Composition analysis of ice particle residuals combining aerosol mass spectrometry and counterflow virtual impactor technique, INUIT-MPIC-TROPOS

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- Introduction and motivation

Ice formation in mixed-phase clouds is an essential prerequisite for the formation of precipitation at mid-latitudes. In such mixed-phase clouds, ice particles can grow at the expense of the supercooled water droplets to sizes large enough to prevent complete evaporation before reaching the ground during precipitation. Only via heterogeneous ice nucleation it is possible to form ice at temperatures warmer than -35°C. Up to now the exact pathways of heterogeneous ice formation are not sufficiently well understood, similarly the chemical properties and surface properties that enable a single aerosol particle to act as an ice nucleus at a given temperature and supersaturation. Laboratory experiments yielded very important result in the recent years, however it is not clear whether realistic atmospheric scenarios were reproduced. For example, it has been shown that mineral dust, which is a good ice nucleus as a pure substance, irreversibly loses its ice activation properties upon treatment with sulfuric acid (Reitz et al., 2011). Previous field investigations, parts of which were conducted at the Jungfraujoch, have shown that mineral dust particles dominate the ice particle residue number (Kamphus et al., 2010) but also black carbon was found to be enriched in these residual particles (Mertes et al., 2007; Cozic et al., 2008). In 2011, a new DFG funded research unit (INUIT = Ice Nuclei Research Unit) was established with the objective to acquire further and better knowledge on atmospheric ice formation processes.

- Scientific objectives

As part of the research unit INUIT, a large field campaign in real atmospheric mixed phase clouds was regarded to be mandatory for the success of the project. The previous data that were obtained from field campaigns (partly during the CLACE experiments at the Jungfraujoch (Mertes et al., 2007; Cozic et al., 2008; Cziczo et al., 2009; Kamphus et al., 2010; Ebert et al., 2011) but also on other mountain stations as Storm Peak (Richardson et al., 2007) or aircraft-based measurements (Pratt et al., 2009) yielded results that have shown to be not unambiguous. The role of lead in ice nucleation was found to be important by (Cziczo et al., 2009) and (Kamphus et al., 2010). The role of primary biological particles acting as ice nuclei was found to be very high by (Pratt et al., 2009) but this was not found at the Jungfraujoch. Also the role of black carbon that was observed to be enhanced in ice residuals (Cozic et al., 2008) is not yet understood.
Thus, the scientific objectives of the INUIT-JFJ field project of our group were: Operating two aerosol mass spectrometers at the Jungfraujoch station together with our partner groups in order to

- analyze ice particle residuals from ambient mixed phase clouds
- analyze ice nuclei that were activated by an ice nucleus chamber and selected by a CVI
- Clarify the role of different particle types for ice nucleation under realistic atmospheric conditions
- Characterize the background aerosol in the free troposphere

- Reason for choosing station

Atmospheric processing of aerosol particles involves different processes (e.g., coating by organic material, by nitric and sulfuric acid, reaction with Ozone etc.) such that it is not straightforward to extrapolate laboratory results on real atmospheric data. It is therefore necessary to study real atmospheric ice nuclei under ambient conditions in mixed phase clouds at the relevant temperature range between -20 and 0°C. Such conditions can be met at the altitude of the Jungfraujoch (3500 m) in winter, when the probability of mixed phase clouds is sufficiently high. The infrastructure of the High Alpine Research Station Jungfraujoch is excellent, and the experiences gathered in previous projects (CLACE3-6) strongly encouraged the INUIT group to conduct the field campaign at the Jungfraujoch again.

- Method and experimental set-up

Sampling of ice crystals out of mixed-phase clouds was conducted by a counterflow virtual impactor (Ice-CVI, Leibniz Institute for Tropospheric Research (Mertes et al., 2007)) and additionally by the newly developed Ice Selective Inlet (ISI) by PSI, Switzerland. The Ice-CVI samples small, freshly formed ice crystals ($d < 20$ µm) that have not yet scavenged ambient aerosol particles. Thus it is expected that the residuals of these small ice crystal have acted as the original ice nucleus. The ice particle residuals (IPR) sampled by these inlets were analyzed by a laser ablation single particle aerosol mass spectrometer ALABAMA (Brands et al., 2011).
Additionally, we operated a newly developed combination of an ice nucleation chamber (FINCH, Goethe-University Frankfurt) and the ALABAMA via an additional CVI (IN-CVI, Leibniz Institute for Tropospheric Research). Although the number of sampled particles from this combination was low, a proof of concept could be achieved but it has become clear that the transmission and sampling efficiency of the whole system needs to be improved. The measurements are complemented by a large set of aerosol and cloud measurements, like number concentration, size distribution, chemical composition of the background aerosol by aerosol mass spectrometry, ice crystal number density and shape, etc.

- Preliminary results and conclusions

The laser ablation mass spectrometer acquired more than 600 mass spectra of IPR sampled by the Ice-CVI out of which 573 showed useful mass spectra. During operation of ALABAMA connected to the ISI the instrument obtained 45 usable mass spectra. The evaluation of the data is in progress and is done with the software package CRISP(Klimach et al., 2010). This program allows for the assignment of the mass spectra into different clusters that contain similar mass spectra. In this case the spectra are sorted with the fuzzy c-means algorithm (Hinz et al., 1999).
The first preliminary analysis of the acquired IPR data shows that the most abundant particle type (17% of all mass spectra) has components of mineral dust like lithium (Li), sodium (Na), potassium (K), aluminum (Al), iron (Fe) but also organic compounds (Fig. 1). Another particle type (11% of all mass spectra) found in the IPR contains carbon fragments, organic compounds (OC), sodium, aluminum and potassium. These results are valid for the IPR sampled from both inlets, although the statistic signification of the 45 mass spectra sampled behind the ISI I too low to draw further conclusions. On the other hand, the agreement of both data sets indicates that both inlets work reliably and sample the same type of ice particles. Figure 2 gives the relative abundance of all ice particle residuals sampled from both ISI and the Ice-CVI. A more detailed analysis of the data will give further insights into the chemical nature of ice nuclei and ice particle residuals.

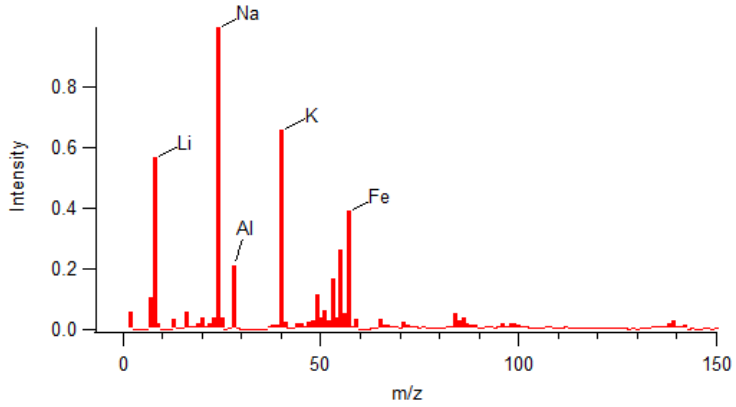
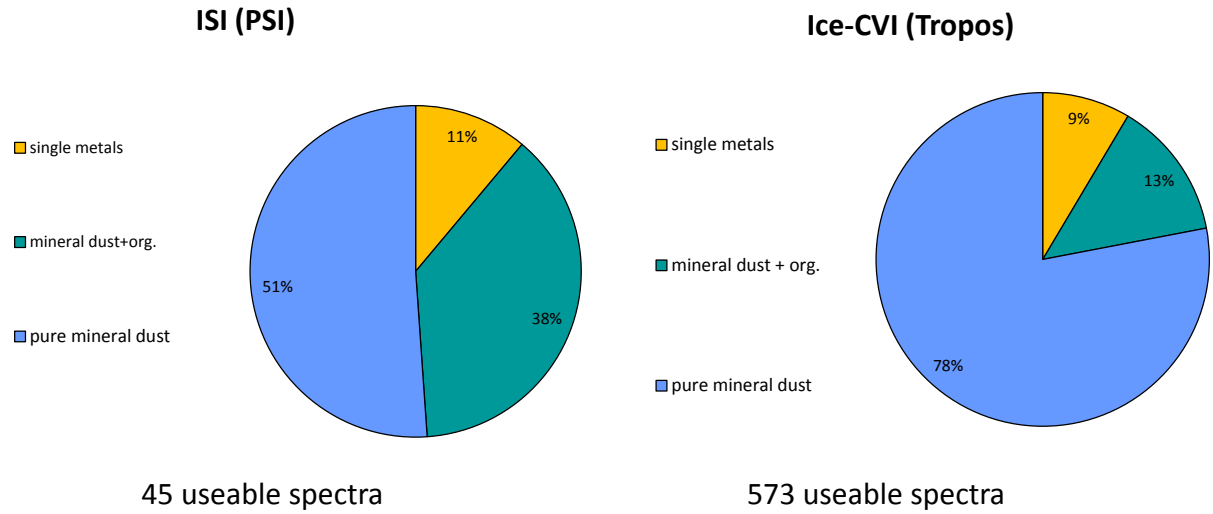


Fig. 1: Average mass spectrum of those mass spectra of ice residuals that were assigned to the largest cluster. The observed ions are characteristic for mineral dust.



45 useable spectra 573 useable spectra

Figure 2. Relative abundance of particle types sampled by the laser ablation aerosol mass spectrometer ALABAMA in mixed phase clouds when connected to the Ice Selective Inlet (left) and to the Ice-CVI (right).

- Outcome and future studies

The results obtained by our group during the INUIT-JFJ campaign indicate several new and interesting results:

a) Mineral dust is dominating the ice residual particles sampled from mixed phase clouds in a winter high Alpine station
b) No indications for biological particles acting as IN were observed by the aerosol mass spectrometer
c) No enrichment of soot or black carbon was observed by mass spectrometry in the IPR
d) The fraction of particles containing lead was in the order of 6% and thereby in the range of background aerosol as reported by (Cziczo et al., 2009) and not as high as observed in IPR by the same authors.

While result a) supports many previous findings, results b) through d) are unexpected and will therefore require a thorough analysis of the data in order to confirm the reliability of our methods. A repetition of the experiment is highly desirable, since the year-to-year variability of the IPR composition at the Jungfraujoch station is unknown.

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