation scheme predict the correct number and size of the NAT particles that are responsible for denitrification. The observed small NAT particles in mid-season is not strongly coupled to denitrification. Or it is possible that some of them grow to the size equivalent to the NAT our model predict and have a similar number density, and lead to the denitrification as we predict. It is also found that the denitrification in Antarctic is not as sensitive to the temperature as the Arctic is.
From the study above, we find several important mechanisms that are necessary in future development. The first one is the gravity wave and the temperature fluctuation. In Antarctic area, about 76% of ice clouds and 44% of CALIPSO defined enhanced NAT clouds over the Transantarctic Mountains and Antarctic Peninsula are generated because of orographic gravity waves [Alexander et al., 2013]. The second one is a microphysical formation of ice particles and the interaction between ice and other PSC types. Both NAT and ice optical properties will be more precise if these processes are include in the model. From the model analysis, both the gravity wave and NAT formed from ice seems necessary in order to obtain NAT particles with large number density. Other possibilities such as heterogeneous nucleation of NAT particles [Hoyle et al., 2013]could be taken into account because stratospheric sulfates commonly contain micrometeorites.
Appendix

A. Growth and evaporation process for STS and NAT particles

The growth and evaporation rate equation [Toon et al., 1989] we use is similar to the expression by Barkstrom [Barkstrom, 1978] and Ramaswamy and Detwiler [Ramaswamy and Detwiler, 1986]. In this equation, we ignore the effects of solutes on the vapor pressure and we ignore radiative heating of the particles:

\[
\frac{dm}{dt} = g_0(p_\infty - A_kp_v)/(1 + g_0g_1p_v)
\]  

(A1)

Here \( \frac{dm}{dt} \) is the mass growth rate (g/cm\(^3\)/s) for one particle, \( p \) is the partial pressure of the condensing gas infinitely far from the particle (e.g. environmental gas pressure), and \( p_v \) is the saturation vapor pressure (e.g. the pressure over a flat surface of the liquid in equilibrium with the gas). \( A_k \) is the Kelvin correction term, which represents the curvature effects of particles on the vapor pressure:

\[
A_k = \exp \left( \frac{2M_c\sigma}{RT\rho_s r} \right)
\]

Here \( \sigma \) is the surface tension, \( \rho_s \) is the particle density, \( M_c \) is the molecular weight of the appropriate vapor (water, nitric acid, or sulfuric acid), \( r \) is drop radius, the \( R \) is the gas constant and \( T \) is the environment temperature.

The \( g_0 \) and \( g_1 \) terms in equation (A1) are growth kernels which include vapor diffusivity for the appropriate vapor \( (D) \), and thermal conductivity \( (K) \) considering the size of the particle relative to the mean free path, as well as the latent heat of condensation \( (L) \) [Toon et al., 1989]:

\[
g_0 = 4\pi rD_v M_c/(RT)
\]

\[
g_1 = M_c l^2/(RT^2 f_v K 4\pi r)
\]

Where \( f_v \) and \( f_t \) terms are ventilation factors to represent the effects of the motion of particles through the air on condensation and thermal conduction.
We use the full equations in our model for all particle sizes. For large particles, such as NAT, the equations have the dependencies that are obvious from the equations presented above. However, for sulfate and STS particles in stratosphere, the particle size \((r)\) is generally smaller than the mean free path \((H)\). At a typical stratospheric pressure of 50 hPa and temperature of 200 K, the mean free path is about 0.8 micron. That means the Knudsen numbers \((K_{nd} = H_d/r\) and \(K_{nt} = H_t/r\)) are often larger than 1 in stratosphere. In that case the equations have different dependencies. The vapor diffusivity \((D)\), and thermal conductivity \((K)\) can be written as:

\[
D = D' C / (r + \lambda C K_{nd} / \Phi_0) \\
K = K' C / (r + \lambda_t C K_{nt} / \Phi_0)
\]

where

\[
\lambda = (1.33 + 0.71/K_{nd})/(1 + 1/K_{nd}) + 1.33(1 - \alpha_a) / \alpha_a \\
\lambda_t = (1.33 + 0.71/K_{nt})/(1 + 1/K_{nt}) + 1.33(1 - \alpha_t) / \alpha_t
\]

Here \(\alpha_a\) (the sticking coefficient) and \(\alpha_t\) (the thermal accommodation coefficient) are assumed to be unity for STS [Toon et al., 1989]. Some data suggest that they may be less than one for HNO\(_3\) condensing [Crowley et al., 2010]. \(D'\) is the temperature dependent diffusivity of the appropriate vapor in air. The diffusion coefficient \(D'\) for water vapor is given by Pruppacher and Klett [1997]. For HNO\(_3\), we use the similar expression [Larsen, 2000]:

\[
D'_{HNO_3} = A \times D'_{H_2O}
\]

In Larsen’s paper [Larsen, 2000], \(A\) is 0.559. Here, we tune \(A\) to match measurements for the diffusivity of HNO\(_3\) in air at 296 K, 1 atm [Tang et al., 2014]. Here, \(A\) is 0.466.

\(K'\) is the thermal conductivity of air; and \(C\) is the capacitance of the particles [Pruppacher and Klett, 1997]. The definitions of Knudsen numbers can also be written as:

\[
K_{nd} = H_d/r = 3D'/(\nu_w r)
\]
\[ K_{nt} = \frac{H_t}{r} = 3K'/(\rho v_t(C_p - 0.5R)r) \]

Here, \( v_w \) is the mean thermal velocity of a water molecule and \( C_p \) is the heat capacity of air. Since we assume spherical particles, \( C \) has a value of unity, as does \( \Phi_0 \), which is a shape correction for thermal diffusion. Therefore, for the stratospheric small particle limit, the diffusivity and conductivity can be simplified as:

\[ D = D'/(\lambda_{nt}) = D'/\left(3\lambda D'/v_w r\right) = v_w r / (3\lambda) \]

\[ K = K'/(\lambda_{nt}) = K'/\left(3\lambda K'/(\rho v_t(C_p - 0.5R)r)\right) = \rho v_t(C_p - 0.5R)r / (3\lambda_t) \]

In the growth rate equation we ignore the possibility that the vapor pressures might be modified by dissolved species such as HCl [Toon et al., 1986; Weisser et al., 2006] and micrometeorites, which could alter the vapor pressure for pure substances. When multiple species grow, we sum their growth rates. Strictly speaking the terms should not be summed because the latent heat release from the condensational growth of each species affects all the others. However, latent heat release is negligible for PSCs.

From equation (A1), we can get the particle growth/evaporation rate, and how much H\(_2\)SO\(_4\) and HNO\(_3\) mass should be moved between bins. Therefore, the aerosol continuity equation can be solved to obtain the new particle concentration:

\[ \frac{\partial C(m)}{\partial t} = -\frac{\partial C(m)g(m)}{\partial m} \]

Where \( C(m) \) is the concentration of particles with mass \( m \); \( g(m) \) is the growth or evaporation rate for particles with mass \( m \). Here, \( g(m) \) is the same as \( \frac{dm}{dt} \) in equation (A1). The meaning of the equation is that the rate of change of the particle concentration is determined by the divergence of the flux of particles moving from other masses to mass \( m \) and from mass \( m \) to other masses. A mass conserving, ratio conserving advection scheme [Lin and Rood, 1996, 1997] is used to solve this advection equation.
The growth equation requires equations for acid concentrations, vapor pressures and surface tensions among others to calculate the growth rate. These are described below.

A.1 Acid concentration

The acid concentration, or weight percent, is required to calculate vapor pressure, surface tension and solution density for ternary particles. The weight percent of HNO$_3$, H$_2$SO$_4$ and H$_2$O are based on Luo et al.’s scheme [Luo et al., 1995], which assumes that water vapor is in equilibrium with the particles.

There are several other models that consider either STS or binary sulfuric acid water vapor pressures and weight percentages. The Tabazadeh’s scheme [Tabazadeh et al., 1997] has been successfully used to calculate the weight percent of sulfuric acid and aerosol size in the WACCM/CARMA sulfate model [English et al., 2011]. However, Tabazadeh’s scheme doesn’t consider a ternary solution. We find two schemes that treat STS. We find that both Luo et al.’s [Luo et al., 1995] and Zhang et al.’s [Zhang et al., 1993] methods agree well with Tabazadeh et al.’s scheme between 185 K to 235 K assuming the HNO$_3$ amount is zero. However, the scheme of Zhang et al. is quantized and more time consuming to use in the model. Therefore, Luo’s scheme is used in this STS-PSC model.

It is more complex to determine the weight percents when HNO$_3$ is present in the particles, and a vapor pressure equation is needed. We discuss this case in the next section.

A.2 Vapor pressures

We use the H$_2$SO$_4$ vapor pressure equation given by Kulmala and Laaksonen [1990], which is valid for a wide range of temperatures for a given weight percent solution. This formulation does not consider HNO$_3$ condensed on the particles. However,
the vapor pressure of H$_2$SO$_4$ is very low for polar night temperatures, so it is not a limiting factor in condensational growth, although ignoring the effects of HNO$_3$ on the sulfuric acid vapor pressure might impact the sulfuric acid nucleation calculations.

The HNO$_3$ vapor pressure (in hPa) for STS particles is expressed as [Luo et al., 1995]:

$$\ln p_{HNO_3} = A_{HNO_3} + B_{HNO_3}/T + \ln [\omega_1 (\omega_1 + 0.09 \omega_2)]$$

Where $\omega_1$ and $\omega_2$ are the weight percent of H$_2$SO$_4$ and HNO$_3$. $A_{HNO_3}$ and $B_{HNO_3}$ are constants and $T$ is the temperature. CARMA tracks the abundance of H$_2$SO$_4$ and HNO$_3$ in each particle size class so the ratio of $\omega_1$ and $\omega_2$ is determined for each particle size class by CARMA.

We assume H$_2$O is in equilibrium with the particles so that the vapor pressure of water over the particles is also known. Given the water vapor pressure, and the ratio of $\omega_1$ to $\omega_2$, the empirical equation below contains only one unknown parameter, so it can be solved iteratively to determine the weight percents:

$$\ln p_{H_2O} = 23.306 - 4.5261 \omega_1 - 5.3465 \omega_2 + \omega_h (7.451 \omega_1 + 12 \omega_2) - \omega_h^2 (4 \omega_1 + 8.19 \omega_2)$$

$$+ [-5814 + 1033 \omega_1 + 928.9 \omega_2 - \omega_h (2309 \omega_1 + 1876.7 \omega_2)]/T$$

Where $\omega_h = \omega_1 + 1.4408 \omega_2$ and $\omega_1 = \omega_2 \times \text{ratio}$.

The HNO$_3$ vapor pressure (in Torr) for NAT particles is expressed as [Hanson and Mauersberger, 1988]:

$$\log_{10}(P_{HNO_3}) = m(T) \cdot \log_{10}(P_{H_2O}) + b(T)$$

Where

$$m(T) = -2.7836 - 0.000887 T$$

$$b(T) = 38.9855 - 11398/T + 0.009179 T$$

In the equations, temperature, $T$, needs to be in the range from 180 K to 200 K. $P_{HNO_3}$ and $P_{H_2O}$ are in Torr.
A.3 Surface tension and density

The surface tension, $\gamma$, and the density, $\rho$, of ternary solutions is calculated by using empirical polynomial equations [Martin et al., 2000]:

$$\gamma(x,y) = \frac{\sum_{i=0}^{5} \sum_{j=0}^{5} \gamma_{ij} x^i y^j}{(\gamma_0 + \gamma_1 x + \gamma_2 y)^2}$$

$$\rho(x,y) = \sum_{i=0}^{4} \sum_{j=0}^{3} \rho_{ij} x^i y^j$$

Where $\gamma_{ij}$, $\gamma_0$, $\gamma_1$ and $\gamma_2$ are the coefficients in the polynomial equation at temperatures of 293 K and 253 K. $x$ and $y$ are the weight percent of $\text{H}_2\text{SO}_4$ and $\text{HNO}_3$ in each particle respectively. Using the coefficients listed in Martin et al. [2000], we can calculate the surface tension and particle density of the ternary solution at 293 K and 253 K for each bin. We assume the surface tension and the density depend linearly on temperature, and interpolate the surface tension and the density to other temperatures.
B. Coagulation equation and coagulation kernel set-up in the model

The basic coagulation equation is:

\[
\frac{\partial C(m)}{\partial t} = \frac{1}{2} \int_{0}^{m} K_c(u,m-u)c(u)c(m-u)du - C(m)\int_{0}^{\infty} K_c(u,m)C(u)du
\]

The two terms on the right represent the coagulation production rate for particles of mass \( m \) due to coagulation of smaller particles and the second term is the loss rate of mass \( m \) particles due to coagulating to form larger particles.

\( K_c \) is the coagulation kernel. We use the Brownian coagulation kernel. A correction for the effect of Van der Waals forces between particles on Brownian coagulation [Chan and Mozurkewich, 2001] has been included in the CARMA model [English et al., 2011].

Although we use a general formulation, under the limit when the mean free path is much larger than the particle size (which roughly applies to sulfuric acid and STS particles), the Brownian coagulation kernel \( K_c \) is:

\[
K_c = \alpha_s \pi (r_1 + r_2)^2 \sqrt{(v_1^2 + v_2^2)}
\]

In this equation, two particles with radius \( r_1 \) and \( r_2 \) coagulate with each other with kinetic speeds of \( v_1 \) and \( v_2 \). \( \alpha_s \) is the probability that the two particles will stick together. The coagulation kernel expresses the volume swept out by coagulating particles in a second and has units of \( \text{cm}^3 \text{s}^{-1} \). Figure B 1 shows the coagulation kernel as a function of particle sizes at 50 hPa in the CARMA model. The coagulation kernel varies only slightly with pressure. The Brownian coagulation kernel ranges from \( 10^{-10} \) cm\(^3\)/s to \( 10^{-2} \) cm\(^3\)/s.
Figure B 1 Brownian coagulation kernel at 50 hPa for particle sizes typical of polar sulfate aerosols and STS.
C. Sedimentation of particles

The WACCM model transports the particles via resolved winds and eddy diffusion. However the PSC vertical movement due to gravitational sedmentation and Brownian diffusion is simulated in CARMA:

\[
\frac{\partial C}{\partial t} = -\frac{\partial (V_{\text{fall}}C)}{\partial z} + \frac{\partial}{\partial z} \left[ \rho K_z \frac{\partial (C/\rho)}{\partial z} \right] \tag{C1}
\]

Where \(C\) is a given particle concentration in a fixed mass bin, \(V_{\text{fall}}\) is the fall velocity calculated in CARMA, and \(K_z\) is the Brownian diffusion coefficient. For Reynolds numbers less than \(10^{-2}\) (particle radius less than about 10 \(\mu\)m, which is suitable for stratosphere sulfate aerosols and PSCs), CARMA uses the Stokes-Cunningham equation [Toon et al., 1989]:

\[
V_{\text{fall}} = 2Br^2\rho_p g/\rho
\]

Where \(r\) is the radius of the particle, \(\rho_p\) is the density, and \(\mu\) is the dynamic viscosity of air. \(B\) is the slip correction for the kinetic limit in which particles are smaller than the mean free path of air. For sphere, \(B\) is written as:

\[
B = 1 + 1.246Kn + 0.42Kn e^{-0.87/Kn}
\]

\(Kn\) is the Knudsen number, which is the ratio of mean free path and the particle radius. In the stratosphere, the sulfate particles are generally smaller than the mean free path (at a typical stratosphere condition with 50 hPa and 200 K, the mean free path is about 0.8 micon). For those particles which have large \(Kn\), \(B\) is simplified as \(B=1.666Kn\) and the fall velocity equation can be written in kinetic limit:

\[
V_{\text{fall-kinetic}} = \beta \rho_p g r / 2n_a \sqrt{\frac{\pi}{2m_a kT}}
\]

Where, \(n_a\) is the number density of air molecules; \(m_a\) is the mass of an air molecule; \(\beta = 1.35\) for diffuse molecular scattering; = 1 for specular reflection.
For those particles which have large Reynolds number, the fall velocity equation needs to use the drag coefficient for correction. The relation between Reynolds number and drag coefficient is expressed by *Le Clair et al.* [1970].

The second term on the right of equation (C1) includes the Brownian diffusion coefficient. CARMA treats Brownian diffusion of aerosols, which is important above 100 km, and not well treated by algorithms in WACCM [English et al., 2011]. The vertical advection equation is solved by using the finite-volume scheme to guarantee mass conservation and tracer ratio conservation [Lin and Rood, 1996, 1997].

Figure C 1 shows the fall velocity as a function of particle size at different pressure levels, assuming the environmental temperature is 200 K and particle density is 1.9 g/cm³. The figure indicates that the STS particles, with a typical radius of 0.5 micron, have a fall velocity of $10^{-2}$-$10^{-1}$ cm/s, or about 0.3-3 km/month. While, NAT particles, with a size of 10 µm fall about 3 cm/s, or about 3 km/day. The high fall velocity of large NAT particles causes NAT particles to be important for denitrification.

![Figure C 1 Fall velocity as a function of particle size at different stratospheric pressure levels.](image)


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