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SUPPLEMENTARY INFORMATION
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Supplementary Information

Methods

Three types of experiments were undertaken to determine the nature of ice nuclei and ice residue. First, ice crystals were formed from ambient aerosol within a liter-sized continuous flow diffusion chamber (CFDC)[1]. Ice crystals were then separated for analysis using a counterflow virtual impactor (CVI)[2]. Second, ice crystals in naturally occurring mixed-phase clouds were separated for analysis using an 'Ice-CVI' specifically designed for mixed-phase conditions[3]. Third, experiments were conducted within the aerosol interactions and dynamics in the atmosphere (AIDA) cloud chamber[4] on collected samples of mineral dust. Experiments were also performed on collected samples of mineral dust doped with lead with a CFDC. Analysis was in all cases performed using single particle mass spectrometry (SPMS)[5,6]. Electron microscopy (EM) coupled to energy dispersive X-ray microanalysis[7] was also used for ambient ice residue characterization.

CFDC

A diffusion chamber functions by generating an environment with a defined temperature below the melting point of water and a supersaturated relative humidity with respect to ice. These conditions are produced in the space between two ice coated walls held at different temperatures and mimic those at which atmospheric mixed-phase and ice clouds form. Diffusion leads to a linear gradient in temperature and absolute humidity between the walls but, because of the exponential relation between temperature and saturation vapor pressure, a supersaturation is achieved close to the center. A sample aerosol flow layered between two particle-free sheath flows constrains the conditions to which the

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sample is exposed. CFDC volumes were a few liters with a residence time on the order of 10-30 seconds[1].

CVI

A conventional CVI inertially separates particles by directing a dry, particle-free, flow of gas in a direction opposite that of the sample. The rate of this 'counterflow' can be adjusted to create a specific inertial cutpoint[2]. A conventional CVI was used for ice crystal separation during droplet-free conditions in the CFDC and AIDA experiments[8].

One limitation is that a conventional CVI can not be used to distinguish frozen and liquid hydrometeors of the same inertia when sampling in mixed-phase conditions. A custom built Ice-CVI[3] was used in order to overcome this limitation for field studies. A vertically oriented inlet horn in combination with a virtual impactor (VI) was used to remove precipitating ice particles larger than 20 µm diameter. The upper limit of 20 µm assured an aspiration efficiency of ~1 for smaller ice particles. Downstream of the VI a pre-impactor (PI) removed supercooled drops by contact freezing on cold impaction plates. Ice particles bounced and passed the impaction plates. A conventional CVI was located downstream of the PI to reject interstitial particles smaller than 5 µm. Ice particles in the 5 - 20 µm diameter range were thus passed by the Ice-CVI. As with a conventional CVI these small ice crystals were injected into a particle-free and dry carrier gas which led to evaporation and allowed for the analysis of the residual material.

AIDA

The ice nucleation properties of laboratory-prepared aerosol, including re-dispersed mineral dust samples, can be investigated at simulated conditions of natural clouds in the AIDA chamber at the Forschungszentrum Karlsruhe[4,5]. Experiments typically begin at ice

saturated conditions in the 84 m^3 actively-cooled cloud chamber due to a thin ice coating on the chamber walls. The formation of a cloud is induced by expansion cooling via vacuum pumping which mimics an updrafting atmospheric air parcel. Droplets and ice particles are detected by optical particle counters, in situ scattering and depolarization measurements, and Fourier transform infrared spectroscopy. Clouds typically exist within the AIDA chamber for several minutes.

SPMS

The single particle mass spectrometers used in this study draw aerosol into the instrument through an aerodynamic inlet which imparts a size dependent velocity. Light scattering as particles pass through two visible lasers beams set a known distance apart indicates the presence of a sample and, when combined with the size dependant velocity, provides the aerodynamic diameter. A near ultraviolet laser is triggered by the light scattering event to desorb the aerosol material and ionize it. The chemical composition can then be inferred from ions detected using a time of flight mass spectrometer. Analysis is performed in situ and in real time on a particle by particle basis. A recent review of SPMS was conducted by Murphy[6].

The lower size limit of a SPMS is set by the detection limit of scattered light; this is normally between 150-250 nm aerodynamic diameter. The upper limit is set by the aerodynamic properties of the inlet and this is normally between 2 and 3 □m diameter[6]. It is noteworthy that previous studies have shown that atmospheric ice nuclei are found within this range[9,10].

Without extensive laboratory testing particle matrix effects and the disparate ionization efficiencies of common aerosol materials single particle mass spectrometers produce

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qualitative, not quantitative, data[11]. Isotopic abundance can be used to identify specific elements, as is shown in Figure S1 for lead in an ice residual from a naturally occurring mixed-phase cloud. Gallavardin *et al.* showed that specific mineralogical information was difficult to ascertain on the single particle level, however, and we therefore use the broad classifications 'mineral dust' and 'lead containing' in this study[12]. A list of the number of spectra analyzed for each study is given in Table S1.

EM

Size, morphology, and elemental composition of individual ice residue and interstitial particles (i.e., those which did not form droplets or ice) were analyzed during the field studies using environmental scanning EM and transmission electron microscopy (TEM), each combined with energy dispersive X-ray microanalysis[7]. Samples from the Ice-CVI were impacted onto EM grids which were analyzed at the Institute for Applied Geosciences at the Technical University Darmstadt. Lead inclusions of <100 nm diameter were studied with High Resolution-TEM.

Field Sites

Storm Peak Laboratory (SPL)

Field experiments were conducted on ambient aerosol at SPL located at 3200 meters above sea level (m.s.l.) in the Colorado Rocky Mountains. The high altitude and absence of local sources results in access to free tropospheric conditions, typically during overnight periods when subsidence of the planetary boundary layer occurs[13]. Experiments at SPL were performed during the fall of 2001 and spring of 2004 by exposing free

tropospheric aerosol to cirrus cloud formation conditions with a CFDC. Ice crystals were then separated with a CVI and analyzed using SPMS[14].

Jungfraujoch Research Station (JRS)

The JRS is located at 3600 m.s.l. in the Swiss Alps in a region with minimal local particle sources. Mixed-phase clouds occur with a frequency of 40% during late winter and early spring at this site[15]. Ice crystals were separated when mixed-phase clouds were present using the Ice-CVI. Residue was analyzed with SPMS and samples were collected for off-line EM during the late winter and early spring of 2006 and 2007.

Laboratory Particle Preparation

Laboratory studies at the AIDA chamber were conducted on Arizona Test Dust (Powder Technology, Inc.). The mineral samples were dispersed into a particle-free flow of dry synthetic air with a small scale powder disperser (TSI, Inc.). Large dust particles were removed in an inertial impactor with a cutoff diameter of 1 □m diameter before being added to the aerosol chamber.

Laboratory CFDC experiments were performed on kaolinite clay (Fluka, Inc.). The kaolinite was dispersed in distilled deionized water and aerosolized with a custom build atomizer. Aerosol both in an un-doped state and associated with 1% lead sulfate by mass was produced and size selected at 200 nm diameter with a differential mobility analyzer (TSI, Inc.). The internal mixing state of mineral dust and lead was ascertained with SPMS.

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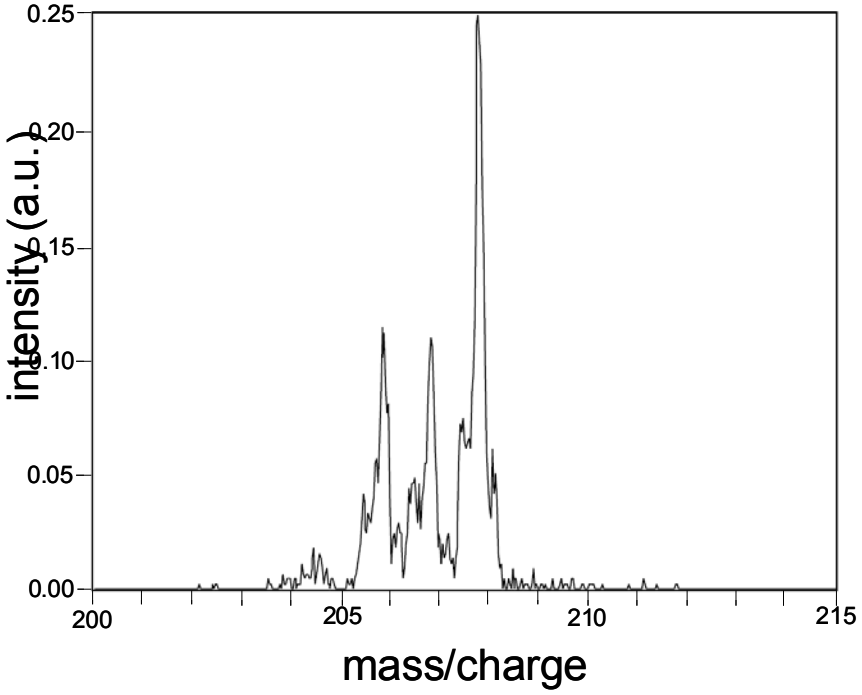
Global Climate Model Simulations

For the global climate simulations the ECHAM5 general circulation model was used. ECHAM5 includes a two-moment cloud microphysics scheme[16] coupled to the ECHAM5-HAM two-moment aerosol scheme which predicts the aerosol mixing state in addition to the aerosol mass and number concentrations[17]. The size-distribution is represented by a superposition of log-normal modes including the major global aerosol compounds sulfate, black carbon, organic carbon, sea salt and mineral dust. In order to avoid changes in meteorology, both the pre-industrial and present-day simulations were nudged to the ECMWF ERA40 reanalysis data for the year 2000 after an initial spin-up of 3 months[17]. The aerosol emissions of the pre-industrial simulations are representative of the year 1750[17]. The simulations were conducted in T42 horizontal resolution (~2.8º x 2.8º) with 19 vertical layers.

Supplementary Figure 1



Supplementary Figure 1: Identification of lead from isotopic abundances. This exemplary ice residual, shown in arbitrary units (a.u.) of signal intensity versus positive ion mass to charge, is from a mixed-phase cloud at the Jungfraujoch Research Station. The isotopic abundance of lead at mass 204, 206, 207, and 208 is 1.4, 24.1, 22.1, and 52.4 %, respectively. This pattern, discernable using SPMS, was used to identify lead.

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Supplementary Table 1

Experiment	Cloud Source	Location	Ice Nuclei	Ice Residue	Aerosol	SPMS Spectra	Mineral Dust	Lead
1	CFDC (cloud chamber)	SPL	X		Ambient	~2500 total ~250 IN	49%	32%
2	Natural clouds (mixed-phase)	JRS		X	Ambient	~1750 total ~500 residue	67%	42%
3	AIDA (cloud chamber)	AIDA	X		Resuspended mineral dust	~2400	100%	44%

Supplementary Table 1: Source, location, ice crystal and aerosol origin, and spectral statistics for the 3 experimental studies. Experiments 1 and 3 utilized ice chambers while 2 was performed from within naturally occurring clouds. Experiments 1 and 2 were conducted on ambient aerosol while 3 was performed on resuspended mineral dust. In total ~3150 ice-forming aerosols were analyzed of which 42% contained lead. Note that lead is present at the 5-10% level in ambient aerosol[18].

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