Name of research institute or organization:

Technische Universität Darmstadt, Institut für Angewandte Geowissenschaften, Umweltmineralogie

Title of project:

In-situ environmental scanning electron microscopic investigation of the ice nucleating abilities of aerosol particles from mixed-phase clouds from the CLACE 6 campaign

Project leader and team:

Dr. Martin Ebert, Dr. Annette Worringen, Dr. Nathalie Benker, Dipl.-Met. Dörthe Müller-Ebert, Dr. Frank Zimmermann and Prof. Dr. S. Weinbruch (project leader)

Project description:

The aerosol-cloud interaction processes in mixed-phase clouds were studied during the CLCE 6 campaign in February/March 2007 at the high alpine research station Jungfraujoch.

During the CLACE 5 campaign we have performed individual particle analysis of ice residuals, which were sampled by an ice-counterflow virtual impactor (ice-cvi), developed by the Institute for Tropospheric Research in Leipzig (Mertes et al., 2007).

The main focus of our electron microscopic work during CLACE 6 lies on the in-situ environmental scanning electron microscopic investigation of the ice nucleating abilities of ice resiudials sampled during the CLACE 6 campaign. Additionally, the single particle analysis approach is used for the chemical identification of the ice forming fraction and to characterize the remaining interstitial particle fraction of the total aerosol in mixed-phase clouds. For particle sampling we have used two self constructed 2-stage impactors (cut off diameters 0.9 µm and 0.06 µm) behind different inlet systems. The interstitial aerosol was sampled behind an interstitial inlet operated with a PM2 cyclone impactor. An ICE-CVI (Counterflow Virtual Impactor) inlet was used to sample resiudal particles of small ice nuclei (IN).

For the electron microscopical analysis a FEI Quanta 200 FEG environmental scanning electron microscope (ESEM) and a JEOL J3010 transmission electron microscope (TEM) each combined with energy dipsersive X-ray analysis (EDX) were used.

Pb-containing agglomerates

The most obvious difference between IN- and interstitial-samples, observed in the CLACE 5 campaign, was the enhanced occurrence of Pb-containing particles in the IN-samples. These particles are predominantly internally mixed with (aged) sea salt, carbonaceous particles or silicates. Our observation of these lead-containing particles in the IN-fraction is in agreement with findings of other participants of the CLACE 5 campaign. As a possible source for the lead component in these particles aircraft emissions are assumed, because lead is still added as additive to avitation gasoline. The potential behaviour of Pb-containing particles as ice nuclei is discussed by Szymer and Zawadzki [1997].

The phase composition of the Pb containing particles could be identified with TEM. In Figure 1-left a section of an aged sea salt particle with small Pb-containing inclusions (black dots) are shown.

The Pb inclusions are generally smaller than 10 nm (with a maximum at 5-6 nm), what prevents the direct phase determination of the Pb containing phase by selected area electron diffraction. According to high-resolution images in the TEM and "pseudo" electron diffraction patterns, obtained by Fourier transformation of the bright field images (see Figure 1-right), the predominant part of the Pb inclusions could be identified as PbS and in single cases as elemental Pb.

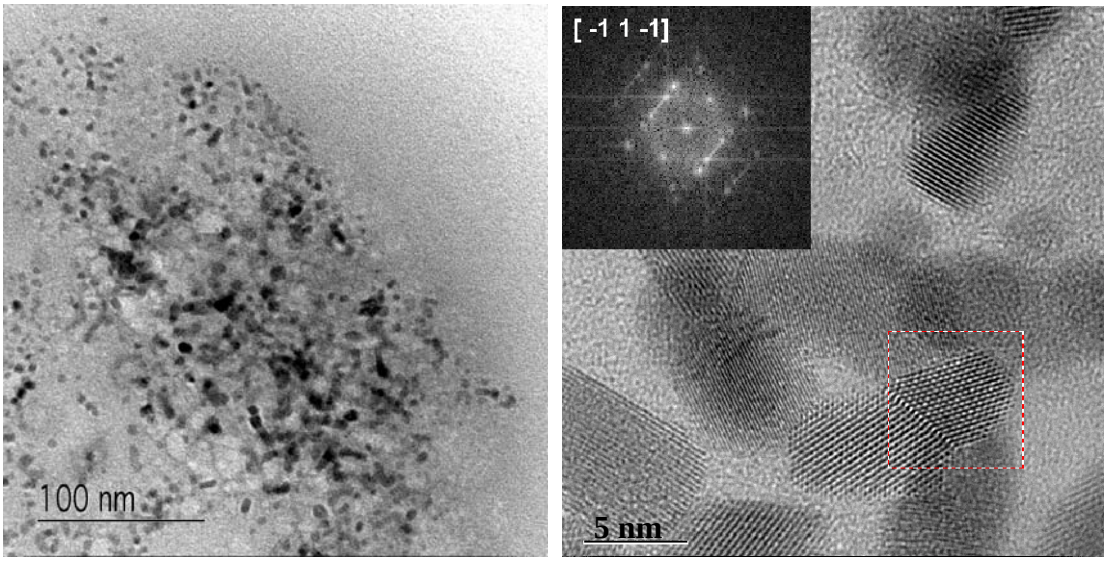

Figure1: (left) TEM-bright field image; section of an aged sea salt particle with Pb-containing particles (black dots); (right) TEM-bright field image and „pseudo" electron diffraction pattern of PbS inclusions.

First ice activation experiments

First in-situ ice nucleating experiments in the ESEM of ice resiudial samples from the CLACE 6 campaign were performed.

For this purpose IN samples (ice-CVI) were collected on silicon substrates. These samples were transferred in the environmental scanning electron microscope.

Environmental scanning electron microscopy (ESEM) enables in-situ observation of interactions between water vapor and aerosol particles in the sub-micrometer range (e.g., Ebert et al., 2002). By varying the water partial pressure and using a Peltier element to realize temperatures below the freezing point it is possible to obtain supersaturated conditions relative to ice in the sample chamber of such an instrument (Zimmermann et al., 2007). Ice nucleation experiments of the CLACE 6 ice-CVI samples were performed at temperatures between -13 °C and -21°C. The temperature was changed in steps of 1K, and at each temperature the H_2O vapor pressure was increased from subsaturation to supersaturation values (relative to ice). The special

design of the vacuum system allows working pressures up to approximately 40 hPa in the sample chamber during imaging with secondary and backscattered electrons. The working pressure can be set by any non-flammable and non-corrosive gas including H_2O. In our experiments, the total pressure in the sample chamber was always equal to the partial pressure of H_2O, i.e., no other gas species was present inside the sample chamber. Prior to the ice nucleation experiments, the temperature of the Peltier element was calibrated by determination of the deliquescence relative humidity (DRH) of different salts (Ebert et al., 2002). In order to check that ice nucleation is initiated by the particles, an experiment with a pure silicon substrate (i.e., without particles) was performed. In this case, ice formation was not observed, even at high supersaturation values up to approximately 140 % (relative to ice). More details of the calibration procedures and ice nucleation experiments are given by Zimmermann et al. (2007).

sampling start	sampling end	particle diameter (µm)	Ice nucleation observed		
			-13°C	-17°C	-21°C
02/24/07	02/25/07	> 0.9	**Yes**	**Yes**	**Yes**
02/24/07	02/25/07	0.06 – 0.9	No	No	No
02/25/07	02/26/07	> 0.9	No	No	No
02/25/07	02/26/07	0.06 – 0.9	No	No	No
02/26/07	02/27/07	> 0.9	No	No	No
02/26/07	02/27/07	0.06 – 0.9	No	No	No
02/27/07	02/28/07	> 0.9	No	No	No
02/28/07	03/01/07	> 0.9	No	No	No
03/06/07	03/06/07	> 0.9	**Yes**	**Yes**	**Yes**
03/08/07	03/08/07	0.06 – 0.9	No	No	No
03/09/07	03/10/07	> 0.9	No	No	No

Table 1: Results of the in-situ ice nucleating experiments of ice residual samples from the CLACE 6 campaign.

In total 33 ice nucleating experiments of eleven IN samples (ice-CVI inlet system) at three different temperatures (-13°C, -17°C, and -21°C) were performed. Unexpectedly, ice nucleation could be observed only for 2 of these 11 samples (see Figure 2).

For all other samples no growing ice crystals could be observed, even at supersaturation values (relative to ice) and temperatures of -21°C.

It is important to notice in this context that in these ESEM in-situ ice nucleating experiments only ice formation by the condensation freezing and deposition freezing

modes can be reproduced. Other ice forming processes like contact or immersion freezing are not possible to follow by this method. Further on, in some cases, activation of a particle is not reproducible, i.e., a particle that acted as an ice nucleus cannot be activated in further cycles (e.g., Soulage, 1957).

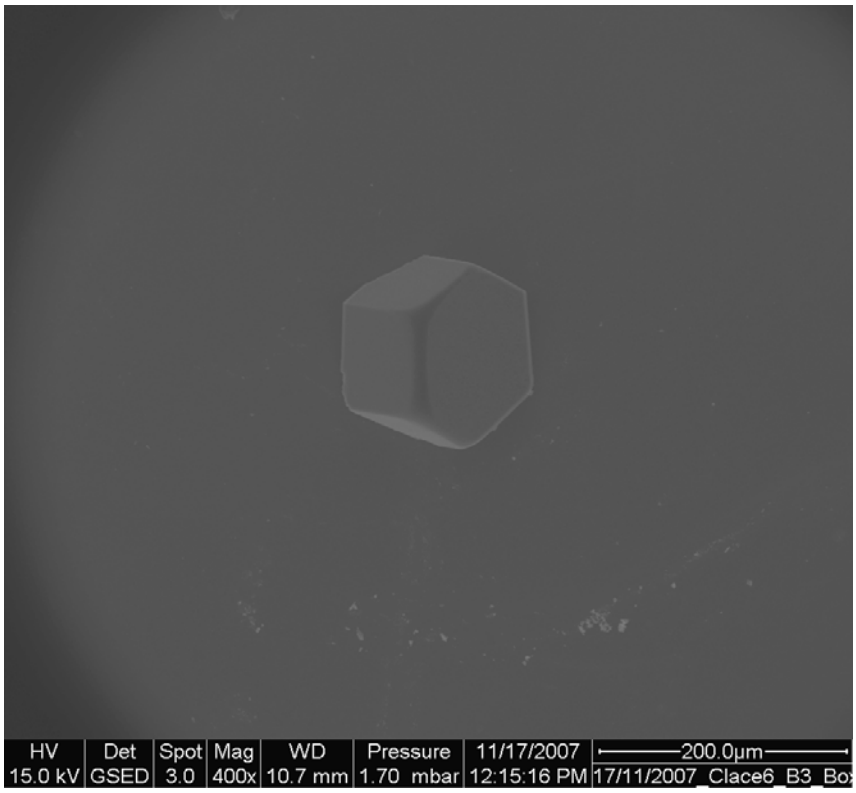

Figure 2: Reactivated ice residual particle from the CLACE 6 campaign (6th of March 2007).

References

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Zimmermann F., M. Ebert, A. Worringen, S. Weinbruch, Environmental scanning electron microscopy (ESEM) as a new tool to determine the ice nucleation capability of individual aerosol particles, *Atmospheric Environment* **41**, 8219-8227, 2007.

Key words:

Ice nuclei, ESEM, individual particle analysis, chemical composition

Collaborating partners/networks:

Institut für Troposphären Forschung, Leipzig, Germany
Institut für Physik der Atmosphäre, Johannes Gutenberg-University und Max-Planck Institut für Chemie, Mainz, Germany
Institute for Atmospheric and Climate Science, ETH Zurich, Switzerland

Scientific publications and public outreach 2007:

Refereed journal articles

Mertes S., B. Verheggen, S. Walter, M. Ebert, P. Conolly, E. Weingartner, J. Schneider, K. Bower, S. Weinbruch, J. Cozic, J. Heintzenberg, Counterflow virtual impactor based collection of small ice particles in mixed-phase clouds for the physico-chemical characterisation of tropospheric ice nuclei: sampler description and first case study, Aerosol Sci. Technol. **41**, 9, 848-864, 2007.

Zimmermann F., M. Ebert, A. Worringen, S. Weinbruch, Environmental scanning electron microscopy (ESEM) as a new tool to determine the ice nucleation capability of individual aerosol particles, Atmospheric Environment **41**, 8219-8227, 2007.

Conference paper

Worringen, A., N. Benker, M. Ebert, F. Zimmermann, S. Mertes, E. Weingartner, and S. Weinbruch, Characterization of ice residuals from the CLACE 5 experiment, EAC Salzburg, 2007.

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