Cloud Condensation Nuclei and Immersion Freezing Abilities of Al$_2$O$_3$ and Fe$_2$O$_3$ Particles Measured with the Meteorological Research Institute’s Cloud Simulation Chamber

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Abstract

Aluminum oxide (Al$_2$O$_3$) and iron oxide (Fe$_2$O$_3$) particles have been observed not only in industrial areas and their surroundings, but also in natural atmospheric environments. These types of aerosols can influence aerosol–cloud interactions. In this study, physicochemical properties such as size distribution and the ability to act as cloud condensation nuclei (CCN) as well as ice nucleating particles (INPs) of surrogates of ambient Al$_2$O$_3$ and Fe$_2$O$_3$ particles were investigated using a CCN counter, the Meteorological Research Institute’s (MRI) cloud simulation chamber, the MRI’s continuous-flow-diffusion-chamber-type ice nucleus counter (CFDC-type INC), and an array of aerosol instruments. The results indicated that their hygroscopicity parameter ($\kappa$-value) ranged from 0.01 to 0.03. This range is compatible with that of surrogates of mineral dust particles and is smaller than typical $\kappa$-values of atmospheric aerosols. On the other hand, based on their ice nucleation active surface site (INAS) densities, these materials may act as effective INPs via immersion freezing (i.e., ice nucleation triggered by particles immersed in water droplets). In the cloud chamber experiments, Al$_2$O$_3$ and Fe$_2$O$_3$ particles continuously nucleated ice crystals at temperatures below $-14^\circ$C and $-20^\circ$C, respectively. This result indicates that the Al$_2$O$_3$ particles were better INPs than the Fe$_2$O$_3$ particles were. Moreover, the INAS density of the Al$_2$O$_3$ particles was comparable to that of natural ambient dust.

Keywords hygroscopicity; activated fraction; ice nucleation active surface site density; immersion freezing; CFDC-type ice nucleus counter

1. Introduction

Metal oxides have been observed frequently in the atmosphere near industrial areas and their surroundings. Metals have also been found to be enriched in ambient ice crystal residual measurements (Chen et al. 1998; DeMott et al. 2003; Cziczo et al. 2009; Prenni et al. 2009; Ebert et al. 2011). However, in previous studies, there have been no detailed investigations of the abilities of metal oxides to act as both cloud condensation nuclei (CCN) and ice nucleating particles (INPs). These roles of metal oxide particles need to be reexamined because related anthropogenic forcing, such as by aerosol–cloud interactions, especially the modulation of ice formation in clouds by aerosols acting as INPs, remains largely uncertain (IPCC 2013).

In addition to being components of Earth’s crust, aluminum oxides and iron oxides are found in anthropogenic emissions. Such emissions include those from industrial and metallurgical processes, combustion of fossil fuels, transport sources such as diesel vehicles, tire wear, brake wear, and shipping, and the resuspension of crustal materials and road dust. Metal oxides have also been reported in soot particles emitted from sources where catalytic additives are used (Sanderson et al. 2017).

Anthropogenic emissions contribute 13 % of atmospheric aluminum (Lantzy and MacKenzie 1979). It has been shown in previous studies that concentrations of aluminum in rural air typically range from 0.005 to 0.18 μg m$^{-3}$ (Hoffman et al. 1969; Pötzl 1970; Sorenson et al. 1974), whereas those in urban and industrial areas range from 0.4 to 8.0 μg m$^{-3}$ (Pillay and Thomas 1971; Sorenson et al. 1974). The major anthropogenic sources of aluminum-containing particulate matter include coal combustion, aluminum production, and other industrial activities, such as smelting to process crustal minerals. Motor vehicle emissions contribute an estimated 0.9–9 % of the observed elemental concentration of aluminum in the cities of the U.S. (Ondov et al. 1982).

Recent observations have indicated that the emission of iron oxide particles resulting from anthropogenic activities tends to be in the form of aggregated FeO$_x$ nanoparticles (Hu et al. 2015; Adachi et al. 2016). Moteki et al. (2017) used a modified single-particle soot photometer and electron microscopy to investigate atmospheric aerosols that were transported directly to the sampling point along a flight track at an altitude lower than 2 km without undergoing wet removal. They concluded that the number fraction of natural mineral dust in all Fe-bearing particles in the continental outflows from East Asia (except for Asian dust periods) was less than 0.10.

A few studies presented observed iron- and aluminum-containing particle results in elemental form due to the limitations of the measuring methods (e.g., energy-dispersive X-ray spectroscopy combined with electron microscopy and inductively coupled plasma mass spectroscopy provide chemical properties of materials in elemental form but do not provide their chemical composition). However, in reality, iron and aluminum in the atmosphere can oxidize easily and exist in the form of oxides. Atmospheric aerosol particles comprised of aluminum oxides and iron oxides have diameters ranging from submicrons to microns (Utsunomiya et al. 2004; Ntziachristos et al. 2007; Amato et al. 2011; Liati et al. 2012; Smith et al. 2012; Adachi et al. 2016; Sanderson et al. 2016). In a roadside sampling at two urban sites in the UK, iron and aluminum accounted for 52.6 % and 23.1 % of the mass of the particulate matter with diameters of less than 18 μm (PM$_{18}$), respectively. The median diameter of Fe$_2$O$_3$ particles is approximately 0.03 μm; however, these particles tend to agglomerate to form clusters ranging from 0.2 to 1 μm in diameter (Sanderson et al. 2016). A similar composition was found for roadside samples collected in California, USA (Ntziachristos et al. 2007). Linak et al. (2007) indicated that fly ash consists of aluminum and iron oxides with diameters of less than 2.5 μm. In a study conducted in Abidjan, Côte d’Ivoire, particle sizes in rural, urban, and industrial areas were found to be smaller than 2.5 μm in diameter and aluminum and iron accounted for PM$_{2.5}$ concentrations of 56–79 μg mg$^{-1}$ and 34–54 μg mg$^{-1}$, respectively (Kouassi et al. 2010). More than 60 % by volume of blast furnace kish (containing 40–60 % Fe$_2$O$_3$) around iron and steel manufacturing facilities was found to be comprised of particles less than 5 μm in diameter, more than half of which (about 37 % of the total) consisted of particles less than 1 μm in diameter (Machemer 2004). High concentrations of Fe-bearing particles with diameters ranging from 0.2 to 2.4 μm have been observed in the area of Tokyo (Adachi et al. 2016). Another study has shown that space shuttle exhaust air collected at altitudes of 2–7 km is characterized by high concentrations, up to several hundred particles per cubic centimeter, of aluminum oxide particles ranging in diameter from 0.3 μm to 7 μm (Cofer III et al. 1991).

Due to the abundance of aluminum oxide (0.008–0.37 μg m$^{-3}$) and iron oxide (0.003–0.39 μg m$^{-3}$) in the atmosphere (Duce et al. 1975; Losno et al. 1992; Cakmak et al. 2014; Chance et al. 2015) and their...
enrichment in ambient ice crystal residual particles (Chen et al. 1998; DeMott et al. 2003; Cziezko et al. 2009; Prenni et al. 2009; Ebert et al. 2011), in several previous studies, the abilities of these two metal oxides to act as INPs have been investigated. Saunders et al. (2010) used the Aerosol Interactions and Dynamics in the Atmosphere (AIDA) chamber to observe the deposition nucleation of Fe$_2$O$_3$ at relative humidity with respect to ice (RHi) ranging from 105% to 140% and temperatures below −53°C. Approximately 10% of the amorphous Fe$_2$O$_3$ particles (modal diameter = 0.03 µm) nucleated ice crystals at RH$_i$ = 140% at an initial chamber temperature of −91°C. In an experiment with a higher initial chamber temperature, Fe$_2$O$_3$ acted as CCN at −32°C, and these droplets froze at temperatures below −35°C, close to the homogeneous freezing point. These results indicate that Fe$_2$O$_3$ particles do not act as INPs under conditions pertinent to tropospheric mixed-phase clouds, which exist at temperatures higher than −38°C. Hiranuma et al. (2014) also used the AIDA chamber to investigate the capability of Fe$_2$O$_3$ (hematite) particles with diameters of ~1 µm to act as immersion freezing mode INPs and to assess the sensitivity of this process to surface irregularities of Fe$_2$O$_3$. The immersion freezing mode ice nucleation efficiency of milled Fe$_2$O$_3$ particles was nearly an order of magnitude higher at −35.2°C < T < −33.5°C than that of cubic Fe$_2$O$_3$ particles, indicating a substantial effect of morphological irregularities on immersion mode freezing.

Archuleta et al. (2005) used a continuous-flow-diffusion-chamber-type ice nucleus counter (CFDC-type INC) and examined the potential role of Al$_2$O$_3$ and Fe$_2$O$_3$ particles with sulfuric acid coating as heterogeneous INPs at cirrus temperatures. Among the size-selected particles, ranging from 0.05 µm to 0.2 µm in diameter, particles with a size of 0.2 µm were the most effective INPs. The authors also demonstrated heterogeneous ice nucleation of Al$_2$O$_3$ and Fe$_2$O$_3$ particles at an RH$_i$ of approximately 140% and at temperatures ranging from −45°C to −60°C. Additionally, the authors suggested the possibility of initiating ice crystal formation at relatively high temperatures characteristic of mixed-phase clouds. Yakobi-Hancock et al. (2013) tested the deposition ice nucleation abilities of nine atmospheric metal oxide particles (various mineral compositions), size-selected at 0.2 µm, using a CFDC-type INC at −40.0 ± 0.3°C. The results indicated that metal oxides, including Al$_2$O$_3$ and Fe$_2$O$_3$, might not be effective INPs.

On the other hand, the hygroscopicity of aluminum oxide was indicated as 0 (reported to one significant digit) in Table 1 in the paper by Carrico et al. (2010). However, to the best of our knowledge, almost no full-scale research on the hygroscopicity of metal oxide particles has been conducted to date.

Previous studies have demonstrated the ability of metal oxide particles to act as INPs at lower temperatures, suggesting potential aerosol–cloud interactions in the upper-level atmosphere (Archuleta et al. 2005; Saunders et al. 2010; Yakobi-Hancock et al. 2013; Hiranuma et al. 2014). In this study, the CCN and INP abilities of Al$_2$O$_3$ and Fe$_2$O$_3$ particles were examined at higher temperatures to determine their role in mixed-phase cloud processes. A cluster of aerosol instruments and a CCN counter were used to measure the CCN ability (hygroscopicity), and the cloud simulation chamber of the Meteorological Research Institute (MRI) (Tajiri et al. 2013) and the MRI’s CFDC-type INC (Saito et al. 2011) were used to measure the INP ability. Additionally, a cross-instrument comparison was conducted and the sensitivities of the metal oxides to nucleation events and experimental conditions were evaluated.

The MRI’s cloud simulation chamber was used previously to investigate the ability of surrogates of atmospheric dust and biological aerosols to act as INPs (Tajiri et al. 2013; Hiranuma et al. 2015a, b) and to investigate the abilities of hygroscopic and glaciogenic seeding materials (hygroscopic flare, salt micropowder, and AgI particles) to act as CCN and INPs, along with their effects on the initial microphysical structures of clouds (Tajiri et al. 2015). The MRI’s CFDC-type INC has been used to investigate the ability of surrogates of atmospheric dust particles to act as INPs (Saito et al. 2011; Tajiri et al. 2013) as well as the seasonal variation and vertical distributions of atmospheric INPs (Murakami et al. 2012; Yamashita et al. 2014; Orikasa et al. 2016).

In this study, the abilities of Al$_2$O$_3$ and Fe$_2$O$_3$ particles to act as CCN and INPs at temperatures relevant to mixed-phase clouds were obtained mainly from cloud simulation chamber experiments. The experimental methods are described in Section 2, followed by the results in Section 3, discussion in Section 4, and conclusions in Section 5. We also measured INP number concentrations of the metal oxides using a CFDC-type INC, but the ice nucleation active surface site (INAS) densities obtained from the CFDC-type INC measurements were significantly different from those obtained from the cloud chamber experiments. Since the source of this discrepancy could not be assuredly identified and requires further research, the results of the CFDC-type INC measurements are...
described and the possible causes for the significant differences are discussed briefly in the Appendix.

2. Methods

2.1 Experimental procedure

In this study, the abilities of two metal oxides (Al\(_2\)O\(_3\) and Fe\(_2\)O\(_3\)) to act as CCN and INPs were measured using an array of instruments. These included the MRI’s cloud simulation chamber (Tajiri et al. 2013), the MRI’s CFDC-type INC (Saito et al. 2011), a CCN counter (CCNC, model CCN-200; DMT Inc.), and other aerosol measuring instruments. Measurements to assess the ability to act as CCN were performed twice for each material (Section 2.2). The cloud simulation chamber experiments were performed under different conditions, which are described in Section 2.3. The CFDC-type INC measurements were performed once for each material and are described in the Appendix.

Two types of Fe\(_2\)O\(_3\) (Fe\(_2\)O\(_3\)#1 and Fe\(_2\)O\(_3\)#2, both hematite) and one type of Al\(_2\)O\(_3\) (white fused alumina), all commercially available (TETSUGEN and APPIE, respectively), were used. Table 1 shows the material specifications. A rotating brush disperser (model RBG 1000; Palas) was used for dry particle generation. The dispersed particles were either introduced directly into the cloud simulation chamber via two-stage cyclones (with 50% cut-off diameters of 2.5 µm and 1.0 µm) or stored in the aerosol buffer tank (volume: 4 m\(^3\)) via two-stage cyclones and subsequently supplied to the aerosol instruments. The size distribution measurements of the aerosol particles in the cloud simulation chamber and the aerosol buffer tank were made using a scanning mobility particle sizer spectrometer (SMPS, model 3936; TSI Inc.) and an aerodynamic particle sizer spectrometer (APS 3321; TSI Inc.). During the merging of APS and SMPS data, the default value for bulk density of particles (1 g cm\(^{-3}\)) was used, and the dynamic shape factor was not applied because the exact values of bulk density and dynamic shape factor were unknown. This may have caused a slight overestimation of the sizes and surface areas of the metal oxide particles. In this study, the size ranges measured with the combination of SMPS and APS, the cloud aerosol spectrometer (CAS; DMT Inc.), and the CFDC-type INC’s optical particle counter (OPC) were 0.013–14.86 µm, 0.34–26.75 µm, and 0.5–6.79 µm, respectively. Figure 1 shows the number and area size distributions of the Al\(_2\)O\(_3\) and Fe\(_2\)O\(_3\) particles. The surface areas of the metal oxide particles were computed assuming a spherical shape, which was based on the particle size measured by the aerosol instruments. The total surface area (\(S_{\text{total}}\)) and the average surface area (\(S_{\text{ave}}\)) can be obtained from aerosol size distributions (Hinds 1999; Niemand et al. 2012). The size-related information for the three materials is also shown in Table 2. The Al\(_2\)O\(_3\) particles introduced into the cloud simulation chamber had a broader size distribution than that of the Fe\(_2\)O\(_3\) particles, especially for the size range larger than 1 µm. All samples (Al\(_2\)O\(_3\), Fe\(_2\)O\(_3\)#1, and Fe\(_2\)O\(_3\)#2) aerosolized in the chamber and had similar size distributions for particles smaller than 1 µm. Note that the number size distribution for Al\(_2\)O\(_3\) peaked at approximately 0.3 µm, which was slightly larger than the peak values of the number size distributions for Fe\(_2\)O\(_3\)#1 and Fe\(_2\)O\(_3\)#2. In addition, Fe\(_2\)O\(_3\)#1 and Fe\(_2\)O\(_3\)#2 particles had lower number concentrations in the size range larger than 1 µm, implying a rapid decrease in concentration with increasing size when compared to the concentration of Al\(_2\)O\(_3\) particles.

2.2 CCN ability measurement

A differential mobility analyzer (DMA, model 3080; TSI Inc.), a CCNC, and a condensation particle counter (CPC, model 3772; TSI Inc.) were used to measure the hygroscopicity parameter (\(\kappa\)) as a function of the dry particle diameter and the critical supersaturation (Petters and Kreidenweis 2007). The particles classified by the DMA were subsequently measured with the CPC and CCNC for aerosol particle and CCN concentrations, respectively. The activated fraction (AF) of the aerosol particles was defined as the ratio of the CCN concentration (\(N_{\text{CCN}}\), measured with the CCNC) to the condensation nuclei (CN) concentration (\(N_{\text{CN}}\), measured with the CPC). By changing the particle size periodically using the DMA (from 100 nm to 490 nm for ~ 15 minutes), the critical diameter was defined as the dry particle diameter at

<table>
<thead>
<tr>
<th>Aerosol (source)</th>
<th>Purity (wt. %)</th>
<th>Density (g cm(^{-3}))</th>
<th>Other content</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(_2)O(_3) (APPIE)</td>
<td>&gt; 99 %</td>
<td>3.9</td>
<td>unknown</td>
</tr>
<tr>
<td>Fe(_2)O(_3)#1 (TETSUGEN)</td>
<td>99.24 %</td>
<td>5.2</td>
<td>H(_2)O 0.1 %, Cl 0.073 %, SO(_4) 0.04 %</td>
</tr>
<tr>
<td>Fe(_2)O(_3)#2 (TETSUGEN)</td>
<td>99.05 %</td>
<td>5.2</td>
<td>H(_2)O 0.06 %, Cl 0.04 %, SO(_4) 0.02 %</td>
</tr>
</tbody>
</table>
which a minimum of 50% of the particles activated into cloud droplets at a given supersaturation. The supersaturation was increased in a stepwise manner after each cycle of scanning the particle sizes (Koehler et al. 2007; Rose et al. 2008; Yamashita et al. 2011).

2.3 Cloud simulation chamber

The MRI’s cloud simulation chamber was equipped with various optical devices for sensing cloud formation and measuring the size distributions, shapes, and asphericity of aerosols and cloud particles with diameters ranging from 0.01 µm to several hundred micrometers. The size distributions and total concentrations of aerosols, cloud droplets, and ice crystals were measured continuously during the expansion experiments by the CAS, Welas OPC (Promo 2000...
H, size range 2–105 mm; Palas), and cloud particle imager (CPI; SPEC Inc.). The aerosol particle concentrations were measured continuously using the CPC. The CPC could measure particle concentrations in the chamber at pressures as low as 300 hPa with a normalized asymptotic detection efficiency of more than 85% (Takegawa and Sakurai 2011). The expansion caused adiabatic cooling of the simulated ascending air, and the temperature of the inner chamber wall was controlled to match the air temperature to minimize heat and water vapor exchanges between the air and the wall. Therefore, the temperature distribution in the chamber was fairly uniform, even during expansion experiments, within the range of ± 0.3°C. The inner chamber could be cooled to any temperature between 30°C and −100°C. A detailed description can be found in the paper by Tajiri et al. (2013).

Table 3 shows the aerosol types, particle concentrations, total surface areas, examined temperature range, initial dewpoint temperature, temperature at the lifting condensation level, maximum cloud droplet concentration, maximum ice crystal concentration, and maximum INAS density for the seven cloud chamber experiments. Each material was tested at the same initial temperature (except for experiments Fe21 and Fe22), but at different initial dewpoint temperatures. This led to different lifting condensation levels, which were used to determine the timing of cloud formation in the cloud chamber. All experiments were conducted with an evacuation rate corresponding to a simulated updraft velocity of 5 m s⁻¹.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Aerosol</th>
<th>(N_{\text{aerosol}}) (cm⁻³)</th>
<th>(S_{\text{total}}) (m² cm⁻³)</th>
<th>(T_{\text{range}}) (°C)</th>
<th>(T_{\text{din}}) (°C)</th>
<th>(T_{\text{LCL}}) (°C)</th>
<th>(N_{\text{droplet}}) (cm⁻³)</th>
<th>(N_{\text{ice}}) (cm⁻³)</th>
<th>(n_s) (m⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al1</td>
<td>Al₂O₃</td>
<td>2059</td>
<td>4.4 × 10⁻⁹</td>
<td>−23–−5</td>
<td>−13.3</td>
<td>−16.9</td>
<td>1477</td>
<td>6.15</td>
<td>1.4 × 10⁰</td>
</tr>
<tr>
<td>Al2</td>
<td>Al₂O₃</td>
<td>1897</td>
<td>7.2 × 10⁻⁹</td>
<td>−29–−5</td>
<td>−8.7</td>
<td>−11.5</td>
<td>1214</td>
<td>73.0</td>
<td>1.0 × 10¹</td>
</tr>
<tr>
<td>Al3</td>
<td>Al₂O₃</td>
<td>1896</td>
<td>5.0 × 10⁻⁹</td>
<td>−28–−5</td>
<td>−6.5</td>
<td>−8.9</td>
<td>618</td>
<td>26.5</td>
<td>5.3 × 10¹</td>
</tr>
<tr>
<td>Fe11</td>
<td>Fe₂O₃#1</td>
<td>4225</td>
<td>3.4 × 10⁻⁹</td>
<td>−2–−5</td>
<td>−5.2</td>
<td>−7.5</td>
<td>1234</td>
<td>1.94</td>
<td>5.7 × 10¹</td>
</tr>
<tr>
<td>Fe12</td>
<td>Fe₂O₃#1</td>
<td>4593</td>
<td>6.1 × 10⁻⁹</td>
<td>−30–−5</td>
<td>−10.5</td>
<td>−13.6</td>
<td>1182</td>
<td>9.25</td>
<td>1.5 × 10¹</td>
</tr>
<tr>
<td>Fe21</td>
<td>Fe₂O₃#2</td>
<td>3927</td>
<td>4.2 × 10⁻⁹</td>
<td>−32–−5</td>
<td>−13.9</td>
<td>−15.7</td>
<td>648</td>
<td>7.72</td>
<td>1.8 × 10¹</td>
</tr>
<tr>
<td>Fe22</td>
<td>Fe₂O₃#2</td>
<td>3139</td>
<td>3.0 × 10⁻⁹</td>
<td>−33–−5</td>
<td>−11.0</td>
<td>−12.5</td>
<td>1220</td>
<td>8.06</td>
<td>2.7 × 10¹</td>
</tr>
</tbody>
</table>

3. Results

3.1 Ability to act as CCN

The hygroscopicity values (κ-values) of Al₂O₃, Fe₂O₃#1, and Fe₂O₃#2 ranged from 0.01 to 0.03 and appeared to increase slightly with decreasing particle size (Fig. 2). The size dependency of the hygroscopicity could be related to the mixing ratio of the metal oxides and other Cl- and SO₄-bearing trace materials whose hygroscopicity values are higher than those of the metal oxides. Therefore, the hygroscopicity of the pure metal oxide particles could be approximately 0.01. The κ-values were comparable to those for surrogates of mineral dust particles (0.01 ≤ κ ≤ 0.08; Koehler et al. 2009; Yamashita et al. 2011) and were smaller than the typical mean κ-values of atmospheric aerosols (κ ~ 0.3 for continental air mass and κ ~ 0.7 for maritime air mass; Andreae and Rosenfeld 2008; κ ~ 0.1 in early summer in western Japan; Murakami et al. 2015; Yamashita et al. 2015).

Fig. 2. Hygroscopicity (κ-value) of the three types of metal oxide particles.
3.2 IN ability obtained from the cloud simulation chamber experiments

Figures 3–9 indicate the results of individual INP measurements using a 1-second averaged dataset, except for the time variation of particle size distributions in the fourth row, which were plotted using 10-second averaged data (although the Welas OPC acquired the data at 1 Hz). The results pertinent to the INP ability (Figs. 10, 11) are also presented using a 10-second averaged dataset.

In general, the onset of cloud droplet formation in the chamber experiments was determined more easily and precisely than that of ice crystal formation. The timing of the onset of ice crystal formation was usually affected by the detection limit of the minimum concentration of ice crystals and the accuracy of discrimination between droplets and ice crystals. However, in this study, the temporal evolution of the particle size distributions measured by the Welas OPC readily indicated the onset of ice formation, as described in the following subsection. Since the CAS is installed on the side wall of the chamber and the Welas OPC is installed on the bottom plate (Tajiri et al. 2013), when the air temperature and humidity in the chamber have a significant heterogeneity due to insufficient initialization, the onset of cloud formation is sometimes measured by the two instruments with a slight time lag.

a. Al₂O₃

Three experiments (Al1, Al2, and Al3) were performed with the same initial air temperature of 5°C, but with different initial dewpoint temperatures \(T_{\text{din}}\). A comparison of the three experiments indicated that the onset of cloud droplet formation appeared to be controlled by the initial dewpoint temperatures. In the driest case Al1 \(T_{\text{din}} = -13.3°C\), Fig. 3), the Welas OPC indicated that cloud droplet formation started at approximately 530 s. The cloud droplet formation during Al2 \(T_{\text{din}} = -8.7°C\), Fig. 4) and Al3 \(T_{\text{din}} = -6.5°C\),

![Fig. 3](image-url)
Fig. 4. Time series of various parameters collected during the Al2 experiment. Description as indicated in Fig. 3.

Fig. 5. Time series of various parameters collected during the Al3 experiment. Description as indicated in Fig. 3.
The cloud droplet concentrations during the Al1, Al2, and Al3 experiments were 1500 cm$^{-3}$, 1200 cm$^{-3}$, and 620 cm$^{-3}$, respectively, and the AFs of aerosol particles larger than 0.3 μm as CCN were 0.72, 0.64, and 0.33, respectively. The low concentration of cloud droplets in Al3 could be attributed to the drier air in the outer chamber. It is likely that the air in the outer chamber was not adjusted to the same humidity as that of the air in the inner chamber during the initialization process and could have leaked slightly into the inner chamber, resulting in the suppression of the maximum supersaturation in the inner chamber.

The onset of ice crystal formation (the appearance of particles larger than 30 μm, as indicated in the fourth row of Fig. 3) during Al1 occurred around the same time as the cloud droplet formation, even though the ice formation ability was limited because of the deceleration and leveling off of the cooling rate immediately after the onset of ice formation. The conversion of liquid-phase cloud particles to ice-phase particles was first detected by the Welas OPC and the CPI. The Welas OPC showed a large increase in particle sizes ranging from less than 20 μm to greater than 30 μm upon ice nucleation and initial ice crystal formation. This increase in the particle sizes was primarily caused by the strong sideward scattering of light by ice crystals; it was also influenced by the fast growth of ice crystals at the expense of supercooled droplets (Wagner et al. 2011). The onset of ice crystal formation during Al2 occurred at approximately 500 s, whereas that during Al3 occurred at 430 s. The difference in the onset times between the three experiments may have been affected by the timing of cloud formation. The ice crystal concentrations in the three experiments reached 6 cm$^{-3}$, 73 cm$^{-3}$, and 26 cm$^{-3}$, respectively (Table 3). The large variation in the ice crystal concentrations could have resulted from the fallout (settlement) effect of ice crystals and the slight inhomogeneity of ice crystal concentrations in the chamber.

b. Fe$_2$O$_3$#1

Two experiments (Fe11 and Fe12) were performed with the same initial air temperature of 5°C, but with different $T_{\text{din}}$. The time series of the key parameters for Fe11 ($T_{\text{din}} = -5.2^\circ\text{C}$) and Fe12 ($T_{\text{din}} = -10.5^\circ\text{C}$) are shown in Figs. 6 and 7, respectively. Even though the concentrations of aerosol particles larger than 0.3 μm during Fe11 and Fe12 were twice those obtained for the Al$_2$O$_3$ particle experiments, the cloud droplet concentrations were approximately 1200 cm$^{-3}$. Consequently, the CCN AF of aerosol particles larger than 0.3 μm ranged from 0.25 to 0.3. The onset of cloud droplet formation at 350 s in the Fe11 experiment was earlier than that observed for Fe12. However, the onset of ice crystal formation in both experiments occurred at 550–600 s, which corresponded to air temperatures of approximately −22°C. The ice crystal concentrations for Fe11 and Fe12 reached 2 cm$^{-3}$ and 9 cm$^{-3}$, respectively.

c. Fe$_2$O$_3$#2

In the Fe21 ($T_{\text{din}} = -13.9^\circ\text{C}$, Fig. 8) and Fe22 ($T_{\text{din}} = -11.0^\circ\text{C}$, Fig. 9) experiments using Fe$_2$O$_3$#2 particles, the initial temperature was set to −5°C instead of 5°C (the initial air temperature for all other experiments including Fe11 and Fe12) to ensure that the cloud droplets started to form earlier than they did in Fe11 and Fe12. The onsets of cloud droplet formation for Fe21 and Fe22 were at 300 s and 250 s, respectively. The cloud droplet concentration of ~1200 cm$^{-3}$ obtained for Fe22 was greater than that observed for Fe21 (650 cm$^{-3}$), resulting in AFs of 0.17 and 0.39 for Fe21 and Fe22, respectively. The temperature at the onset of ice crystal formation was approximately −22°C, and the ice crystal concentrations reached ~8 cm$^{-3}$ in both experiments.

d. AF

Figure 10 presents the AF of Al$_2$O$_3$ and Fe$_2$O$_3$ particles as INPs obtained from the cloud chamber experiments. The AF of aerosol particles as INPs ($f_{\text{INP}} = N_{\text{ice}}/N_{\text{aerosol}}$) was obtained from the number concentration of the activated ice crystals ($N_{\text{ice}}$) measured by the Welas OPC and the number concentration of aerosol particles with diameters of > 0.3 μm ($N_{\text{aerosol}}$) measured by the CAS immediately before the cloud droplet formation during the expansion experiments. In an overall comparison, as shown in Fig. 10, the Al3 experiment (navy-blue-colored curve) had the highest onset temperature of −19°C for an AF of 0.001. The Al2 experiment (magenta curve) had the highest AF of ~0.02 at −26°C. Fe$_2$O$_3$#1 (yellow and brown curves) and Fe$_2$O$_3$#2 (light-blue and blue curves) had relatively poor IN abilities with an AF of 0.003 at approximately −30°C. Both Fe$_2$O$_3$#1 and Fe$_2$O$_3$#2 experiments with different dewpoint temperature settings appeared to show less deviated results with regard to the temperature dependency of AF than the three Al$_2$O$_3$ experiments. The results from the Al2 and Al3 experiments indicated small dips in the AF before reaching the highest AF due to a slight inhomogeneity of ice crystals in the chamber. Also, note that no cor-
Fig. 6. Time series of various parameters collected during the Fe11 experiment. Description as indicated in Fig. 3.

Fig. 7. Time series of various parameters collected during the Fe12 experiment. Description as indicated in Fig. 3.
Fig. 8. Time series of various parameters collected during the Fe21 experiment. Description as indicated in Fig. 3.

Fig. 9. Time series of various parameters collected during the Fe22 experiment. Description as indicated in Fig. 3.
rection for the fallout (settlement) effect was applied to the data (Fig. 10). The effects thought to influence the measured INP ability are discussed in Section 4.

e. INAS density

Figure 11 shows the INAS density \( n_S \) obtained in this study and those quoted from past studies for comparison. The INAS concept for immersion freezing investigated in this study postulates that the ice crystal formation observed in the experiments was only a function of the temperature (Connolly et al. 2009; Niemand et al. 2012). The INAS density was obtained by dividing \( N_{\text{ice}} \) by \( S_{\text{total}} \), which was measured immediately before the cloud droplet formation for each experiment by the CAS. Assuming a uniform distribution of ice nucleation sites and their size independence over a given total aerosol surface area, the surface-area-based ice nucleation efficiencies of the three independent metal oxide samples were compared in this study. The uncertainty of the INAS density obtained from the cloud chamber experiments, which was propagated from the measurement error of ice crystal number concentration by the Welas OPC (±20 %; Möhler et al. 2006) and the surface area estimation error of ±17 %, was evaluated to be ±26 %.

Considering the fallout (settlement) effect and the temporal failure of the refrigeration system, the INAS densities were plotted in temperature ranges of −18°C to −20°C, −16°C to −25°C, and −14°C to −22°C for Al1, Al2, and Al3, respectively, from −19°C to −26°C for Fe11 and Fe12, and from −18°C to −30°C for Fe21 and Fe22. Fitting formulas were applied to the data obtained during Al2 and Al3, as well as those obtained during Fe11, Fe12, Fe21, and Fe22. The Fe2O3#1 (Fe11 and Fe12) and Fe2O3#2 (Fe21 and Fe22) experiments showed nearly the same temperature dependency of the INAS density, although the manufacturing processes of the two types of Fe2O3 particles differed and the Fe11 and Fe12 experiments were limited to a temperature range higher than −28°C. The Fe2O3#1 and Fe2O3#2 particles showed an INAS density of \( 3 \times 10^4 \) m\(^{-2} \) at approximately −30°C. The Al2 and Al3 experiments showed a similar temperature dependency for the INAS density, although the INAS density for Al3 was slightly larger than that for Al2. The Al1 experiment indicated a steep rise in the INAS density after the onset of ice nucleation, likely due to the short residence time of particles in the droplets (although the temperature range was limited to higher than −20°C because of a temporal failure of the refrigeration system). From the viewpoint of both number (AF) and total surface (INAS density), Al2O3 appears to have a better INP ability than that of Fe2O3 by one or more orders of magnitude; the AF and INAS density values at −23°C for Al2O3 and Fe2O3 were 0.01 and \( 2 \times 10^{-9} \) m\(^{-2} \), and \( 9 \times 10^{-5} \) and \( 1 \times 10^{-8} \) m\(^{-2} \), respectively.

Fig. 10. Activated fractions (AFs) of Al2O3 and Fe2O3 particles as INPs obtained from the cloud simulation chamber experiments.

Fig. 11. INAS densities of Al2O3 and Fe2O3 particles obtained from the cloud simulation chamber experiments. Reference INAS densities are included for immersion freezing nucleation of Fe2O3 (Hiranuma et al. 2014), dust (Niemand et al. 2012), and illite (Broadley et al. 2012).
4. Discussion

The ability of metal oxide particles to act as CCN depends on their size. Pure metal oxide particles larger than 0.1 μm can be activated as CCN at a supersaturation with respect to water (SSw) of 0.1–0.5 % (frequently seen just above cloud bases) because the critical diameters of particles activated at an SSw of 0.1–0.5 % range from 0.1 μm to 0.5 μm (based on the extrapolation of the measurement results shown in Fig. 2), whereas particles smaller than 0.1 μm may not act as effective CCN. However, metal oxide particles coated with or internally mixed with other hygroscopic materials can act as CCN at much smaller sizes. This means that metal oxide particles smaller even than 0.1 μm that are coated and/or internally mixed with hygroscopic materials may act as CCN and, subsequently, nucleate ice crystals via the immersion/condensation freezing mechanisms in mixed-phase clouds.

Cloud chamber experiments for all metal oxide particles indicated cloud droplet formation followed by ice crystal formation. The lowest temperatures at the lifted condensation levels in the expansion (cloud formation) experiments for Al2O3 and Fe2O3 particles were −17°C and −16°C, respectively. Therefore, the metal oxide particles acted as immersion freezing mode INPs but not as deposition mode INPs at temperatures of −17°C and −16°C, respectively. Adding surface area information as a comparison standard, the temperature dependencies of the metal oxide particles with regard to the INAS density were similar to those of several mineral dust particles and illite NX, which have been well investigated. In several studies, it has been indicated that mineral dust and other materials (such as cellulose) have INAS densities of ~ 10^−2 m^−2.

The Al2O3, Fe2O3#1, and Fe2O3#2 had similar size distributions for particles smaller than 1 μm. However, in comparison to the Al2O3, the Fe2O3#1 and Fe2O3#2 particles had much smaller number concentrations in the size range larger than 1 μm. Both Al2O3 and Fe2O3 particles examined in this study showed broad number (area) size distributions with a mode diameter of ~ 0.3 μm (~ 1.3 μm).

The hygroscopicity values (κ-values) of the three types of metal oxide particles were between 0.01 and 0.03 and showed a weak size dependency. Additionally, the hygroscopicity of the Al2O3 particles was slightly larger than those of the Fe2O3#1 and Fe2O3#2 particles.

Both Al2O3 and Fe2O3 particles nucleated ice crystals via the immersion freezing mechanism, presumed from the rather short time period between the cloud droplet and ice crystal formations in the cloud chamber experiments. However, the possibility that some particles existed as interstitial aerosols acting as contact freezing mode INPs cannot be rejected. No deposition nucleation was observed for Al2O3 and Fe2O3 particles at temperatures ranging from 0°C to −17°C and from 0°C to −16°C, respectively, which represent temperatures of cloud droplet formation. However, Hiranuma et al. (2014) reported that 24 % of ice crystals were generated by deposition nucleation in the temperature range of −33°C to −35°C. The INP abilities of these metal oxide particles, which were determined in the cloud chamber experiments, indicated that the INAS density of Al2O3 was 2 × 10^9 m^−2 at approximately −23°C and was one or more orders of magnitude greater than that of Fe2O3. In addition, Al2O3 activated as INP at temperatures 4–5°C higher than Fe2O3 for the same AF or INAS density.

The INAS densities of both metal oxides were comparable to those of surrogates of mineral dust and other atmospheric INPs, indicating that these metal...
oxide particles are effective INPs if their total surface area is sufficiently large (i.e., if their sizes are sufficiently large and/or their concentrations are sufficiently high). For metal oxide particles to act as immersion freezing mode INPs, they first need to be incorporated into cloud droplets. The most effective process is for them to act as CCN. If the particles are larger than 0.1 µm, the metal oxide particles themselves may act as CCN and be incorporated into cloud droplets; however, particles smaller than 0.1 µm may need to be coated and/or internally mixed with hygroscopic materials to enhance their hygroscopicity.

In this study, the possibility of metal oxide particles to act as efficient INPs and influence aerosol–cloud–precipitation interactions was demonstrated. However, to understand their role in the atmosphere, a series of future studies investigating the ice nucleation activity of metal oxide particles in greater detail through observations of natural and anthropogenic emissions of metal oxide particles in terms of their concentrations, size distributions, and state of coating and/or internal mixing with other materials are strongly recommended. In our ongoing work, experiments considering the entire range of temperature and humidity are being conducted to understand the role of metal oxide particles in natural cloud formation processes.

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Appendix: Immersion freezing abilities of Al₂O₃ and Fe₂O₃ particles measured with the CFDC-type INC

A.1 CFDC-type INC

In addition to the cloud simulation chamber experiments, the MRI’s CFDC-type INC was employed to conduct INP measurements for temperatures ranging from −15°C to −35°C and humidity ranging from ice saturation to water supersaturation of ~ 15 %. A detailed description of the instrument can be found in the paper by Saito et al. (2011); however, the outer cylinder of the evaporation section was recently modified by adding a refrigerant coil to keep its temperature close to that of the outer cylinder of the growth section and to mitigate the adverse effects of ice crystal evaporation (Saito et al. 2012).

Metal oxide particles stored in the aerosol buffer tank via the two-stage cyclones were supplied to the CFDC-type INC via its inlet double impactors with a cut-off diameter of 1 µm. In this study, the abilities of the Al₂O₃, Fe₂O₃#1, and Fe₂O₃#2 to act as INPs were measured while scanning RH at several different temperatures. The threshold channel for ice crystal detection was set to channel #63, which corresponded to a particle size of 3.36 µm.

A.2 INP ability obtained from the CFDC-type INC measurements

The 15-second-running-mean results indicated that only the measurements for Al₂O₃ particles showed notable results. The AF of Al₂O₃ particles (d > 0.5 µm) as INPs was approximately 0.01 at a temperature of −35°C. Figure A1 shows the INAS density obtained from the CFDC-type INC measurements. The INAS density was obtained by dividing N_{ice} by S_{total}, which was measured by the INC’s OPC. Data that were assumed to have measured falling frosts and evaporating water droplets are excluded from this figure. In addition, data showing number concentrations close to the noise level of the INP measurements were excluded. The uncertainty of the INAS density obtained from the CFDC-type INC measurements, which was propagated from the measurement error of ice crystal number concentrations by the INC’s OPC (±10 %; Hiranuma et al. 2015a) and the surface area estimation error of ±7 %, was evaluated to be ±12 %. However,
when evaluating this uncertainty, underestimation of INP number concentrations due to humidity inhomogeneity in aerosol laminae and short residence time of aerosol particles in the CFDC-type INC (described later) was not considered. The Al$_2$O$_3$ particles indicated a large INAS density compared to the Fe$_2$O$_3$ particles. The INAS density for Al$_2$O$_3$ particles increased with decreasing temperature and reached $10^{10}$ m$^{-2}$ at $-35^\circ$C. Conversely, both types of Fe$_2$O$_3$ particles showed poor INP abilities in the CFDC-type INC measurements. The INAS density for Fe$_2$O$_3$ particles did not show any systematic increase with decreasing temperature but showed unexpectedly low values, most of which were not clearly resolvable above the instrument noise level. A possible reason for the poor INAS density measured by the INC is discussed in the next subsection.

A.3 Cross-instrument comparison of INP ability

The measured INP abilities appeared to be significantly different for the cloud simulation chamber experiments and the CFDC-type INC measurements. The INP abilities of Fe$_2$O$_3$, as indicated by the INAS density, when measured with the CFDC-type INC, were smaller by two or more orders of magnitude than those obtained from the cloud chamber experiments. The CFDC-type INC measurements showed a reasonable temperature dependence of the INP abilities for the Al$_2$O$_3$ particles beyond water saturation; however, INPs were not detectable below water saturation. The increase in the INP concentrations beyond water saturation was likely due to the increase in the AF of particles as CCN and not due to the SS$_{w}$ dependency of their ability as immersion freezing mode INPs. The immersion freezing mechanism requires particles to be within droplets; however, SS$_{w}$, in principle, is irrelevant to the nucleation efficiency of immersion freezing, which is determined by the droplet temperature. Parts of aerosol particles were exposed to target RH in the CFDC-type INC due to the non-uniform RH distribution in the aerosol lamina and the diffusion (broadening) of the aerosol lamina itself. Consequently, the AF of aerosol particles as CCN increased with increasing target SS$_{w}$ beyond water saturation (DeMott et al. 2015; Burkert-Kohn et al. 2017; Garimella et al. 2017). Therefore, immersion freezing was thought to be the dominant mechanism for ice nucleation in the CFDC-type INC. CFDC-type INC is also less sensitive in the detection of INPs with low nucleation rates in comparison to cloud simulation chamber experiments. The CFDC-type INC measurements demonstrated that ice nucleation occurred sporadically and probabilistically, especially for Fe$_2$O$_3$ particles.

A.4 Possible causes for the large difference in apparent INP abilities obtained from cloud chamber experiments and CFDC-type INC measurements

The large difference in the INAS density between the cloud chamber experiments and the CFDC-type INC measurements could be attributable to the short residence time (on the order of a few seconds) of particles under the activation conditions (within a droplet at the nucleation temperature) in the CFDC-type INC. Conversely, in the cloud chamber experiments, the particles experienced activation conditions for much longer time periods (on the order of a few tens of seconds); however, this was dependent on the ascent rate. In this study, a deterministic (or singular) interpretation of immersion freezing nucleation, which approximated immersion freezing as being dependent only on the temperature and did not quantify the time-dependent ice nucleation behavior, was employed. An alternate, purely stochastic interpretation quantifies the time-dependent characteristics of ice nucleation.

In general, the nucleation rate of a given nucleation site is a function of temperature and decreases at higher temperatures. If the time constant of a nucleation rate is 1 s (high nucleation rate), the AF for a short residence time (e.g., 3 s) under nucleation conditions in the CFDC-type INC will be 0.95. However, if the time constant is 60 s (low nucleation rate), the AF will be 0.064. This implies that only a portion of the ice nucleation sites can be activated in the CFDC-type INC when the nucleation rate is low. The time constant of 60 s is not unrealistically long, and much longer time constants have been observed in previous studies (Welti et al. 2012; Herbert et al. 2014; Vali 2014).

The large difference in the INAS density between the cloud chamber experiments and the INC measurements could also be attributable to the difference in the size distributions of the metal oxide particles in the cloud chamber experiments and the CFDC-type INC measurements. As indicated in Fig. 1, during the INC measurements, nearly all particles larger than 1 µm were removed by the inlet double impactors (cut-off size of 1 µm) and the very fine airflow structures of the INC’s inlet manifold. For simplicity, we adopted a definition of the INAS density based on the geometric surface area instead of the Brunauer–Emmett–Teller (BET) surface area, which is determined by the N$_2$-absorption technique and is sensitive to much finer surface structures (textures). If the ratio of the
BET surface area to the geometric surface area has a strong size dependency (i.e., the ratio increases with the particle size), the INAS density measured by the INC could be smaller than that obtained from the cloud chamber experiments, although electron micrographs showed no significant difference in the surface microstructure between submicron particles and supermicron particles. More detailed and well-organized inter-instrument comparisons are needed to resolve this issue.

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