# TNA User Report

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| | |
|---|---|
| Project title | MAN-INUIT09 |
| Project objectives (max 100 words) | The objective of the project was to assess the role of mineralogy in the ice nucleating (IN) efficiency of natural desert dust samples. Using a LAAP-TOF single particle mass spectrometer and our novel method for the real time differentiation of mineral phase in dust we attempted to answer the following questions:<br>1. How much does feldspar and other minerals affect the IN ability of natural desert dust aerosols?<br>2. In how far is single particle mass spectrometry capable to differentiate between aerosol particles of different mineralogical composition?<br>3. Is there a preference for certain minerals to nucleate ice? |
| Description of work (max 100 words): | This work ran in parallel with the experiments undertaken as part of the INUIT09 project at the AIDA chamber. The LAAP-TOF was used to evaluate the single particle composition of several natural desert dust samples from Africa that were dispersed in the NAUA and AIDA chambers prior to the commencement of simulated ice nucleation conditions. |

| Principal Investigator's and group's information | |
|---|---|
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| Researcher status | Postdoctoral researcher |
| New user | Yes |
| Number of users in the group *(including the project leader)* | 1 |
| Number of access days | 14 |

# Trans-National Access (TNA) Scientific Report

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## Instructions

Please limit the report to max 5 pages, you can include tables and figures. Please make sure to address any comments made by the reviewers at the moment of the project evaluation (if applicable, in this case you were informed beforehand). Please do not alter the layout of the document and keep in Word version.
The report will be made available on the eurochamp.org website. Should any information be confidential or not be made public, please inform us accordingly (in this case it will only be accessible by the European Commission, the EUROCHAMP-2020 project partners, and the reviewers). Please include:

- Introduction and motivation
- Scientific objectives
- Reason for choosing the simulation chamber/ calibration facility
- Method and experimental set-up
- Data description
- Preliminary results and conclusions
- Outcome and future studies
- References

**Name of the PI and of the group members (include affiliation): Nicholas Marsden (University of Manchester).**
**Chamber name and location: AIDA Chamber, Karlsruhe, Germany.**
**Campaign name and period: MAN-INUIT09, 6th – 21st July 2017**
**Text:**

## Introduction and Motivation

Indirect radiative forcing of the atmosphere by clouds represents the biggest uncertainty in climate change modelling due to a lack of understanding of how aerosol-cloud interactions affect the microphysical properties of clouds [1]. Heterogeneous ice nucleation in cold and mixed phase cloud is particularly difficult to predict because the onset conditions for ice formation is partly dependent on the composition of the ice-nucleating particle (INP). Mineral dust is suspected as being an important source of INP due to its atmospheric abundance[2] and the relatively high temperature of ice nucleation observed in the laboratory [3]. Furthermore, experiments with nominally pure mineral samples have shown that ice nucleation is dependent on mineral type [4]. Expanding these findings to mineralogically heterogeneous natural dust samples is difficult however, because of lack of an effective analytical method to deduce mineral phase on a single particle basis.

The Laser Ablation Aerosol Particle Time-of-Flight (LAAP-ToF) mass spectrometer has the ability to measure composition of single particles online. This technique is particularly well suited to evaluating particle composition in dynamic simulations of ice nucleation, such as those simulated in controlled expansion cloud-simulation chambers (CECC), because of the high time resolution of the measurement. However, matrix effects during the ionisation processes result in a non-quantitative composition measurement which hinders the identification of mineral phase by traditional mass spectral peak area analysis. To overcome this problem, in a recent study Marsden et al introduced a novel technique that was able to differentiate clay mineral standards by exploiting apparent differences in ion formation mechanism between particles of different mineralogy, using relative shift in ion arrival times in addition to the peak area measurement in single particle mass spectra [5].

In this project, we have applied the newly developed mass spectrometry technique to the composition measurement of natural dust samples in tandem with ice nucleation experiments in the AIDA chamber. The data is expected to provide valuable insights into the ice nucleating characteristics of atmospherically relevant dust during realistic cloud forming conditions.

## Scientific Objectives

The objective of the project would be to assess the role of mineralogy in the ice nucleating (IN) efficiency of natural desert dust samples. Using a customised LAAP-TOF single particle mass spectrometer we would attempt to provide an answer to the following questions:

1. How much does feldspar and other minerals affect the IN ability of natural desert dust aerosols?

2. In how far is single particle mass spectrometry capable to differentiate between aerosol particles of different mineralogical composition?

3. Is there a preference for certain minerals to nucleate ice?

Deployed to the AIDA cloud simulation chamber, our novel method for the real time differentiation of mineral phase in dust aerosol, especially the ability to differentiate feldspar from clay mineral such as illite, offers a unique opportunity to evaluate the role of mineralogy in IN processes.

## Reasons for Choosing the AIDA Chamber

The team at the AIDA chamber have vast amount of experience in simulating ice nucleation by mineral dust in cold and mixed phase clouds and are in possession of the natural desert dust samples collected from potential source areas in Africa. The AIDA facility has the capability to disperse these samples in atmospherically relevant conditions. In addition a counterflow virtual impactor (CVI) is available at AIDA which extract the particle residue from melted ice crystals.

## Method and Experimental Setup

The LAAP-ToF is a single particle mass spectrometer that is commercially available from AeroMegt GmbH. Aerosol is directly introduced into the instrument via an aerodynamic lens inlet which produces a narrow particle beam along the instrument axis. An optical particle detection system identifies the presence of a particle in the ion source of the mass spectrometer and triggers a high powered pulse (193nm) from an excimer laser.  If certain threshold conditions are met, the interaction with the laser pulse vaporizes the particle and produces a cloud of ions, fragments and neutrals. The ions are analysed my bipolar time-of-flight mass spectrometry which outputs a positive and negative ion mass spectra for each particle analysed.

Natural dust samples were dispersed in the NAUA and AIDA chambers using rotating brush generator (Model RBG 1000, Palas GmbH) and small scale powder disperser (model 3433, TSI inc). Measurements of the size distribution of the dispersed dust were made using the host APS and SMPS instruments and filter samples were collected for off-line composition analysis.

The LAAP-ToF sampled the dust in three ways:

1. Directly from the NAUA chamber at high concentration.
2. Directly from the AIDA chamber at low concentration prior to expansion to cloud forming conditions.
3. Downstream of the CVI after ice formation at atmospherically relevant conditions.

## Data Description

The LAAp-ToF produces a positive and negative mass spectrum which represents the composition of a single particle. The techniques is subject to a number of measurement biases due to instrument function, which means that only approximately 10% of detected dust particles produce an informative mass spectrum. Table 1 shows the number of informative mass spectra that were acquired for selected natural dust samples after filtering the data.

**Table 1. The number of informative bipolar mass spectra of natural dust samples obtained from the NAUA and AIDA chambers (after filtering).**

| | Sample | Origin | NAUA | AIDA |
|---|---|---|---|---|
| North Sahara | DDS01 | Soil sample from Mhamid region, near border to Algeria, SE of Atlas mountains, river sediments 29.83773 °N, -5.76143 °E | 2043 | 340 |
| | DDS02 | soil sample from Mhamid region, Hamada with large amounts of dust 29.84957 °N, -6.01508 °E | 5213 | 599 |
| | DDS03 | Soil sample from Mhamid region, border of dry salt/ silt plain of Lac Iriqui close to sand dune fields 29.86202 °N, -6.156760°E | 2581 | |
| | SDT01 | Maouna near Tataouine, Tunesia 33°1'N, 10°40'E | | 271 |
| South Sahara /Sahel | DDA01 | Dano, Burkina Faso | 3962 | 319 |
| | SDN02 | Banizoumbou, Niamey, Niger 13.516667 °N, 2.633333 °E | 2921 | |
| | SDN05 | Grand Mosque in Niamey, Niger 13.522203 °N, 2.133011 °E | 5077 | |
| | SDB01 | Bodele Depression, Chad 16.135650 °N, 18.598833 °E | | 319 |

## Preliminary Results and Conclusions

Preliminary examination of the data indicates that the mass spectra are of sufficient quality to perform composition analysis on most dust samples. An example of a bipolar mass spectrum acquired from the analysis of DDS02, showing typical markers of mineral dust is shown in Figure 1. Elemental ion of Na (m/z 23), Al (m/z 27), K (m/z 39) anf Fe (m/z 56) are observed in the positive in spectrum; and fragment ions $SiO_2$ (m/z 60) and $SiO_3$ (m/z 76) are observed in the negative ion spectrum.

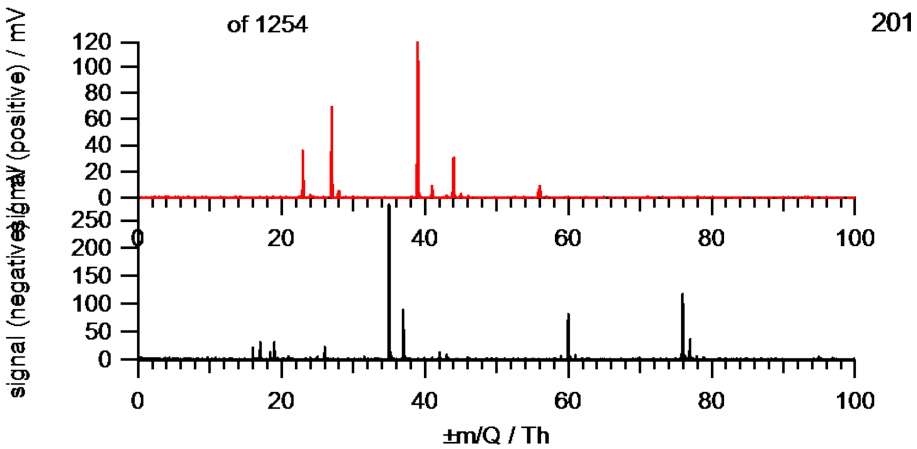


**Figure 1. Example of bipolar mass spectrum of a single particle of Moroccan dust (DDS02).**

In addition, we have applied the novel technique of mineral differentiation by ion formation mechanism using peak shift analysis to the Moroccan dust samples DDS01, DDS02 and DDS03. Preliminary results, shown in Figure 2, hint at subtle differences in mineralogy when compared to the calibration with illite nx and microcline feldspar.

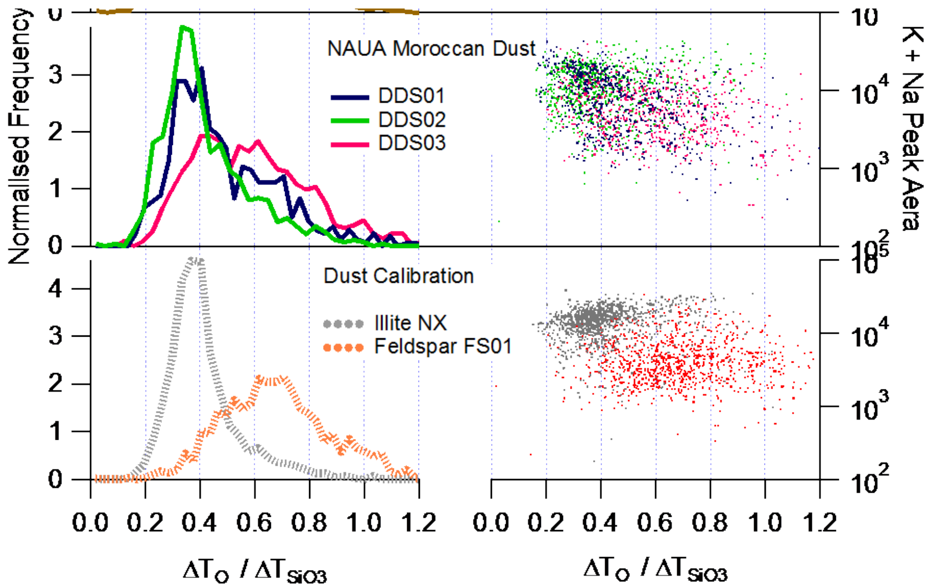


**Figure 2. Peak shift analysis of Moroccan dust with reference to sodium and potassium content.**

## Outcome and Future Studies

We expect to be able to characterise the dust composition by traditional peak area analysis, and make a comparison between North Saharan dust samples and South Saharan / Sahelian dust samples which are expected to be significantly different in mineralogy. In addition, a more detailed mineralogical analysis of the Moroccan dust samples may provide important clues to the mineralogical influence on ice nucleation when compared to the ice nucleating efficiency derived from the AIDA chamber experiments.

## References

1. Boucher O, Randall D, Artaxo P, et al. Clouds and Aerosols. *Clim Chang 2013 Phys Sci Basis Contrib Work Gr I to Fifth Assess Rep Intergov Panel Clim Chang*. 2013:571-657. doi:10.1017/CBO9781107415324.016.

2. DeMott PJ. African dust aerosols as atmospheric ice nuclei. *Geophys Res Lett*. 2003;30(14):1732. doi:10.1029/2003GL017410.

3. Connolly PJ, Möhler O, Field PR, et al. Studies of heterogeneous freezing by three different desert dust samples. *Atmos Chem Phys Discuss*. 2009;9(1):463-514. doi:10.5194/acpd-9-463-2009.

4. Atkinson JD, Murray BJ, Woodhouse MT, et al. The importance of feldspar for ice nucleation by mineral dust in mixed-phase clouds. *Nature*. 2013;498(7454):355-358. doi:10.1038/nature12278.

5. Marsden NA, Flynn MJ, Allan JD, Coe H. On-line differentiation of mineral phase in aerosol particles by ion formation mechanism using a LAAP-ToF single particle mass spectrometer. 2017;(July).