nature geoscience

LETTERS

PUBLISHED ONLINE: 19 APRIL 2009 | DOI: 10.1038/NGEO499

Inadvertent climate modification due to anthropogenic lead

Daniel J. Cziczo[1,2]*, Olaf Stetzer[2], Annette Worringen[3], Martin Ebert[3], Stephan Weinbruch[3], Michael Kamphus[4], Stephane J. Gallavardin[2,4], Joachim Curtius[4,5], Stephan Borrmann[4,6], Karl D. Froyd[7], Stephan Mertes[8], Ottmar Möhler[9] and Ulrike Lohmann[2]

Aerosol particles can interact with water vapour in the atmosphere, facilitating the condensation of water and the formation of clouds. At temperatures below 273 K, a fraction of atmospheric particles act as sites for ice-crystal formation. Atmospheric ice crystals—which are incorporated into clouds that cover more than a third of the globe[1]—are thought to initiate most of the terrestrial precipitation[2]. Before the switch to unleaded fuel last century, the atmosphere contained substantial quantities of particulate lead; whether this influenced ice-crystal formation is not clear. Here, we combine field observations of ice-crystal residues with laboratory measurements of artificial clouds, to show that anthropogenic lead-containing particles are among the most efficient ice-forming substances commonly found in the atmosphere[3]. Using a global climate model, we estimate that up to 0.8 W m^{-2} more long-wave radiation is emitted when 100% of ice-forming particles contain lead, compared with when no particles contain lead. We suggest that post-industrial emissions of particulate lead may have offset a proportion of the warming attributed to greenhouse gases.

It is highly certain that the anthropogenic addition of greenhouse gases to the atmosphere has caused global warming[4]. Conversely, the addition of small aerosol particles has caused regional 'solar dimming' phenomena[5] that counteract some greenhouse-gas warming in a so-called direct effect. Aerosol particles can also interact with atmospheric water vapour by acting as sites of condensation and can thereby lead to the formation of clouds. Clouds, in turn, affect the global radiative balance by reflecting solar energy or trapping terrestrial radiation[6]; this is termed an aerosol 'indirect effect'. Net warming or cooling is dependent on cloud properties such as altitude and thickness. Depending on the ambient temperature and saturation, warm liquid water clouds, cold ice clouds or intermediate-temperature mixed-phase clouds can form. Owing to the typically high altitude and often remote location, the nucleation of ice is the less well-understood process. Despite this uncertainty, cirrus ice clouds can influence the Earth's radiative budget owing to their large global coverage[7]. For example, it has been shown[8] that indirect aerosol perturbations to ice clouds can cause radiative changes of the same magnitude as the direct radiative impact of all anthropogenic particles.

Ice can nucleate homogeneously from the aqueous droplets commonly found in the atmosphere, but this requires a supercooling of ~40 K below the equilibrium freezing temperature[9,10]. Atmospheric ice formation at higher temperatures requires the presence of a special solid particle that acts as an ice nucleus[10]. Owing to the presence of a surface that enhances the stability of an ice embryo, this process is known as heterogeneous ice nucleation. An ice nucleus can cause ice nucleation by several modes, for example from within a liquid water droplet or by acting as a site for the direct deposition of water vapour. Not all solid aerosol particles enhance ice nucleation, but several materials have been shown to act as ice nuclei. These include, but are not limited to, mineral dust, anthropogenic metal oxides, pollen and bacteria[9]. Each aerosol type shows a characteristic saturation and temperature, which varies depending on the mode by which freezing occurs. This freezing onset point is dependent on the surface area of the particle and some researchers have theorized that there are specific 'active sites' that stabilize an ice embryo[10]. Larger particles and materials that inherently contain more active sites thus exhibit a higher nucleation temperature[11]. The exact nature of these sites remains unknown, but features such as surface defects are one candidate. Another atmospherically important property of ice nuclei is their abundance. For example, silver iodide and some biological materials are known to be effective ice nuclei, but it is uncertain if their abundance is large enough to induce a global radiative impact[12].

Here, we have determined the nature of ice nuclei using three complementary methods: (1) creating artificial clouds by exposing ambient aerosol to controlled supersaturation and temperature, thereby mimicking atmospheric cloud formation, (2) examining the residue of ice crystals from naturally occurring clouds and (3) creating artificial clouds on laboratory-prepared aerosol particles (Supplementary Information contains a full discussion of the methods and data statistics in Supplementary Table S1). For all methods, mass spectrometry was used as the analytical technique and the percentage represents a number fraction of analysed particles. Using the first method, we find that mineral dust is the most common atmospheric aerosol type that acts as an

[1]Atmospheric Sciences and Global Change Division, Pacific Northwest National Laboratory, 902 Battelle Blvd, Richland, Washington 99354, USA, [2]Institute for Atmospheric and Climate Science, ETH Zurich, Universitätstrasse 16, CH-8092 Zürich, Switzerland, [3]Institute for Applied Geosciences, Technical University Darmstadt, Schnittspahnstraße 9, D-64287 Darmstadt, Germany, [4]Institute for Atmospheric Physics, Johannes Gutenberg-University of Mainz, Joh.-Joachim-Becher-Weg 21, D-55099 Mainz, Germany, [5]Institute for Atmospheric and Environmental Sciences, Goethe-University Frankfurt am Main, Altenhöferallee 1, D-60438 Frankfurt am Main, Germany, [6]Particle Chemistry Department, Max Planck-Institute for Chemistry, D-55128 Mainz, Germany, [7]Chemical Sciences Division, National Oceanic and Atmospheric Administration, 325 Broadway Ave., Boulder, Colorado 80305, USA, [8]Leibniz-Institute for Tropospheric Research, D-04318 Leipzig, Germany, [9]Institute for Meteorology and Climate Research, Forschungszentrum Karlsruhe, Postfach 3640, D-76021 Karlsruhe, Germany. *e-mail: daniel.cziczo@pnl.gov.

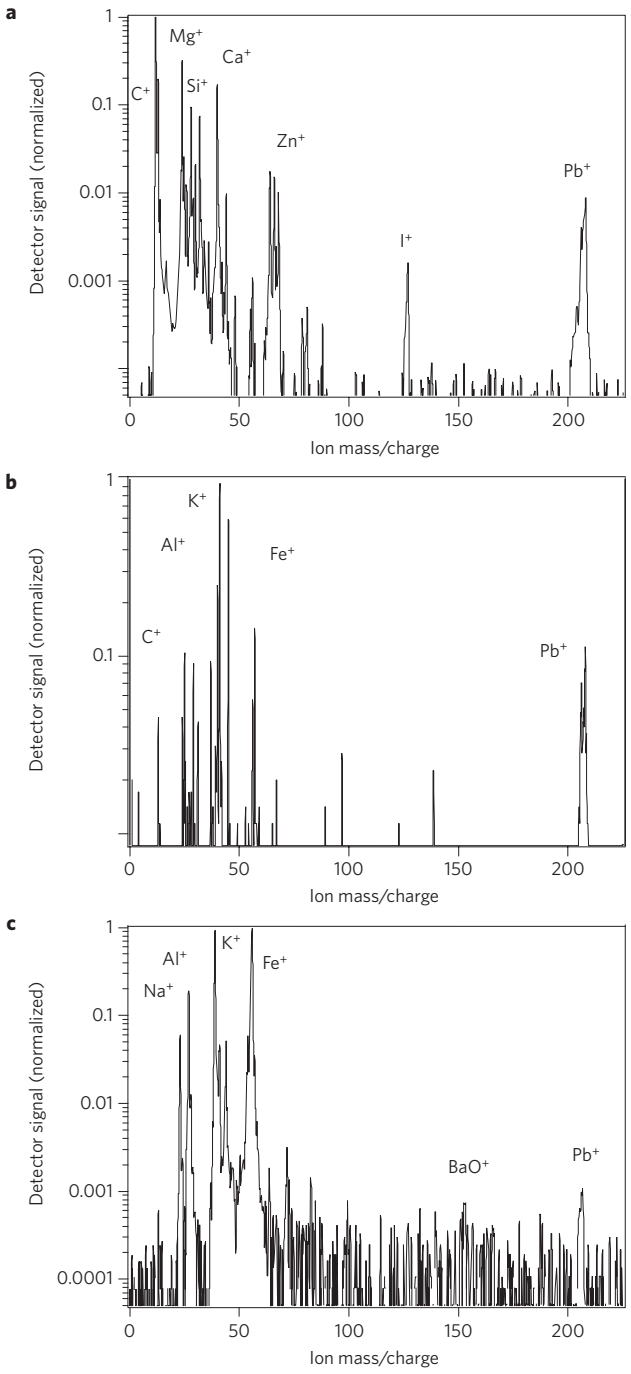

Figure 1 | Positive ion mass spectra of single ice-crystal residual particles. a, Spectrum obtained at the Storm Peak Laboratory (3,200 m above sea level) in the Colorado Rocky Mountains when ambient aerosol was exposed to cirrus cloud conditions within a CFDC. **b**, Spectrum obtained at the JRS (3,600 m above sea level) in the Swiss Alps from the residue of an ice crystal from a mixed-phase cloud. **c**, Spectrum obtained during experiments when Arizona Test Dust was exposed to cirrus cloud conditions within the AIDA chamber.

effective ice nucleus, representing 49% of all analysed particles[13]. Figure 1a is the mass spectrum of one exemplary particle. The single component found with the highest frequency was lead, present in 32% of ice nuclei (an example of the isotopic identification of lead is given in Supplementary Fig. S1). The second method, the separation of ice crystals from naturally occurring clouds, yielded similar results for ice residue. The distinction between ice nuclei

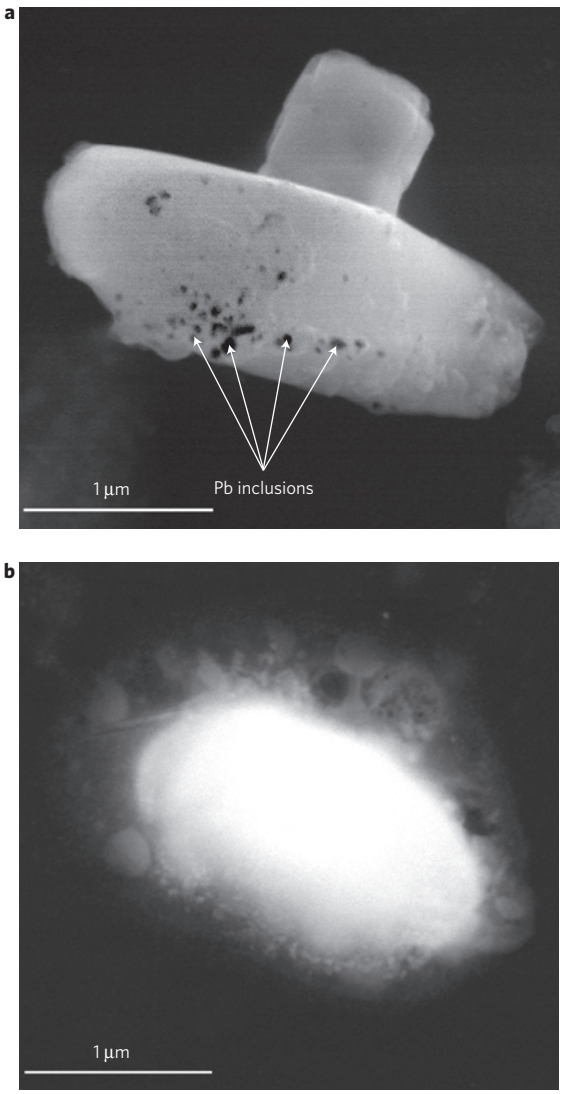

Figure 2 | Secondary electron images of ice-crystal residual particles from mixed-phase clouds at the JRS. a, Lead inclusions (black dots), visible from an overlay of a scanning electron image and lead mapping by energy dispersive X-ray microanalysis of this residual silicate particle. **b**, A carbon-, chlorine- and lead-containing residual particle where lead is in the form of organic lead and/or lead halides.

and ice residue is that the latter contains the ice nuclei and any gas and particle-phase material that adhered to the ice crystal during its atmospheric lifetime. As an example, Fig. 1b shows that the most common class of ice residue was again mineral dust, observed for 67% of the residue. The most common component was lead, observed in 42% of this residue. The frequency of mineral dust found using the first and second methods is in agreement with past studies, including identification of the central aerosol particle embedded within snowflakes[9]. The correlation between lead and ice nucleus concentration was observed in a previous study of bulk ice nucleus properties[14], although this was attributed to both also being correlated to particle size. The authors suggested studies at the single-particle level to verify this[14] as have been carried out in this study.

The results using the first two methods motivated the third set of studies, the formation of artificial clouds on collected samples of mineral dust prepared in a laboratory environment. This allowed control of conditions with greater precision than was possible in a field setting; previous studies on idealized mineral dust samples

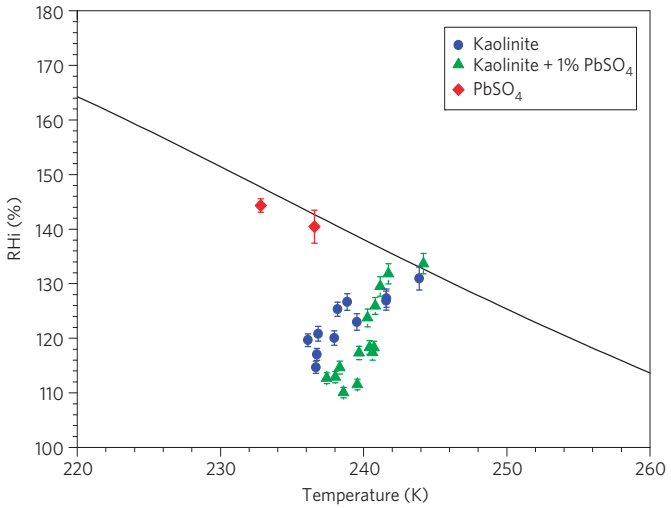

Figure 3 | Temperature and relative humidity required for the onset of ice nucleation using a cloud chamber. Conditions required for ice nucleation by kaolinite mineral dust and kaolinite doped with lead sulphate are shown. Below ~240 K, the lead-doped kaolinite particles, which mimic atmospheric aerosol that coagulated with lead, induce ice nucleation at a lower saturation for a given temperature than undoped kaolinite. Pure lead sulphate is, in contrast, an inefficient nucleus. The solid line represents the saturation vapour pressure of liquid water.

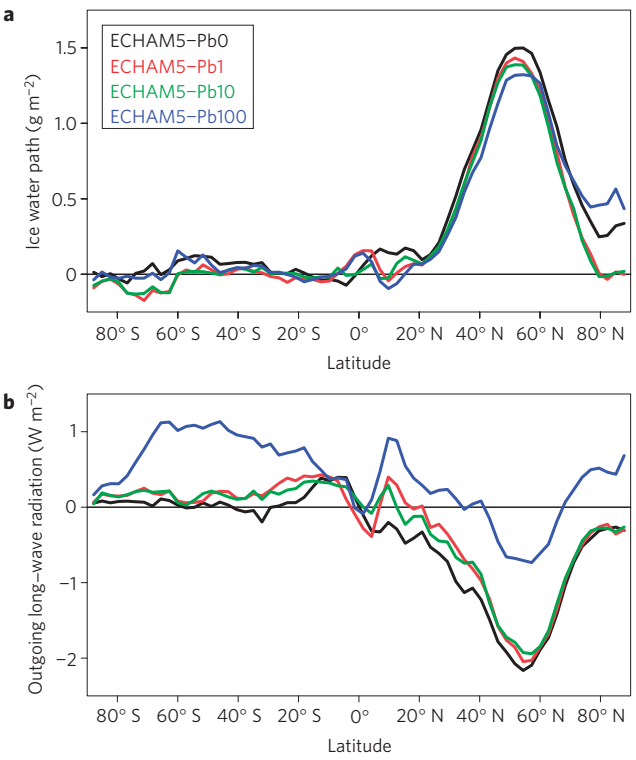

Figure 4 | Atmospheric properties with and without the influence of anthropogenic lead. a,**b**, Ice water path (**a**) and outgoing long-wave radiation (**b**) difference between the present-day and pre-industrial times. The four sensitivity conditions are 0, 1, 10 and 100% of mineral dust containing lead inclusions.

have been used to determine specific ice nucleation threshold conditions[15]. For the collected samples of mineral dust, lead was present in 8% of the aerosol particles, but in the subset that caused ice nucleation, lead was found in 44%. Figure 1c is an example of a lead-containing particle that nucleated ice under controlled laboratory conditions.

By analysis of Antarctic ice cores, Boutron and Patterson[16] showed that lead from mineral dust and volcanic emissions were the main atmospheric sources during pre-industrial times. Anthropogenic activities now dominate, accounting for >99% in the mid-1980s. At that time, most of the lead introduced to the atmosphere was from tetraethyl lead (TEL) added to automotive petrol. With regulation of TEL, total lead has dropped significantly, with a 20-fold decrease reported in the continental United States in the two decades since 1980 (ref. 17). TEL in light aviation fuel is now thought to be the dominant new source, although the uncertain and increasing emissions from coal combustion and smelting could be equivalent or greater[3,17]. In a study of atmospheric particles from 50 nm to 2 μm diameter, Murphy *et al.*[3] showed that lead was detectable in ~5–10%. The size dependence of the lead concentration and the mixing state supported the coagulation of small (<50 nm) primary lead particles with pre-existing atmospheric aerosol as the source of most of the particles[3].

Since the mid-1940s it has been known that artificial ice nuclei could be produced[18]. Two materials found to nucleate ice as high as a few degrees below 273 K were silver and lead iodide[19], although the high toxicity of the latter limited its use. Lead oxides and mixtures with ammonium iodide were subsequently found to be similar, if not better, ice nuclei than silver and lead iodide (ref. 20). Baklanov *et al.* showed that pure lead-containing materials were not required for ice nucleation; instead, lead need only be present as a surface inclusion on an inert core so long as its size remains at or above that of an active site, assumed to be ~30–50 nm in diameter[21]. Figure 2 contains electron microscope images of lead-containing ice residuals from the Jungfraujoch Research Station (JRS). Using energy-dispersive X-ray microanalysis, lead was identified in ~15% of the ice residuals. Surface inclusions, detected on 80% of the lead-containing particles, are denoted as black dots. Chemical analysis shows lead bound in several forms including lead sulphide, lead halides, organic lead and lead oxide. Individual inclusions are of the order of 10 nm diameter, consistent with coagulation of small primary lead particles onto pre-existing atmospheric aerosol as it passes through lead source regions[3]. This is the method recommended by Baklanov *et al.* for maximizing the ice nucleating potential of an inert aerosol, unintentionally carried out, by adding surface inclusions of ice nucleus material[21]. We therefore contend that anthropogenic emissions of lead to the atmosphere have had the effect of 'supercharging' pre-existing particles, making them highly efficient ice nuclei. Furthermore, we note that the altitude at which light aircraft fly is above the planetary boundary layer and directly places the emitted lead at an altitude where ice and mixed-phase clouds form.

The ice nucleation potential of atmospheric aerosol that coagulated with small primary lead particles has not previously been investigated. Previous research has instead focused on the production of artificial ice nuclei for weather modification[19–21]. The form of atmospheric lead may vary, depending on the specific emission, with lead sulphate and oxide being two common forms[3]. The former has not been investigated as an ice nucleus. Laboratory studies were carried out by atomization of the precipitate of lead sulphate crystals in a water slurry containing kaolinite mineral dust. The results are illustrated in Fig. 3. Doping was at an atmospherically relevant level of 1% lead sulphate to kaolinite by mass[3] and this was compared with undoped particles. The presence of lead decreased the saturation required for the nucleation of ice when compared with pure kaolinite by ~10–20% relative humidity with respect to water ice at temperatures below ~240 K.

To estimate the climatic effect of lead-containing ice nuclei, global climate model simulations were carried out with homogeneous and heterogeneous nucleation in cirrus clouds with

temperatures below 238 K (refs 22, 23). We assume that 0, 1, 10 or 100% of the internally mixed mineral dust particles in a present-day climate simulation contain lead and that lead-containing particles initiate freezing at 110% relative humidity with respect to ice (RHi). The first case is a modern world with no lead emissions, the second and third are estimates for the present day and the fourth may be similar to conditions if TEL was unregulated. The remaining immersed dust particles initiate freezing at 130% RHi and all other supercooled solution droplets freeze homogeneously. As shown in Fig. 4, the change in the ice water path, the vertically integrated ice water content in mixed-phase and cirrus clouds, since pre-industrial times is largest in the mid-latitudes of the Northern Hemisphere. The increase is similar in the four sensitivity simulations despite the fact that the increase in lead-containing mineral dust particles causes more particles to initiative freezing at lower RHi. This increase in lead-containing particles corresponds to warmer temperatures and lower cloud altitudes, and thus, more emitted long-wave radiation. As compared with the case where mineral dust particles contain no lead in the present day, up to 0.8 W m^{-2} more long-wave radiation is emitted when 100% of the mineral dust aerosols contain lead.

Methods

Three types of experiment were undertaken to determine the nature of ice nuclei and ice residue. First, ice crystals were formed from ambient aerosol within a litre-sized continuous flow diffusion chamber[24] (CFDC). Also known as 'cloud chambers', CFDCs are used to mimic the atmospheric temperature and relative humidity at which clouds form to facilitate experiments in a controlled laboratory or field setting. Ice crystals formed within the CFDC were isolated for analysis using counterflow virtual impaction[25]. Second, crystals from naturally occurring mixed-phase clouds at the Jungfraujoch Research Station (JRS) were separated for analysis using an ice counterflow virtual impaction[26]. Third, experiments were conducted within the Aerosol Interactions and Dynamics in the Atmosphere (AIDA) cloud chamber, an 84 m^3 actively cooled vessel[27], as well as a CFDC on collected samples of mineral dust. Subsequent experiments were conducted on collected samples doped with lead. Size and compositional analysis of ice nuclei and ambient aerosol was carried out using single-particle mass spectrometry[28,29] and electron microscopy coupled to energy-dispersive X-ray microanalysis[30]. Supplementary Information contains a full discussion of the methods. Data statistics are given in Supplementary Table S1.

Received 4 December 2008; accepted 19 March 2009; published online 19 April 2009

References

1. Wylie, D. P. & Menzel, W. P. Eight years of high cloud statistics using HIRS. *J. Clim.* **12**, 190–184 (1999).
2. Lohmann, U. *et al.* Cloud microphysics and aerosol indirect effects in the global climate model ECHAM5-HAM. *Atmos. Chem. Phys.* **7**, 3425–3446 (2007).
3. Murphy, D. M. *et al.* Distribution of lead in single atmospheric particles. *Atmos. Chem. Phys.* **7**, 3763–3804 (2007).
4. Solomon, S. *et al.* (eds) *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the IPCC* (Cambridge Univ. Press, 2007).
5. Liepert, B. G. Observed reductions of surface solar radiation at sites in the United States and worldwide from 1961 to 1990. *Geophys. Res. Lett.* **29**, 61.1–61.4 (2002).
6. Yau, M. K. & Rogers, R. R. *Short Course in Cloud Physics* 3rd edn (Butterworth-Heinemann, 1996).
7. Liou, K.-N. Influence of cirrus clouds on weather and climate processes: A global perspective. *Mon. Weath. Rev.* **114**, 1167–1199 (1986).
8. Lohmann, U. A glaciation indirect aerosol effect caused by soot aerosols. *Geophys. Res. Lett.* **29**, 11.1–11.4 (2002).
9. DeMott, P. J. in *Cirrus* (eds Lynch, D. K., Sassen, K., Starr, D. C. & Stephens, G.) 102–135 (Oxford Univ. Press, 2002).
10. Pruppacher, H. R. & Klett, J. D. *Microphysics of Clouds and Precipitation* 2nd edn (Kluwer, 1997).
11. Archuleta, C. M., DeMott, P. J. & Kreidenweis, S. M. Ice nucleation by surrogates for atmospheric mineral dust and mineral dust/sulfate particles at cirrus temperatures. *Atmos. Chem. Phys.* **5**, 2617–2634 (2005).
12. Möhler, O., DeMott, P. J., Vali, G. & Levin, Z. Microbiology and atmospheric processes: The role of biological particles in cloud physics. *Biogeosciences* **4**, 1059–1071 (2007).
13. DeMott, P. J. *et al.* Measurements of the concentration and composition of nuclei for cirrus formation. *Proc. Natl Acad. Sci.* **100**, 14655–14660 (2003).
14. Borys, R. D. & Duce, R. A. Relationships among lead, iodine, trace metals and ice nuclei in a coastal urban atmosphere. *J. Appl. Meteorol.* **18**, 1490–1494 (1979).
15. Möhler, O. *et al.* Efficiency of the deposition mode ice nucleation on mineral dust particles. *Atmos. Chem. Phys.* **6**, 3007–3021 (2006).
16. Boutron, C. F. & Patterson, C. C. Lead concentration changes in Antarctic ice during the Wisconsin/Holocene transition. *Nature* **323**, 222–225 (1986).
17. Environmental Protection Agency. *Latest findings on National Air Quality, 2002 Status and Trends* (US Environmental Protection Agency, 2003); available at <http://www.epa.gov/air/airtrends/aqtrnd02/2002_airtrends_final.pdf>.
18. Vonnegut, B. The nucleation of ice formation by silver iodide. *J. Appl. Phys.* **18**, 593–595 (1947).
19. Schaefer, V. J. Silver and lead iodides as ice-crystal nuclei. *J. Meteorol.* **11**, 417–419 (1954).
20. Reischel, M. T. Lead nuclei from reactions involving lead, ammonia, and iodine. *Atmos. Environ.* **9**, 955–958 (1975).
21. Baklanov, A. M. *et al.* The influence of lead iodide aerosol dispersity on its ice-forming activity. *J. Aerosol. Sci.* **22**, 9–14 (1991).
22. Lohmann, U., Spichtinger, P., Jess, S., Peter, T. & Smit, H. Cirrus cloud formation and ice supersaturated regions in a global climate model. *Environ. Res. Lett.* **3**, 045022 (2008).
23. Stier, P. *et al.* The aerosol-climate model ECHAM5-HAM. *Atmos. Chem. Phys.* **5**, 1125–1156 (2005).
24. Stetzer, O., Baschek, B., Lüönd, F. & Lohmann, U. The Zurich ice nucleation chamber (ZINC)—a new instrument to investigate atmospheric ice formation. *Aerosol. Sci. Technol.* **42**, 64–74 (2008).
25. Ogren, J. A., Heintzenberg, J. & Charlson, R. J. In situ sampling of clouds with a droplet to aerosol converter. *Geophys. Res. Lett.* **12**, 121–124 (1985).
26. Mertes, S. *et al.* Counterflow virtual impactor based collection of small ice particles in mixed-phase clouds for the physico-chemical characterization of tropospheric ice nuclei: Sampler description and first case study. *Aerosol. Sci. Technol.* **41**, 848–864 (2007).
27. Möhler, O. *et al.* Experimental investigation of homogenous freezing of sulphuric acid particles in the aerosol chamber AIDA. *Atmos. Chem. Phys.* **3**, 211–223 (2003).
28. Gallavardin, S. J. *et al.* Single particle laser mass spectrometry applied to differential ice nucleation experiments at the AIDA chamber. *Aerosol. Sci. Technol.* **42**, 773–791 (2008).
29. Murphy, D. M. The design of single particle laser mass spectrometers. *Mass Spectrom. Rev.* **26**, 150–165 (2007).
30. Zimmermann, F., Ebert, M., Worringen, A., Schütz, L. & Weinbruch, S. Environmental scanning electron microscopy (ESEM) as a new technique to determine the ice nucleation capability of individual atmospheric aerosol particles. *Atmos. Environ.* **41**, 8219–8227 (2007).

Acknowledgements

We thank P. J. DeMott, D. M. Murphy and D. S. Thomson for their assistance with the measurements. We also acknowledge the effort of all of the participants of the INSPECT and CLACE field studies, the support of the High Altitude Research Foundation Gornergrat and Jungfraujoch and the experimental group at AIDA. This research was supported by the Atmospheric Composition Change the European Network for Excellence, ETH Zurich, the German Research Foundation and Pacific Northwest National Laboratory directed research funding.

Author contributions

D.J.C., single-particle mass spectrometry, data analysis and paper writing; O.S., ice nucleation experiments and data analysis; A.W., M.E. and S.W., sample acquisition, electron microscopy and data interpretation and analysis; M.K., S.J.G., J.C. and S.B., mass spectrometer development, sample acquisition for single-particle mass spectrometry and data analysis; S.M., ice crystal sample acquisition and data analysis; O.M. and K.D.F., conducted AIDA experiments and data analysis; U.L., GCM programming and data analysis.

Additional information

Supplementary information accompanies this paper on www.nature.com/naturegeoscience. Reprints and permissions information is available online at http://npg.nature.com/reprintsandpermissions. Correspondence and requests for materials should be addressed to D.J.C.