The global influence of dust mineralogical composition on heterogeneous ice nucleation in mixed-phase clouds

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Abstract
Mineral dust is the dominant natural ice nucleating aerosol. Its ice nucleation efficiency depends on the mineralogical composition. We show the first sensitivity studies with a global climate model and a three-dimensional dust mineralogy. Results show that, depending on the dust mineralogical composition, coating with soluble material from anthropogenic sources can lead to quasi-deactivation of natural dust ice nuclei. This effect counteracts the increased cloud glaciation by anthropogenic black carbon particles. The resulting aerosol indirect effect through the glaciation of mixed-phase clouds by black carbon particles is small (+0.1 W m⁻² in the shortwave top-of-the-atmosphere radiation in the northern hemisphere).

Keywords: aerosol indirect effect, heterogeneous freezing, ice nuclei deactivation, mixed-phase clouds

1. Introduction

Aerosol particles interact with clouds in several ways. Their influence on liquid clouds has been studied extensively (e.g., Twomey 1974, Albrecht 1989). Anthropogenic aerosols add to the number of condensation nuclei available for droplet nucleation. An increased number of droplets at fixed cloud water content leads to a higher cloud albedo. Furthermore, the suppression of precipitation through more but smaller droplets increases the cloud lifetime. The magnitude of the different indirect aerosol forcings is still unclear (Lohmann and Feichter 2005).

In mixed-phase clouds a third effect, the cloud glaciation effect, has been hypothesized (Lohmann 2002a). Mixed-phase clouds, containing both liquid and frozen water, are frequent in mid-latitude and polar regions (Quante 2004). At temperatures below 0°C, water droplets do not freeze spontaneously, but can persist as supercooled liquid until approximately −38 °C, the homogeneous freezing temperature. At warmer temperatures, freezing of droplets occurs only through heterogeneous nucleation on ice nuclei. Ice nuclei are predominantly insoluble particles, such as mineral dust or metallic material (Richardson et al 2007). The relative importance of the different nucleation modes (deposition, immersion, condensation and contact freezing) is still unclear. For immersion freezing an ice nucleus within a supercooled cloud droplet initiates the freezing process, while during contact freezing a supercooled droplet collides with a dry ice nucleus, such that the freezing process is initiated from the outside. Deposition refers to the direct growth of ice from the vapour on a dry ice nucleus, while for condensation freezing first a liquid layer condenses on a particle, which subsequently initiates the freezing. Although these ice nucleation processes are more efficient the lower the temperature and the higher the supersaturation over ice, observed ice crystal number concentrations are highly variable for a given temperature and do not generally increase with lower temperatures (Gultepe et al 2001).

As long as unfrozen droplets remain, the in-cloud air is saturated with respect to supercooled liquid water, and thus is supersaturated with respected to ice. This leads to rapid growth of the ice crystals and vaporization of the droplets (Bergeron–Findeisen process) (Findeisen 1938). Therefore precipitation formation is more efficient in mixed-phase clouds than in...
warm clouds (Rogers and Yau 1989). For anthropogenic ice nuclei, such as black carbon (soot), this is called the "glaciation indirect effect". Natural ice nuclei, which have not increased through human activity, do not add to the glaciation indirect effect.

Lohmann and Diehl (2006) have presented sensitivity experiments with the ECHAM4 general circulation model. This was the first general circulation model study which took the efficiencies of ice nuclei of different chemical composition into account. However, for freezing on mineral dust, only the two extreme cases of (1) all dust consisting of kaolinite, a less efficient ice nucleus, or (2) all dust consisting of montmorillonite, a highly efficient ice nucleus (Pitter and Pruppacher 1973), were considered. They showed that whether dust is assumed to be composed of kaolinite or montmorillonite had significant implications for the total indirect aerosol effect, with the decrease in top-of-the-atmosphere net radiation between preindustrial and present-day climate varying between 1 ± 0.3 and 2.1 ± 0.1 W m⁻².

Whether anthropogenic activity actually increases or decreases ice nuclei (IN) concentrations is a matter of debate. As reviewed by Szyrner and Zawadzki (1997), emissions from vegetation fires, rocket exhaust, and certain industries have been shown to be prolific IN sources. However, some studies have also reported a decrease of IN concentration due to human activity. Brahm and Spyers-Duran (1974) found significant deactivation of natural IN, measured at a fixed temperature of -16.6 °C, in passing over a big city. Borys (1989) reported that pollution-derived Arctic haze aerosol has a factor of 10–1000 lower fraction of ice nucleating particles, measured at -25 °C and water saturation, than the Arctic aerosol during clean conditions. Based on these data, Girard et al (2005) formulated an IN reduction factor, depending on sulfuric acid mass concentration. Deactivation of ice nuclei can be due to the coating of insoluble, highly active contact IN with soluble material. With a coating of, for example, sulfuric acid, these particles could act as immersion or condensation nuclei instead, but these processes require lower freezing temperatures. For example, Pitter and Pruppacher (1973) measured a median freezing temperature for kaolinite particles in the contact mode of -12 °C and of -28 °C in the immersion mode. Dust particles often get coated with sulfate, e.g. by cloud processing, as observed in the eastern Mediterranean by Levin et al (1996). Ansmann et al (2005) put forward deactivation of dust ice nuclei by coating and mixing with hygroscopic material as an explanation for an observed nonglaciated cloud at -9 to -16 °C in the presence of a layer of Saharan dust transported over Europe. Storelvmo et al (2007) were the first to test this hypothesis in a global model, assuming that dust particles act as immersion nuclei rather than contact nuclei if enough sulfuric acid is present in a gridbox for a coating of one monolayer. This resulted in less efficient freezing in the present-day climate than in the preindustrial climate.

In this study, we use the coupled aerosol–climate model ECHAM5-HAM, taking into account the coating of dust and black carbon particles with sulfate. By introducing monthly mean mineralogical compositions, which vary regionally depending on the origin of the dust, we aim at constraining the model between the two extreme cases of pure kaolinite or pure montmorillonite dust. For this we use a database by Claquin et al (1999), who have compiled the mineralogical composition of mineral dust for all global source areas. For the clay fraction, i.e. particles smaller than 3 μm in diameter, the kaolinite, smectite (montmorillonite), illite, calcite and quartz mass fractions are given for a variety of soils. Kaolinite, smectite and illite together make up more than 70% in mass of the clay fraction of all investigated soils, for most cases even more than 85%. Illite is on average more abundant than smectite, but its ice nucleating properties have rarely been investigated. Hoffer (1961) found a very similar behaviour of illite and montmorillonite with respect to immersion freezing. Therefore we do not distinguish these two minerals in the present study.

2. Model description

We use the coupled aerosol–climate model ECHAM5-HAM (Stier et al 2005) with a microphysics module that includes prognostic equations for the cloud droplet number concentration (Lohmann et al 1999) and ice crystal number concentration (Lohmann 2002b, Lohmann et al 2007). The treatment of heterogeneous freezing is described below. The model we use is a preliminary version of ECHAM5.302 with only four instead of six shortwave spectral bands and without the cirrus scheme by Kärlcher and Lohmann (2002) and Lohmann and Kärcher (2002), which gives a slightly different aerosol indirect effect than in Lohmann et al (2007). However, this study mainly aims at comparing the different sensitivity scenarios and not at giving robust forcing estimates. Furthermore, only heterogeneous ice nucleation in mixed-phase clouds is studied here.

2.1. Heterogeneous freezing parameterization

The parameterizations of heterogeneous freezing processes between 0° and -35 °C are based on the parameterizations used in ECHAM4 as described in Lohmann and Diehl (2006), but they have been modified for this study to make use of the aerosol fields of ECHAM5-HAM and the offline dust mineralogy. We account for contact and immersion/condensation freezing. Homogeneous freezing and deposition nucleation is thought to be negligible in mixed-phase clouds.

The freezing rate via contact nucleation (cnt) is based on Young (1974) and Cotton et al (1986). It takes into account contact through Brownian diffusion, depending on the size of the droplets and of the aerosol particles. In contrast to Lohmann and Diehl (2006), we do not prescribe the initial mass of an individual ice crystal but set this mass equal to the droplet’s mass before freezing. This reflects the assumption that the droplets do not break up during freezing.

\[ Q_{\text{frz,cnt}} = -\frac{dN_t}{dt}_{\text{frz,cnt}} = D_{ap}4\pi r_lN_{a,cnt}N_t. \]  \( (1) \)
Table 1. Parameters $a_x$ and $b_x$ for contact freezing (Diehl et al. 2006) and parameter $c_x$ for immersion freezing (Diehl and Wurzler 2004).

| $x$ | $a_x$ (K$^{-1}$) | $b_x$ | $c_x$ (m$^{-1}$) |
|-----|-----------------|-------|-----------------|
| BC  | 0.0614          | 0.5730| 0.00291         |
| KAO | 0.1007          | 0.6935| 0.0615          |
| MON | 0.1014          | 0.3277| 32.3            |

$N_i$ is the concentration of liquid cloud droplets, $D_{ap}$ is the size-dependent Brownian aerosol diffusivity, and $n_i$ is the volume mean droplet radius. $N_{a,\text{cnt}}$ is the number of contact nuclei. It is parameterized (in deviation from the original formulation by Young (1974)) as follows, taking into account the ice nucleation efficiencies of different aerosols:

$$N_{a,\text{cnt}} = \sum_x \max(1, \min(0, (-a_x(T - 273.15 \text{ K}) - b_x))) \times \frac{N_{\text{cnt},x}}{N_{\text{aer,insol}}(N_l + N_i)}$$

with

$$x = \text{BC (black carbon), KAO (kaolinite), MON (montmorillonite).}$$

$N_i$ is the ice crystal number concentration, $N_{\text{aer,insol}}$ the total insoluble aerosol number concentration and $N_{\text{cnt},x}$ a number concentration of the maximum available contact ice nuclei of material $x$. $T$ is the temperature in K. The parameters $a_x$ and $b_x$ (see table 1) are related to the material’s effectiveness to act as ice nuclei in the contact freezing mode and have been determined from a compilation of experimental data by Diehl et al. (2006). Equation (2) has been derived from the parameterization of the number of frozen droplets as a function of the total (frozen plus unfrozen) droplet number, which is equivalent to $N_l + N_i$, by Diehl et al. (2006). Note that $N_{a,\text{cnt}}$ does not directly transfer into ice crystal concentrations, because the collision rate (equation (1)) is the limiting process for contact nucleation.

In ECHAM5-HAM, aerosol particles are represented as an external mixture of internally mixed modes (see table 2). Coating of insoluble particles is simulated online. Only uncoated particles are assumed to act as contact nuclei. Therefore $N_{\text{cnt},x}$ is obtained by summing up the number concentrations of all insoluble modes which contain that component and weighting this number with the surface area.

$$N_{\text{cnt,BC}} = \left(\frac{m_{\text{BC,KI}}}{m_{\text{BC,KI}} + m_{\text{OC,KI}}}\right)^{2/3} N_{\text{KI}}$$

$$N_{\text{cnt,KAO}} = (N_{\text{AI}} + N_{\text{CI}}) x_{\text{KAO}}$$

$$N_{\text{cnt,MON}} = (N_{\text{AI}} + N_{\text{CI}}) x_{\text{MON}}.$$  

$m$ are mass mixing ratios. The indices of the variables in these equations refer to the different modes and aerosol components in ECHAM5-HAM and are listed in table 2. $x_{\text{KAO}}$ and $x_{\text{MON}}$ are the mass fractions of the dust components kaolinite and montmorillonite, which are not calculated in ECHAM5-HAM, but are obtained from an offline transport model as described in section 2.2. Here we assume that the different dust mineralogical components are externally mixed. As discussed by Balkanski et al. (2006), both external and internal mixtures of different minerals can possibly be generated during dust emission.

The aerosol modes and components in ECHAM5-HAM (SO4 = sulphate, BC = black carbon, OC = organic carbon, SS = sea salt, DU = dust).

Table 2. The aerosol modes and components in ECHAM5-HAM (SO4 = sulphate, BC = black carbon, OC = organic carbon, SS = sea salt, DU = dust).

- **Internally mixed/soluble modes**
  - KS: Aitken mode, soluble
  - AS: accumulation mode, soluble
  - CS: coarse mode, soluble

- **Externally mixed/insoluble modes**
  - NS: nucleation mode, soluble
  - KS: Aitken mode, insoluble
  - AS: accumulation mode, insoluble
  - CS: coarse mode, insoluble

The contributions $N_{\text{imm},x}$ of the three different potential immersion freezing nuclei are calculated by

$$N_{\text{imm,BC}} = \left(\frac{m_{\text{BC,KS}}/\rho_{\text{BC}}}{V_{\text{KS}}}\right)^{2/3} N_{\text{KS}}$$

$$+ \left(\frac{m_{\text{BC,AS}}/\rho_{\text{BC}}}{V_{\text{AS}}}\right)^{2/3} N_{\text{AS}}$$

$$+ \left(\frac{m_{\text{BC,CS}}/\rho_{\text{BC}}}{V_{\text{CS}}}\right)^{2/3} N_{\text{CS}}.$$
In the previous equations, $V_{KS}$, $V_{AS}$ and $V_{CS}$ are the total dry volumes per kg of aerosol particles in the Aitken, accumulation and coarse soluble/mixed modes, respectively.

$$
V_{KS} = m_{SO4,KS}/\rho_{SO4} + m_{BC,KS}/\rho_{BC}
+ m_{OC,KS}/\rho_{OC}
$$

$$
V_{AS} = m_{SO4,AS}/\rho_{SO4} + m_{BC,AS}/\rho_{BC}
+ m_{OC,AS}/\rho_{OC} + m_{SS,AS}/\rho_{SS}
+ m_{DU,AS}/\rho_{DU}
$$

$$
V_{CS} = m_{SO4,CS}/\rho_{SO4} + m_{BC,CS}/\rho_{BC}
+ m_{OC,CS}/\rho_{OC} + m_{SS,CS}/\rho_{SS}
+ m_{DU,CS}/\rho_{DU}.
$$

The densities of the components are $\rho_{SO4} = 1841$ kg m$^{-3}$, $\rho_{BC} = 2000$ kg m$^{-3}$, $\rho_{OC} = 2000$ kg m$^{-3}$, $\rho_{SS} = 2165$ kg m$^{-3}$ and $\rho_{DU} = 2650$ kg m$^{-3}$.

The cooling rate $dT/dr$ in equation (5) is derived from the vertical velocity $w$, which is obtained for liquid and mixed-phase clouds from $w = \bar{w} + 1.33\sqrt{TKE}$, with the large-scale vertical velocity $\bar{w}$ plus a subgrid-scale contribution estimated from the turbulent kinetic energy TKE (Lohmann et al. 2007). The turbulent contribution is usually much larger than the large-scale vertical velocity. For an adiabatic temperature gradient, this converts into the following temperature tendency:

$$
\frac{dT}{dr} = -\frac{g}{c_p}w.
$$

This trend is significantly larger than the large-scale temperature tendency $dT/dr$ alone which was used by Lohmann and Diehl (2006) for immersion freezing in ECHAM4. This increases the relative importance of immersion freezing compared tocontact freezing.

Figure 1 depicts $Q_{frz, cnt}$ and $Q_{frz, imm}$ for pure black carbon, montmorillonite and kaolinite aerosol, for typical values of cloud properties and aerosol radii of freshly emitted particles from Stier et al. (2005). Contact freezing on montmorillonite sets in at the highest temperatures (~4°C), followed by kaolinite. Contact freezing on black carbon sets in below ~9°C, but then attains two orders of magnitude higher values than contact freezing on mineral dust. This is due to the higher aerosol diffusivity $D_{ag}$ of the Aitken mode black carbon particles compared to the accumulation mode dust particles.

Immersion freezing on montmorillonite becomes significant compared to contact freezing below ~25°C, and immersion freezing on kaolinite only below ~31°C. Immersion freezing on black carbon is negligible for this set of cloud parameters until close to the homogeneous freezing threshold, where heterogeneous freezing is switched off in the model.

Freezing by Aitken-mode particles has not been definitely proven to occur in the atmosphere. On the one hand, residuals from ice particles are often found to be on average larger than ambient particles (e.g., by Richardson et al. 2007). On the other hand, Seifert et al. (2003) reported that small ($d < 100$ nm) aerosol particles dominated the number density of residuals for measurements in cirrus clouds during the INCA campaign (Interhemispheric differences in cirrus properties from anthropogenic emissions), and related this finding to heterogeneous nucleation. Most laboratory studies investigated freezing only on ice nuclei with a diameter of 100 nm or larger. Sax and Goldsmith (1972), however, showed that silver iodide particles with a radius of 10 nm can act as efficient contact ice nuclei, colliding with droplets in free fall by Brownian diffusion.

The Bergeron–Findeisen process is parameterized as a threshold process (Lohmann et al. 2007). Once heterogeneous freezing leads to an ice water mixing ratio larger than the threshold value of 0.5 mg kg$^{-1}$, the remaining cloud droplets evaporate within one model timestep and the water mass is deposited onto the existing ice crystals. Ice crystal multiplication at temperatures between ~3 and ~8°C via the Hallett–Mossop process is also taken into account (Lohmann 2002b).

2.2. Dust mineralogical composition

The dust mineralogy fields have been calculated offline with the chemistry transport model TM3 (Tegen et al. 2002). The mineral dust source strength is governed by the wind speed and soil parameters. The source scheme of this model includes preferential sources of dust emission (topographic depressions), a seasonally changing vegetation masking dust emissions (Tegen et al. 2002) and satellite retrieved roughness lengths (Prigent et al. 2005). The computation of the
The mineralogical composition is based on Claquin et al. (1999), but is simplified by using only 27 major soil types, averaging the results by Claquin et al. (1999) for 107 soil types with area-weighted means. The mineralogical composition of the soil obtained in this way is shown in figure 2 for the four components illite, smectite, kaolinite and calcite/quartz in the clay fraction. The clay fraction is defined here as fine particles up to a radius of 1.5 μm, even though this fraction also contains some quartz/calcite. This corresponds to the dust calculated by ECHAM5-HAM, which does not contain the large dust fraction.

The four components are transported as tracers in the model such that the mineralogical composition of airborne dust at each grid point can be calculated. TM3 was driven with meteorological fields from the ERA15 reanalysis for the year 1987. The timestep for computing the dust sources was 6 h. The source fields were computed with 1.125° × 1.125° horizontal resolution.

ECHAM5-HAM also includes the Tegen et al. (2002) dust emission scheme. The mass flux of emitted dust is distributed into two lognormal modes with mass-median radii of 0.37 and 1.75 μm (Stier et al. 2005). These size distribution parameters have been obtained by a fit of multi-annual global mean emitted size distribution, represented by 24 size bins in the emission scheme by Tegen et al. (2002), with three lognormal modes. The super-coarse mode is neglected in ECHAM5-HAM because of its short lifetime. The dust emissions are attributed to the insoluble accumulation and coarse modes AI and CI (table 2). Subsequent coating or coagulation with soluble material transfers the dust particles into the internally mixed modes AS and CS.

As in this study montmorillonite is also used as a proxy for illite (with respect to its freezing behaviour), the montmorillonite fraction \( x_{\text{MON}} \) (equations (3c) and (6c)) is defined as the ratio of the sum of the illite and smectite (which is a synonym for the montmorillonite clay group) mixing ratio divided by total clay mixing ratio. The kaolinite fraction \( x_{\text{KAO}} \) (equations (3b) and (6b)) is the kaolinite mixing ratio divided by the total clay mixing ratio.

The montmorillonite and kaolinite fractions were stored as monthly mean three-dimensional fields and used as input to ECHAM5-HAM. Figure 3 shows the annual mean kaolinite and montmorillonite fractions of the total atmospheric clay burden. Montmorillonite (49–60%) is more abundant than kaolinite (30–42%). In general, the kaolinite fraction is larger in the southern hemisphere because the kaolinite fraction in the soil is also largest in southern Africa, South America and Australia (see figure 2). The montmorillonite fraction on average behaves reciprocally to kaolinite. The monthly fields on individual levels (not shown) exhibit a stronger variance.

2.3. Evaluation of the dust mineralogical composition fields

The simulated mineralogical composition on the lowest level has been compared to various measurements of airborne particles and wet deposition samples. Figure 4 shows that overall the model simulates excessively uniform values for the kaolinite and montmorillonite fraction. Kaolinite tends to be underestimated, while montmorillonite (compared to the sum over illite and smectite measurements) shows less of a bias. This suggests that the calcite/quartz content of the measurements was higher than simulated. In part, this bias can be due to the inclusion of particles larger than 3 μm in diameter, which tend to be richer in quartz, in the analysis. The observations refer to individual events at precise locations, while the model simulates the mean mineralogical composition.
for a larger area, averaged over a time period of one month. Additionally, the observations rely on a number of different techniques, so that individual values might not be comparable. The observations do not show any clustering regarding their large-scale source area (colour-coded in figure 4). Therefore some lack of variability in the model is not surprising. In the coherent dataset by Stuut et al. (2005), which has been measured on a 8000 km cruise along the west African coast, a north-to-south increase of the kaolinite fraction has been observed. This is also reproduced in the model, although with an offset to higher values (see red squares in figure 4, left plot).

2.4. Simulations

Three pairs of simulations have been carried out (see table 3). In the simulation MIX the dust mineralogy described above has been used. In the sensitivity experiments KAO and MON, dust is assumed to be composed completely of one mineralogical component. Simulations with this assumption have also been studied by Lohmann and Diehl (2006). The simulations are run for 5 years (after a 3-month spin-up) in T42L19 resolution ($2.8^\circ \times 2.8^\circ$, 19 vertical levels with a top at 10 hPa, and a timestep of 15 min), using climatological sea surface temperatures and sea ice extent. Each simulation has been carried out once with present-day aerosol emissions and once with emissions representative for the preindustrial era, as described in Lohmann et al. (2007). For the preindustrial (PI) simulations, the greenhouse gas concentrations and sea surface temperatures are held constant at their present-day values in order to isolate the aerosol effect. Mineral dust aerosol is considered as natural aerosol (i.e., no changes in soil properties between preindustrial and present-day conditions are taken into account), although the percentage of mineral dust emission caused directly or indirectly by human activity is still under discussion. Tegen et al. (2004) estimate it at less than 10%. In our simulations, differences in the mineral dust emissions are caused solely by changes in the wind field.
3. Results

3.1. Simulations of present-day climate

A thorough evaluation of ECHAM5-HAM is presented by Lohmann et al. (2007). Here we focus on differences between the three simulations MIX, KAO and MON. Annual zonal means of cloud liquid and ice water path, which can be compared to satellite observations, are shown in Figure 5. The three sensitivity studies differ only slightly. Figure 5(a) shows the liquid water path (LWP) over the ocean surface compared to SSM/I retrievals by Greenwald et al. (1993), Weng and Grody (1994) and Wentz (1997). The global mean values amount to 67.6 g m\(^{-2}\) in simulation MIX, 67.9 g m\(^{-2}\) in simulation KAO and 67.4 g m\(^{-2}\) in simulation MON. This falls within the observed range of 50–84 g m\(^{-2}\). The zonal distribution is only partly captured in the simulations. Around the equator, ECHAM5-HAM simulates a too low liquid water path, while it is comparable to observations in the subtropics and mid-latitudes.

The ice water path (IWP) is 27.8 g m\(^{-2}\) in simulations KAO and MIX and 27.9 g m\(^{-2}\) in simulation MON, which compares well to an estimate derived from ISCCP data by Storelvmo et al. (2007) of 29.5 g m\(^{-2}\). The zonal distribution is well captured between 60\(^\circ\)S and 60\(^\circ\)N. At high latitudes, the comparison is more uncertain, because no satellite observations are available during the polar night.

In order to study the differences between the three sensitivity studies KAO, MON and MIX, we analyse the vertically integrated heterogeneous freezing rate, which reflects the effectiveness of freezing of the mineral dust. The zonal mean freezing rate, given as the number of frozen droplets in a vertical column per unit time and area, is highest in simulation MON and lowest in simulation KAO (Figure 6).

Figure 7 shows the global distributions of the vertically integrated number freezing rates. Here ‘freezing on dust’ includes both contact and immersion freezing on dust, and ‘freezing on BC’ both contact and immersion freezing for black carbon. The freezing rates are in general larger at higher latitudes and larger over the continents than over the ocean, due to higher cloud droplet number concentrations over continents, resulting in more contact freezing. Additionally, the chance of cloud supercooling is enhanced at higher latitudes and also higher altitudes over orography. Overall, freezing by black carbon is simulated more frequently because of the high number concentrations and small sizes, thus high contact efficiencies, of insoluble black carbon particles. In some regions, e.g. south-east Asia, black carbon clearly dominates over freezing on dust. On the other hand, dust dominates the freezing at higher latitudes. Freezing on black carbon is very similar in the three simulations, such that the total freezing rate is essentially modulated by the freezing efficiency of dust.

Figure 6. Vertically integrated zonal and annual mean total heterogeneous freezing rates.

Dust and BC particle number burdens (Figure 8), calculated by equations (3a)–(3c) and (6a)–(6c), are 1–2 orders of magnitude higher in the coated modes (which constitute the maximum available immersion nuclei) than in the uncoated modes (the maximum available contact nuclei). Black carbon is more abundant in number, because the particles are smaller. While no global observations of the fraction of coated particles are available, field campaigns at selected locations support these model results. For example, Andreae et al. (1986) report that over remote oceans, 80–90% of the sampled silicate particles were associated with sea salt.
3.2. Anthropogenic climate forcing

A set of simulations for the preindustrial era has been run in order to study the sensitivity of the anthropogenic climate forcing by aerosols to heterogeneous freezing processes. The differences between present-day and preindustrial simulations are summarized in table 4 and shown as zonal averages in figure 9. They include both the direct aerosol effect and aerosol indirect effects on warm and mixed-phase clouds. Aerosol optical depth (AOD) increases from preindustrial to present-day times because of anthropogenic aerosol and precursor emissions. Cloud cover increases slightly because of the indirect cloud lifetime effect: more aerosol particles result in more cloud droplets, which (at constant liquid water content) have smaller sizes and therefore form precipitation less efficiently. Cloud lifetime increases and with it the mean cloud cover. The liquid water path increases because of the longer cloud lifetime. The ice water path remains nearly constant, because glaciated clouds dissipate quickly. The smaller cloud droplets also lead to increased scattering of incoming solar radiation (cloud albedo effect). The top-of-

Additionally, dust particles which are not internally mixed with sea salt can react with volatile and semi-volatile atmospheric compounds. Asian dust particles collected over the sea of Japan during ACE-Asia, filtered to exclude particles associated with sea salt, were mixed with nitrate (on average 26% of the individually sampled particles), sulfate (18%) and chloride (18%), with only a few particles containing more than one secondary acid (Sullivan et al. 2007). For black carbon, rapid ageing is observed, too. At the high-altitude Alpine research station Jungfraujoch, with no local sources nearby, BC was found to be scavenged into hydrometeors to the same extent as the bulk aerosol, which suggests that BC was covered with soluble material (Cozic et al. 2007).
Table 4. Global annual mean difference in liquid water path (LWP), ice water path (IWP), cloud droplet number burden \( (N_d) \), ice crystal number burden \( (N_i) \), cloud cover (CC) and top-of-the-atmosphere shortwave \( (F_{SW}) \), longwave \( (F_{LW}) \) and net \( (F_{net}) \) radiative fluxes between present-day and preindustrial simulations, with interannual standard deviations. \( F_{SW} \) and \( F_{net} \) are downward positive, \( F_{LW} \) is upward positive.

| Simulation   | KAO        | MON        | MIX        | MIX-nBC     |
|--------------|------------|------------|------------|-------------|
| \( \Delta \text{LWP} \) (g m\(^{-2}\)) | 7.26 ± 1.00 | 6.72 ± 0.81 | 7.25 ± 0.89 | 7.54 ± 0.92 |
| \( \Delta \text{IWP} \) (g m\(^{-2}\)) | 0.23 ± 0.28 | 0.28 ± 0.29 | 0.20 ± 0.15 | 0.39 ± 0.18 |
| \( \Delta N_i \) (10\(^{10}\) m\(^{-2}\)) | 1.030 ± 0.066 | 1.037 ± 0.067 | 1.069 ± 0.045 | 1.117 ± 0.076 |
| \( \Delta N_d \) (10\(^{10}\) m\(^{-2}\)) | 0.058 ± 0.012 | 0.063 ± 0.007 | 0.064 ± 0.009 | 0.072 ± 0.009 |
| CC (%)       | 0.63 ± 0.30 | 0.48 ± 0.20 | 0.48 ± 0.24 | 0.49 ± 0.27 |
| \( \Delta F_{SW} \) (W m\(^{-2}\)) | -2.24 ± 0.51 | -2.03 ± 0.41 | -2.25 ± 0.50 | -2.38 ± 0.43 |
| \( \Delta F_{LW} \) (W m\(^{-2}\)) | -0.16 ± 0.31 | -0.22 ± 0.22 | -0.20 ± 0.18 | -0.43 ± 0.15 |
| \( \Delta F_{net} \) (W m\(^{-2}\)) | -2.08 ± 0.43 | -1.80 ± 0.36 | -2.04 ± 0.56 | -1.86 ± 0.37 |

Figure 8. Particle number burdens (zonal and annual means) of coated and uncoated black carbon and dust particles, which provide the maximum available immersion \( (N_{imm,BC} \) and \( N_{imm,KAO} + N_{imm,MON} \) and contact \( (N_{cnt,BC} \) and \( N_{cnt,KAO} + N_{cnt,MON} \) nuclei numbers, respectively.

The differences between the three simulations are small and do not reflect a larger glaciation indirect effect in simulation KAO than in simulation MON. In the modelling study with ECHAM4 by Lohmann and Diehl (2006), assuming dust as a less efficient ice nucleus (kaolinite) increased the relative importance of freezing on black carbon and therefore increased the aerosol indirect effect on mixed-phase clouds and reduced the total aerosol indirect effect on the shortwave radiation. Only because of the larger compensating emission of longwave radiation was the net radiation also most negative in the ECHAM4 simulation KAO.

Splitting up the global mean vertically integrated freezing rate into contributions by contact freezing on dust, immersion freezing on dust, contact freezing on black carbon and immersion freezing on black carbon (figure 10) gives an explanation for this finding in the present study. Present-day total freezing rates are a factor of 4–6 higher than preindustrial freezing rates, partly because of higher droplet concentrations stemming from the aerosol indirect effect on warm clouds (especially over the continents) and partly because of higher black carbon concentrations. Immersion freezing on black carbon is negligible, but contact freezing on black carbon constitutes the major contribution to the total freezing rate. Its magnitude is very similar in KAO, MON and MIX. Uncoated black carbon particles, although they are far less abundant than coated black carbon particles (figure 8), trigger most of the freezing events in present-day conditions. Large differences are seen in the freezing on dust, where the lower ice nucleation efficiency of kaolinite is visible. In simulations MON and MIX, contact freezing amounts to ≈27% of the freezing on dust in the preindustrial climate and 15% in the present-day climate. In contrast, in simulation KAO, it amounts to 80% (preindustrial) and 68% (present-day), although the absolute value is lower. Note that the number freezing rates in figure 10 are not proportional to the mass of frozen water, as droplets in polluted regions (where freezing by black carbon is most important) are smaller than in remote regions and the frozen water mass is thus relatively smaller.

The partitioning between contact and immersion freezing on mineral dust is related to the ageing of the particles. Only uncoated mineral dust particles are potential contact nuclei, while coated (aged) particles can potentially initiate immersion freezing. Figure 11 shows the simulated present-day and preindustrial dust mass burden and the contributions of insoluble (uncoated) and soluble/mixed (coated) modes. The total dust burden is relatively constant, with 9.3 Tg (preindustrial) and 8.9 Tg (present-day), but the simulated contribution of uncoated dust to the total dust burden has shifted from 61% in preindustrial conditions to 48% in present-day conditions. Anthropogenic emissions of sulfate and SO\(_2\) lead to a faster ageing of the dust aerosol and thus a slightly larger removal rate. This shift is more pronounced in the northern hemisphere. Uncoated dust particles are found closer to the source regions and are on average larger than the aged, coated dust particle population, from which the largest particles have been removed by sedimentation and efficient wet deposition. Therefore the uncoated particles are less abundant in number (figure 8).

Translated to dust ice nuclei concentrations, in the present-day climate fewer potential contact nuclei and more potential immersion nuclei are available. As kaolinite ice nuclei are very inefficient in the immersion mode, this shift signifies a quasi-deactivation. Montmorillonite particles, on the other hand, are still active ice nuclei even when coated. Thus, the deactivation of kaolinite ice nuclei through coating by anthropogenic sulfate is the main difference between simulations KAO and MIX.
and MON. This deactivation dominates over the glaciation indirect effect (caused by anthropogenically increased black carbon concentrations) in simulation KAO. In simulation MIX, the immersion freezing stems from the contribution of the montmorillonite particles, and only the kaolinite part of the dust ice nuclei is quasi-deactivated. This effect was not taken into account by Lohmann and Diehl (2006).

### 3.3. Sensitivity to freezing on black carbon

As another sensitivity experiment, simulation MIX has been rerun (for present-day and preindustrial emissions) with suppression of both contact and immersion freezing on black carbon (simulation MIX-nBC). This can give an upper estimate of the glaciation indirect effect. Results from the 5-year simulation are included in table 4. However, contrary to expectations, the simulation MIX-nBC does not yield a larger change in the global mean liquid water path or in the TOA shortwave radiation. In the zonal distribution, systematic differences between the northern and the southern hemisphere are evident (figure 12 and table 5). In the northern hemisphere, if freezing on black carbon is suppressed (simulation MIX-nBC), the liquid water path, cloud cover and
cloud droplet number burden increase more than in simulation MIX. Therefore the shortwave radiative forcing is stronger (more negative). When freezing on black carbon is included, more clouds glaciate and therefore the increase in liquid water path is lower. Note that the shift of dust ice nuclei from the contact to the immersion mode by coating with sulfate is taken into account in both simulations MIX and MIX-nBC. In the southern hemisphere, the heterogeneous freezing rates are in general much lower (see figure 6) because larger areas are ocean. Changes in liquid water path, cloud cover, cloud droplet number burden and shortwave radiative forcing in simulations MIX and MIX-nBC show an opposite behaviour than in the northern hemisphere. A detailed analysis has shown that this is not related to mixed-phase cloud processes, but to different wind-dependent emission fluxes of sea salt aerosol. Through dynamic, nonlinear feedbacks, surface winds decrease in simulation MIX-nBC, leading to fewer sea salt particles, while they increase in simulation MIX (figure 13). This results in different concentrations of cloud condensation nuclei and slightly different effects on warm clouds, which are not the focus of this study. The decrease of surface winds is not a robust feature of model studies of the preindustrial era, and we therefore omit the southern hemisphere from further analysis of this simulation.

From this sensitivity study, we can give an upper estimate of the glaciation indirect effect for the northern hemisphere, where mixed-phase cloud processes are more important. The difference in shortwave radiative forcing between simulations MIX and MIX-nBC is +0.11 W m\(^{-2}\), which is offset by the difference in longwave radiation (less outgoing terrestrial radiation because of a higher cloud cover) of \(-0.22\) W m\(^{-2}\). The actual glaciation indirect is expected to be even slightly smaller, as it only includes effects of freezing on anthropogenic black carbon, while the simulation MIX-nBC also excluded freezing on natural black carbon particles.
Figure 13. Difference between present-day and preindustrial runs of annual mean sea salt emission fluxes in simulations (a) MIX and (b) MIX-nBC.

Figure 14. Schematic of aerosol indirect effects in warm and mixed-phase clouds. The glaciation indirect has been introduced by Lohmann (2002a). The ‘deactivation indirect effect’ proposed in this study is strongest for dust composed of a mineral which is inefficient in initiating freezing in the immersion mode (like kaolinite).

4. Discussion and conclusions

In the global climate model ECHAM5-HAM, we take the dependence of heterogeneous freezing on the composition of aerosol particles available for ice nucleation into account. Two types of mineral dust, montmorillonite and kaolinite, and black carbon are considered as ice nuclei. Uncoated particles can initiate contact freezing, while coated particles are potential immersion nuclei, which are active at lower temperatures.

In addition to sensitivity simulations which assume all dust to act as kaolinite/montmorillonite ice nuclei, we present simulations with a three-dimensional atmospheric dust mineralogical composition, which is calculated offline. The simulated dust composition is more uniform than point measurements of atmospheric dust samples from different continents. In general, the kaolinite content seems to be overestimated.

In our simulations, contact freezing by black carbon is the dominating freezing process, due to high black carbon number concentrations, and due to the small particle size and high Brownian collision efficiency of black carbon. Freezing on dust occurs in both the contact and immersion freezing modes if the dust is composed of montmorillonite (a highly efficient ice nucleus), and almost exclusively in the contact mode if the dust is composed of kaolinite (a less efficient ice nucleus). In the present-day climate, anthropogenic sulfate emissions lead to enhanced coating of dust particles, and therefore quasi-deactivate kaolinite ice nuclei. This deactivation effect counteracts the glaciation indirect effect, which suggests an increase of cloud glaciation and precipitation formation resulting from the increase of black carbon ice nuclei resulting from anthropogenic activity (figure 14). The coating and deactivation of natural IN leads to less frequent glaciation of mixed-phase clouds, and therefore less precipitation via the ice phase, longer cloud lifetimes, and increased cloud cover and a higher global cloud albedo, resulting in an increase in reflected solar radiation. It reinforces the aerosol indirect effects on warm clouds. The magnitude of the deactivation effect depends on the freezing efficiency of dust and thus on the mineralogical composition.

In general, we find a smaller effect of the different dust compositions than a previous study with the ECHAM4 model by Lohmann and Diehl (2006). First of all, the coating and deactivation of dust ice nuclei by anthropogenic sulfate, which counteracts the glaciation indirect effect, was not taken into account in ECHAM4. Furthermore, in
Table 5. Hemispheric annual mean difference in liquid water path (LWP), ice water path (IWP), cloud droplet number burden (NC), ice crystal number burden (NC), cloud cover (CC) and top-of-the-atmosphere shortwave (FSW), longwave (FW) and net (Fnet) radiative fluxes between present-day and preindustrial simulations for the northern (NH) and southern hemisphere (SH) in simulations MIX and MIX-nBC.

| Simulation | MIX | MIX-nBC | MIX | MIX-nBC |
|------------|-----|---------|-----|---------|
| ΔLWP (g m⁻²) | 11.44 | 12.01 | 3.07 | 2.07 |
| ΔFWP (g m⁻²) | 0.40 | 0.61 | 0.01 | 0.19 |
| ΔNC (10¹⁸ m⁻²) | 1.74 | 1.82 | 0.39 | 0.32 |
| ΔNC (10¹⁰ m⁻²) | 0.16 | 0.12 | 0.01 | 0.01 |
| ΔCC (%) | 0.87 | 0.97 | 0.09 | 0.01 |
| ΔFSW (W m⁻²) | −3.69 | −3.80 | −0.81 | −0.46 |
| ΔFFW (W m⁻²) | −0.38 | −0.60 | +0.02 | +0.14 |
| ΔFnet (W m⁻²) | −3.31 | −3.20 | −0.78 | −0.60 |

ECHAM5-HAM, heterogeneous freezing acts as a trigger to initiate the Bergeron–Findeisen process, which rapidly glaciates clouds. In ECHAM4, the Bergeron–Findeisen process could last several time steps. Although the Bergeron–Findeisen process in ECHAM5-HAM is described as a simple instantaneous threshold process, which might mask the effects of different ice nuclei concentrations, it results in a reasonable partitioning between the liquid and ice phases (Lohmann et al. 2007), and is a considerable improvement over ECHAM4. A more sophisticated parameterization of the Bergeron–Findeisen process, taking into account time-dependent liquid-to-ice conversion as a function of vertical velocities and ice crystal numbers, could enhance the difference between the sensitivity simulations in ECHAM5-HAM.

Finally, we present a sensitivity study with suppressed freezing on black carbon. The glaciation indirect effect is only apparent in the northern hemisphere, where heterogeneous freezing is largest. Here it amounts to a reduction in reflected shortwave radiation at the top-of-the-atmosphere of +0.11 W m⁻² and an increase in longwave radiation emitted to space of −0.22 W m⁻². In the southern hemisphere, the glaciation indirect effect is masked by changes in sea salt emissions due to variation in surface winds.

We conclude that coating and deactivation of ice nuclei has to be considered next to the emission of additional ice nuclei by anthropogenic activity for estimation of the anthropogenic indirect aerosol effect on mixed-phase clouds. As these two effects counteract each other, the total anthropogenic effect on mixed-phase clouds is small compared to the aerosol indirect effect on warm clouds. As uncertainties regarding the parameterization of mixed-phase cloud processes (heterogeneous freezing, Bergeron–Findeisen process) persist, further field observations of ice nuclei concentrations, composition and related cloud properties are needed in order to permit model validation.

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