Cloud condensation nuclei (CCN) and ice nuclei (IN) abilities of Al\textsubscript{2}O\textsubscript{3} and Fe\textsubscript{2}O\textsubscript{3} using MRI dynamic cloud chamber and CFDC-type IN counter

Tzu-Hsien KUO\textsuperscript{1}, Masataka MURAKAMI\textsuperscript{1,2}
Takuya TAJIRI\textsuperscript{1}, and Narihiro ORIKASA\textsuperscript{1}
\textsuperscript{1}MRI; \textsuperscript{2}ISEE, Nagoya U.

2017/02/17@極地研
Outline

• General information of two metal oxide
  o Reviewed articles in atmospheric composition
• Reviewed articles in cloud chamber and CFDC experiments
• MRI experiments during 2016/10/17-2017/01/16
  o Particle size distribution
  o CCN abilities (κ-value)
  o IN abilities (dynamic cloud chamber/CFDC type IN counter)
• Discussion
• Conclusion and ongoing work
General information of two metal oxide

- Metal oxide sources in the atmosphere
  - Natural - volcano, soil, biomass burning
  - Anthropogenic - engineered, fuel, industrial pollution, firework, aircraft emission, hygroscopic flare
Aluminium oxide observed in the atmosphere

Aluminium accounts for 8.3% of Earth crust; Corundum is the most common naturally occurring crystalline form of aluminium oxide.

Industrial proposes

Space shuttle exhausted air at 2-7 km high with 98.9% aluminum oxide in 0.3 µm diameter and below. (Cofer III et al., 1991)

Linak et al., (2007): Fly-ash includes Al, Ca, Ti, Mg, and iron oxide is below 2.5 µm

In Abidjan- a rural (Pasteur), an urban (Cocody), an industrial (Vridi) sites, particles are mostly smaller than 2.5 µm, aluminum, iron, calcium account for 56-79 µg/mg, 34-54 µg/mg and 31-37 µg/mg. (Kouassi et al., 2010)

Roadside: 23.1% in aluminum oxide (Sanderson et al., 2016)

Component Bituminous Subbituminous Lignite

<table>
<thead>
<tr>
<th>Al₂O₃</th>
<th>5-35</th>
<th>20-30</th>
<th>20-25</th>
</tr>
</thead>
</table>

From wikipedia
Iron oxide observed in the atmosphere

Iron accounts for 4.5% of Earth crust; Industrial proposes

In urban background, iron oxide distributes in 25-116 nm (Belosi et al., 2013)

Iron oxide distributes 200-2400 nm in Tsukuba. (Adachi et al., 2016)

Around iron and steel manufacturing facilities, iron oxide distributes 5-10 μm or less 5 μm. (Machemer, 2004)

Roadside: 52.6% iron in PM\textsuperscript{18}, iron oxide’s median diameter 27 and 37nm. (Sanderson et al., 2016)
Anthropogenic forcing

Radiative forcing of climate between 1750 and 2011

Forcing agent

Well Mixed Greenhouse Gases
- CO₂
- Halocarbons
- Other WMGHG (CH₄, N₂O)

Ozone
- Stratospheric
- Tropospheric

Stratospheric water vapour from CH₄

Surface Albedo
- Land Use
- Black carbon on snow

Contrails
- Contrail induced cirrus

Aerosol-Radiation Interac.

Aerosol-Cloud Interac.

Total anthropogenic

Solar irradiance

Radiative Forcing (W m⁻²)

Fig 3. Bar chart for RF (hatched) and ERF (solid) for the period 1750–2011, where the total ERF is derived from Figure 8.16. Uncertainties (5 to 95% confidence range) are given for RF (dotted lines) and ERF (solid lines).

(IPCC, AR5)
Aerosol—cloud—climate interaction

Fig 4. Aerosol-cloud-climate interaction (J.-P. Chen 2004)
Ice nucleation

Fig 5. Modes of ice formation in clouds (from ETH Zürich)
Ice nucleation active surface site (INAS) densities

- INAS density ($ns$) based on geometric aerosol size is a method to parameterize surface area-scaled immersion freezing activities (Connolly et al., 2009; Niemand et al., 2012)
- postulates that ice crystal formation observed in experiments is a solely function of temperature (and ice saturation)
- activated ice crystals ($Nice$) and CN was measured simultaneously during the expansion experiments, the activated fraction of aerosol particles as ice nuclei ($fIN = Nice/Ncn$) was obtained
- dividing the activated fraction by the volume equivalent surface area of an individual particle ($Sve$) measured in advance for each experiment
- on the assumption of a uniform distribution of ice nucleation sites and their size-independency over a given total aerosol surface area ($Sve \cdot Ncn$).

\[
n_s(T, S_i) = -\frac{1}{A_{aer}} \cdot \ln(1 - f_{IN}(T, S_i)) \\
\approx f_{IN}(T, S_i)/A_{aer}
\]
Hiranuma et al. (2014) used AIDA chamber, shown with immersion nucleation, tested surface irregularities of Fe$_2$O$_3$ particles. The immersion mode ice nucleation efficiency of milled Fe$_2$O$_3$ particles is almost an order of magnitude higher at $-35.2^\circ C < T < -33.5^\circ C$ ($RHi = 125\%$) than that of the cubic Fe$_2$O$_3$ particles, indicating a substantial effect of morphological irregularities on immersion mode freezing.

Fig 8. Results in INAS form
Saunders et al. (2010) used AIDA chamber, observed deposition nucleation of Fe$_2$O$_3$ at RH$_i$ ranging from 105% to 140% for temperatures below -53°C.

- Approximately 10% of amorphous Fe$_2$O$_3$ particles (modal diameter = 30 nm) generated at RH$_i$ = 140% with an initial chamber temperature of -91°C.

Conditions studied in the chamber which correspond to cirrus cloud formation in the upper troposphere.

![Graph](image.png)

Fig 7. calculated number of active sites per unit area of material that become active at the given sice for the iron oxide aerosol experiments as indicated.

$$ns \text{ (-83°C )}=10^{(3.33 \times S_{ice})+8.16}$$
12

0.1% of the total number of injected aerosol particles had nucleated ice (i.e. formed 5 µm crystals) Yakobi-Hancock et al. (2013) using a CFDC at $-40.0 \pm 0.3{ }^\circ\text{C}$ and particles size-selected at 200 nm.

### Table 1. Tested substances in order of increasing critical RH$_i$ for deposition activation of 0.1% of 200 nm particles at $-40{ }^\circ\text{C}$. The electrical conductivity ($\mu$S) of the suspensions is indicated in parentheses for MDD, ATD, orthoclase, and TiO$_2$ after the sample names.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Critical RH$_i$ (%)</th>
<th>Category</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbI$_2$</td>
<td>122.8 ± 2.0</td>
<td>Anthropogenic</td>
<td>Sigma-Aldrich, 99 %</td>
</tr>
<tr>
<td>MDD unwashed (70 µS)</td>
<td>125.4 ± 1.8</td>
<td>Mineral dust</td>
<td>Peters et al. (2008)</td>
</tr>
<tr>
<td>MDD (50 µS)</td>
<td>126.3 ± 3.4</td>
<td>Mineral dust</td>
<td>Peters et al. (2008)</td>
</tr>
<tr>
<td>Orthoclase (K-feldspar) (18 µS)</td>
<td>127.1 ± 6.3</td>
<td>Feldspar mineral</td>
<td>Department of Earth Sciences, University of Toronto</td>
</tr>
<tr>
<td>ATD (30 µS)</td>
<td>129.5 ± 5.1</td>
<td>Mineral dust</td>
<td>Powder Technology Inc., 0–5 µm</td>
</tr>
<tr>
<td>ATD unwashed (89 µS)</td>
<td>132.9 ± 0.5</td>
<td>Mineral dust</td>
<td>Powder Technology Inc., 0–5 µm</td>
</tr>
<tr>
<td>Orthoclase (K-feldspar) unwashed (50 µS)</td>
<td>135.0 ± 3.6</td>
<td>Feldspar mineral</td>
<td>Department of Earth Sciences, University of Toronto</td>
</tr>
<tr>
<td>Plagioclase (Na/Ca-feldspar)</td>
<td>136.2 ± 1.3</td>
<td>Feldspar mineral</td>
<td>Department of Earth Sciences, University of Toronto</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>136.4 ± 1.9</td>
<td>Clay mineral</td>
<td>Department of Earth Sciences, University of Toronto</td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>139.3 ± 1.0</td>
<td>Clay mineral</td>
<td>Department of Earth Sciences, University of Toronto</td>
</tr>
<tr>
<td>Illite</td>
<td>142.5 ± 2.3</td>
<td>Clay mineral</td>
<td>Department of Earth Sciences, University of Toronto</td>
</tr>
<tr>
<td>Pyrite (FeS)</td>
<td>142.9 ± 0.8</td>
<td>Metal sulfide</td>
<td>Department of Earth Sciences, University of Toronto</td>
</tr>
<tr>
<td>Corundum (Al$_2$O$_3$)</td>
<td>143.2 ± 3.2</td>
<td>Metal oxide</td>
<td>Sigma-Aldrich, ≥98 %</td>
</tr>
<tr>
<td>Calcite (CaCO$_3$)</td>
<td>144.3 ± 0.9</td>
<td>Metal carbonate</td>
<td>Department of Earth Sciences, University of Toronto</td>
</tr>
<tr>
<td>Magnetite (Fe$_2$O$_4$)</td>
<td>144.4 ± 2.2</td>
<td>Metal oxide</td>
<td>Sigma-Aldrich, &lt;5 µm, 95 %</td>
</tr>
<tr>
<td>Quartz (SiO$_2$)</td>
<td>144.7 ± 1.5</td>
<td>Metal oxide</td>
<td>Alfa Aesar, 99.9 %</td>
</tr>
<tr>
<td>Gypsum (CaSO$_4$2H$_2$O)</td>
<td>144.8 ± 1.2</td>
<td>Metal sulfate</td>
<td>Sigma-Aldrich, ≥99 %</td>
</tr>
<tr>
<td>Galena (PbS)</td>
<td>145.0 ± 1.0</td>
<td>Metal sulfide</td>
<td>Sigma-Aldrich, 99.9 % trace metal basis</td>
</tr>
<tr>
<td>Anglesite (PbSO$_4$)</td>
<td>145.1 ± 1.3</td>
<td>Metal sulfide</td>
<td>Sigma-Aldrich, 98 %</td>
</tr>
<tr>
<td>Zn</td>
<td>145.4 ± 0.6</td>
<td>Pure metal</td>
<td>Atlantic Equipment Engineers, 99.8 %</td>
</tr>
<tr>
<td>Massicot (PbO)</td>
<td>145.5 ± 1.3</td>
<td>Metal oxide</td>
<td>Sigma-Aldrich, ≥99.0 %</td>
</tr>
<tr>
<td>Calcite (CaCO$_3$)</td>
<td>145.8 ± 1.4</td>
<td>Metal carbonate</td>
<td>Sigma-Aldrich, ≥99.0 %</td>
</tr>
<tr>
<td>Rutile (TiO$_2$) unwashed (10.8 µS)</td>
<td>146.3 ± 1.0</td>
<td>Metal oxide</td>
<td>Sigma-Aldrich, 99–100.5 %</td>
</tr>
<tr>
<td>Bunsenite (NiO)</td>
<td>146.5 ± 0.8</td>
<td>Metal oxide</td>
<td>Sigma-Aldrich, 99 %</td>
</tr>
<tr>
<td>Cerussite (PbCO$_3$)</td>
<td>146.7 ± 0.6</td>
<td>Metal carbonate</td>
<td>Sigma-Aldrich, ACS reagent grade</td>
</tr>
<tr>
<td>Rutile (TiO$_2$) (1.4 µS)</td>
<td>147.4 ± 0.4</td>
<td>Metal oxide</td>
<td>Sigma-Aldrich, 99–100.5 %</td>
</tr>
<tr>
<td>ZnS</td>
<td>147.7 ± 1.5</td>
<td>Metal sulfide</td>
<td>Sigma-Aldrich, ≥97.0 %</td>
</tr>
<tr>
<td>Zincite (ZnO)</td>
<td>148.6 ± 0.2</td>
<td>Metal oxide</td>
<td>Sigma-Aldrich, ≥99.0 %</td>
</tr>
<tr>
<td>Hematite (Fe$_2$O$_3$)</td>
<td>148.8 ± 1.0</td>
<td>Metal oxide</td>
<td>Sigma-Aldrich, &lt;5 µm, 99+ %</td>
</tr>
</tbody>
</table>
## Summary of reviewed articles

Table 2. Summary of reviewed articles

<table>
<thead>
<tr>
<th></th>
<th>Nucleation mode</th>
<th>Particle size</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hiranuma et al. (2014)</td>
<td>Immersion (AIDA chamber)</td>
<td>modal diameter = 1 µm</td>
<td>milled Fe₂O₃ INAS~1E10 at −35.2 °C &lt; T ≤−33.5 °C (RHᵢ = 125%) (larger particle)</td>
</tr>
<tr>
<td>Saunders et al. (2010)</td>
<td>Deposition (AIDA chamber)</td>
<td>modal diameter = 30 nm</td>
<td>Fe₂O₃ at RHᵢ ranging from 105% to 140% for temperatures below -53 °C. (Upper layer)</td>
</tr>
<tr>
<td>Yakobi-Hancock et al. (2013)</td>
<td>Deposition (CFDC)</td>
<td>200 nm</td>
<td>-40°C, 1%, RHᵢ=143.2% (Al₂O₃) RHᵢ=148.8% (Fe₂O₃)</td>
</tr>
<tr>
<td>Archuleta et al. (2005)</td>
<td>Deposition (CFDC)</td>
<td>50,100,200 nm</td>
<td>200nm, 1%, RHᵢ ~140% -45 (Al₂O₃) -60 °C (Fe₂O₃)</td>
</tr>
</tbody>
</table>
Table 4. Material information

<table>
<thead>
<tr>
<th>Aerosol (source)</th>
<th>Purity wt%</th>
<th>Density (g cm(^{-3}))</th>
<th>Other content</th>
<th>Average surface (m(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(_2)O(_3) (APPIE)</td>
<td>99% up</td>
<td>3.9</td>
<td>unknown</td>
<td>1.61E-12 (11/17)</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>
<td>8.04E-13 (2/13)</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>
<td>3.85E-13 (11/16)</td>
</tr>
</tbody>
</table>
Size distribution in the exp.

Table 5. Material information

<table>
<thead>
<tr>
<th>type</th>
<th>method</th>
<th>Mean diameter</th>
<th>Aave</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>chamber</td>
<td>0.50</td>
<td>1.6E-12</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>CFDC</td>
<td>0.34</td>
<td>4.9E-13</td>
</tr>
<tr>
<td>Fe₂O₃ #1</td>
<td>chamber</td>
<td>0.37</td>
<td>8.0E-13</td>
</tr>
<tr>
<td>Fe₂O₃ #2</td>
<td>chamber</td>
<td>0.30</td>
<td>3.9E-13</td>
</tr>
</tbody>
</table>

Fig 10. Particle size distribution
Activated Fraction (AF)
AF = CCN/CN

Critical Dry diameter: AF = 0.5

SS=0.2%
50% of size-classified dry particles activated as CCN
The results indicated that the hygroscopicity (κ-value) were around 0.01, which are comparable to that of surrogates of mineral dust particles, and less than the average κ-value of atmospheric aerosols.
Aerosol and Cloud particles measurements

### Aerosol Particles
- **CCN Counter** (CCN-200, DMT)
- **IN Counter** (MRI)
- **OPC** (KC-01E, RION)
- **SMPS** (MODEL3936, TSI)

### Cloud Particles
- **Laser sensor**
- **Welas OPC**

### Device specifications
- **Size range:**
  - Aerosol: $10 \text{nm} \sim 1 \text{µm}$
  - Drop/Ice: $1 \text{µm} \sim 100 \text{µm}$

- **Data:**
  - Aerosol size spectra
  - CCN activity spectra
  - Cloud particle size distribution

### Operational Ranges
- **Pressure:** $1000 \sim 30 \text{hPa}$
- **Wall Temperature:** $+30 \sim -100 \degree \text{C}$
- **Ascent Rate:** $0 \sim 30 \text{m/s}$

### Data:
- Onset, Time evolution of size distribution and concentration,
  Particle shape and Habit image and Depolarization ratio
MRI cloud chamber facility System diagram

Cloud simulation Building

Dry Air Supply System

Refrigerator

Coolant Reservoir

Air Supply

FFU/HEPA

Hygro

CCNC

CPC

CAS

Welas

CPI

Diaphram pump

MRI Dynamic Cloud Chamber

Air sampling & Injection

Dry Air Supply

Aerosol Injection

Air Supply

Agitator

Air Exhaust

Vacuum Pump

Air sampling & Injection

Dry Air

Air Injection

Aerosol Injection1

Aerosol Injection2

Air Sampleing

Processed Air Supply

Dry Air Supply System

MV

MV

Agitator

Vacuum Pump

Blower

Vacuum Pump

CCNC

INC

SMPS

CPC

OPC

APS

Aerosol Buffer Tank

Aerosol measurement Building

Air Supply

Air Exhaust

S

S

S

S

S

S

S

S

S

S

S

S

S

S

S

S

S
### MRI dynamic cloud chamber exp.

#### Table 6. Exp. information

<table>
<thead>
<tr>
<th>date</th>
<th>type</th>
<th>Conc. (#/cc)</th>
<th>ascent rate (m/s)</th>
<th>Tini</th>
<th>Tdini</th>
<th>TLCL</th>
<th>AFmax</th>
<th>Aave</th>
<th>INASmax</th>
</tr>
</thead>
<tbody>
<tr>
<td>161117</td>
<td>Al$_2$O$_3$</td>
<td>1360</td>
<td>5</td>
<td>5</td>
<td>-13.3</td>
<td>-16.9</td>
<td>0.0043</td>
<td>1.6E-12</td>
<td>2.7E+09</td>
</tr>
<tr>
<td>161118</td>
<td>Al$_2$O$_3$</td>
<td>2940</td>
<td>5</td>
<td>5</td>
<td>-8.7</td>
<td>-11.5</td>
<td>0.0425</td>
<td>1.6E-12</td>
<td>2.6E+10</td>
</tr>
<tr>
<td>170106</td>
<td>Al$_2$O$_3$</td>
<td>1600</td>
<td>5</td>
<td>5</td>
<td>-6.5</td>
<td>-8.9</td>
<td>0.0205</td>
<td>1.6E-12</td>
<td>1.3E+10</td>
</tr>
<tr>
<td>170110</td>
<td>Fe$_2$O$_3$ #1</td>
<td>4200</td>
<td>5</td>
<td>5</td>
<td>-5.2</td>
<td>-7.5</td>
<td>0.0006</td>
<td>1.2E-12</td>
<td>4.9E+08</td>
</tr>
<tr>
<td>170111</td>
<td>Fe$_2$O$_3$ #1</td>
<td>8640</td>
<td>5</td>
<td>5</td>
<td>-10.5</td>
<td>-13.6</td>
<td>0.0014</td>
<td>1.2E-12</td>
<td>1.1E+09</td>
</tr>
<tr>
<td>170112</td>
<td>Fe$_2$O$_3$ #2</td>
<td>3580</td>
<td>5</td>
<td>-5</td>
<td>-13.9</td>
<td>-15.7</td>
<td>0.0031</td>
<td>3.9E-13</td>
<td>7.9E+09</td>
</tr>
<tr>
<td>170113</td>
<td>Fe$_2$O$_3$ #2</td>
<td>2880</td>
<td>5</td>
<td>-5</td>
<td>-11</td>
<td>-12.5</td>
<td>0.0042</td>
<td>3.9E-13</td>
<td>1.1E+10</td>
</tr>
</tbody>
</table>
Fig 15. MRI dynamic chamber exp.
Activation fraction

Fig 16. Activation fraction
INAS

Fig 17. Results in INAS form

AF: Al$_2$O$_3$ > Fe$_2$O$_3$ #2 > Fe$_2$O$_3$ #1
Particle size (Surface): Al$_2$O$_3$ > Fe$_2$O$_3$ #1 > Fe$_2$O$_3$ #2
INAS: Al$_2$O$_3$ > Fe$_2$O$_3$ #2 > Fe$_2$O$_3$ #1
Fig 18. Previous results in INAS form

\[ n_s(T, S_i) = -1/A_{\text{aer}} \cdot \ln (1 - f_{\text{IN}}(T, S_i)) \approx f_{\text{IN}}(T, S_i)/A_{\text{aer}} \]

Dust:
- Asian dust (AD)
- Saharan dust (SD)
- Canary Island dust (CID)
- Israel dust (ID)
- Arizona test dust (ATD).

Niemand et al. 2012
Niemand et al. 2012
Atkinson et al. 2013
Broadly et al. 2012
Previous study using MRI chamber

Cellulose (セルロース)

Fig 19. (a) Size distribution of cellulose (b) Results in INAS form

Hiranuma et al. (2015)

Ice nucleation by cellulose becomes significant (>0.1 l^{-1}) below about -21 C, temperatures relevant to mixed-phase clouds.
Discussion for cloud chamber exp.

- Coolant temperature issue (not low enough)
- Around -20°C, the ice crystal can be observed in cloud chamber exp.
- Which is the dominated mechanism, condensation or immersion freezing?
- Size issue, \( \text{Al}_2\text{O}_3 \) has broad size distribution inside the cloud chamber.
  - Size matters more than chemistry for cloud-nucleating ability (Dusek et al., 2006)
    - More particles are large than 0.2 \( \mu \text{m} \) of \( \text{Al}_2\text{O}_3 \)
Table 7. Material information

<table>
<thead>
<tr>
<th>type</th>
<th>Mean diameter</th>
<th>Aave</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$_2$O$_3$</td>
<td>0.34</td>
<td>4.9E-13</td>
</tr>
<tr>
<td>Fe$_2$O$_3$ #1</td>
<td>0.35</td>
<td>4.8E-13</td>
</tr>
<tr>
<td>Fe$_2$O$_3$ #2</td>
<td>0.28</td>
<td>3.0E-13</td>
</tr>
</tbody>
</table>

Cut-off 1µm

IN measurement employed
Temperature: -10 °C ~ -35 °C
Relative humidity:
SSi ~ 0 % to SSw ~ +15 %
CFDC-type IN counter exp.

From deposition to condensation-freezing nucleation mode.

Fig.22 CFDC-type INC results
**Discussion**

- Is the metal oxide efficient enough as CCN/IN?
  - Real atmospheric condition, particle size distribution

- How is the difference between laboratory and reality?
  - Internal/external mixing
  - Mixed-phase clouds

- Uncertainties during the experiment processes.
- We suggest a series of future studies investigating the ice nucleation activity of metal oxide in greater detail.
Conclusion and ongoing work

- Kappa of three metal oxide particles are around 0.01-0.04
- Ice nucleation by two metal oxide becomes significant below about -20/-25 °C, temperatures relevant to mixed-phase clouds.
- Al$_2$O$_3$ seems to have better IN ability than Fe$_2$O$_3$ both in cloud chamber exp. and CFDC-type INc exp.
  - Onset temperature is around -20°C in cloud chamber exp.
  - Ability is like illite.
  - Onset temperature is around -30°C in CFDC-type INc exp.

- Parcel model (Chen and Lamb, 1994) – using kappa and INAS for parameterization (Yamashita et al., 2011, 2013; Hoose and Möhler, 2012)
Thanks for listening.