

Invited talk

MASS SPECTROMETRIC ANALYSIS OF SMALL ICE CRYSTAL RESIDUALS IN MIXED PHASE CLOUDS DURING THE CLACE PROJECTS

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1. INTRODUCTION

Heterogeneous nucleation is the main initiation process of precipitation in mid latitudes. However, the relationship between the ability to act as ice nuclei (IN) and the chemical composition of aerosol particles is not yet fully understood. First ambient measurements in pure ice clouds, e.g. cirrus clouds, are described in the literature but these measurements are restricted to aircraft based equipment. Ground based measurements can only be conducted on mountain sites in mixed phase clouds, but separation of ice nuclei from cloud condensation nuclei (CCN), which outnumber the IN by a factor of ~ 100 is necessary. A series of intensive ground based field experiments was carried out from 2001 to 2007 at the Jungfraujoch station in the Swiss Alps under the name CLACE (Cloud and Aerosol Characterization Experiment). During CLACE a newly designed Ice-CVI (counter-flow virtual impactor) was combined with different aerosol mass spectrometers in order to investigate the chemical

composition of ice nuclei in mixed phase clouds.

2. MEASUREMENTS

The Sphinx laboratory at the Jungfraujoch is situated at 3580 meters above sea level in the Swiss Alps at 7° 59' 2" E, 46° 32' 53" N. During the winter months it is mostly located in the free troposphere and frequently surrounded by mixed phase clouds. The CLACE campaigns were conducted from February to mid of March. Here, results from CLACE 3 to 6 (2004 – 2007) are presented.

2.1. Inlet systems

Three different inlet systems were available during the CLACE campaigns, sampling the entire background aerosol, the interstitial (not activated) aerosol particles, and residuals from small ice crystals and supercooled droplets.

The "total" inlet is heated, thereby evaporating cloud water and ice and thus sampling interstitial and activated aerosol particles. It is part of the GAW (Global Atmospheric Watch) project, permanently installed at the Jungfraujoch and operated by the Paul Scherrer Institute (PSI).

The interstitial inlet samples the not activated aerosol with a cut off at 2.5 µm. It

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is installed by the Paul Scherrer Institute especially for the CLACE campaigns.

To separate the ice residuals from the cloud condensation nuclei and the not activated aerosol, an Ice-CVI was operated by the IfT Leipzig during the CLACE campaigns. It consists of four main parts, an omnidirectional, exponentially-tapered, upward looking horn to aspirate the cloud air. In the virtual impactor (VI) particles larger than $20\text{ }\mu\text{m}$ ($D_{50\%}$ cut size diameter) are virtually impacted, whereas smaller particles remain in the sample flow. Downstream of the VI a pre-impactor (PI) is installed which separates the small ice particles from supercooled droplets by freezing the latter upon contact with impaction plates colder than 0°C . The CVI itself is located downstream of the PI to reject the interstitial particles. The CVI inlet is installed inside a wind tunnel to accelerate the incoming air up to 120 m s^{-1} , which is needed to reach a $D_{50\%}$ cut size of about $5\text{ }\mu\text{m}$. A controlled counterflow is blown out of the inlet tip, which allows only hydrometeors of sufficient inertia to enter the system. The supercooled drops and larger ice crystals have already been removed by the PI and VI, respectively, thus only the small ice particles ($5\text{ }\mu\text{m} < D_{\text{ice}} < 20\text{ }\mu\text{m}$) are sampled. Inside the CVI the small ice particles are injected into a particle-free and dry carrier air for complete sublimation. A more detailed description of the Ice-CVI can be found in Mertes et al. (2007).

2.2. Aerosol mass spectrometer

During the CLACE campaigns online mass spectrometry was applied to investigate the chemical composition of ambient aerosol particles. There are two different techniques to perform aerosol mass spectrometry, thermal vaporization of aerosol particles with subsequent electron impact (EI) ionization as used by the Aerodyne AMS instruments and a combined vaporization and ionization with intense laser pulses as used by single particle instruments. Both techniques were deployed during the CLACE campaigns.

Aerosol mass spectrometer (AMS):

The particles enter the instrument through an aerodynamic lens. Particles in the size diameter range from 60 nm to 600 nm are focused into a narrow particle beam. The vacuum-aerodynamic particle diameter can be derived by measuring the particle flight time between a chopper wheel and the mass spectrometric detection. The particles are evaporated with an electric heater at 600°C . The resulting vapor is ionized with EI ionization at 70 eV . The resulting ions are analyzed with different mass filters. During CLACE 3 and 4, a quadrupole mass spectrometer was used. A disadvantage of this mass filter is the low mass scanning velocity and resolution of the mass spectra. Experimental details for the Q-AMS can be found in Jayne et al. (2000). During CLACE 5 and 6 the new generation of the AMS instrument with a time-of-flight (TOF) mass filter (Drewnick et al. (2005)) was deployed at the Jungfraujoch. These instruments combine fast sampling rates with high spectral resolution. Both instruments have in common that only material which is vaporized at temperatures of 600°C can be analyzed. The vaporization and the theoretical well understood EI ionization can be calibrated and quantitative results on sulfate, nitrate, ammonium and organics can be given.

Single particle mass spectrometer:

Refractory material can be analyzed in single particle mass spectrometer with laser ablation on the expense of not being quantitative. The particles enter the instrument through an aerodynamic lens. Particles with a diameter between 300 nm and 3000 nm are focused into a particle beam. At two positions in the particle beam light scattering experiments are performed with two 532 nm cw laser beams. From the time between the two light scattering signals the flight time and hence the diameter of the particles can be derived. The particle velocity is used to trigger the third laser which is a pulsed excimer laser working at 193 nm . Single particles are vaporized and the resulting vapor is ionized within one

laser pulse. The ions are analyzed in a bipolar time-of-flight mass spectrometer. A detailed description of the single particle mass spectrometer deployed at the Jungfraujoch can be found in Kamphus et al. (2008).

3. RESULTS

3.1. Q-AMS mass closure

During the CLACE 3 and 4 campaigns mass spectrometric measurements were conducted with the Q-AMS. Concentrations of sulfate, nitrate, ammonium and organics were measured for the background aerosol, the interstitial aerosol and ice nuclei. Comparison of different sizing techniques (AMS and scanning mobile particle sizer, SMPS) allows the measurement of the mean density for the aerosol population at the Jungfraujoch. Thus, it is possible to derive mass concentrations from the number concentrations measured with a SMPS. A comparison of the mass concentrations measured with the Q-AMS with the SMPS data is shown in Figure 1 for the background aerosol, the interstitial aerosol and the ice nuclei.

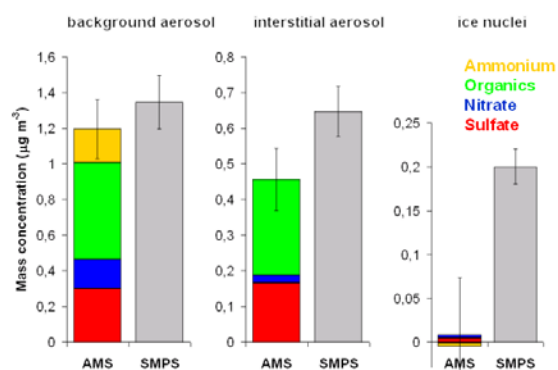


Figure 1: Comparison of Q-AMS and SMPS results at different inlets.

For the background and interstitial aerosol ammonium, nitrate, sulfate and organics account for most of the aerosol mass. But for the ice nuclei a large portion of the aerosol mass detected by the SMPS cannot be detected by the Q-AMS. The aerosol components which are not detected by the

Q-AMS are likely composed of refractory materials like carbon black and mineral dust. Single particle analysis with laser ablation is a suitable technique to detect these refractory materials, so during CLACE 5 and 6 our Single Particle Laser Ablation Time-of-flight mass spectrometer (SPLAT) was deployed at the Jungfraujoch.

3.2. SPLAT background, IN, CCN

During the CLACE 5 and 6 campaigns our single particle laser ablation instrument was applied to especially investigate the refractory components of the ambient aerosol and its role in ice nucleation. In contrast to the Q- and TOF-AMS measurements, the SPLAT instrument can only detect particles larger than 300 nm. In addition to this, only qualitative results can be drawn from the measurements due to the complex theoretically not well understood ablation process, which arranges for slightly different mass spectra even for the same component.

Measurements were conducted at the total inlet and, whenever clouds were present and the Ice-CVI was operational, at the Ice-CVI to sample ice nuclei. In order to measure CCN, the pre-impactor of the CVI was removed during one day. The spectra for the background aerosol, the ice nuclei and cloud condensation nuclei were classified with a k-means algorithm which results in different chemical classes and number of particles belonging to these classes. Figure 2 shows the classification results for the background aerosol particles, ice nuclei and cloud condensation nuclei.

It can clearly be seen that the IN are dominated by the two classes with strong signals from mineral dust (class 1 and 6). They account for 57% of the particles. For the background aerosol and the CCN this value decreases to 8% and 12% respectively. Another component which shows strong variation is sulfate. In the IN it can be found in 44% of the particles (class 4 and 6), whereas sulfate is dominating in 73% of the spectra for background aerosol (class 2, 4 and 5). Finally, in the CCN

sulfate can be found in 92% of the spectra (class 2, 4 and 6).

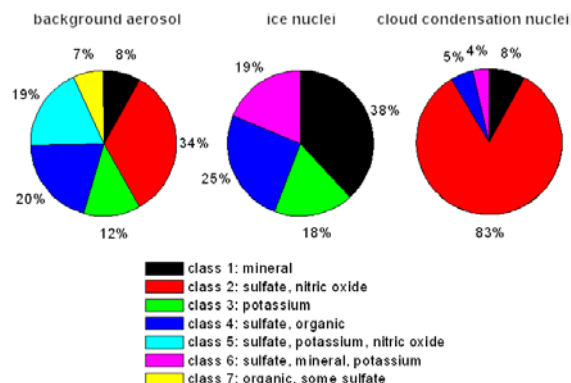


Figure 2: Results from the classification of the particles analyzed with the SPLAT instrument.

All spectra for the IN, CCN and the background aerosol show a high degree of internal mixing. There is hardly any class described by mass signals which cannot be found in one of the other classes. The relation of the intensity of different mass signals is the most important criterion for defining the different particle classes.

A comparison with other studies can be drawn from the CRYSTAL-FACE data presented by Cziczo et al. (2004). With a single particle mass spectrometer they analyzed cirrus IN behind a CVI onboard an aircraft. Their instrument (PALMS) also utilizes 193 nm for the ablation laser. For mineral dust/fly ash an increase from 1% of outside cloud particles to 44% for ice nuclei was found. This value increased further to

64% during a dust event. In the CRYSTAL-FACE data a particle class containing sulfate, potassium, organics and nitric oxide (termed as SKON group) was very dominant. 95% of the outside cloud particles belonged to this group. For the IN there was a decrease to 28% and 8% during a dust event. In our single particle spectra the SKON group is comparable to class 2, 4 and 5. So, for the background aerosol and the CCN 72% and 88% of the particles belong to the SKON corresponding classes. For the IN there is a strong decrease to 25%. In summary, there is a very nice agreement between the CRYSTAL-FACE data from cirrus measurement and our measurements in mixed phase clouds for the mineral dust/fly ash as well as the SKON group.

3.3. TOF-AMS (HOA/OOA)

With the W-TOF-AMS it is possible to separate ions with an identical integer mass, for example $C_2H_3O^+$ (m/z 43.0184) and $C_3H_7^+$ (m/z 43.0551). $C_2H_3O^+$ can be considered as a marker for oxygenated organic aerosol (OOA), whereas $C_3H_7^+$ is related to hydrogenated organic aerosol (HOA). Figure 3 shows the ratio between the two m/z 43 signals at the different inlets during the CLACE 6 campaign. While the background aerosol and the cloud condensation nuclei are mainly composed of oxidized organic components, in the ice residuals predominantly un-oxidized organics (HOA) were found. These results are in agreement with Cozic et al. (2008) who found during CLACE 3 and 4 that

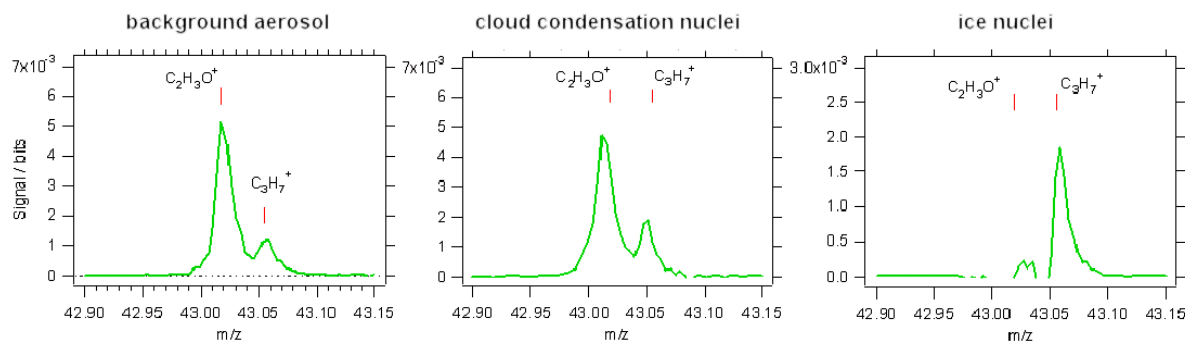


Figure 3: W-TOF-AMS high resolution mass spectra for m/z 43. $C_2H_3O^+$ is a marker for OOA, $C_3H_7^+$ for HOA.

carbonaceous aerosols are enriched in ice residuals.

3.4. Lead in single particles

With the single particle instrument (SPLAT) we were able to detect lead in single aerosol particles at the Jungfraujoch during CLACE 5 and 6. Figure 4 shows the distribution of the lead isotopes for a background aerosol particle. Lead is identified clearly by the isotopic pattern which is close to the natural occurrence of the isotopes (^{204}Pb 1.4%, ^{206}Pb 24.1%, ^{207}Pb 22.1%, ^{208}Pb 52.4%). Approximately 9% of the detected background aerosol particles contained lead. For the cloud condensation nuclei this value decreased to

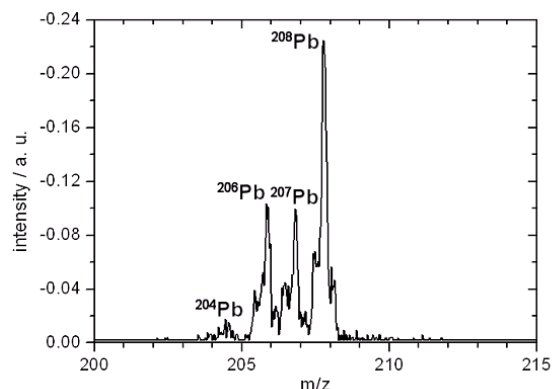


Figure 4: Single particle spectrum showing lead isotopic pattern

4%, while for the ice residuals there was a strong increase to 42%. The reason for the enrichment is not clear. We think that the main source for lead is aviation fuel which contains lead with concentrations up to 0.56 g/l.

4. CONCLUSION

As shown in the previous sections the combination of different mass spectrometric techniques with special inlet systems is an ideal tool to investigate the role of chemistry in heterogeneous ice nucleation in mixed phase clouds. AMS instruments are able to measure the non-refractory part of the aerosol quantitatively and give a detailed

view into the ratio of oxygenated/hydrogenated organic aerosol. With the single particle instrument with laser ablation further information about the refractory aerosol can be obtained. Thus, both instruments complement each other. A large data set on mixed phase clouds was generated during the CLACE campaigns, but for the ice nuclei, where concentrations are lower as 1 cm^{-3} , only general conclusion could be drawn. With further improvements on the efficiency especially of our single particle instrument, we want to perform time resolved measurements and correlate these to meteorological data. Further CLACE campaigns are planned to achieve this goal.

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