The authors would like to thank both anonymous referees for their time, their helpful comments and suggestions and their attention to all the details. We appreciate their contribution. Please find below a detailed point-by-point replies and amendments followed by the marked up manuscript. Referees comments are in blue.

Anonymous Referee #1

Received and published: 30 November 2015

Our main concerns:

In his review, anonymous referee #1 indicates that the new chamber and instrumental measurements have limited audience, implying the majority of atmospheric scientists would be naturally interested in remote sensing. We argue that aerosol chemo-physical properties, modelling and single particle measurements discussed in this paper are not less important but complementing the remote measurements. The relevance of this paper is emphasized in the comparison to real atmospheric measurements made with the same CASPOL airborne instrument (Fig.9) and following the research published in ACP by Glen and Brooks, 2013 of Particle by Particle analysis. Using similar instrument for similar purpose, similar terminology is used. CAPS-CASPOL is widely used in airborne particle by particle measurements and it is an important tool in atmospheric research. It is primarily used in the range (3-50 μm) and the new results presented here of <3 μm small SOA particles observed with this instrument could assist in atmospheric particle by particle CASPOL data interpretation.

The review states that the paper may be more suited to a technical journal. At the same time the reviewer suggests to add more details about signal conversion of a commercially available instrument and detailed inlets description, while overlooking the science of the SOA observations (Table 2, Fig.5, Fig.6, Fig.7, Fig.8, Fig.9) in his comments. The authors would like to highlight that this paper is submitted to the special issue "The CERN CLOUD experiment (ACPD/AMTD Inter-Journal SI)". More detailed replies are listed below.

General comments

This manuscript presents results, primarily taken with the CASPOL instrument, of artificial cloud and secondary organic aerosol (SOA) experiments from the CERN CLOUD chamber. The Cloud and Aerosol Spectrometer with Polarisation detection (CASPOL) measures the total forward-scattered light and orthogonally polarised components of the backscattered light from particles produced in the controlled conditions of the chamber. Based on the relationship between these three measurements a classification scheme for water, ice, and (de)hydrated SOA particles is presented.

The authors discuss the importance of such chamber measurements and describe adequately both the chamber and the CASPOL instrument. The fact that this instrument has been newly installed and the CLOUD chamber has started producing cloud particles (as opposed to doing purely aerosol studies) makes the results new and of interest, at least to a somewhat limited audience. Specific concerns are listed below however the major two are; firstly that results are presented in a highly specific manner such that its general usefulness has been lessened and secondly, that the quality of the writing hinders the reader's understanding and appreciation of the work presented. The former point has ramifications for satisfying the scope of ACP. From the journal 'Aims and Scope' webpage;

"The journal scope is focused on studies with general implications for atmospheric science rather than investigations that are primarily of local or technical interest."

In its current form I would say that the manuscript does not meet this requirement and may be better suited to submission to a more technical journal.

Reply:

- "measures the total forward-scattered light and orthogonally polarised components"

  This instrument version measures the total backscatter and only one polarised component (31441.13-16).
- "The fact that this instrument has been newly installed and the CLOUD chamber has started producing cloud particles…makes the results new and of interest, at least to a somewhat limited audience… that results are presented in a highly specific manner such that its general usefulness has been lessened

  This paper reports laboratory studies of aerosols and clouds and includes modelling and field measurements all of which are included in the scope of this journal. Chemical composition and physical properties and processes are linked throughout the paper:

  Detailed optical observations of the phase transition process in a cloud is described along with optical properties of the particles. Detailed SOA growth and the associated viscosity changes observed, along with an analysis of the optical properties in each SOA state are described, linking these to chemical processes. The reviewer does not provide any critical comment on these aspects of the work.

  To provide relevant atmospheric context for these chamber results, the measured responses of a range of other atmospherically relevant particles from airborne field measurements of volcanic ash, super-cooled water and ice cloud particles are compared with our chamber measurements. This is highly relevant as these field observations were made with the identical instrument used in the chamber experiment.

The study and its results can be used as a contribution to the approaches needed for understanding analysis of airborne field experiments as well as chamber experiments where these and similar instruments are becoming widely used, e.g. the DMT CAPS-CASPOL, BCP-D and DMT SPIN-OPC. The presented results have special relevance for TTL measurements, mixed phase clouds and aerosol cloud interaction studies in general.

A large part of the paper discusses the SOA transitions and existence of two polarising states in simulated atmospheric conditions, together with the SOA reversed transition to a more viscous state. This is scientifically important for understanding many atmospheric processes including ice nucleation and particle radiative scattering properties. Therefore in our view, the observations are not local or technical, and have demonstrated real atmospheric relevance.

- "In its current form I would say that the manuscript does not meet this requirement and may be better suited to submission to a more technical journal"

The focus of the paper is the optical characterisation of atmospheric particles by their unique polarisation signatures with atmospheric relevance and context. The technical discussion of the instrumental design or the chamber setup appears in all CLOUD papers and is not the main point of this paper as these have been discussed by others (and which we have cited). These are used here only to underpin the measurements of important physical properties. The first section explains the initial steps in the analysis, further figures (**Table 2**, **Fig.5** growth rate of SOA, **Fig.6** two distinct polarising states of particles, **Fig.7** reversed transition in viscosity, **Fig.8** decrease in SOA size, **Fig.9** polarisation scatter map for different particles) report and focus on the new results from the SOA experiments. Finally these are placed in context by comparison with atmospheric observations using an identical instrument which was deployed in previous aircraft studies. Whilst we are happy to clarify and improve on the work presented we believe it is entirely relevant to ACP in all respects.

Specific comments

1. There is a tendency by the authors to present results in a manner that makes them less useful to the wider community. One of the draws of using an instrument like the CASPOL is for comparison with the remote sensing community which does not have access to the forward scattering information. For example, polarisation ratio is presented in a slightly different way to the more common β_{PER}/β_{PAR} and the particle classification map is presented as perpendicularly polarised backscatter to total backscatter ratio and forward-scatter ratio. In doing so, the authors have made it impossible to compare these results with a majority of work in the existing literature. The authors also do not explain the reasons for the decision to use these different parameters.

The authors cite the work by Glen and Brooks [1]. This paper presents maps using the same classification mapping space as in this manuscript however they also show the same data in backscatter versus polarisation ratio space which is close to that used extensively for lidar return classification. Different plotting space does highlight different characteristics in the same dataset and it is possible that the map presented in this manuscript is the only one that leads to clear separation between the species under study. However this does seem somewhat unlikely given the volume of data presented in the literature in the more conventional way. At the very least the authors should address this, and more helpfully provide classifications with more common axes.

The afore-mentioned work of Glen and Brooks would also provide a nice comparison to the work presented in this manuscript. This could easily be done despite the different definition of polarisation ratio used in the older paper.

Reply:

- The comparison of remote sensing and particle by particle measurements is not a straightforward process (i.e. bulk vs. single particle and single composition vs mixed composition ensembles of particles). Many single particle laboratory techniques in particular have proven difficult to adopt when translated to real atmospheric mixed-phase, multiple composition aerosol and cloud environments. This is often not acknowledged fully. The efficiency of such techniques in particular can become concentration limited especially in mixed phase or small particle clouds. These techniques therefore provide complementary data rather than comparable data and research in this area continues; “Satellite measurements often unable to detect thin cirrus clouds and other clouds are misclassified as cirrus. In these cases airborne probes are required. The main drawbacks of existing instrumentation are their inability to effectively characterise the small <200μ crystal component and to directly measure ice water content and important optical parameters. Aircraft operations also inherently suffer from limited spatial coverage and limited instrument sampling volumes. IWC becomes largely contributed by smaller particles at temperatures below -45C, However there is still debate as to the importance of smaller crystals for both mass budgets and for determining the radiative properties of clouds… Finally, the soundest approach to research of clouds and cirrus in particular is to synergistically combine as many sensor observations as possible” [2].
  Nevertheless, a paper is being prepared based on a technical comparison between CASPOL single particle measurements and the bulk measurements provided by the SIMONE

instrument based on measurements in CLOUD; this paper will be more relevant to the remote sensing community as SIMONE operates on the same principle as LIDAR, providing bulk cloud depolarisation measurements.

- The ratio mentioned by the reviewer is most commonly defined as the Depolarisation ratio in remote sensing. The Polarisation ratio is what the current version of this instrument can provide and it is a follow up on the work reported by Glen and Brooks in the ACP journal: "*Although depolarization ratio is the working definition for a parameter used in numerous studies, it has been noted that technically the interaction between particles and linearly polarized light does not explicitly depolarize the incident light but instead changes the state of the polarized light".*
- The author appreciates the interest in the results for remote sensing classification of small particles and mixed phase clouds and additional plot will be provided for Total Back vs Dpol/Back space (Fig.3c) as the reviewer suggests.
- "given the volume of data presented in the literature in the more conventional way" – it will be useful to see some citations other than those we have cited to which the reviewer refers to here.
- "The afore-mentioned work of Glen and Brooks would also provide a nice comparison to the work presented in this manuscript".

  Despite the similarity of the instruments, there are differences in defined Polarisation ratios, and which are used by different communities:

  1. Polarisation ratios much higher than unity were observed by Glen and Brooks e.g. White Quartz, which makes it difficult to present a consistent comparison. In the Glen and Brooks study (Fig.5) most of the particles up to 2 μm appear to have polarisation values > 1. In our measurements, less than 1% of the polarisation ratios are above unity. Such a comparison will require thorough analysis of specifications of both detectors from both instruments. DMT is frequently initiating instrument updates, therefore instrumental updates history should be reviewed as well for the suggested quantitative comparison.
  2. Dust and minerals roughly belong to the same category/ range of highly polarising particles. Our general map includes several types and compositions under different conditions. Needless to say more research is to be done to validate this classification under different humidity and temperature variations (31449.15-18).

2. In page 31441, line 10 it is written that most of the light from particles of interest are scattered in the forward direction. However, based on the ratios in figures 3, 6, and 10, the total backscatter signal is greater than that in the forward direction. Specifics of the parameters used to calculate the ratios are not addressed in the paper so I assume that they are some instrument voltage or count that do not directly represent the scattered irradiance. This makes it difficult for those with different but equivalent instruments (or even updated versions of the same instrument) to utilise or reproduce these results.

Reply:

- The reported ratios in Fig.3,6,9 (there is no Fig.10) are from two separate detectors that have different conversion because of different irradiance as the reviewer points out. Some of these differences are described in Table S2, and elsewhere (e.g. [3]), and could be used in equivalent versions of the instruments. The sample volume of the CAS is defined with a pinhole aperture (or mask) and is used to select only the most uniform and intense section of the laser beam [4], 31441.20. Once again, additional technical information could be more suitable for a technical paper but is also described in the cited instrument papers standards, for such instruments. Any inter-comparison of different instruments should be advised by DMT.

3. The discrimination between liquid water and ice with polarised light has a long history so in addition to this, I was hoping to see the identification or classification of different ice habits with this instrument in the chamber. At the end of section 3.1 there is a glimpse of this possibility with a list of different habits formed in the chamber along with the 3V-CPI images in figure 4. Given that all these habits can be created it is unclear why the authors did not make better use them. The sentence on page 31448, line 18 insinuates that there is a limited range of habits within the chamber (at least compared to the real atmosphere). Perhaps the predominant habit cannot be selected with the conditions within the chamber? Perhaps there was only ever a random selection of habits? If so this should be addressed along with a comment on the distribution of habits used when doing the cluster analysis. If discussion about the impact of different ice crystal habits, or even better, the classification of different habits were included this manuscript would be significantly enhanced.

Reply:

- "The discrimination between liquid water and ice with polarised light has a long history" – it has a long history indeed though not a fruitful one for application in real-mixed phase clouds and small particles. Unfortunately, the measurements of ice crystal number and size as well as RH_{ice} have suffered from instrument issues over the last decades [5]. Additional chamber experiments with controlled conditions as this one could shed more light on the nature and origin of particles in the atmosphere.
- "I was hoping to see the identification or classification of different ice habits with this instrument in the chamber"- In these experiments, the vast majority of ice particles were small. Ice habits classification for particles less than 50 μm by using solely the polarisation measured by CASPOL is not realistic. Additional papers using other techniques during CLOUD for this purpose (e.g. PPD small ice detector technology) are being prepared elsewhere. Our 3VCPI (which comprises both a 2DS LED imaging and a CPI CCD imaging instruments) minimal detection threshold was ~20-40 μm, depending on habit, with an imaging resolution of 2.3 μm. The shapes seen in Fig.4 are of bigger particles ~80 μm as stated in the figure. Since the majority of ice crystals are less than 50 μm in size it is not possible to reliably discriminate these crystal habits into the generally used habit classification categories we would use for e.g. airborne studies with 3VCPI (e.g. in Lawson et al. [6] the vast majority of CPI images were >50 μm and only those were sorted into habit categories).
- Initial branching of the small ice crystal or a high aspect ratio (aspherical) shape would definitely affect the polarisation measured by CASPOL (31449.14).

4. Section 3.2 on the ACPIM modelling does not seem to add appreciably to this manuscript compared to a comment on the chamber wall heating and appropriate citation towards the end of section 2.1. See point 31445.15 below.

Reply:

- The ACPIM model was used to plan the experimental conditions prior to the actual experiments and to subsequently compare with the environmental conditions recorded. Therefore the comparison of model and measurements is essential to indicate any discrepancies in current understanding of both the chamber environmental conditions and fundamental cloud nucleation processes. Model validation in a different chamber was one of the purposes of these chamber measurements. This section therefore also presents the first application of use ACPIM for the CLOUD chamber at CERN. This adds to its previous application in the AIDA cloud chamber at KIT as described in detail by Connolly et al. (2009). A good prediction ability of the phase transition onset and water evaporation was demonstrated with the model. Possible reasons for discrepancies are discussed in point 31445.15 below (Chamber vs. Air parcel).

5. The Discussion in section 4 is disjointed and very difficult to understand. Please break this into separate paragraphs of related material.

Corrected to:

The results presented in this paper (Figs. 2, 5 and S3, S4 in the Supplement) illustrate the ability of the CASPOL instrument to provide reliable Particle Size Distribution (PSD) in expansion chamber campaigns, and to classify atmospheric particles of different phases, viscosities, shapes, and sizes. The polarisation ratio was combined with the PBP clustering technique to highlight the time resolved aspherical fraction evolution.

Despite the known limitations and uncertainties in these measurements, e.g., particle sedimentation (Chapter 6 in Kulkarni, 2011), electronic “ringing”, and leakage currents (Kramer, 2002), these did not affect the filtered results (Fig. 3b) shown here. Another uncertainty is contributed by the extremely high aerosol concentrations ~ 40 000 cm^{-3} (with unresolvable interarrival- times between successive particle). These concentrations may not be atmospherically relevant; their role here was solely to grow the larger SOA particles (> 500 nm). This was required to allow the optical detection of particles during growth and liquefaction.

In addition to concentration issues, a derivation of equivalent diameters from dry viscous aerosol particles may be challenging since it has been argued that spherical aerosols can be considered as purely a “figment of the imagination” (Baran et al., 2013). However, the PSD measured by CASPOL and UHSAS during SOA growth corresponded well (Fig. 5). The predicted SOA behaviour (Koop et al., 2011) and the measured slow increase of polarisation may suggest a change in the viscosity of these particles. The polarisation transitions observed were both clear and repeatable which gives confidence in our ability to identify the hypothesised transitions and to place these observations on the general polarisation map for classification in a comparative particle analysis.

The general classification map presented here demonstrates a good agreement between chamber and airborne measurements (Fig. 9). Although super-cooled droplets, ice and other particle polarisation footprints seem to be quite distinct, it is clear that further spatial growth and branching of ice could lead to a significant increase in polarisation and possibly significant overlapping of different species. One of the aims of future studies would be to test aggregation and branching impacts on CASPOL signals. Slightly higher polarisation of the airborne super-cooled droplets and ice might be the result of aerosol ageing. Processes such as aerosol ageing will influence subsequent phase separation processes within the droplet but are difficult to reproduce in a chamber.

In the real atmosphere, the particles are more complex; contain additional polarising constituents and have more branching. Froyd et al. (2010) report the coexistence of mixtures of partially or fully neutralised sulphate with organic material, nucleated ice crystals, dry ammonium sulphate, and glassy particles in the Tropical Troposphere Layer (TTL). Ice residuals were also similar in size to unfrozen aerosol. Lawson et al. (2008) suggests a thorough investigation of nucleation and growth mechanisms of ice particles in TTL at low temperatures is needed, particularly in the presence of sulphates mixed with organics and very high relative humidity. This might be difficult due to increasing anthropogenic SO_2 emissions which may increase the formation of sulphuric acid aerosols and thus small ice crystals in the TTL (Notholt et al., 2005). The increase in small ice concentration in presence of aerosols may complicate ice content measurements even further. The classification map presented here represents one approach to facilitate future CASPOL-PBP data analysis of the TTL and deep convective outflow regions. It could also be useful for particles like ammonium sulphate that often reach high altitudes through the seasonal biomass burning processes and initiate ice nucleation. Using a method such as the classification map presented here to discriminate between different kinds of atmospheric particles (e.g., ice crystals, ammonium sulphate, volcanic ash, SOA) will allow better insight for atmospheric transport and chemical processes.

Technical corrections

The general standard of the text is inadequate, in addition to rectifying the specific corrections below, I would encourage the authors to carefully re-read the manuscript and address this issue. Some of the following points are purely technical and some may also be of a scientific nature. Location of items are given as **page.line**.

Title: The title is very vague and the use of a generic acronym does not help.

Reply:

The paper describes observations of phase change transition in SOA under different environmental conditions. In addition the methods used were also applied to the discrimination of associated nucleated water and ice particles observed during the CLOUD experiments. As mentioned earlier the paper was submitted to the special issue “The CERN CLOUD experiment (ACPD/AMTD Inter-Journal SI)” and should be seen in this context. The special issue has additional papers with the CLOUD acronym which make the experiments more localized and defined. We are happy to emphasise the nature of the phase transition nature of the work by suggesting a change in title. One suggestion is: Phase Transition Observations and Discrimination of Small Cloud Particles by Light Polarisation in Expansion Chamber Experiments

31435.4 This sentence mentions three times that there are both liquid water and ice. Remove the repetition.

Changed to: The detection of aerosol particles, liquid droplets, and ice crystals, especially in the small cloud-particle size range below 50 µm, remains challenging in mixed phase, often unstable environments.

31435.8 The Cloud Aerosol Spectrometer with Polarisation (CASPOL) is an airborne instrument that has the ability to detect such small cloud particles and measure their effects on the backscatter polarisation state. ". . . and measure their effects on the backscatter polarisation state." Rephrase the second half of this sentence.

Changed to: The Cloud Aerosol Spectrometer with Polarisation (CASPOL) is an airborne instrument that has the ability to detect such small cloud particles and measure the variability in polarisation state of their backscattered light.

31435.22 "Finally, we discuss the benefits and limitations of this classification approach for atmospherically relevant concentration and mixtures with respect to the CLOUD 8–9 campaigns and its potential contribution to Tropical Troposphere Layer (TTL) analysis". Since the relevance of the particle categorisation to TTL data is limited to several sentences at the end of the manuscript, mention of it in the abstract can probably be removed.

Reply:

The discussion of potential contribution to TTL analysis has been extended (Specific comment #5)

31436.10 "Scattering analysis is complicated further in small ice crystals and Secondary Organic Aerosol (SOA)". SOAs are not referred to in the previous or current paragraph so remove reference to them in this sentence.

Reply:

Sentence moved to the end of first paragraph in the Introduction section. This way the first paragraph states that scattering analysis is complicated further with ice and SOA and a detailed paragraph with description of ice complication begins, following with a paragraph explaining the aerosol and SOA complications respectively:

"Scattering and absorption due to atmospheric particles can vary widely, leading to net radiative effect that either cool or warm the surface of the Earth. Ice crystals pose a potential challenge since their non-sphericity complicates the theoretical description of their single scattering properties (Macke et al., 1996). Several attempts have been made to model and simulate light interactions with different ice crystal habits, mixtures of crystal types, aggregates, and aerosols (Baran, 2013), but no single method can easily combine all size ranges and types of particles, making accurate, unified modelling nearly impossible. Scattering analysis is complicated further in small ice crystals and Secondary Organic Aerosol (SOA).

Small ice crystals can have different major internal defects (e.g., stacking faults, chemical defects, molecular vacancies, interstitial molecules, ionized states, and orientation defects), surface roughness, and branching with various symmetries; the optical effects of these defects depend strongly on the spatial orientation of the particle in a flow…

Aerosol particles found in the lower confines of the atmosphere are typically internal or external mixtures of inorganic salts, refractory components such as mineral dusts and clays, and organic species; they also contain varying quantities of water…”.

31436.11 “Small ice crystals can have different major internal defects (e.g., stacking faults, chemical defects, molecular vacancies, interstitial molecules, ionized states, and orientation defects), surface roughness, and branching with various symmetries”; These complicating artefacts are unlikely to be limited to small ice crystals as stated (although the implications of such artefacts on measurements of the scattered light may indeed be more important) so rephrase these sentences.

Changed to: Ice crystals can have different major internal defects (e.g., stacking faults, chemical defects, molecular vacancies, interstitial molecules, ionized states, and orientation defects), surface roughness, and branching with various symmetries. These could be even more influential in small ice measurements.

31436.14 The optical effects of these defects depend strongly on the spatial orientation of the particle in a flow. The optical effects of these defects depend on the orientation of the particle relative to the incident radiation not the flow. If there is a preferential particle orientation in a flow relative to the instrument, and thus laser, this then may lead to systematic measurement bias as mentioned. A reference would be good here along with comments about any preferential orientation or lack there-of in the CLOUD chamber.

Reply:

The angle between the flow direction and the laser beam in the instrument is constant therefore the angle to the laser is correlated with the preferred orientation in the laminar flow. Orientation effects on classification were observed previously in the AIDA chamber [7]. Due to the good mixing (two fans) in the CLOUD chamber, the smaller size and low aspect ratio of the measured particles in addition to the short gap between entering the inlet and the actual measurement we assume no orientation preference, nonetheless this is another uncertainty in our measurement as stated. We can’t cite any ice crystal orientation effects from previous work in the CLOUD chamber since these are the first measurements reported from the ice phase experiments. Particles are generally in an air flow of some description, and non-spherical particles will normally tend to orient themselves in a way that minimises aerodynamic drag in the absence of any other forces such as shear in the flow. To avoid confusion, we have removed reference to the air flow in the manuscript.

31436.21 Organic components create hygroscopicity variation that affect the water uptake of the particles (Cziczo et al., 2004; Jimenez et al., 2009; Duplissy et al., 2011). Water uptake variation between pure sulphate and internally mixed organic/sulphate aerosols alter the particle refractive index and may lead to mis-sizing by optical instruments if the composition is not taken into account (see Sect. 2.3). “Organic components create hygroscopicity variation. . . ”, this sentence and the next should be rephrased for clarity.

Changed to: The hygroscopicity of organic particle is derived from their composition (Cziczo et al., 2004; Jimenez et al., 2009; Duplissy et al., 2011). Pure sulphate and internally mixed organic/sulphate aerosols will have different water uptakes, and consequently different refractive indices. This may lead to mis-sizing by optical instruments if the composition is not taken into account (see Sect. 2.3).

31437.13 its derivatives in SOA are optically active materials (Wilberg et al., 2004; Cataldo et al., 2010) that rotate the initial polarisation. Particles do not rotate the initial polarisation, the polarisation of the incident light is unaffected by the presence of a particle. Rewrite this sentence.

Changed to: its derivatives in SOA are optically active materials (Wilberg et al., 2004; Cataldo et al., 2010) that induce a change in the polarisation state of the scattered radiation.

31438.2 Recently, additional experiment focusing on cloud formation (i.e. “Cloudy” experiments) has been added to allow ice nucleation to proceed. “Recently, additional experiment focusing on. . . ” This sentence doesn’t make sense.

Change to: Recently, additional experiments focusing on cloud formation have been performed at the CERN chamber. In this paper we focus particularly on results from this “Cloudy” series of experiments. This addition was driven by the importance of ice particles to the earth’s radiation budget and feedback mechanisms.

31439.7 An in situ system, the Scattering Intensity Measurements for the Optical detection of icE – SIMONE-Junior (Schnaiter et al., 2012), was installed for bulk depolarisation measurements. The SIMONE instrument is described as in situ which suggests that the other instruments are not. Is this because the other instruments operate with inlets? If so, a description of instrument inlets and the impact on sampling should be given (with a reference if required). If not, then remove “in situ”.

Reply:

Some instruments are sampling through inlets. Chamber probes are described in detail elsewhere [8].In CASPOL, penetration efficiency of 10 μm particles was well above 90% in all campaigns. Instrumental setup is presented in Fig.S1.

Changed to: An averaged path system, the Scattering Intensity Measurements for the Optical detection of icE – SIMONE-Junior (Schnaiter et al., 2012), was installed for bulk depolarisation measurements.

31440.25 A more detailed description of the latter can be found in the accompanying paper by Järvinen et al. (2015). “. . . of the latter. . . ” does not make sense here so the sentence needs rewriting.

Changed to: A more detailed description of these experiments can be found in the accompanying paper by Järvinen et al. (2015).

31441.1 The Cloud and Aerosol Spectrometer with Polarisation detection (CASPOL) is part of the Cloud Aerosol and Precipitation Spectrometer (CAPS). Although mentioning the CAPS in the body of this section is sensible (if nothing else it allows a reader to find the instrument on the manufacturer’s website which does not list CASPOL) including it in the title of this section is just confusing. Rename this “The CASPOL Instrument”, “CASPOL Description”, or something like that. In general this section needs to be split up into more than one paragraph and reordered for clarity (eg currently order is forward scattering, backscattering, depolarisation, size and refractive index effects on forward scattering, then effect of qualifier. This does not make for easy reading).

Changed to:

2.3 The CASPOL instrument

The Cloud and Aerosol Spectrometer with Polarisation detection (CASPOL) is part of the Cloud Aerosol and Precipitation Spectrometer (CAPS). The first variant of the instrument was introduced in 1999 and was designed for airborne in situ cloud measurements (Baumgardner et al., 2001; Heymsfield, 2007), although it has subsequently been used for cloud chamber measurements (Krämer 2009). The version of CASPOL employed here has a linearly polarised laser to provide a collimated incident beam of light at a wavelength of 680 nm.

The first two detectors of the instrument are detecting the light scattered in the forward direction with collection angles 4 to 12◦. The near forward angles are used because most of the light scattered from a particle whose diameter is larger than the incident wavelength is in the forward direction. The first detector in the forward direction is used as a qualifier; it has a rectangular optical mask that restricts scattered light from particles that are outside the centre of focus of the laser beam. Only particles within the optimal view volume are counted and characterized. All data are collected on a single particle basis, thus provide a measure of particle-by-particle variability and single particle optical properties. The particle's water equivalent optical diameter in the range 0.51 – 50 μm is determined from the forward scattering signal in the second detector using the standard Mie scattering assumptions, i.e., spherical geometry and isotropic refractive index.

The next pair of detectors measures the backscattered light with collection angles of 168 to 176◦. The first backscattering detector is used for qualitative particle shape discrimination. The second detector has a polarised filter (90◦ to the polarisation of the incident light) to measure the change in polarisation of scattered light caused by asphericity (Baumgardner et al., 2011; Glen and Brooks, 2013) or birefringence. In this configuration, spherical particles produce little response in the perpendicular polarisation backscatter detector. Conversely, frozen water droplets and aspherical ice crystals will show much more distinct signals.

In order to eliminate aerosol particle interference in our cloud measurements, only contributions from a subset of larger particles above 3 μm were included. This threshold is based on work by Baumgardner et al. (2001) and Lance (2012) who selected a similar size range for cloud particle measurements. In the special case of SOA measurements, a subset of small particles (< 3 μm) detected in the lower gain stage, was considered.

31441.9 There are four detectors in the instrument, with collection angles of 4 to 12◦ for the forward detectors and 168 to 176◦ for the backward detectors. It is obvious what is meant, however angles are two dimensional; the instrument collects light over solid angles subtended by the angles given.

Changed to: The first two detectors of the instrument detect the light scattered in the forward direction. The collection of the light cone is subtended by the angles 4 to 12◦.

31441.10 The near forward angles are used because most of the light scattered from a particle whose diameter is larger than the incident wavelength is in the forward direction.The near-forward angles are used for what and instead of what alternative?

Changed to: The near forward angles are used for sizing because light is preferentially scattered in the forward direction from particles whose diameters are larger than the incident wavelength.

31441.27 This threshold is based on work by Baumgardner et al. (2001) and Lance (2012) who selected a similar size range for cloud particle measurements. The entire size range of the CASPOL is not given although various subranges or thresholds are mentioned throughout the manuscript. Add this information to this section.

Reply: Added above.

31442.8 Aspherical particles will be mis-sized with respect to spherical particles, subject to their cross-section as shown by Borrmann et al. (2000). Size of aspherical particles is used throughout the manuscript but only receives a very cursory two sentences here. It is unclear how such particles are sized, as only Mie theory is discussed I assume that an equivalent optical diameter is used however it is still unclear what refractive index is used (particularly in cases such as figure 2 where ice and water particle sizes are presented on the same axis). The final sentence needs significant expansion. The bin size (were the manufacturer's nominal diameter bin widths used or was a calibration done as in the Rosenberg et al. [9] paper cited?) varies across the size range of the instrument but these are not given in the manuscript. Was the error assumed or calculated and was it the same for the ice and SOA particles? No uncertainties are given with the diameter data presented and plotted, this should be rectified.

Reply:

The sizing of the particles is described in 31441.18. The CASPOL was calibrated using Polystyrene Latex Spheres (PSL) with refractive index n=1.51, as described extensively in the cited references (and in DMT User's Manual [10]). The authors have added this instrument's manual citation for those interested. We assume an uncertainty of the size of a bin width as stated in this section. The error for SOA and ice is essentially different due to their different sizes and different bin widths for these sizes.

The inversion of the scattering cross section as was mentioned in the calibration section has an inherent problem with all types of optical particle counters. DMT addresses this problem as follows: the Mie curves were smoothed (by applying a running average) to an extent that yielded a monotonic function across which 30 channels were attributed. This procedure does not account for sizing ambiguities. Despite this, the default manufacturer's channel selection is sufficient for the determination of the total droplet number concentration or the total liquid water content [11]. Moreover, it was shown in this study that despite the different scattering geometries and optics, the different instruments are in a good agreement; The mean equivalent diameter measured by CASPOL agrees with UHSAS measurement during SOA growth experiments (Fig.5) within the bin width error range; CASPOL also agrees with the PPD instrument during the ice phase measurements at -50C (Fig.S1) and with the WELAS instrument for super cooled water droplets at -12C (Fig.S2). These various inter-comparisons add confidence to the performance of the CASPOL.

The uncertainty in the derived polarisation ratio is approximately 20%, as a result of the accuracy of the NIST calibration particles that have a cited standard deviation of ±10%, the variance in the laser intensity that is on the order of 15%, and electronic noise that contributes another 10% as described in [12].

Section changed to: The CASPOL was calibrated using Polystyrene Latex Spheres (PSL), as described elsewhere, e.g., DMT Manual (2011), Meyer (2011), Rosenberg et al. (2012). Size calibration relates the amplitude of the instrument's response to particle scattering cross-sections. Using the Mie–Lorenz curve, the nominal size bin limits can then be defined (Table S2 in the Supplement) in terms of the diameter of water droplets having the same scattering cross-section, giving a reasonable estimate of particle size for liquid droplets and small spherical ice particles. Aspherical particles will be mis-sized with respect to spherical particles, subject to their cross-section as shown by Borrmann et al. (2000). In our instrument this error would normally be in the order of the size bin width. The uncertainty in the derived polarisation ratio is approximately 20% as described by Baumgardner et al., (2005).

- Supplementary materials will include bins table.

31442.15 The polarisation ratio measured with the CASPOL instrument and reported in this paper is defined as the ratio of perpendicularly polarised backscatter intensity to total backscatter intensity and provides a measure of phase, composition, and surface features of the particle. This is an unusual manner of expressing the degree of polarisation rotation in the scattered light. It would be good to see the reason that this definition was used compared to the more common one.

Reply:

This is based on the scattering properties measured by the instrument, as explained in 31442.17-19, and is generally adopted by the user community for this instrument. This ratio differs from the depolarisation ratio that is measured using remote sensing techniques [13]. The two ratios cannot be directly compared, requiring additional calibration [3] with limited efficiency for this purpose. A separate paper addressing this point, comparing SIMONE with CASPOL depolarisation approaches, is being prepared.

31442.16 The polarisation ratio measured with the CASPOL instrument and reported in this paper is defined as the ratio of perpendicularly polarised backscatter intensity to total backscatter intensity and provides a measure of phase, composition, and surface features of the particle. ". . . provides a measure of. . . " perhaps overstates the quantitative utility of the polarisation ratio which varies with one or any combination of the particle characteristics listed.

Reply:

This is in fact what the instrument provides: a measure for the combination of all characteristics together since it is unable to separate the single characteristics, maybe a better phrase would be: "... and provides an indication of the combined phase, composition, and surface features of the particle. Though some of these components effects on polarisation signal can be neglected in our case due to the size, simplicity and reproducibility of the particles.

Changed to: The polarisation ratio measured with the CASPOL instrument and reported in this paper is defined as the ratio of perpendicularly polarised backscatter intensity to total backscatter intensity and provides a measure of the combined phase, composition, and surface features of the particle.

31442.20 The ratio of perpendicularly polarised backscatter to forward scatter (Dpol/Fwd) indicates the contribution of particle size to the scattering. Unless there is precedent, I'd recommend a change of symbol for the perpendicularly polarised backscatter signal. Dpol rolls of the tongue as depolarisation (ratio).

Reply:

There is, somewhat unfortunately, a precedent among the probe user community which took root in the early days of CASPOL measurements. While we agree that the term "Dpol" appears confusing, in the context of the experiments described here, it is the only measurement of the polarisation state of the scattered light.

31442.21 PBP measurements reveal the fraction of aspherical particles population (Fig. 2c) and its evolution. This is not entirely obvious. For a spherical particle in the size range of interest, the forward scattering signal will increase with size however spherical particles are somewhat irrelevant here. With aspherical particles the forward scattering may be non-uniform which makes this sweeping statement somewhat uncertain. This is linked to the use of these ratios as discussed in point 1 above but if this ratio is to be used to link size and asymmetry then further explanation and references are required to address the assumptions and subtleties.

Reply:

This line mentions the fraction of aspherical population. The sizing is done in the forward direction but the aspherical fraction presented in Fig.2C is calculated from the backscatter polarisation thresholds as described in section 2.4.2. The error in sizing would normally be in the order of the size bin width, the uncertainties for the ratios are discussed in comment 31442.8.

31443.8 Clustering analysis is used here to discriminate and assign unique particle properties corresponding to different phases during the experiment (e.g., water, ice), primarily based on polarisation differences (Fig. 3). ". . . based on polarisation differences. . . " could cause confusion with a mathematical difference, use "variation" or something similar.

Changed to: Clustering analysis is used here to discriminate and assign unique particle properties corresponding to different phases during the experiment (e.g., water, ice), primarily based on variations in the polarisation state of the scattered light (Fig. 3).

31443.11 Here we use the MatLab K means cluster function. Use standard nomenclature (of the website); MATLAB (check journal standards to see if this requires a ®), k-Means, and cite the URL for the kmeans function.

Reply: From a brief review of several ACP papers it looks like there are multiple variations of this nomenclature.

Changed to: Here we use the *k*-means cluster function (Seber, 1984; Spath, 1985) from the MATLAB® statistics toolbox.

Added References:

*Seber, G. A. F.: Multivariate Observations, John Wiley & Sons, I., Hoboken, NJ, 1984.

**Spath, H.: Cluster Dissection and Analysis: Theory, FORTRAN Programs, Examples, Halsted Press, New York, 1985.

31444.4 d(i,C) is the average distance of the point i to the other points in the cluster C. The use of d(i;C) here is confusing, is it the same as d(xj ; mji) in equation 1? If not, it would be clearer to define b(i) in words only. If it is, then don't reuse i and rework the sentence for clarity.

Reply: They are different: d(xj,μj) is the squared Euclidean distance of a point to the centroid of the cluster. d(i,C) is the average distance of a point to the other points in the cluster. Sentence rephrased.

Changed to: where a(i) is the average distance of the point i to the other points in its own cluster A. b(i) is the minimal average distance of the point I to the points in the other cluster, over all clusters other than A (Eq. 2).

31444.6 This validation is sufficient for our analysis to indicate the ability of the algorithm to group similar data sets using the prescribed values. What validation is being referred to here? s(i) = 1, s(i) > x, or just the use of a silhouette value?

Reply:

The use of Silhouette to evaluate the clustering.

31444.9 Following cluster analysis, asphericity thresholds are selected based on cluster boundaries identified by the colour transition in Fig. 3. Is the red–blue transition automatically generated by the cluster analysis? Are the particle type boundaries given in the map in figure 9 the asphericity thresholds that are referred to here? Are the thresholds set by 100% coverage of the data points, 90%, two standard deviations, etc? The cluster analysis and map is the focus of this manuscript and yet the reader is left to guess at a number of relevant details.

Reply:

- Yes, the red–blue colours automatically generated and assigned by the algorithm to differentiate the clusters visually.
- No the asphericity thresholds are values derived from single cluster analysis. Fig.9 is collated from tens of experiments. The boxes in Fig.9 represent the space of measurements error and data points' distribution for single cluster as stated in the figure.
- Yes, all 100% of data points are used in the clustering analysis. Thresholds are selected according to colour boundaries and silhouette value above 0.9.
- The cluster analysis and the map is not the only focus of the paper. We also report new results for polarisation response observed for the viscous SOA and the derived transitions states.

Hope it makes things clearer; these answers have been incorporated into the manuscript.

31444.23 These diverse experiments produced ice habits that included needles, hexagonal plates, columns, bullets and dendrites; ice aggregates and spheroids were also detected (Fig. 4). See point 3 above for general comments on this section. Specifically, please comment on how representative the images from the 3V-CPI are to the particles sampled by the CASPOL at the same time?

Reply:

These instruments measure over different size ranges. The 3V-CPI images provide complimentary information regarding the variety of large particles and their habits resulting from the nucleation processes that result from the different experiments and support the observation as stated of ice production. While the 3V-CPI data acts as confirmation of the CASPOL detection of ice, we cannot rule out a size dependence of ice crystal habit. It should not therefore be assumed that the crystal habits shown by the 3V-CPI are the same as those giving rise to the observed polarisation effects. At the same time, there is no fundamental reason to assume the habits are different. These are in fact the first observations of ice habits in this particular chamber.

31445.15 ACPIM was able to replicate the observed particle phase transitions in the mixed phase runs, thereby validating the phase concentration plot (Fig. 2c). Define replicate. There seems to be some significant discrepancies between the model and data for times beyond 60 sec in figure 2c, ie modelled liquid concentration drops quickly to zero around 100 sec and modelled ice concentration remains constant for longer time scales.

Reply:

By replicating we refer to replication of the phase transition time series, decrease in water concentration and increase in ice concentration.

Some of the particles classified as aspherical could be super-cooled droplets with higher polarisation and this would explain the slight underestimation of the ice and overestimation of the water by the model. Later on, the model slightly overestimates the concentration since part of the spherical particle population measured could be sublimated ice at this point in the temperature cycle. These small discrepancies are important since CASPOL is generally able to classify only according to optical sphericity (31445.19: Ambiguous polarisation states of water, e.g., in super-cooled or frozen droplets, might be resolved by comparing ACPIM to CASPOL data and examining the mismatch).

31446.5 During these growth periods (Fig. 5), an increase in the CASPOL backscatter polarisation ratio was observed, while the Dpol/Fwd ratio did not change significantly, suggesting the change in size had less effect on the measurements than did the polarisation. The meaning of the final phrase of this sentence is unclear. Does this mean that as the particles grew the asymmetry increased faster than the optical equivalent size? If so it would be very interesting to see some supporting data from one of the other instruments or a previous work on the growth of such particles. In any case some clarification is required here. It may be useful to add a plot of the ratio onto a second y-axis of figure 5.

Reply:

Once particles grew into the CASPOL detectable size range their size did not increase much further (being concentrated in the lower size bins, with equivalent mean diameter ≤ 1 μm), while the

Dpol/Bck ratio changed very significantly as seen in the experimental runs shown in Fig.6. We do not refer to the rate of change here. Adding another y axis to Fig.5 for the whole growth period in CASPOL would be inaccurate due to coincidence effects as explained in the paragraph. In addition to counting and sizing artefacts, particle coincidence can result in erroneously high S-polarised measurements as a result of multiple scattering. For this reason Fig.6 was plotted for periods when the coincidence was negligible.

Comparison with the SIMONE is impossible since both instruments were measuring reliably in different periods; SIMONE needs higher concentrations of particles to provide a signal while the CASPOL particle by particle measurement generally operates best at lower concentrations. More detail on growth and depolarisation is discussed elsewhere [14].

31446.16 As concentrations decreased below the CASPOL operating threshold of 1300 cm−3 , a significantly lower particle polarisation (more optically spherical) state was detected by the CASPOL. "As concentrations decreased below the CASPOL operating threshold of 1300 cm-3. . . " makes it sound like the concentration is lower than the minimum detection threshold. A slight rewording is required, or even better, remove this as it has already been stated that only concentrations below 1300 cm-3 are considered in this analysis.

Changed to: A significantly lower particle polarisation (more optically spherical) state was detected by the CASPOL at this stage.

31446.21 The two clusters are overlaid for several experiments as shown in Fig. 6. How did cases with significant overlap of the clusters affect the classification map boundaries? Were such cases used for classification? As mentioned in 31444.6, was there a threshold silhouette value required for a dataset to be added to the classification map?

Reply:
For PBP data clustering there was no overlap (Fig.2). In case there is too much overlap- the data can't be clustered or get a low silhouette value. These cases were not used for classification. The threshold silhouette value will be noted in the manuscript.

31447.15 It is clear that classification of particles has wide reaching effects on our understanding of the atmosphere. This is an unfortunate choice of words as this sentence is anything but clear. Surely understanding precedes classification?

Reply: Will be removed.

31447.21 A plot of the total backscatter intensity as a function of the polarisation ratio for various types of dust clearly shows the difference in their signatures. A list of different classification mapping schemes is given and then the map used here is different to these. This is discussed as a major shortcoming of the manuscript in point 1 above however if nothing else the authors should justify their choice of classification space.

Reply:

We list recent methods for classification by light properties. Both methods for classification in remote and in situ are presented. These techniques are different. Our technique is very similar to the one used for insitu measurements. The difference in the nature of the experiments and the type of particles allowed clearer separation in this particular classification space. Nonetheless, a plot will be added for comparison in the exact classification space of Glen and Brooks.

31448.4 Further separation by size might be possible on the x axis. Mention is made of segregation by size which would be useful however it has not been done. Further information is required here.

Reply:

X axis Dpol/Fwd encompasses information about the particle size as was mentioned previously:

- Typical sizes for ice and water are presented in Fig.2 and discussed in comment 31442.21
- SOA growth periods shown in Fig. 5 (comment 31446.5 the Dpol/Fwd ratio did not change significantly, suggesting the change in size had small effect).

It is very difficult to completely separate the combination of features that can result in the observed net Dpol/Fwd ratio, particularly if some of them are subtle. But might be possible with additional information from other instruments.

31448.11 The classification of ice and water is limited by size. This is unclear, does it mean that the boundaries of the regions of liquid water and that of ice are based solely on the particle size? Rewording of sentence required.

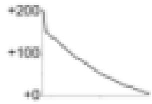
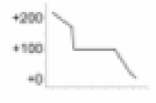
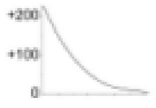
Changed to: Previous classifications of small ice and water by size had limited accuracy [15].

31449.8 However, the PSD measured by CASPOL and UHSAS during SOA growth corresponded well (Fig. 5). Figure 5 does not show a PSD.

Changed to: However, particle sizes measured by CASPOL and UHSAS during SOA growth corresponded well.

Table 1:

Table 1. Experimental parameters of the expansion runs presented in this paper. Excess pressure profile *x* axis is of the order of several minutes.

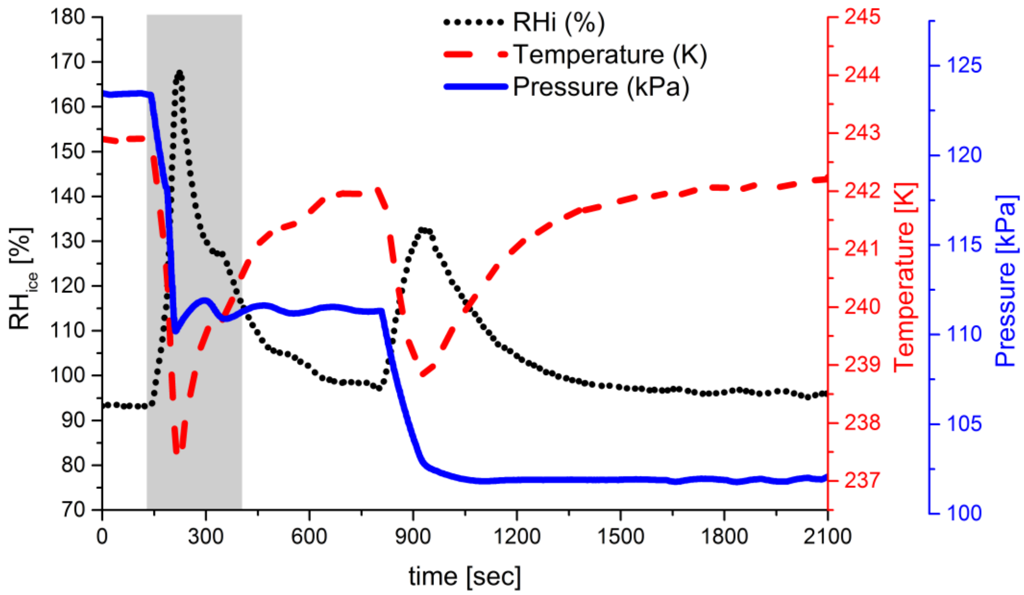
Run#	Seed type	Seed concentration [cm^{-3}]	Excess Pressure profile [mb]	$T_{initial}$ [°C]	RH_{ice}^{max} [%]
1248.13	Ammonium Sulphate	3000		+ 10	107
1291.16	Sulphuric Acid	75		−30	168, 135
1298.20	Sulphuric Acid	700		−50	148
1311.03	Sulphuric Acid	3260		−10	123
1471.34	Oxalic Acid	100		−20	165

31459

Why are there two values for RH for run 1291.16?

Reply: max RH reached, in a multi-step (here 2 steps) expansion (Fig.1).

Figure 1



It would be useful to have the x-axis of this plot presented in the same way (and scale?) as those in figure 2.

Reply: Fig.1 presents a full time scale of a multistep expansion produced in the chamber, and the behaviour of the physical variables. It is usually during the 2nd step (31444.17) that we were able to observe the larger particles (e.g. as shown by the 3VCPI images).

Fig.2 focuses on a specific step (<200sec) of the phase transition. The grey shaded background indicates the time period analysed in Fig.2, 3.

The x-axis will begin from 0.

Figure 2

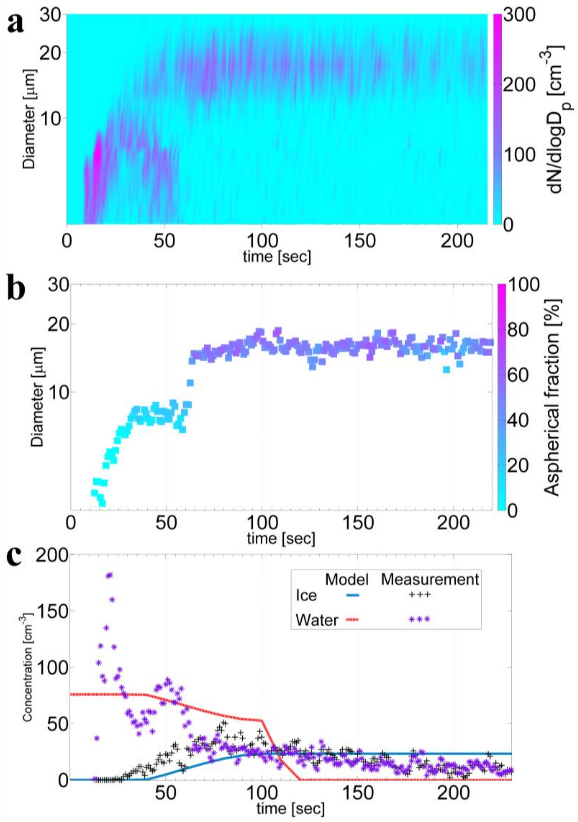


Figure 2. Mixed phase cloud, phase transition period (Run #1291.16). The uncertainty in sizing is in the order of the size bin width (Table S2). The error of the polarisation ratio and asperisity is approximately 20 %. (a) CASPOL particle size distribution, (b) CASPOL PBP aspherical fraction, (c) CASPOL measured water and ice concentrations derived from asphericity compared to ACPIM.

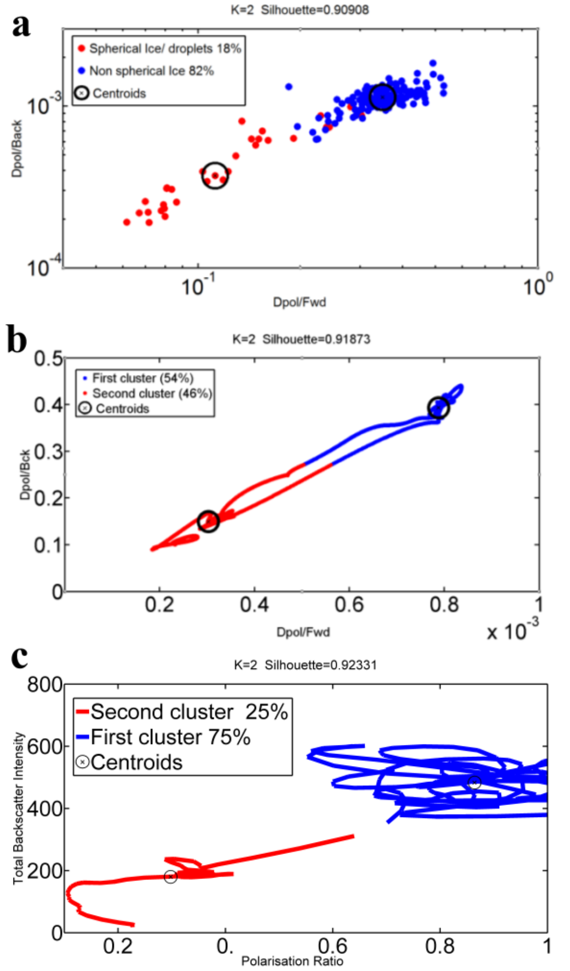
As mentioned previously, how is the diameter defined here? The colour maps are different to those used in the other concentration contour plots; these should be unified if possible. Remove the blue background from 2b, an increase in the size of the data points would also assist the reader. Add size uncertainty bars to 2b (with associated discussion of their derivation in the text).

Reply: The optical diameter is defined based on calibration and binning of the forward scattered intensity (comment 31442.8).

Addition of size uncertainty bars on all the data points in Fig.2b produces an unclear phase transition and overloads the plot, the uncertainty will be described in the caption.

- Colour maps unified
- Fig.2B background removed, size of data points increased

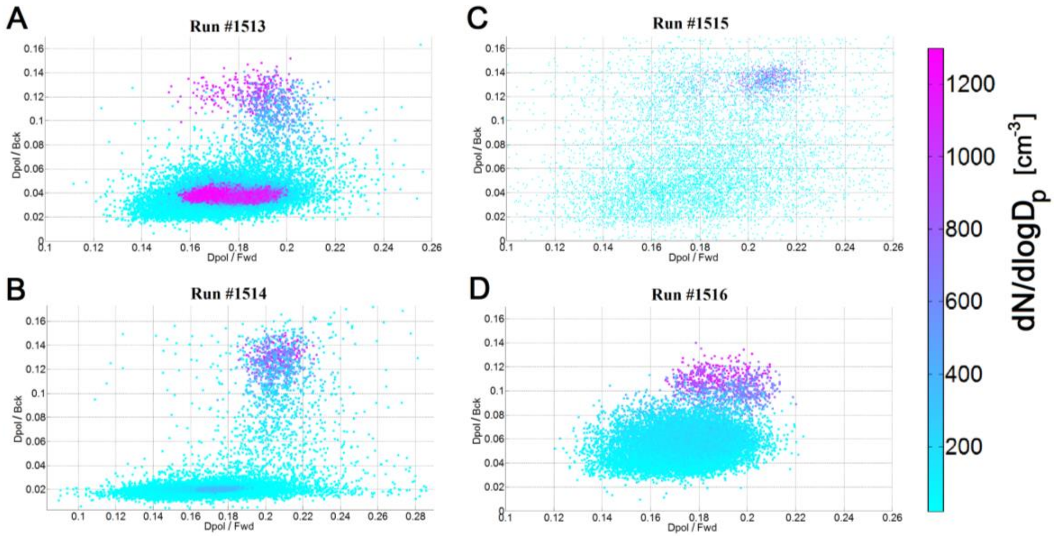
Figure 3



Refine size of plots and size of text to make full use of column width. The symbol for the cluster centroid in the caption is incorrect.

Changed: text size enlarged, instructions will be given to the publisher to make full use of column width, the symbol of the centroid in the caption will be changed to ⦿. A figure comparable to Glen and Brooks has been added.

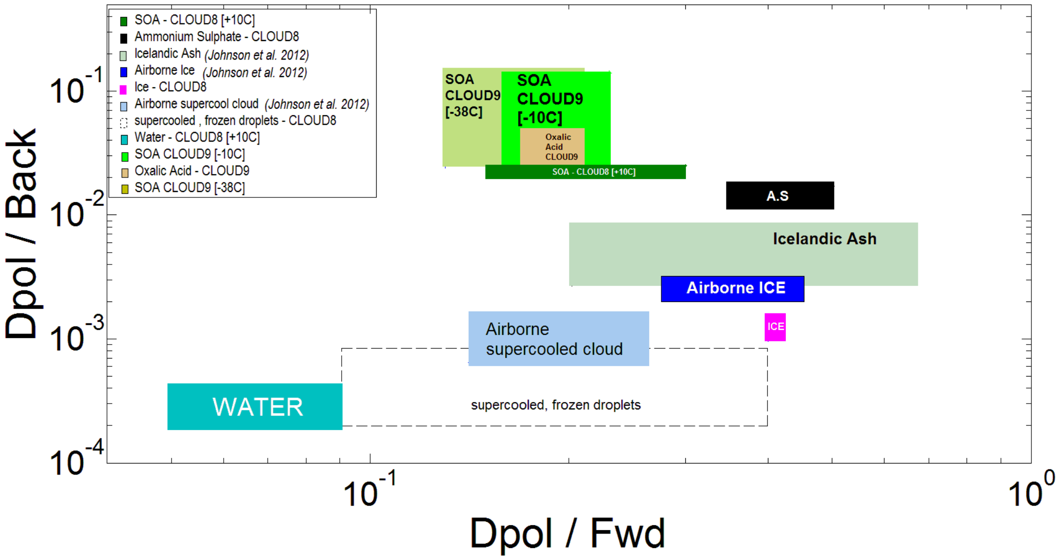
Figure 6



Refine size of plots and size of text to make full use of column width.

<u>Reply:</u> Instructions will be given to the publisher to make full use of column width

Figure 9

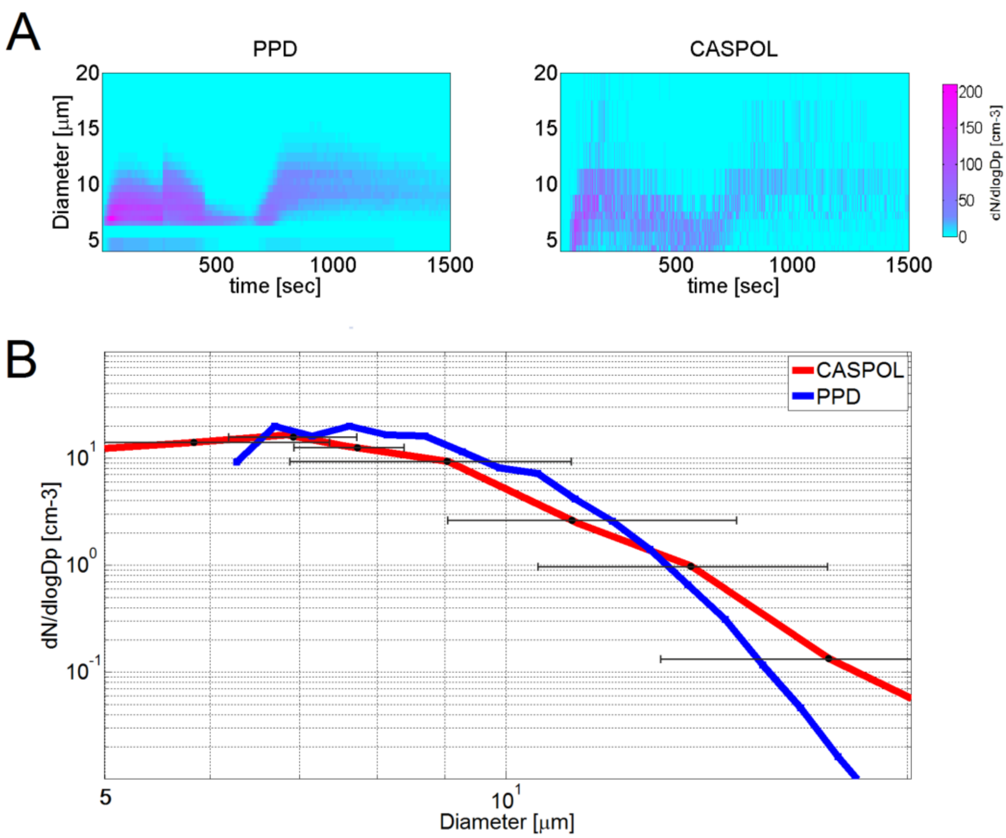


The labels are almost illegibly small. Several colours (especially the dark blues) are too similar.

Changed:

Colours changed, labels slightly bigger

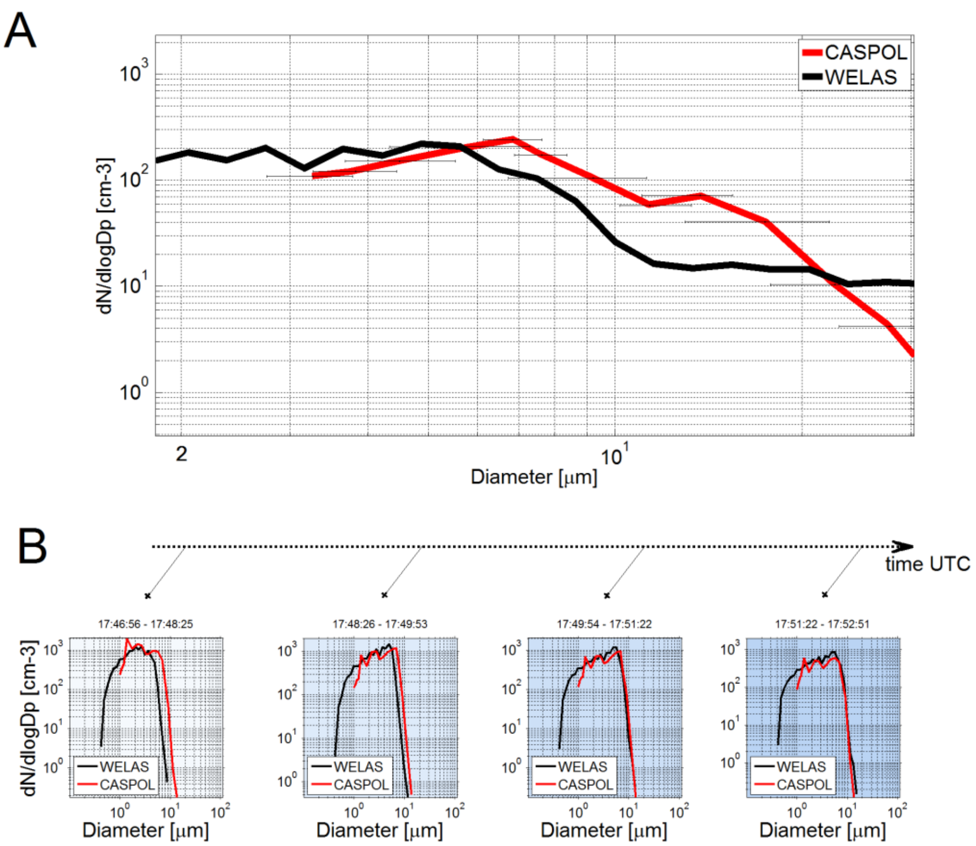
Figure S3



Add uncertainties to PSD in S3b. Improve axis labels so that there is more than a single number on the x-axis.

Changed.

Figure S4



Add uncertainties to PSD in S4a. Improve axis labels so that there is more than a single number on the x-axis.

<u>Changed.</u>

References

[1] Glen, A. and Brooks, S. D. “A new method for measuring optical scattering properties of atmospherically relevant dusts using the Cloud and Aerosol Spectrometer with Polarization (CASPOL)”, Atmos. Chem. Phys., 13, 1345–1356, doi:10.5194/acp-13-1345-2013, 2013.

[2] Lynch, D. K.: Cirrus, Oxford University Press, 2001.

[3] Meyer, J.: Ice crystal measurements with SIMONE and CAS DPOL, Ph.D. thesis, Julich 25 Forschungszentrum, Wuppertal, Germany, 140 pp., 2011.

[4] Baumgardner, D., Jonsson, H., Dawson, W., O'Connor, D., and Newton, R.: The cloud, aerosol and precipitation spectrometer: a new instrument for cloud investigations, Atmospheric Research, 59, 251-264, 10.1016/S0169-8095(01)00119-3, 2001.

[5] Krämer, M., Rolf, C., Luebke, A., Afchine, A., Spelten, N., Costa, A., Zöger, M., Smith, J., Herman, R., Buchholz, B., Ebert, V., Baumgardner, D., Borrmann, S., Klingebiel, M., and Avallone, L.: A microphysics guide to cirrus clouds – Part 1: Cirrus types, Atmos. Chem. Phys. Discuss., 15, 31537-31586, doi:10.5194/acpd-15-31537-2015, 2015.

[6] Lawson, R. P., Baker, B. A., Zmarzly, P., O’Connor, D., Mo, Q., Gayet, J.-F., and Shcherbakov, V.: Microphysical and Optical Properties of Atmospheric Ice Crystals at South Pole Station, Journal of Applied Meteorology and Climatology, 45, 1505-1524, 10.1175/JAM2421.1, 2006.

[7] Abdelmonem, A., Schnaiter, M., Amsler, P., Hesse, E., Meyer, J., and Leisner, T.: First correlated measurements of the shape and light scattering properties of cloud particles using the new Particle Habit Imaging and Polar Scattering (PHIPS) probe, Atmos. Meas. Tech., 4, 2125-2142, doi:10.5194/amt-4-2125-2011, 2011.

[8] Duplissy, J., Merikanto, J., Franchin, A., Tsagkogeorgas, G., Kangasluoma, J., Wimmer, D., Vuollekoski, H., Schobesberger, S., Lehtipalo, K., Flagan, R. C., Brus, D., Donahue, N. M., Vehkämäki, H., Almeida, J., Amorim, A., Barmet, P., Bianchi, F., Breitenlechner, M., Dunne, E. M., Guida, R., Henschel, H., Junninen, H., Kirkby, J., Kürten, A., Kupc, A., Määttänen, A., Makhmutov, V., Mathot, S., Nieminen, T., Onnela, A., Praplan, A. P., Riccobono, F., Rondo, L., Steiner, G., Tome, A., Walther, H., Baltensperger, U., Carslaw, K. S., Dommen, J., Hansel, A., Petäjä, T., Sipilä, M., Stratmann, F., Vrtala, A., Wagner, P. E., Worsnop, D. R., Curtius, J., and Kulmala, M.: Effect of ions on sulfuric acid-water binary particle formation II: Experimental data and comparison with QC-normalized classical nucleation theory, Journal of Geophysical Research: Atmospheres,, 10.1002/2015JD023539, 2015.

[9] Rosenberg, P. D., Dean, A. R., Williams, P. I., Dorsey, J. R., Minikin, A., Pickering, M. A., and Petzold, A. “Particle sizing calibration with refractive index correction for light scattering optical particle counters and impacts upon PCASP and CDP data collected during the Fennec campaign”, Atmos. Meas. Tech., 5, 1147–1163, doi:10.5194/amt-5-1147-2012, 2012.

[10] DMT Manual: CAPS operator manual, DOC-0066 Revision F,DMT, Boulder, Colorado, USA, 2011.

[11] Spiegel 2012 Spiegel, J. K., Zieger, P., Bukowiecki, N., Hammer, E., Weingartner, E., and Eugster, W.: Evaluating the capabilities and uncertainties of droplet measurements for the fog droplet spectrometer (FM-100), Atmos. Meas. Tech., 5, 2237-2260, 10.5194/amt-5-2237-2012, 2012.

[12] Baumgardner, D., Chepfer, H., Raga, G. B., and Kok, G. L.: The shapes of very small cirrus particles derived from in situ measurements, Geophysical Research Letters, 32, 10.1029/2004GL021300, 2005.

[13] Groß, S., Esselborn, M., Weinzierl, B., Wirth, M., Fix, A., and Petzold, A.: Aerosol classification by airborne high spectral resolution lidar observations, Atmos. Chem. Phys., 13, 2487-2505, 10.5194/acp-13-2487-2013, 2013.

[14] Järvinen, E., Ignatius, K., Nichman, L., Kristensen, T. B., Fuchs, C., Höppel, N., Corbin, J. C., Craven, J., Duplissy, J., Ehrhart, S., El Haddad, I., Frege, C., Gates, S. J., Gordon, H., Hoyle, C. R., Jokinen, T., Kallinger, P., Kirkby, J., Kiselev, A., Naumann, K.-H., Petäjä, T., Pinterich, T., Prevot, A. S. H., Saathoff, H., Schiebel, T., Sengupta, K., Simon, M., Tröstl, J., Virtanen, A., Vochezer, P., Vogt, S., Wagner, A. C., Wagner, R., Williamson, C., Winkler, P. M., Yan, C., Baltensperger, U., Donahue, N. M., Flagan, R. C., Gallagher, M., Hansel, A., Kulmala, M., Stratmann, F., Worsnop, D. R., Möhler, O., Leisner, T., and Schnaiter, M.: Observation of viscosity transition in α-pinene secondary organic aerosol, Atmos. Chem. Phys. Discuss., 15, 28575–28617, doi:10.5194/acpd-15-28575-2015, 2015.

[15] Heymsfield, A. J., Schmitt, C., Bansemer, A., van Zadelhoff, G.-J., McGill, M. J., Twohy, C., and Baumgardner, D.: Effective Radius of Ice Cloud Particle Populations Derived from Aircraft Probes, Journal of Atmospheric and Oceanic Technology, 23, 361-380, 10.1175/JTECH1857.1, 2006.

Anonymous Referee #2

Received and published: 4 January 2016

Main comments

The purpose of this paper remain somethat unclear for the reader. First of all, no explicit scientific goals are given in section 1. It is merely stated that "We prope this viscous that in this paper" (lines 21-22 on page 31437) and "In this paper we highlight results from. . ." (lines 12-14 on page 31438). Second, the title give a hint what might be the main purpose of this paper, yet the contents of the paper is not fully in line with the this title. Section 5 finally provides some concrete results obtained from this study. Maybe the authors could build on these main results, rather than giving the reader an impression of very general goal (title) or hardly no scientiric goals at all (introduction).

Reply:

31436.17 “However, single particle-by-particle analysis of the backscatter polarisation state is useful for particle discrimination as we shall show”. – Our goal here is to find a method to discriminate particles based on their physical properties.
31437.11 “In this study we examine Alpha-pinene... ; its derivatives in SOA are optically active materials… We probe this viscous state in this paper”. - The importance of viscosity is introduced in previous paragraph and the goal is described in this paragraph: Detection of the different states of alpha pinene SOA by light polarisation.
31.438.12 Another goal was to produce, detect and analyse small-ice fraction in mixed phase clouds which is still a challenging task. The results of these experiments are highlighted here.

I am not fully comfortable with the structure of the paper. The paper has a section "2. Methodology", yet the authors present methodological issues also in the introduction (introduction of the CLOUD chamber) and in the middle of results (short description of ACPIM model in section 3.2).

Reply:

- The CLOUD Chamber and Cloudy experiments section includes the history and overview of the CLOUD PROJECT, 31438.5-7 the principle of operation is mentioned briefly for the sake of comparison to other chambers in the world. Line 31438.8 will be moved to the Methodology section.
- The Methodology section includes the instrumentation, technical description of the facility and the CLOUD experiments.
- The description of ACPIM in section 3.2 is too brief to have a separate paragraph in the Methodology section; ACPIM’s structure is not in the scope of this paper and is cited for further reading.

The result are given in 4 separate subsections (sections 3.1-3-4). While these results are probably somehow connected with each other, such a connection is very difficult to catch when reading the paper. The authors should do a better job in tighing up these apparantly separate results.

Reply:

First we present a technique to discriminate between ice and water in mixed phase clouds (3.1). Then we present ice fraction model validation (3.2). Next we broaden the classification method to discriminate between the different states of SOA in the lower size range (3.3). This is finally broadened to include classification of various types of particles (3.4). The story plot will be modified.

Minor comments

1. I do not see the agreement between measurements and modeling in Fig. 2c as convincing as stated in the paper (lines 15-24 on page 31445).

Reply:

Please see reply to 1st referee in specific comment #4 and comment 31445.15

2. Lines 1-8 on page 31447: The authors use 3 times the word"“this" without clearly specifying what "this" is referring to (something mentioned before these two paragraphs).

Reply:

1st This 31447.1 refers to the preceding sentence: “As a result of this drying process and the dynamics of partitioning, CASPOL measures an increase in polarisation”.

2nd This 31447.4 refers to the preceding sentence: “Transition to an amorphous aerosol phase with high viscosity”.

3rd This 31447.7 refers to the preceding sentence: “ability of the CASPOL to identify very significant polarisation shifts in the aerosol scattering properties that are likely associated with changes in their physico-chemical properties”.

- Rephrased:

This increase could be explained as transition to an amorphous aerosol phase with high viscosity at RH ∼ 10 %, T = −30 to −38 ◦C, P = 102 kPa as suggested by the hysteresis plot of Koop et al. (2011). Our results cannot, however, be unambiguously ascribed to the viscosity transition based solely on the measurements here. We simply note the ability of the CASPOL to identify very significant polarisation shifts in the aerosol scattering properties that are likely associated with changes in their physico-chemical properties.

Additional support for this hypothesis comes from SMPS measurements. No particles were detected in the SMPS size range in the transition period;

3. I do not undertand the purpose of the first sentence of section 3.4

Reply: removed.

Phase Transition Observations and Discrimination of Small Cloud Particles by Light Polarisation in Expansion Chamber Experiments ~~Discrimination of Water, Ice and Aerosols by light polarisation in the CLOUD experiment~~

L. Nichman[1], C. Fuchs[2], E. Järvinen[3], K. Ignatius[4], N.F. Höppel[3], A. Dias[5], M. Heinritzi[6], M. Simon[6], J. Tröstl[2], A.C. Wagner[6], R. Wagner[7], C. Williamson[6,*], C. Yan[7], P. J. Connolly[1], J.R. Dorsey[1,8], J. Duplissy[9], S. Ehrhart[5], C. Frege[2], H. Gordon[5], C.R. Hoyle[2,10], T.B. Kristensen[4], G. Steiner[7,11,], N.M. Donahue[12], R. Flagan[13], M. W. Gallagher[1], J. Kirkby[5,6], O. Möhler[3], H. Saathoff[3], M. Schnaiter[3], F. Stratmann[4] and A. Tomé[14]**

[1] {School of Earth, Atmospheric and Environmental Sciences, University of Manchester, Manchester, M13 9PL, UK}

[2] {Laboratory of Atmospheric Chemistry, Paul Scherrer Institut, 5232 Villigen, Switzerland}

[3] {Karlsruhe Institute of Technology, Karlsruhe, Germany}

[4] {Institute for Tropospheric Research (TROPOS), 04318 Leipzig, Germany}

[5] {CERN, PH Department, Geneva, Switzerland}

[6] {Institute for Atmospheric and Environmental Sciences, Goethe-University Frankfurt, Frankfurt am Main, Germany}

[7] {Department of Physics, University of Helsinki, P.O.Box 64, 00014 University of Helsinki, Finland}

[8] {National Centre for Atmospheric Science, Manchester, UK}

[9] {Helsinki Institute of Physics, Finland}

[10] {Swiss Federal Institute for Forest Snow and Landscape Research (WSL)-Institute for Snow and Avalanche Research (SLF), Davos, Switzerland}

Comment [L.N1]: Technical corrections: The title is very vague and use of a generic acronym does not help
Reply:
The paper describes observations of ph change transition in SOA under differen environmental conditions. In addition t methods used were also applied to the discrimination of associated nucleated water and ice particles observed during the CLOUD experiments. As mentioned earlier the paper was submitted to the special issue "The CERN CLOUD experiment (ACPD/AMTD Inter-Journal SI)" and should be seen in this context. The special issue has additional papers with the CLOUD acronym which make t experiments more localized and define We are happy to emphasise the nature the phase transition nature of the work suggesting a change in title. One suggestion is: Phase Transition Observations and Discrimination of Sma Cloud Particles by Light Polarisation in Expansion Chamber Experiments

Comment [L.N2]: Referee 2, main comment 1:
The purpose of this paper remain somethat unclear for the reader. First c all, no explicit scientific goals are given section 1. It is merely stated that "We prope this viscous that in this paper" (li 21-22 on page 31437) and "In this pape we highlight results from. . ." (lines 12- on page 31438). Second, the title give a hint what might be the main purpose o this paper, yet the contents of the pape not fully in line with the this title. Sectio 5 finally provides some concrete results obtained from this study. Maybe the authors could build on these main resu rather than giving the reader an impression of very general goal (title) o hardly no scientiric goals at all (introduction).
Reply:
31436.17 "However, single particle-by-particle analysis of the backscatter polarisation state is useful for particle discrimination as we shall show". – Ou goal here is to find a method to discriminate particles based on their physical properties.
31437.11 "In this study we examine Alp pinene... ; its derivatives in SOA are optically active materials... We probe th viscous state in this paper". - The importance of viscosity is introduced in previous paragraph and the goal is described in this paragraph: Detection the different states of alpha pinene SO by light polarisation.
31.438.12 Another goal was to produce detect and analyse small-ice fraction in mixed phase clouds which is still a challenging task. The results of these experiments are highlighted here.

[11] {Ion Molecule Reactions & Environmental Physics Institute of Ion Physics and Applied Physics Leopold-Franzens University, Innsbruck, Austria}

[12] {Centre for Atmospheric Particle Studies, Carnegie Mellon University, Pittsburgh PA 15213 USA}

[13] {California Institute of Technology, Division of Chemistry and Chemical Engineering, Pasadena, California 91125, USA}

[14] {CENTRA-SIM, University of Lisbon and University of Beira Interior, 1749-016 Lisbon, Portugal}

[*] {now at Chemical Sciences Division NOAA Earth System Research Laboratory, Boulder, CO. Also at Cooperative Institute for Research in Environmental Sciences, University of Colorado Boulder, Boulder, Colorado, USA}

[**] {now at Aerosol Physics and Environmental Physics Faculty of Physics, University of Vienna, Wien, Austria}

Correspondence to: L. Nichman (Leonid.Nichman@manchester.ac.uk)

Abstract

Cloud microphysical processes involving the ice phase in tropospheric clouds are among the major uncertainties in cloud formation, weather and General Circulation Models (GCMs). The detection of aerosol particles, liquid droplets, and ice crystals, especially in the small cloud-particle size range below 50 µm, remains challenging in mixed phase, often unstable environments.~~The simultaneous detection of aerosol particles, liquid droplets, and ice crystals, especially in the small cloud-particle size range below 50 µm, remains challenging in mixed phase, often unstable ice-water phase environments.~~ The Cloud Aerosol Spectrometer with Polarisation (CASPOL) is an airborne instrument that has the ability to detect such small cloud particles and measure the variability in polarisation state of their backscattered light.~~The Cloud Aerosol Spectrometer with Polarisation (CASPOL) is an airborne instrument that has the ability to detect such small cloud particles and measure their effects on the backscatter polarisation state.~~ Here we operate the versatile Cosmics-Leaving-OUtdoor-Droplets (CLOUD) chamber facility at the European Organisation for Nuclear Research (CERN) to produce controlled mixed phase and other clouds by adiabatic expansions in an ultraclean environment, and use the CASPOL to discriminate between

Comment [L.N3]: 31435.4 This sentence mentions three times that the are both liquid water and ice. Remove t repetition.

Comment [L.N4]: 31435.8 The Clou Aerosol Spectrometer with Polarisation (CASPOL) is an airborne instrument tha has the ability to detect such small clou particles and measure their effects on t backscatter polarisation state. ". . . and measure their effects on the backscatte polarisation state." Rephrase the secon half of this sentence.

different aerosols, water and ice particles. In this paper, optical property measurements of mixed phase clouds and viscous Secondary Organic Aerosol (SOA) are presented. We report observations of significant liquid - viscous SOA particle polarisation transitions under dry conditions using CASPOL. Cluster analysis techniques were subsequently used to classify different types of particles according to their polarisation ratios during phase transition. A classification map is presented for water droplets, organic aerosol (e.g., SOA and oxalic acid), crystalline substances such as ammonium sulphate, and volcanic ash. Finally, we discuss the benefits and limitations of this classification approach for atmospherically relevant concentration and mixtures with respect to the CLOUD 8 - 9 campaigns and its potential contribution to Tropical Troposphere Layer (TTL) analysis.

1 Introduction

Scattering and absorption due to atmospheric particles can vary widely, leading to net radiative effect that either cool or warm the surface of the Earth. Ice crystals pose a potential challenge since their non-sphericity complicates the theoretical description of their single scattering properties (Macke et al., 1996). Several attempts have been made to model and simulate light interactions with different ice crystal habits, mixtures of crystal types, aggregates, and aerosols (Baran, 2013), but no single method can easily combine all size ranges and types of particles, making accurate, unified modelling nearly impossible.

Scattering analysis is complicated further in small ice crystals and Secondary Organic Aerosol (SOA).

~~Small ice~~ Ice crystals can have different major internal defects (e.g., stacking faults, chemical defects, molecular vacancies, interstitial molecules, ionized states, and orientation defects), surface roughness, and branching with various symmetries~~;–~~. These could be even more influential in small ice measurements. T~~t~~he optical effects of these defects depend strongly on the spatial orientation of the particle~~ in a flow~~. They can lead to systematic biases since particles with a high width to height aspect ratio can have a preferred orientation in chamber measurements (Abdelmonem et al., 2011). However, single particle-by-particle analysis of the backscatter polarisation state is useful for particle discrimination as we shall show.

Aerosol particles found in the lower confines of the atmosphere are typically internal or external mixtures of inorganic salts, refractory components such as mineral dusts and clays, and organic species; they also contain varying quantities of water. The hygroscopicity of organic particle is derived from their composition (Cziczo et al., 2004; Jimenez et al., 2009; Duplissy et al., 2011). Pure sulphate and internally mixed organic/sulphate aerosols will have

Comment [L.N5]: 31435.22 "Finally, we discuss the benefits and limitations of this classification approach for atmospherically relevant concentration and mixtures with respect to the CLOUD 8–9 campaigns and its potential contribution to Tropical Troposphere Layer (TTL) analysis". Since the relevanc of the particle categorisation to TTL dat limited to several sentences at the end the manuscript, mention of it in the abstract can probably be removed.
Reply:
The discussion of potential contributior TTL analysis has been extended (Specifi comment #5)

Comment [L.N6]: 31436.10 "Scattering analysis is complicated furt in small ice crystals and Secondary Orga Aerosol (SOA)". SOAs are not referred t in the previous or current paragraph so remove reference to them in this sentence.
Reply:
Sentence moved to the end of first paragraph in the Introduction section. T way the first paragraph states that scattering analysis is complicated furthe with ice and SOA and a detailed paragr with description of ice complication begins, following with a paragraph explaining the aerosol and SOA complications respectively.

Comment [L.N7]: 31436.11 "Small crystals can have different major intern defects (e.g., stacking faults, chemical defects, molecular vacancies, interstitia molecules, ionized states, and orientati defects), surface roughness, and branching with various symmetries"; These complicating artefacts are unlike to be limited to small ice crystals as sta (although the implications of such artefacts on measurements of the scattered light may indeed be more important) so rephrase these sentences

Comment [L.N8]: 31436.14 "The optical effects of these defects depend strongly on the spatial orientation of th particle in a flow". The optical effects o these defects depend on the orientatio of the particle relative to the incident radiation not the flow. If there is a preferential particle orientation in a flo relative to the instrument, and thus lase this then may lead to systematic measurement bias as mentioned. A reference would be good here along wi comments about any preferential orientation or lack there-of in the CLOU chamber.
Reply:
The angle between the flow direction a the laser beam in the instrument is constant therefore the angle to the lase correlated with the preferred orientatic in the laminar flow. Orientation effects classification were observed previously the AIDA chamber [7]. Due to the good

different water uptakes, and consequently different refractive indices. This may lead to mis-sizing by optical instruments if the composition is not taken into account (see Sect. 2.3).~~Organic components create hygroscopicity variation that affect the water uptake of the particles (Cziczo et al., 2004; Jimenez et al., 2009; Duplissy et al., 2011). Water uptake variation between pure sulphate and internally mixed organic/sulphate aerosols alter the particle refractive index and may lead to mis-sizing by optical instruments if the composition is not taken into account (see Sect. 2.3).~~ In addition to the familiar liquid and crystalline states, atmospheric aerosol may also exist in semi-solid and solid amorphous states (i.e., lacking an ordered, repeating structure) such as soft polymers, gels, or glasses (Mikhailov et al., 2009). The viscous SOA is expected to appear either in low relative humidity (RH), low temperature environments or both. A subset of these viscous particles, sometimes referred to as "glassy", (e.g. Koop et al., 2011) or amorphous, are thought to be important components in the atmosphere because of their low volatility, long lifetimes, and their potential impact on several competing processes which occur during updraft of an air parcel. These include: heterogeneous ice nucleation in the deposition mode onto the glassy solid aerosol surface; diffusion of water into the particle, inducing a gradual phase transition towards the liquid state; and immersion freezing during the transition between the states, (Berkemeier et al., 2014). Some terpenoids can affect these processes by formation of particles in the glassy state.

In this study we examine alpha-pinene, the most widely encountered terpenoid in nature (Noma and Asakawa, 2010); its derivatives in SOA are optically active materials (Wilberg et al., 2004; Cataldo et al., 2010) that induce a change in the polarisation state of the scattered radiation.~~its derivatives in SOA are optically active materials (Wilberg et al., 2004; Cataldo et al., 2010) that rotate the initial polarisation~~. The resulting change to the polarisation state of the back-scattered light from these aerosol particles can, therefore, be used to probe these effects. Small molecules such as water can soften the structural matrix (as water acts as a plasticizer) of SOA, thus reducing viscosity. As water molecules are removed by drying, the SOA viscosity increases. These highly viscous particles (Renbaum-Wolff et al., 2013) are, therefore, likely to be optically-anisotropic (having aspherical shape, branches, roughness, or variations in internal structure) that accentuate the polarisation shift of the incident beam in Cloud Aerosol Spectrometer with Polarisation (CASPOL). We probe this viscous state in this paper.

Comment [L.N9]: 31436.21 Organi components create hygroscopicity variation that affect the water uptake o the particles (Cziczo et al., 2004; Jimene et al., 2009; Duplissy et al., 2011). Wate uptake variation between pure sulphat and internally mixed organic/sulphate aerosols alter the particle refractive ind and may lead to mis-sizing by optical instruments if the composition is not taken into account (see Sect. 2.3). "Organic components create hygroscopicity variation. . . ", this sentence and the next should be rephrased for clarity.

Comment [L.N10]: 31437.13 its derivatives in SOA are optically active materials (Wilberg et al., 2004; Cataldo al., 2010) that rotate the initial polarisation. Particles do not rotate the initial polarisation, the polarisation of t incident light is unaffected by the presence of a particle. Rewrite this sentence.

1.1 The CLOUD Chamber and Cloudy Experiments

The Cosmics Leaving OUtdoor Droplets (CLOUD) chamber was designed to simulate different atmospheric conditions to reduce the uncertainties for cloud, weather and general circulation models (Chapter 7 of IPCC 2013; Boucher et al., 2013) and provide new data for the parametrisation and modelling of atmospheric processes. The first series of CLOUD experiments at the European Organisation for Nuclear Research (CERN) began in 2006 (Duplissy et al., 2010). For several years these experiments were mainly dedicated to aerosol nucleation and growth. Recently, additional experiments focusing on cloud formation have been performed at the CERN chamber. In this paper we focus particularly on results from this "Cloudy" series of experiments. This addition was driven by the importance of ice particles to the earth's radiation budget and feedback mechanisms~~Recently, additional experiment focusing on cloud formation (i.e. "Cloudy" experiments) has been added to allow ice nucleation to proceed. This was driven by the importance of ice particles to the earth's radiation budget and feedback mechanisms~~. The CLOUD chamber utilises the adiabatic expansion principle to generate super-cooled water and ice clouds, similar to other atmospheric cloud chambers (Möhler et al., 2006; Schnaiter, 2009; Tajiri et al., 2013). ~~Controlled supersaturated conditions are created in the chamber by allowing air to expand and cool at prescribed rates.~~ In order to investigate the microphysics of homogeneous ice nucleation in situ, two sets of Cloudy experiments were conducted during two campaigns at CERN in 2013 and 2014, hereafter referred to as CLOUD 8 and 9, respectively. In this paper we highlight results from some of the mixed-phase cloud measurements as well as new polarisation transition measurements for SOA from the photo-oxidation and ozonolysis of alpha-pinene.

2 Methodology

2.1 CLOUD chamber and instrumentation

The CLOUD chamber was designed in order to achieve excellent temperature stability and very low background aerosol and trace gas concentration levels in order to identify small changes in nucleation rates due to the influence of cosmic rays (Duplissy et al., 2010; Kirkby et al., 2011). An overview of the chamber and more detailed information is presented in the Supplement (Fig. S1). The CLOUD chamber was equipped with a range of instruments that can measure atmospheric constituents. Aerosol concentrations were measured by a combination of Scanning Mobility Particle Sizer (SMPS with TSI-type, custom-built DMA), and an Ultra High Sensitivity Aerosol Spectrometer (UHSAS, DMT) to determine potential

Comment [L.N11]: 31438.2 Recent additional experiment focusing on cloud formation (i.e. "Cloudy" experiments) h been added to allow ice nucleation to proceed. "Recently, additional experim focusing on. . . " This sentence doesn't make sense.

Comment [L.N12]: Referee 2, main comment 2:
I am not fully comfortable with the structure of the paper. The paper has a section "2. Methodology", yet the auth present methodological issues also in th introduction (introduction of the CLOUD chamber) and in the middle of results (short description of ACPIM model in section 3.2).
Reply:
The CLOUD Chamber and Cloudy experiments section includes the histor and overview of the CLOUD PROJECT, 31438.5-7 the principle of operation is mentioned briefly for the sake of comparison to other chambers in the world. Line 31438.8 will be moved to t Methodology section.
The Methodology section includes the instrumentation, technical description the facility and the CLOUD experiments The description of ACPIM in section 3.2 too brief to have a separate paragraph the Methodology section; ACPIM's structure is not in the scope of this pap and is cited for further reading.

Cloud Condensation Nuclei (CCN) concentrations. During CLOUD 8 and 9, instruments for the measurements of cloud droplets and ice particles were added. Cloud particle formation and evolution was measured using several optical spectrometers including a WELAS optical particle counter (WELAS Promo 2000, Palas GmbH) (Benz et al., 2005), a Particle Phase Discriminator (PPD-2K), (Kaye et al., 2008), a 3-View Cloud Particle Imager (3V-CPI, SPEC Inc.), (Lawson et al., 2003) and a Cloud Aerosol Spectrometer – with Polarisation (CASPOL, DMT) (Baumgardner et al., 2001, 2011; Glen and Brooks, 2013). The latter will be described in more detail in Sect. 2.3. An averaged path system, the Scattering Intensity Measurements for the Optical detection of icE – SIMONE-Junior (Schnaiter et al., 2012), was installed for bulk depolarisation measurements.~~An in situ system, the Scattering Intensity Measurements for the Optical detection of icE – SIMONE-Junior (Schnaiter et al., 2012), was installed for bulk depolarisation measurements.~~

The procedure for operation of the CLOUD facility as an expansion cloud chamber for ice nucleation studies along with full schematics are described in detail by Guida et al. (2012, 2013) and will only briefly be reviewed here. Controlled supersaturated conditions are created in the chamber by allowing air to expand and cool at prescribed rates.The basic operating procedure adopted for all the cloud microphysics experiments was as follows: the chamber was slowly pressurised to +220 mb relative to ambient pressure; CCN were then vaporised and injected through the gas lines; after the CCN had mixed throughout the chamber volume, a valve was opened allowing the air to expand with the pressure reached +5 mb. The pressure, temperature, and humidity traces for a typical expansion are shown in Fig. 1. Super-saturation occurs due to the pressure reduction and resultant temperature decrease.

Before the beginning of the expansion, RH with respect to liquid water of approximately 92–96 % was achieved. The total humidity in the chamber was measured by dew point mirror instruments (model MBW973 during CLOUD 9 and MBW373LX during CLOUD 8, both from "MBW calibration Ltd.") attached to a heated sampling line. Together with the in situ measured gas temperature (6 calibrated thermocouples, type K) these instruments provide the RH in the chamber and might overestimate it in the presence of clouds (assuming additional evaporation of cloud droplets in the heated sampling line). During CLOUD 9 a tuneable diode laser (TDL) hygrometer, comparable to the APicT instrument as described by Fahey et al. (2014), was used to measure the water vapour content with 1 Hz time resolution using a single optical path of 314 cm once across the middle plane of the CLOUD chamber. Thus, this instrument provides the RH also in the presence of clouds. Subtracting the water vapour

Comment [L.N13]: 31439.7 An in si system, the Scattering Intensity Measurements for the Optical detectio of icE – SIMONE-Junior (Schnaiter et al. 2012), was installed for bulk depolarisation measurements. The SIMONE instrument is described as in si which suggests that the other instrume are not. Is this because the other instruments operate with inlets? If so, a description of instrument inlets and the impact on sampling should be given (wi a reference if required). If not, then remove "in situ".
Reply:
Some instruments are sampling throug inlets. Chamber probes are described in detail elsewhere [8].In CASPOL, penetration efficiency of 10 µm particle was well above 90% in all campaigns. Instrumental setup is presented in Fig.S

content from the total water content results in the condensed (ice or liquid) water content. Sulphuric acid, ammonium sulphate, and oxalic acid particles were used to seed the chamber with CCN concentrations ranging from 0.5 to several thousand particles cm^{-3}. The CCN number concentrations determined the cloud droplet size, with higher CCN concentration producing higher concentrations of smaller ice particles in CLOUD.

Although the expansion is, ideally, adiabatic, heat is continuously transferred to the cooled air from the chamber walls, as the temperature control system is maintained at the pre-expansion temperature, resulting in eventual evaporation of the cloud. The cloud lifetime in the CLOUD experiments could be controlled (e.g., by fan speed or by number of steps in the expansion profile) from several minutes to greater than forty minutes when required (e.g., for ice evolution experiments).

2.2 Cloud Experiment Overview

A series of experiments was conducted to generate liquid clouds (Hoyle et al., 2015), mixed phase clouds, and pure ice clouds. Controlling stepwise the rate of expansion and the humidity flow into the chamber in the mixed phase experiments, it was possible to obtain water super saturation followed by ice super saturation, allowing CCN activation to form a cloud for a short period of several minutes. The adiabatic expansion experiments on which this paper focuses are summarised in Table 1, but results based on a much broader data base of several hundred CLOUD expansions will also be considered for the discussions.

Several additional experiments were conducted to examine any aerosol polarisation state changes arising from possible viscosity changes in response to RH variations, using CASPOL. A more detailed description of these experiments can be found in the accompanying paper by Järvinen et al. (2015). ~~A more detailed description of the latter can be found in the accompanying paper by Järvinen et al. (2015).~~

2.3 The ~~CAPS~~ CASPOL Instrument

The Cloud and Aerosol Spectrometer with Polarisation detection (CASPOL) is part of the Cloud Aerosol and Precipitation Spectrometer (CAPS). The first variant of the instrument was introduced in 1999 and was designed for airborne in situ cloud measurements (Baumgardner et al., 2001; Heymsfield, 2007), although it has subsequently been used for cloud chamber measurements (Krämer 2009). The version of CASPOL employed here has a linearly polarised laser to provide a collimated incident beam of light at a wavelength of 680 nm.

Comment [L.N14]: 31440.25 A mo[re] detailed description of the latter can be found in the accompanying paper by Järvinen et al. (2015). ". . . of the latter. " does not make sense here so the sentence needs rewriting.

Comment [L.N15]: 31441.1 The Cl[oud] and Aerosol Spectrometer with Polarisation detection (CASPOL) is part [of] the Cloud Aerosol and Precipitation Spectrometer (CAPS). Although mentioning the CAPS in the body of thi[s] section is sensible (if nothing else it allo[ws] a reader to find the instrument on the manufacturer's website which does not list CASPOL) including it in the title of th[e] section is just confusing. Rename this " CASPOL Instrument", "CASPOL Description", or something like that. In general this section needs to be split up into more than one paragraph and reordered for clarity (eg currently order forward scattering, backscattering, depolarisation, size and refractive index effects on forward scattering, then effe[cts] of qualifier. This does not make for eas[y] reading).

The first two detectors of the instrument detect the light scattered in the forward direction. The collection of the light cone is subtended by the angles 4 to 12°. The near forward angles are used for sizing because light is preferentially scattered in the forward direction from particles whose diameters are larger than the incident wavelength. The first detector in the forward direction is used as a qualifier; it has a rectangular optical mask that restricts scattered light from particles that are outside the centre of focus of the laser beam. Only particles within the optimal view volume are counted and characterized. All data are collected on a single particle basis, thus provide a measure of particle-by-particle variability and single particle optical properties. The particle's water equivalent optical diameter in the range 0.51 – 50 µm is determined from the forward scattering signal in the second detector using the standard Mie scattering assumptions, i.e., spherical geometry and isotropic refractive index.

The next pair of detectors measures the backscattered light with collection angles of 168 to 176°. The first backscattering detector is used for qualitative particle shape discrimination. The second detector has a polarised filter (90° to the polarisation of the incident light) to measure the change in polarisation of scattered light caused by asphericity (Baumgardner et al., 2011; Glen and Brooks, 2013) or birefringence. In this configuration, spherical particles produce little response in the perpendicular polarisation backscatter detector. Conversely, frozen water droplets and aspherical ice crystals will show much more distinct signals.

In order to eliminate aerosol particle interference in our cloud measurements, only contributions from a subset of larger particles above 3 µm were included. This threshold is based on work by Baumgardner et al. (2001) and Lance (2012) who selected a similar size range for cloud particle measurements. In the special case of SOA measurements, a subset of small particles (< 3 µm) detected in the lower gain stage, was considered.~~The Cloud and Aerosol Spectrometer with Polarisation detection (CASPOL) is part of the Cloud Aerosol and Precipitation Spectrometer (CAPS). The first variant of the instrument was introduced in 1999 and was designed for airborne in situ cloud measurements (Baumgardner et al., 2001; Heymsfield, 2007), although it has subsequently been used for cloud chamber measurements (Krämer 2009). The version of CASPOL employed here has a linearly polarised laser to provide a collimated incident beam of light at a wavelength of 680 nm. There are four detectors in the instrument, with collection angles of 4 to 12° for the forward detectors and 168 to 176° for the backward detectors. The near forward angles are used because most of the light scattered from a particle whose diameter is larger than the incident wavelength is in the forward direction. The backscattering signal is used for qualitative particle shape~~

Comment [m16]: Referee 1, specifi
comment 2:
In page 31441, line 10 it is written that most of the light from particles of inter are scattered in the forward direction. However, based on the ratios in figures 6, and 10, the total backscatter signal is greater than that in the forward directi Specifics of the parameters used to calculate the ratios are not addressed i the paper so I assume that they are son instrument voltage or count that do no directly represent the scattered irradiance. This makes it difficult for th with different but equivalent instrumer (or even updated versions of the same instrument) to utilise or reproduce thes results.
Reply:
The reported ratios in Fig.3,6,9 (there is Fig.10) are from two separate detector that have different conversion because different irradiance as the reviewer poi out. Some of these differences are described in Table S2, and elsewhere (e [3]), and could be used in equivalent versions of the instruments. The sampl volume of the CAS is defined with a pinhole aperture (or mask) and is used select only the most uniform and intens section of the laser beam [4], 31441.20 Once again, additional technical information could be more suitable for technical paper but is also described in cited instrument papers standards, for such instruments. Any inter-comparison different instruments should be advised by DMT.

Comment [L.N17]: 31441.27 This threshold is based on work by Baumgardner et al. (2001) and Lance (2012) who selected a similar size range for cloud particle measurements. The entire size range of the CASPOL is not given although various subranges or thresholds are mentioned throughout t manuscript. Add this information to thi section.
Reply: Added above.

Comment [L.N18]: 31441.9 There a four detectors in the instrument, with collection angles of 4 to 12◦ for the forward detectors and 168 to 176◦ for t backward detectors. It is obvious what meant, however angles are two dimensional; the instrument collects lig over solid angles subtended by the angl given.

Comment [L.N19]: 31441.9 There a four detectors in the instrument, with collection angles of 4 to 12◦ for the forward detectors and 168 to 176◦ for t backward detectors. It is obvious what meant, however angles are two dimensional; the instrument collects lig over solid angles subtended by the angl given.

discrimination. The CASPOL has an additional back-scatter detector with a polarised filter (90° to the polarisation of the incident light) to measure the change in polarisation of scattered light caused by aspherical particles (Baumgardner et al., 2011; Glen and Brooks, 2013). In this configuration, spherical particles produce little response in the perpendicular polarisation backscatter detector. Conversely, frozen water droplets and aspherical ice crystals will show much more distinct signals. The particle's water equivalent optical diameter is determined from the forward scattering signal using the standard Mie scattering assumptions, i.e., spherical geometry and isotropic refractive index. An additional detector in the forward direction is used as a qualifier; it has a rectangular optical mask that restricts scattered light from particles that are outside the centre of focus of the laser beam. Only particles within the optimal view volume are counted and characterized. All data are collected on a single particle basis, thus provide a measure of particle-by-particle variability and single particle optical properties. In order to eliminate aerosol particle interference in our cloud measurements, only contributions from a subset of larger particles above 3 µm were included. This threshold is based on work by Baumgardner et al. (2001) and Lance (2012) who selected a similar size range for cloud particle measurements. In the special case of SOA measurements, a subset of small particles (< 3 µm) detected in the lower gain stage, was considered.

Calibration

The CASPOL was calibrated using Polystyrene Latex Spheres (PSL), as described elsewhere, e.g., DMT Manual (2011), Meyer (2011), Rosenberg et al. (2012). Size calibration relates the amplitude of the instrument's response to particle scattering cross-sections. Using the Mie–Lorenz curve, the nominal size bin limits can then be defined (Table S2 in the Supplement) in terms of the diameter of water droplets having the same scattering cross-section, giving a reasonable estimate of particle size for liquid droplets and small spherical ice particles. Aspherical particles will be mis-sized with respect to spherical particles, subject to their cross-section as shown by Borrmann et al. (2000). In our instrument this error would normally be in the order of the size bin width. The uncertainty in the derived polarisation ratio is approximately 20% as described by Baumgardner et al., (2005).Size calibration of CASPOL, as described in Rosenberg et al. (2012), relates the amplitude of the instrument's response to particle scattering cross-sections. Using the Mie–Lorenz curve, the nominal size bin limits can then be defined in terms of the diameter of water droplets having the same scattering cross-section, giving a reasonable estimate of particle size for liquid droplets and small spherical ice particles. Aspherical particles will be mis-sized with respect to spherical particles, subject to their cross-section as shown by Borrmann et al. (2000). In our instrument the error would normally be in the order of the size bin width.

2.4 Data processing

2.4.1 Particle-by-Particle analysis

The polarisation ratio measured with the CASPOL instrument and reported in this paper is defined as the ratio of perpendicularly polarised backscatter intensity to total backscatter intensity and provides a measure of the combined phase, composition, and surface features of the particle. The polarisation ratio measured with the CASPOL instrument and reported in this paper is defined as the ratio of perpendicularly polarised backscatter intensity to total backscatter intensity and provides a measure of phase, composition, and surface features of the particle. This ratio differs from the depolarisation ratio that is measured using remote sensing techniques (Groß et al., 2013). The two ratios cannot be directly compared, requiring additional calibration for this purpose (Meyer, 2011). The ratio of perpendicularly polarised backscatter to forward scatter ($Dpol/Fwd$) indicates the contribution of particle size to the scattering. PBP measurements reveal the fraction of aspherical particles population (Fig. 2c) and its evolution. Here we employ cluster analysis on PBP data (Sect. 2.4.2) for phase discrimination and for data quality assurance. This method can also be used to classify highly polarising particles. Corrections to the forward, backward and the Dpol channels have been applied and summarized in Table S2 S3 in the Supplement.

2.4.2 Cluster analysis

Clustering or grouping of data by the similarity in one variable or a matrix of variables reveals the size of the population with similar properties and the number of the unique groups in the dataset, as well as the spread in each group. Clustering analysis is used here to discriminate and assign unique particle properties corresponding to different phases during the experiment (e.g., water, ice), primarily based on variations in the polarisation state of the scattered light (Fig. 3). Clustering analysis is used here to discriminate and assign unique particle properties corresponding to different phases during the experiment (e.g., water, ice), primarily based on polarisation differences (Fig. 3). Clustering approaches have been previously used for aerosol property classification, e.g., Omar et al. (2005), Robinson et al. (2013), Crawford et al. (2015). Here we use the *k*-means cluster function (Seber, 1984; Spath, 1985) from the MATLAB® statistics toolbox. Here we use the MatLab K means cluster

Comment [L.N20]: 31442.8 Aspher particles will be mis-sized with respect spherical particles, subject to their cros section as shown by Borrmann et al. (2000). Size of aspherical particles is use throughout the manuscript but only receives a very cursory two sentences here. It is unclear how such particles ar sized, as only Mie theory is discussed I assume that an equivalent optical diameter is used however it is still uncle what refractive index is used (particular in cases such as figure 2 where ice and water particle sizes are presented on th same axis). The final sentence needs

Comment [m21]: Referee 1, specifi comment 1:
There is a tendency by the authors to present results in a manner that makes them less useful to the wider communi One of the draws of using an instrumen like the CASPOL is for comparison with remote sensing community which does not have access to the forward scatteri information. For example, polarisation ratio is presented in a slightly different

Comment [L.N22]: 31442.15 The polarisation ratio measured with the CASPOL instrument and reported in this paper is defined as the ratio of perpendicularly polarised backscatter intensity to total backscatter intensity a provides a measure of phase, composition, and surface features of th particle. This is an unusual manner of expressing the degree of polarisation rotation in the scattered light. It would

Comment [L.N23]: 31442.20 The ra of perpendicularly polarised backscatte forward scatter (Dpol/Fwd) indicates th contribution of particle size to the scattering. Unless there is precedent, I'd recommend a change of symbol for the perpendicularly polarised backscatter signal. Dpol rolls of the tongue as depolarisation (ratio).
Reply:

Comment [L.N24]: 31442.21 PBP measurements reveal the fraction of aspherical particles population (Fig. 2c) and its evolution. This is not entirely obvious. For a spherical particle in the s range of interest, the forward scatterin signal will increase with size however spherical particles are somewhat irrelevant here. With aspherical particle the forward scattering may be non-uniform which makes this sweeping

Comment [L.N25]: 31443.8 Cluster analysis is used here to discriminate an assign unique particle properties corresponding to different phases durin the experiment (e.g., water, ice), prima based on polarisation differences (Fig. 3 ". . . based on polarisation differences. could cause confusion with a mathematical difference, use "variation or something similar.

~~function. First the number of clusters, k, is specified.~~ The algorithm then calculates the minimum total intra-cluster variance (Eq. 1)

$$\sum_{i=1}^{K} \sum_{x_j \in S_i} d(x_j, \mu_i) \qquad (1)$$

where S_i is the ith cluster ($i = 1, \ldots, K$), μ_i is the ith centroid of all the points x_j in cluster S_i, and d is the distance function (e.g., squared Euclidean). In this case the function is applied to a matrix of parameter vectors including polarisation, size, asphericity, concentration, inter-arrival-time, time, etc. This approach should, by itself, be sufficient for discriminating a simple mixture consisting of two discrete and well-separated phases as may be found in the water-ice particle population. In our aerosol-cloud nucleation experiments, an a-priori assumption of cluster number is challenging due to the variability of particles. Initial estimates of cluster numbers (1–7) were tested in sequential iterations. A silhouette index, $s(i)$, was then used to quantitatively assess the quality of clustering, This is a composite index reflecting the compactness and separation of clusters; a larger average silhouette index indicates a better overall quality of the clustering result (Chen et al., 2002). The silhouette value of a point is a measure of the similarity of points within a given cluster compared to these in other clusters; it is defined as

$$s(i) = \frac{b(i) - a(i)}{\max(a(i), b(i))} \qquad (2)$$

where $a(i)$ is the average distance of the point i to the other points in its own cluster A. ~~$d(i,C)$ is the average distance of the point i to the other points in the cluster C.~~ $b(i)$ ~~is the minimal $d(i,C)$ over all clusters other than A~~ $b(i)$ is the minimal average distance of the point i to the points in the other cluster, over all clusters other than A (Eq. 2). For the best possible fit, the silhouette index is, $s(i) = 1$. This validation is sufficient for our analysis to indicate the ability of the algorithm to group similar data sets using the prescribed values. Following cluster analysis, asphericity thresholds are selected based on cluster boundaries identified by the colour transition in Fig. 3 and silhouette values greater than 0.9.

3 Results

3.1 CASPOL Water-Ice measurements

As the temperature in the chamber decreases in the multistep expansions, liquid cloud starts to form when the RH exceeds water saturation (Fig. 1). Figure 2a shows the formation of a

Comment [L.N26]: 31443.11 Here use the MatLab K means cluster functio Use standard nomenclature (of the website); MATLAB (check journal standards to see if this requires a ®), k-Means, and cite the URL for the kmeans function.
Reply:
From a brief review of several ACP pape it looks like there are multiple variation of this nomenclature.

Comment [L.N27]: 31444.4 d(i,C) is the average distance of the point i to th other points in the cluster C. The use of d(i;C) here is confusing, is it the same a d(xj ; mji) in equation 1? If not, it would clearer to define b(i) in words only. If it then don't reuse i and rework the sentence for clarity.
Reply:
They are different: d(xj,μj) is the square Euclidean distance of a point to the centroid of the cluster. d(i,C) is the average distance of a point to the other points in the cluster. Sentence rephrase

Comment [L.N28]: 31444.6 This validation is sufficient for our analysis t indicate the ability of the algorithm to group similar data sets using the prescribed values. What validation is be referred to here? s(i) = 1, s(i) > x, or just the use of a silhouette value?
Reply:
The use of Silhouette to evaluate the clustering.

Comment [L.N29]: 31444.9 Followi cluster analysis, asphericity thresholds a selected based on cluster boundaries identified by the colour transition in Fig Is the red–blue transition automatically generated by the cluster analysis? Are t particle type boundaries given in the m in figure 9 the asphericity thresholds th are referred to here? Are the threshold set by 100% coverage of the data points 90%, two standard deviations, etc? The

Comment [L.N30]: Referee 2, main comment 3:
The result are given in 4 separate subsections (sections 3.1-3-4). While th results are probably somehow connect with each other, such a connection is ve difficult to catch when reading the pape The authors should do a better job in tighing up these apparantly separate results.
Reply:

Comment [m31]: Referee 1, specifi comment 3:
The discrimination between liquid wate and ice with polarised light has a long history so in addition to this, I was hopi to see the identification or classification different ice habits with this instrumen the chamber. At the end of section 3.1 there is a glimpse of this possibility wit list of different habits formed in the chamber along with the 3V-CPI images

mixed phase cloud as a function of time. Droplets formed at sub-zero temperatures are super-cooled and some of them freeze. During the stabilisation period, when pressure remains constant, some of the super-cooled droplets evaporate as the walls reheat the chamber. During the second step of the expansion, the ice grows further. The rapid growth of ice particles depletes the available water vapour, causing the remaining liquid droplets to evaporate by the Bergeron–Findeisen mechanism. The aspherical fraction (Fig. 2b), and the concentrations of water and ice (Fig. 2c) were calculated from the PBP cluster analysis for each of these conditions during the run. Images of some typical ice particles (diameter < 150 μm) from the Cloudy experiments were captured by the 3VCPI. These diverse experiments produced ice habits that included needles, hexagonal plates, columns, bullets and dendrites; ice aggregates and spheroids were also detected (Fig. 4). These habits scatter the light differently. However, CASPOL data were in good agreement with ice measurements by the PPD, small water droplets measured with WELAS (Figs. ~~S3~~ S4 and ~~S4~~ S5 in the Supplement).

3.2 ACPIM modelling

Validation of ice formation was done by modelling. A modelling tool used in this analysis is the Aerosol–Cloud–Precipitation Interaction Model (ACPIM), which has been developed at the University of Manchester in collaboration with the Karlsruhe Institute of Technology (Connolly et al., 2009). Temperature time series were plotted using the initial experimental conditions (e.g., chamber temperature, pressure, RH, and CCN concentration) in the model. Subsequent fitting of the simulated temperature drop to chamber data enabled us to find the rate at which the chamber reheats after expansion (0.007 s^{-1}) for the runs specified in Table 1. This heat exchange coefficient is in a good agreement with the results found by Dias et al. (2015). It quantifies how effectively heat is transferred from the chamber walls and mixed throughout the gas in this chamber.

ACPIM was able to replicate the observed particle phase transitions in the mixed phase runs, thereby validating the phase concentration plot (Fig. 2c). Phase concentration deviations at the beginning of the expansion were probably caused by inhomogeneity in the chamber due to incomplete mixing, or by variations in the expansion rate. Ambiguous polarisation states of water, e.g., in super-cooled or frozen droplets, might be resolved by comparing ACPIM to CASPOL data and examining the mismatch. This simulation of the experiment makes it possible to predict phase concentrations and sizes, supporting the planning of future experiments and validation of the theories behind the model.

Comment [L.N32]: 31444.23 These diverse experiments produced ice habit that included needles, hexagonal plates columns, bullets and dendrites; ice aggregates and spheroids were also detected (Fig. 4). See point 3 above for general comments on this section. Specifically, please comment on how representative the images from the 3V- are to the particles sampled by the CASPOL at the same time?
Reply:
These instruments measure over differ size ranges. The 3V-CPI images provide t complimentary information regarding t variety of large particles and their habit resulting from the nucleation processes that result from the different experime and support the observation as stated c ice production. While the 3V-CPI data a as confirmation of the CASPOL detectio of ice, we cannot rule out a size dependence of ice crystal habit. It shou not therefore be assumed that the crys habits shown by the 3V-CPI are the sam as those giving rise to the observed

Comment [m33]: Referee 1, specifi comment 4:
Section 3.2 on the ACPIM modelling do not seem to add appreciably to this manuscript compared to a comment or the chamber wall heating and appropri citation towards the end of section 2.1. See point 31445.15 below.
Reply:
The ACPIM model was used to plan the experimental conditions prior to the actual experiments and to subsequentl compare with the environmental conditions recorded. Therefore the comparison of model and measuremen is essential to indicate any discrepancie current understanding of both the

Comment [L.N34]: Referee 2, mino comment 1:
I do not see the agreement between measurements and modeling in Fig. 2c convincing as stated in the paper (lines 24 on page 31445).
Reply:
Please see reply to 1st referee in specifi comment #4 and comment 31445.15

Comment [L.N35]: 31445.15 ACPIM was able to replicate the observed part phase transitions in the mixed phase ru thereby validating the phase concentration plot (Fig. 2c). Define replicate. There seems to be some significant discrepancies between the model and data for times beyond 60 se figure 2c, ie modelled liquid concentrat drops quickly to zero around 100 sec ar modelled ice concentration remains constant for longer time scales.
Reply:
By replicating we refer to replication of the phase transition time series, decrea in water concentration and increase in i concentration.

3.3 Viscous SOA measurements

The validated discrimination method used in water-ice phase transition analysis was subsequently applied to investigate SOA phase transition. The viscous SOA growth experiments reported here were achieved using a controlled, constant flow of precursor gases and ozone into the chamber at constant, near-ambient pressure, dry conditions, and constant temperatures, as shown in Table 2 (for details see Järvinen et al., 2015). We observe a growth in particle diameter from tens of nanometres to more than 1 μm size particles. During these growth periods (Fig. 5), an increase in the CASPOL backscatter polarisation ratio was observed, while the ***Dpol/Fwd*** ratio did not change significantly, suggesting the change in size had less effect on the measurements than did the polarisation. A large part of the experiment produced extreme particle concentrations above the recommended CASPOL concentration limit of 1300 cm^{-3}, where significant coincidence errors would be likely to occur (D. Baumgardner, personal communication, 2015). Therefore, we limit our discussion to conditions in which growth to sizes larger than 0.56 μm in diameter, and concentrations below 1300 cm^{-3} occur (for details see Sect. 4). After the growth, RH was increased up to 80% in each experiment in order to observe the phase transitions using optical depolarisation measurements made with the SIMONE instrument (Järvinen et al., 2015). Several repetitions of these growth experiments followed by humidification and phase transition were conducted. The subsequent glass transition formed liquid particles at the end of each experiment. A significantly lower particle polarisation (more optically spherical) state was detected by the CASPOL at this stage~~As concentrations decreased below the CASPOL operating threshold of 1300 cm^{-3}, a significantly lower particle polarisation (more optically spherical) state was detected by the CASPOL~~. As a consequence, we observed the presence of two distinct polarisation clusters during the growth where highly viscous SOA is expected and after the phase transition where we expect to see liquid particles. The two clusters are overlaid for several experiments as shown in Fig. 6.

While cooling the chamber and reducing the RH (Run #1515.16) (Fig. 7), the larger optically semi-spherical particles started to dry. Oxidized α-pinene SOA compounds generally have added functional groups (oxygen containing substituents), high polarity, and, thus, lower vapour pressure (Pandis et al., 1992) than water. As a result of this drying process and the dynamics of partitioning, CASPOL measures an increase in polarisation. The detailed dynamics of partitioning in SOA from alpha-pinene ozonolysis is described in Donahue et al. (2014).

Comment [L.N36]: 31446.5 During these growth periods (Fig. 5), an increas in the CASPOL backscatter polarisation ratio was observed, while the Dpol/Fwd ratio did not change significantly, suggesting the change in size had less effect on the measurements than did th polarisation. The meaning of the final phrase of this sentence is unclear. Does this mean that as the particles grew the asymmetry increased faster than the optical equivalent size? If so it would be very interesting to see some supporting data from one of the other instruments a previous work on the growth of such particles. In any case some clarification required here. It may be useful to add a plot of the ratio onto a second y-axis of figure 5.
Reply:
Once particles grew into the CASPOL detectable size range their size did not increase much further (being concentrated in the lower size bins, wit equivalent mean diameter ≤1 μm), whi the Dpol/Bck ratio changed very significantly as seen in the experimenta runs shown in Fig.6. We do not refer to the rate of change here. Adding anothe axis to Fig.5 for the whole growth perio in CASPOL would be inaccurate due to coincidence effects as explained in the paragraph. In addition to counting and sizing artefacts, particle coincidence ca result in erroneously high S-polarised measurements as a result of multiple scattering. For this reason Fig.6 was

Comment [L.N37]: 31446.16 As concentrations decreased below the CASPOL operating threshold of 1300 cm , a significantly lower particle polarisati (more optically spherical) state was detected by the CASPOL. "As concentrations decreased below the CASPOL operating threshold of 1300 cm . . " makes it sound like the concentrati is lower than the minimum detection threshold. A slight rewording is require or even better, remove this as it has already been stated that only concentrations below 1300 cm-3 are considered in this analysis.

Comment [L.N38]: 31446.21 The tw clusters are overlaid for several experiments as shown in Fig. 6. How di cases with significant overlap of the clusters affect the classification map boundaries? Were such cases used for classification? As mentioned in 31444.6 was there a threshold silhouette value required for a dataset to be added to th classification map?
Reply:
For PBP data clustering there was no overlap (Fig.2). In case there is too muc overlap- the data can't be clustered or a low silhouette value. These cases wer not used for classification. The thresho silhouette value will be noted in the manuscript.

This increase could be explained as transition to an amorphous aerosol phase with high viscosity at RH ~ 10 %, T = −30 to −38°C, P = 102 kPa as suggested by the hysteresis plot of Koop et al. (2011). Our results cannot, however, be unambiguously ascribed to the viscosity transition based solely on the measurements here. We simply note the ability of the CASPOL to identify very significant polarisation shifts in the aerosol scattering properties that are likely associated with changes in their physico-chemical properties.

Additional support for this hypothesis comes from SMPS measurements. No particles were detected in the SMPS size range in the transition period;~~This could be explained as transition to an amorphous aerosol phase with high viscosity at RH ~ 10 %, T = -30 to -38°C, P = 102 kPa as suggested by the hysteresis plot of Koop et al. (2011). Our results cannot, however, be unambiguously ascribed to this based solely on the measurements here. We simply note the ability of the CASPOL to identify very significant polarisation shifts in the aerosol scattering properties that are likely associated with changes in their physico-chemical properties.~~

~~Additional support for this hypothesis comes from SMPS measurements. No particles were detected in the SMPS size range in this period;~~ the upper cut-off of the measurement was about 400 nm. Small decay of the averaged diameter is observed in CASPOL (Fig. 8). These data indicate a wet to dry transformation of essentially large particles. This reversed transition of the viscosity is then followed by much slower partitioning or dissociation within these particles, and a decrease in their concentration and sizes due to constantly decreasing RH.

3.4 Particle classification maps

~~It is clear that classification of particles has wide reaching effects on our understanding of the atmosphere.~~ In order to map the whole range of atmospheric processes under future emissions scenarios, it will be necessary to identify the particles. A new strategy to categorize dust groupings was developed by Glen and Brooks (2013, 2014) whereby optical scattering signatures from CASPOL measurements were used to develop a set of threshold rules based on polarisation ratios. These rules can be used to classify types of dust sampled in the laboratory and during field campaigns. A plot of the total backscatter intensity as a function of the polarisation ratio for various types of dust clearly shows the difference in their signatures. Similar techniques for classifying aerosols are already in use by the LIght Detection And Ranging (LIDAR) community (Burton et al., 2012; Petzold et al., 2010). To explore the feasibility of using the signature method in CLOUD, we have collated polarisation ratio ranges of many particles measured in the CLOUD 8 and 9 campaigns. Here

Formatted: Space After: 10 pt, Adjust space between Latin and Asia text, Adjust space between Asian te and numbers

Comment [L.N39]: Referee 2, mino comment 2:
Lines 1-8 on page 31447: The authors u 3 times the word""this" without clearly specifying what "this" is referring to (something mentioned before these tw paragraphs).
Reply:
1st This 31447.1 refers to the preceding sentence: "As a result of this drying process and the dynamics of partitionin CASPOL measures an increase in polarisation".
2nd This 31447.4 refers to the preceding sentence: "Transition to an amorphous aerosol phase with high viscosity".
3rd This 31447.7 refers to the preceding sentence: "ability of the CASPOL to identify very significant polarisation shi in the aerosol scattering properties tha are likely associated with changes in th physico-chemical properties".

Comment [L.N40]: 31447.15 It is cl that classification of particles has wide reaching effects on our understanding o the atmosphere. This is an unfortunate choice of words as this sentence is anything but clear. Surely understandin precedes classification?

Referee 2, minor comment 3:
I do not undertand the purpose of the f sentence of section 3.4

Comment [L.N41]: 31447.15 It is cl that classification of particles has wide reaching effects on our understanding o the atmosphere. This is an unfortunate choice of words as this sentence is anything but clear. Surely understandin precedes classification?
Reply: Will be removed.

Comment [L.N42]: 31447.21 A plot the total backscatter intensity as a function of the polarisation ratio for various types of dust clearly shows the difference in their signatures. A list of different classification mapping scheme given and then the map used here is different to these. This is discussed as a major shortcoming of the manuscript ir point 1 above however if nothing else t authors should justify their choice of classification space.
Reply:
We list recent methods for classification by light properties. Both methods for classification in remote and in situ are presented. These techniques are different. Our technique is very similar the one used for insitu measurements. The difference in the nature of the experiments and the type of particles allowed clearer separation in this particular classification space. Nonetheless, a plot will be added for

we present the polarisation map (Fig. 9) combining the CLOUD campaign measurements with those obtained from aircraft flights over the North sea (Johnson et al., 2012) using the same CASPOL instrument. This map makes it possible to predict the coordinates of other potential organic compounds in the upper area. Salts, ash, and ice are in the mid-range of the $Dpol/Bck$ ratio; spherical liquids are at the bottom. Further separation by size might be possible on the x axis. In comparison between SIMONE and CASPOL for SOA data points from CLOUD, we can see on the map that SOA – CLOUD 8 (+10°C) data points have lower polarisation ratio compared to other organic aerosols. This measurement implies lower viscosity and could explain the non-existent phase transition in SIMONE depolarisation measurements for this experiment. More experimental data is needed to fill the space for other particles, temperatures and RH.

Classification of small ice and water by size characteristics has limited accuracy (Heymsfield et al., 2006).~~The classification of ice and water is limited by size~~. As explained earlier CASPOL can ~~only~~ differentiate between the asphericities of the particles. The ice presented on this map is aspherical. Slight changes in the polarisation state of droplets can also be observed as the droplets cool and a crystalline pattern emerges. This discrimination technique could be used in chamber measurements with mixtures of CCN and Ice Nuclei (IN) and with some limitations could be applied in explicit atmospheric measurements albeit with higher uncertainty due to potentially significant overlap in polarisation responses, particularly in real environment with high diversity of particles.

4 Discussion

The results presented in this paper (Figs. 2, 5 and S4, S5 in the Supplement) illustrate the ability of the CASPOL instrument to provide reliable Particle Size Distribution (PSD) in expansion chamber campaigns, and to classify atmospheric particles of different phases, viscosities, shapes, and sizes. The polarisation ratio was combined with the PBP clustering technique to highlight the time resolved aspherical fraction evolution.

Despite the known limitations and uncertainties in these measurements, e.g., particle sedimentation (Chapter 6 in Kulkarni, 2011), electronic “ringing”, and leakage currents (Kramer, 2002), these did not affect the filtered results (Figs. 3b,3c) shown here. Another uncertainty is contributed by the extremely high aerosol concentrations ~ 40 000 cm^{-3} (with unresolvable interarrival- times between successive particle). These concentrations may not be atmospherically relevant; their role here was solely to grow the larger SOA particles (>

Comment [L.N43]: 31448.4 Furthe separation by size might be possible on the x axis. Mention is made of segregat by size which would be useful however has not been done. Further information required here.
Reply:
X axis Dpol/Fwd encompasses informat about the particle size as was mentione previously:
- Typical sizes for ice and water are presented in Fig.2 and discussed in comment 31442.21
- SOA growth periods shown in Fig. 5 (comment 31446.5 the Dpol/Fwd rat did not change significantly, suggesti the change in size had small effect).

It is very difficult to completely separat the combination of features that can result in the observed net Dpol/Fwd rat particularly if some of them are subtle. But might be possible with additional information from other instruments.

Comment [L.N44]: 31448.11 The classification of ice and water is limited size. This is unclear, does it mean that t boundaries of the regions of liquid wate and that of ice are based solely on the particle size? Rewording of sentence required.

Comment [L.N45]: Referee 1, Spec comment 5: The Discussion in section 4 disjointed and very difficult to understa Please break this into separate paragra of related material.
Amended

500 nm). This was required to allow the optical detection of particles during growth and liquefaction.

In addition to concentration issues, a derivation of equivalent diameters from dry viscous aerosol particles may be challenging since it has been argued that spherical aerosols can be considered as purely a "figment of the imagination" (Baran et al., 2013). However, particle sizes measured by CASPOL and UHSAS during SOA growth corresponded well. The predicted SOA behaviour (Koop et al., 2011) and the measured slow increase of polarisation may suggest a change in the viscosity of these particles. The polarisation transitions observed were both clear and repeatable which gives confidence in our ability to identify the hypothesised transitions and to place these observations on the general polarisation map for classification in a comparative particle analysis.

Comment [L.N46]: 31449.8 Howev the PSD measured by CASPOL and UHS/ during SOA growth corresponded well (Fig. 5). Figure 5 does not show a PSD.

changed

The general classification map presented here demonstrates a good agreement between chamber and airborne measurements (Fig. 9). Although super-cooled droplets, ice and other particle polarisation footprints seem to be quite distinct, it is clear that further spatial growth and branching of ice could lead to a significant increase in polarisation and possibly significant overlapping of different species. One of the aims of future studies would be to test aggregation and branching impacts on CASPOL signals. Slightly higher polarisation of the airborne super-cooled droplets and ice might be the result of aerosol ageing. Processes such as aerosol ageing will influence subsequent phase separation processes within the droplet but are difficult to reproduce in a chamber.

In the real atmosphere, the particles are more complex; contain additional polarising constituents and have more branching. Froyd et al. (2010) report the coexistence of mixtures of partially or fully neutralised sulphate with organic material, nucleated ice crystals, dry ammonium sulphate, and glassy particles in the Tropical Troposphere Layer (TTL). Ice residuals were also similar in size to unfrozen aerosol. Lawson et al. (2008) suggests a thorough investigation of nucleation and growth mechanisms of ice particles in TTL at low temperatures is needed, particularly in the presence of sulphates mixed with organics and very high relative humidity. This might be difficult due to increasing anthropogenic SO_2 emissions which may increase the formation of sulphuric acid aerosols and thus small ice crystals in the TTL (Notholt et al., 2005). The increase in small ice concentration in presence of aerosols may complicate ice content measurements even further. The classification map presented here represents one approach to facilitate future CASPOL-PBP data analysis of the

TTL and deep convective outflow regions. It could also be useful for particles like ammonium sulphate that often reach high altitudes through the seasonal biomass burning processes and initiate ice nucleation. Using a method such as the classification map presented here to discriminate between different kinds of atmospheric particles (e.g., ice crystals, ammonium sulphate, volcanic ash, SOA) will allow better insight for atmospheric transport and chemical processes.

5 Conclusions

The CLOUD 8–9 campaigns at the CERN facility, introduced a new capability of this facility for cloud particle measurements (Cloudy). In this paper the first CASPOL Cloudy measurements of mixed phase and ice clouds are presented. We discuss the advantages of particle by particle analysis of the polarisation. Single-particle polarisation was used here to discriminate water, ice, SOA, and other atmospheric particles. The capability to detect viscous oxidized alpha-pinene with the CASPOL is reported for the first time.

We present observation of reversed transition from liquid to viscous based on CASPOL, SMPS measurements, and SOA modelling. In our experiments, the SOA viscous to liquid transition is shown to be a reversible process. This result contributes to our understanding of viscous SOA appearance in the atmosphere, ageing and potentially to the solar radiation budget calculations.

Classification using the clustering technique produced a classification map that can contribute to future chamber and, possibly, atmospheric measurements of small particles with CASPOL in a heterogeneous environment. Small ice particles formed during different stages of the cloud still pose a great challenge for the optical instruments. Future efforts will focus on classification of additional cloud particles using CASPOL.

Acknowledgements. We would like to thank CERN for supporting CLOUD with important technical and financial resources, and for providing a particle beam from the CERN Proton Synchrotron. We express great appreciation for the CLOUD collaboration and the volunteers for the night shifts. We would also like to thank Darrel Baumgardner for CASPOL data filtering advice and review of the manuscript. T. B. Kristensen gratefully acknowledges funding from the German Federal Ministry of Education and Research (BMBF) through the CLOUD12 project. This research has received funding from the EC Seventh Framework Programme (Marie Curie Initial Training Network “CLOUD-TRAIN” no. 316662) and Swiss National Science Foundation (SNSF) grant no. 200 021_140 663. The CAPS instrument used in this work was supplied by the National Centre for Atmospheric Science. The UHSAS was funded by NERC grant NE/B504873/1.

References

Abdelmonem, A., Schnaiter, M., Amsler, P., Hesse, E., Meyer, J., and Leisner, T.: First correlated measurements of the shape and light scattering properties of cloud particles using the new Particle Habit Imaging and Polar Scattering (PHIPS) probe, Atmos. Meas. Tech., 4, 2125-2142, doi:10.5194/amt-4-2125-2011, 2011.

Baran, A.: Light scattering by irregular particles in the Earth's atmosphere, in: Light Scattering Reviews 8, edited by: Kokhanovsky, A. A., Springer Praxis Books, Berlin, Heidelberg, Germany, 3–68, 2013.

Baumgardner, D., Brenguier, J. L., Bucholtz, A., Coe, H., DeMott, P., Garrett, T. J., Gayet, J. F., Hermann, M., Heymsfield, A., Korolev, A., Krämer, M., Petzold, A., Strapp, W., Pilewskie, P., Taylor, J., Twohy, C., Wendisch, M., Bachalo, W., and Chuang, P.: Airborne instruments to measure atmospheric aerosol particles, clouds and radiation: a cook's tour of mature and emerging technology, Atmos. Res., 102, 10–29, doi:10.1016/j.atmosres.2011.06.021, 2011.

Baumgardner, D., Chepfer, H., Raga, G. B., and Kok, G. L.: The shapes of very small cirrus particles derived from in situ measurements, Geophys. Res. Lett., 32, doi: 10.1029/2004GL021300, 2005.

Baumgardner, D., Jonsson, H., Dawson, W., O'Connor, D., and Newton, R.: The cloud, aerosol and precipitation spectrometer: a new instrument for cloud investigations, Atmos. Res., 59, 251-264, 10.1016/S0169-8095(01)00119-3, 2001.

Benz, S., Megahed, K., Möhler, O., Saathoff, H., Wagner, R., and Schurath, U.: T - dependent rate measurements of homogeneous ice nucleation in cloud droplets using a large atmospheric simulation chamber, J. Photoch. Photobio. A, 176, 208–217, doi:10.1016/j.jphotochem.2005.08.026, 2005.

Berkemeier, T., Shiraiwa, M., Pöschl, U., and Koop, T.: Competition between water uptake and ice nucleation by glassy organic aerosol particles, Atmos. Chem. Phys., 14, 12513–12531, doi:10.5194/acp-14-12513-2014, 2014.

Comment [L.N47]: References list cited in authors replies:
[1] Glen, A. and Brooks, S. D. "A new method for measuring optical scatterin properties of atmospherically relevant dusts using the Cloud and Aerosol Spectrometer with Polarization (CASPO Atmos. Chem. Phys., 13, 1345–1356, doi:10.5194/acp-13-1345-2013, 2013.
[2] Lynch, D. K.: Cirrus, Oxford Universit Press, 2001.
[3] Meyer, J.: Ice crystal measurements with SIMONE and CAS DPOL, Ph.D. thes Julich 25 Forschungszentrum, Wuppert Germany, 140 pp., 2011.
[4] Baumgardner, D., Jonsson, H., Daws W., O'Connor, D., and Newton, R.: The cloud, aerosol and precipitation spectrometer: a new instrument for clo investigations, Atmospheric Research, 251-264, 10.1016/S0169-8095(01)0011 3, 2001.
[5] Krämer, M., Rolf, C., Luebke, A., Afchine, A., Spelten, N., Costa, A., Zöge M., Smith, J., Herman, R., Buchholz, B., Ebert, V., Baumgardner, D., Borrmann, Klingebiel, M., and Avallone, L.: A microphysics guide to cirrus clouds – Pa 1: Cirrus types, Atmos. Chem. Phys. Discuss., 15, 31537-31586, doi:10.5194/acpd-15-31537-2015, 201
[6] Lawson, R. P., Baker, B. A., Zmarzly, O'Connor, D., Mo, Q., Gayet, J.-F., and Shcherbakov, V.: Microphysical and Optical Properties of Atmospheric Ice Crystals at South Pole Station, Journal o Applied Meteorology and Climatology, 1505-1524, 10.1175/JAM2421.1, 2006.
[7] Abdelmonem, A., Schnaiter, M., Amsler, P., Hesse, E., Meyer, J., and Leisner, T.: First correlated measureme of the shape and light scattering properties of cloud particles using the r Particle Habit Imaging and Polar Scatte (PHIPS) probe, Atmos. Meas. Tech., 4, 2125-2142, doi:10.5194/amt-4-2125-2011, 2011.
[8] Duplissy, J., Merikanto, J., Franchin, Tsagkogeorgas, G., Kangasluoma, J., Wimmer, D., Vuollekoski, H., Schobesberger, S., Lehtipalo, K., Flagan, C., Brus, D., Donahue, N. M., Vehkämäk H., Almeida, J., Amorim, A., Barmet, P., Bianchi, F., Breitenlechner, M., Dunne, M., Guida, R., Henschel, H., Junninen, H Kirkby, J., Kürten, A., Kupc, A., Määttän A., Makhmutov, V., Mathot, S., Niemine T., Onnela, A., Praplan, A. P., Riccobono F., Rondo, L., Steiner, G., Tome, A., Walther, H., Baltensperger, U., Carslaw, S., Dommen, J., Hansel, A., Petäjä, T., Sipilä, M., Stratmann, F., Vrtala, A., Wagner, P. E., Worsnop, D. R., Curtius, and Kulmala, M.: Effect of ions on sulfu acid-water binary particle formation II: Experimental data and comparison with QC-normalized classical nucleation theo Journal of Geophysical Research: Atmospheres,, 10.1002/2015JD023539, 2015.

Borrmann, S., Luo, B., and Mishchenko, M.: Application of the T-matrix method to the measurement of aspherical (ellipsoidal) particles with forward scattering optical particle counters, J. Aerosol Sci., 31, 789–799, doi:10.1016/S0021-8502(99)00563-7, 2000.

Boucher, O., Randall, D., Artaxo, P., Bretherton, C., Feingold, G., Forster, P., Kerminen, V.-M., Kondo, Y., Liao, H., Lohmann, U., Rasch, P., Satheesh, S. K., Sherwood, S., Stevens, B., and Zhang, X. Y.: Clouds and aerosols, in: Climate Change 2013: The Physical Science Basis, Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change, edited by: Stocker, T. F., Qin, D., Plattner, G.-K., Tignor, M., Allen, S. K.,Boschung, J., Nauels, A., Xia, Y., Bex, V., and Midgley, P. M., Cambridge University Press, Cambridge, UK, New York, USA, 571–657, 2013.

Burton, S. P., Ferrare, R. A., Hostetler, C. A., Hair, J. W., Rogers, R. R., Obland, M. D., Butler, C. F., Cook, A. L., Harper, D. B., and Froyd, K. D.: Aerosol classification using airborne high spectral resolution lidar measurements – methodology and examples, Atmos. Meas. Tech., 5, 73–98, doi:10.5194/amt-5-73-2012, 2012.

Cataldo, F., Ursini, O., Lilla, E., and Angelini, G.: Ozonolysis of *α*-pinene, *β*-, *d*- and *l*-turpentine oil studied by chirooptical methods; some implications on the atmospheric chemistry of biogenic volatile organic compounds, Ozone-Sci. Eng., 32, 274–285, doi:10.1080/01919512.2010.493550, 2010.

Chen, G., Jaradat, S. A., Banerjee, N., Tanaka, T. S., Ko, M. S. H., and Zhang, M. Q.: Evaluation and comparison of clustering algorithms in analyzing ES cell gene expression data, Stat. Sinica, 12, 1503997, 241–262, 2002.

Connolly, P. J., Möhler, O., Field, P., Saathoff, H., Burgess, R., Choularton, T., and Gallagher, M.: Studies of heterogeneous freezing by three different desert dust samples, Atmos. Chem. Phys., 9, 2805–2824, doi:10.5194/acp-9-2805-2009, 2009.

Crawford, I., Ruske, S., Topping, D. O., and Gallagher, M. W.: Evaluation of hierarchical agglomerative cluster analysis methods for discrimination of primary biological aerosol, Atmos. Meas. Tech. Discuss., 8, 7303–7333, doi:10.5194/amtd-8-7303-2015, 2015.

Cziczo, D. J., DeMott, P. J., Brooks, S. D., Prenni, A. J., Thomson, D. S., Baumgardner, D., Wilson, J. C., Kreidenweis, S. M., and Murphy, D. M.: Observations of organic species and atmospheric ice formation, Geophys. Res. Lett., 31, L12116, doi:10.1029/2004GL019822, 2004.

DMT Manual: CAPS operator manual, DOC-0066 Revision F,DMT, Boulder, Colorado, USA, 2011.

Donahue, N., Robinson, A., Trump, E., Riipinen, I., and Kroll, J.: Volatility and aging of atmospheric organic aerosol, in: Atmospheric and Aerosol Chemistry, edited by: McNeill, V. F., and Ariya, P. A., Topics in Current Chemistry, Springer, Berlin, Heidelberg, Germany, 97–143, 2014.

Dias, A., Ehrhart, S., Vogel, A., Williamson, C., Simões, J., Kirkby, J., Mathot, S., and Onnela, A.: Analysis of temperature homogeneity of the CLOUD chamber at CERN, in preparation, 2015.

Duplissy, J., DeCarlo, P. F., Dommen, J., Alfarra, M. R., Metzger, A., Barmpadimos, I., Prevot, A. S. H., Weingartner, E., Tritscher, T., Gysel, M., Aiken, A. C., Jimenez, J. L., Canagaratna, M. R., Worsnop, D. R., Collins, D. R., Tomlinson, J., and Baltensperger, U.: Relating hygroscopicity and composition of organic aerosol particulate matter, Atmos. Chem. Phys., 11, 1155-1165, 10.5194/acp-11-1155-2011, 2011.

Duplissy, J., Enghoff, M. B., Aplin, K. L., Arnold, F., Aufmhoff, H., Avngaard, M., Baltensperger, U., Bondo, T., Bingham, R., Carslaw, K., Curtius, J., David, A., Fastrup, B., Gagné, S., Hahn, F., Harrison, R. G., Kellett, B., Kirkby, J., Kulmala, M., Laakso, L., Laaksonen, A., Lillestol, E., Lockwood, M., Mäkelä, J., Makhmutov, V., Marsh, N. D., Nieminen, T., Onnela, A., Pedersen, E., Pedersen, J. O. P., Polny, J., Reichl, U., Seinfeld, J. H., Sipilä, M., Stozhkov, Y., Stratmann, F., Svensmark, H., Svensmark, J., Veenhof, R., Verheggen, B., Viisanen, Y., Wagner, P. E., Wehrle, G., Weingartner, E., Wex, H., Wilhelmsson, M., and Winkler, P. M.: Results from the CERN pilot CLOUD experiment, Atmos. Chem. Phys., 10, 1635–1647, doi:10.5194/acp-10-1635-2010, 2010.

Fahey, D. W., Gao, R.-S., Möhler, O., Saathoff, H., Schiller, C., Ebert, V., Krämer, M., Peter, T., Amarouche, N., Avallone, L. M., Bauer, R., Bozóki, Z., Christensen, L. E., Davis, S. M., Durry, G., Dyroff, C., Herman, R. L., Hunsmann, S., Khaykin, S. M., Mackrodt, P., Meyer, J., Smith, J. B., Spelten, N., Troy, R. F., Vömel, H., Wagner, S., and Wienhold, F. G.: The AquaVIT-1 intercomparison of atmospheric water vapor measurement techniques, Atmos. Meas. Tech., 7, 3177–3213, doi:10.5194/amt-7-3177-2014, 2014.

Froyd, K. D., Murphy, D. M., Lawson, P., Baumgardner, D., and Herman, R. L.: Aerosols that form subvisible cirrus at the tropical tropopause, Atmos. Chem. Phys., 10, 209–218, doi:10.5194/acp-10-209-2010, 2010.

Glen, A. and Brooks, S. D.: A new method for measuring optical scattering properties of atmospherically relevant dusts using the Cloud and Aerosol Spectrometer with Polarization (CASPOL), Atmos. Chem. Phys., 13, 1345–1356, doi:10.5194/acp-13-1345-2013, 2013.

Glen, A. and Brooks, S. D.: Single particle measurements of the optical properties of small ice crystals and heterogeneous ice nuclei, Aerosol Sci. Tech., 48, 1123–1132, doi:10.1080/02786826.2014.963023, 2014.

Groß, S., Esselborn, M., Weinzierl, B., Wirth, M., Fix, A., and Petzold, A.: Aerosol classification by airborne high spectral resolution lidar observations, Atmos. Chem. Phys., 13, 2487–2505, doi:10.5194/acp-13-2487-2013, 2013.

Guida, R., Carrie, P., De Menezes, L., Duplissy, J., Fayet, F., Haider, S., Kirkby, J., Mathot, S., Minginette, P., Onnela, A., Rochez, J., Thomas, G., Wasem, A., and Wilhelmsson, M.: Development of the gas system for the CLOUD experiment at CERN, in: Nuclear Science Symposium and Medical Imaging Conference (NSS/MIC), 2013 IEEE, Seoul 27 October–2 November 2013, 1–5, 2013.

Guida, R., Carrie, P., De Menezes, L., Duplissy, J., Fayet, F., Kirkby, J., Mathot, S., Minginette, P., Onnela, A., Rochez, J., Thomas, G., Wasem, A., and Wilhelmsson, M.: An ultra-pure gas system for the CLOUD experiment at CERN, in: Nuclear Science Symposium and Medical Imaging Conference (NSS/MIC), 2012 IEEE, Anaheim, CA 27 October–3 November 2012, 1199–1203, 2012.

Heymsfield, A. J.: On measurements of small ice particles in clouds, Geophys. Res. Lett., 34, L23812, doi:10.1029/2007GL030951, 2007.

Heymsfield, A. J., Schmitt, C., Bansemer, A., van Zadelhoff, G.-J., McGill, M. J., Twohy, C., and Baumgardner, D.: Effective Radius of Ice Cloud Particle Populations Derived from Aircraft Probes, J. Atmos. Ocean. Tech., 23, 361-380, 10.1175/JTECH1857.1, 2006.

Hoyle, C. R., Fuchs, C., Järvinen, E., Saathoff, H., Dias, A., El Haddad, I., Gysel, M., Coburn, S. C., Tröstl, J., Bernhammer, A.-K., Bianchi, F., Breitenlechner, M., Corbin, J. C., Craven, J., Donahue, N. M., Duplissy, J., Ehrhart, S., Frege, C., Gordon, H., Höppel, N., Heinritzi, M., Kristensen, T. B., Molteni, U., Nichman, L., Pinterich, T., Prevot, A. S. H., Simon, M., Slowik, J. G., Steiner, G., Tomé, A., Vogel, A. L., Volkamer, R., Wagner, A. C., Wagner, R., Wexler, A. S., Williamson, C., Winkler, P. M., Yan, C., Amorim, A., Dommen, J., Curtius, J., Gallagher, M. W., Flagan, R. C., Hansel, A., Kirkby, J., Möhler, O., Stratmann, F., Worsnop, D., and Baltensperger U.: Aqueous phase oxidation of sulphur dioxide by ozone in cloud droplets, Atmos. Chem. Phys. Discuss., 2015.

Järvinen, E., Ignatius, K., Nichman, L., Kristensen, T. B., Fuchs, C., Höppel, N., Corbin, J. C., Craven, J., Duplissy, J., Ehrhart, S., El Haddad, I., Frege, C., Gates, S. J., Gordon, H., Hoyle, C. R., Jokinen, T., Kallinger, P., Kirkby, J., Kiselev, A., Naumann, K.-H., Petäjä, T., Pinterich, T., Prevot, A., Saathoff, H., Schiebel, T., Sengupta, K., Simon, M., Tröstl, J., Virtanen, A., Vochezer, P., Vogt, S.,Wagner, A. C.,Wagner, R., Williamson, C., Winkler, P. M., Yan, C., Baltensperger, U., Donahue, N. M., Flagan, R. C., Gallagher, M., Hansel, A., Kulmala, M., Stratmann, F., Worsnop, D. R., Möhler, O., Leisner, T., and Schnaiter, M.: Observation of viscosity transition in α-pinene secondary organic aerosol, Atmos. Chem. Phys. Discuss., 15, 28575–28617, doi:10.5194/acpd-15-28575-2015, 2015.

Jimenez, J. L., Canagaratna, M. R., Donahue, N. M., Prevot, A. S. H., Zhang, Q., Kroll, J. H., DeCarlo, P. F., Allan, J. D., Coe, H., Ng, N. L., Aiken, A. C., Docherty, K. S., Ulbrich, I. M., Grieshop, A. P., Robinson, A. L., Duplissy, J., Smith, J. D., Wilson, K. R., Lanz, V. A., Hueglin, C., Sun, Y. L., Tian, J., Laaksonen, A., Raatikainen, T., Rautiainen, J., Vaattovaara, P., Ehn, M., Kulmala, M., Tomlinson, J. M., Collins, D. R., Cubison, M. J., E., Dunlea, J., Huffman, J. A., Onasch, T. B., Alfarra, M. R., Williams, P. I., Bower, K., Kondo, Y., Schneider, J., Drewnick, F., Borrmann, S., Weimer, S., Demerjian, K., Salcedo, D., Cottrell, L., Griffin, R., Takami, A., Miyoshi, T., Hatakeyama, S., Shimono, A., Sun, J. Y., Zhang, Y. M., Dzepina, K., Kimmel, J. R., Sueper, D., Jayne, J. T., Herndon, S. C., Trimborn, A. M., Williams, L. R., Wood, E. C., Middlebrook, A. M., Kolb, C. E., Baltensperger, U., and Worsnop, D. R.: Evolution of organic aerosols in the atmosphere, Science, 326, 1525–1529, doi:10.1126/science.1180353, 2009.

Johnson, B., Turnbull, K., Brown, P., Burgess, R., Dorsey, J., Baran, A. J., Webster, H., Haywood, J., Cotton, R., Ulanowski, Z., Hesse, E., Woolley, A., and Rosenberg, P.: In situ observations of volcanic ash clouds from the FAAM aircraft during the eruption of Eyjafjallajökull in 2010, J. Geophys. Res.-Atmos., 117, D00U24, doi:10.1029/2011JD016760, 2012.

Kaye, P. H., Hirst, E., Greenaway, R. S., Ulanowski, Z., Hesse, E., DeMott, P. J., Saunders, C., and Connolly, P.: Classifying atmospheric ice crystals by spatial light scattering, Opt. Lett., 33, 1545–1547, doi:10.1364/OL.33.001545, 2008.

Kirkby, J., Curtius, J., Almeida, J., Dunne, E., Duplissy, J., Ehrhart, S., Franchin, A., Gagne, S., Ickes, L., Kurten, A., Kupc, A., Metzger, A., Riccobono, F., Rondo, L., Schobesberger, S., Tsagkogeorgas, G.,Wimmer, D., Amorim, A., Bianchi, F., Breitenlechner, M., David, A., Dommen, J., Downard, A., Ehn, M., Flagan, R. C., Haider, S., Hansel, A., Hauser, D., Jud, W., Junninen, H., Kreissl, F., Kvashin, A., Laaksonen, A., Lehtipalo, K., Lima, J., Lovejoy,

E. R., Makhmutov, V., Mathot, S., Mikkila, J., Minginette, P., Mogo, S., Nieminen, T., Onnela, A., Pereira, P., Petaja, T., Schnitzhofer, R., Seinfeld, J. H., Sipila, M., Stozhkov, Y., Stratmann, F., Tome, A., Vanhanen, J., Viisanen, Y., Vrtala, A., Wagner, P. E., Walther, H., Weingartner, E., Wex, H., Winkler, P. M., Carslaw, K. S., Worsnop, D. R., Baltensperger, U., and Kulmala, M.: Role of sulphuric acid, ammonia and galactic cosmic rays in atmospheric aerosol nucleation, Nature, 476, 429–433, 2011.

Koop, T., Bookhold, J., Shiraiwa, M., and Pöschl, U.: Glass transition and phase state of organic compounds: dependency on molecular properties and implications for secondary organic aerosols in the atmosphere, Phys. Chem. Chem. Phys., 13, 19238–19255, doi:10.1039/C1CP22617G, 2011.

Kramer, J.: An integrated optical transient sensor, Circuits and Systems II: Analog and Digital Signal Processing, IEEE Transactions on Circuits and Systems – II, 49, 612–628, doi:10.1109/TCSII.2002.807270, 2002.

Krämer, M.: HALO ice crystal spectrometer intercomparison at the AIDA-chamber: first results from the Novel Ice Experiment NIXE-CAPS, Geophys. Res. Abstr., Vol. 11, EGU General Assembly, Vienna, Austria, 2009.

Kulkarni, G., Pekour, M., Afchine, A., Murphy, D. M., and Cziczo, D. J.: Comparison of experimental and numerical studies of the performance characteristics of a pumped counterflow virtual impactor, Aerosol Sci. Tech., 45, 382–392, doi:10.1080/02786826.2010.539291, 2011.

Lance, S.: Coincidence errors in a Cloud Droplet Probe (CDP) and a Cloud and Aerosol Spectrometer (CAS), and the improved performance of a modified CDP, J. Atmos. Ocean. Tech., 29, 1532–1541, doi:10.1175/JTECH-D-11-00208.1, 2012.

Lawson, R. P., Pilson, B., Baker, B., Mo, Q., Jensen, E., Pfister, L., and Bui, P.: Aircraft measurements of microphysical properties of subvisible cirrus in the tropical tropopause layer, Atmos. Chem. Phys., 8, 1609-1620, 10.5194/acp-8-1609-2008, 2008.

Lawson, R. P. B., Baker, B. A., and Pilson, B. A.: In-situ measurements of microphysical properties of mid-latitude and anvil cirrus, in: Proceedings, 30th International Symposium on Remote Sensing Environment, Honolulu, Hawaii, 10–14 November, 707–710, 2003.

Macke, A., Mueller, J., and Raschke, E.: Single scattering properties of atmospheric ice crystals, J. Atmos. Sci., 53, 2813–2825, doi:10.1175/1520-0469(1996)053<2813:SSPOAI>2.0.CO;2, 1996.

Meyer, J.: Ice crystal measurements with SIMONE and CAS DPOL, Ph.D. thesis, Julich Forschungszentrum, Wuppertal, Germany, 140 pp., 2011.

Mikhailov, E., Vlasenko, S., Martin, S. T., Koop, T., and Pöschl, U.: Amorphous and crystalline aerosol particles interacting with water vapor: conceptual framework and experimental evidence for restructuring, phase transitions and kinetic limitations, Atmos. Chem. Phys., 9, 9491–9522, doi:10.5194/acp-9-9491-2009, 2009.

Möhler, O., Field, P. R., Connolly, P., Benz, S., Saathoff, H., Schnaiter, M., Wagner, R., Cotton, R., Krämer, M., Mangold, A., and Heymsfield, A. J.: Efficiency of the deposition mode ice nucleation on mineral dust particles, Atmos. Chem. Phys., 6, 3007–3021, doi:10.5194/acp-6-3007-2006, 2006.

Noma, Y. and Asakawa, Y.: Biotransformation of monoterpenoids by microorganisms, insects, and mammals, in: Handbook of Essential Oils: Science, Technology, and Applications, CRC Press, Boca Raton, FL, USA, 585–736, 2010.

Notholt, J., Luo, B. P., Fueglistaler, S., Weisenstein, D., Rex, M., Lawrence, M. G., Bingemer, H., Wohltmann, I., Corti, T., Warneke, T., von Kuhlmann, R., and Peter, T.: Influence of tropospheric SO2 emissions on particle formation and the stratospheric humidity, Geophys. Res. Lett., 32, L07810, 10.1029/2004GL022159, 2005.

Omar, A. H., Won, J.-G., Winker, D. M., Yoon, S.-C., Dubovik, O., and McCormick, M. P.: Development of global aerosol models using cluster analysis of Aerosol Robotic Network (AERONET) measurements, J. Geophys. Res.-Atmos., 110, D10S14, doi:10.1029/2004JD004874, 2005.

Pandis, S. N., Harley, R. A., Cass, G. R., and Seinfeld, J. H.: Secondary organic aerosol formation and transport, Atmos. Environ. A-Gen., 26, 2269–2282, doi:10.1016/0960-1686(92)90358-R, 1992.

Petzold, A., Esselborn, M., Weinzierl, B., Ehret, G., Ansmann, A., Müller, D., Donovan, D., van Zadelhoff, G.-J., Berthier, S., Wiegner, M., Gasteiger, J., Buras, R., Mayer, B., Lajas, D., and Wehr, T.: ICAROHS inter-comparison of aerosol retrievals and observational requirements for multi-wavelength HSRL systems, in: Proceedings of the ESA Living Planet

Symposium, Bergen, Norway, 28 June–2 July 2010, edited by: Lacoste-Francis, H., Vol. SP-686 (European Space Agency, 2010), p. 102, 2010.

Renbaum-Wolff, L., Grayson, J. W., Bateman, A. P., Kuwata, M., Sellier, M., Murray, B. J., Shilling, J. E., Martin, S. T., and Bertram, A. K.: Viscosity of alpha-pinene secondary organic material and implications for particle growth and reactivity, P. Natl. Acad. Sci. USA, 110, 8014–8019, doi:10.1073/pnas.1219548110, 2013.

Robinson, E. S., Saleh, R., and Donahue, N. M.: Organic aerosol mixing observed by single particle mass spectrometry, J. Phys. Chem. A, 117, 13935–13945, doi:10.1021/jp405789t, 2013.

Rosenberg, P. D., Dean, A. R., Williams, P. I., Dorsey, J. R., Minikin, A., Pickering, M. A., and Petzold, A.: Particle sizing calibration with refractive index correction for light scattering optical particle counters and impacts upon PCASP and CDP data collected during the Fennec campaign, Atmos. Meas. Tech., 5, 1147–1163, doi:10.5194/amt-5-1147-2012, 2012.

Schnaiter, M.: The Ice Cloud Characterisation Campaign HALO-02, Geophys. Res. Abstr., Vol. 11, EGU General Assembly, Vienna, Austria, 2009.

Schnaiter, M., Büttner, S., Möhler, O., Skrotzki, J., Vragel, M., and Wagner, R.: Influence of particle size and shape on the backscattering linear depolarisation ratio of small ice crystals– cloud chamber measurements in the context of contrail and cirrus microphysics, Atmos. Chem. Phys., 12, 10465–10484, doi:10.5194/acp-12-10465-2012, 2012.

Seber, G. A. F.: Multivariate Observations, John Wiley & Sons, I., Hoboken, NJ, 1984.

Spath, H.: Cluster Dissection and Analysis: Theory, FORTRAN Programs, Examples, Halsted Press, New York, 1985.

Tajiri, T., Yamashita, K., Murakami, M., Saito, A., Kusunoki, K., Orikasa, N., and Lilie, L.: A novel adiabatic-expansion-type cloud simulation chamber, J. Meteorol. Soc. Jpn., 91, 687–704, doi:10.2151/jmsj.2013-509, 2013.

Wiberg, K. B., Wang, Y.-G., Murphy, M. J., and Vaccaro, P. H.: Temperature dependence of optical rotation: α-pinene, β-pinene, pinane, camphene, camphor and fenchone, J. Phys. Chem. A, 108, 5559–5563, doi:10.1021/jp040085g, 2004.

Table 1. Experimental parameters of the expansion runs presented in this paper. Excess pressure profile $\boldsymbol{x}$ axis is of the order of several minutes.

Run#	Seed type	Seed concentration [cm^{-3}]	Excess Pressure profile [mb]	$T_{initial}$ [^oC]	RH_{ice}^{max} [%]
1248.13	Ammonium Sulphate	3000		+10C	107
1291.16	Sulphuric Acid	75		-30C	168, 135
1298.20	Sulphuric Acid	700		-50C	148
1311.03	Sulphuric Acid	3260		-10C	123
1471.34	Oxalic Acid	100		-20C	165

Comment [L.N48]: Why are there t values for RH for run 1291.16?
Reply:
Max RH reached, in a multi-step (here 2 steps) expansion (Fig.1).

Table 2. SOA growth experimental conditions of the presented runs.

Run	T [^oC]	Initial RH [%]	Max. concentration [x1000 cm^{-3}] (Diameter>10nm)
1313	+10	12	30
1513	-20	60	45
1514	-20	4	40
1515	-30	2	30
1516	-38	5	45

Figure 1. Example of programmable multistep expansion to form a mixed phase cloud (Run #1291.16). Relative humidity with respect to ice (RHice) calculated from MBW and Thermocouples. Second step grows the present ice particles in the cloud period (25 min). Shaded time period is analysed in Fig. 3.

Comment [L.N49]: It would be use
to have the x-axis of this plot presented
the same way (and scale?) as those in
figure 2
Reply:
Fig.1 presents a full time scale of a
multistep expansion produced in the
chamber, and the behaviour of the
physical variables. It is usually during th
2nd step (31444.17) that we were able
observe the larger particles (e.g. as sho
by the 3VCPI images).
Fig.2 focuses on a specific step (<200se
of the phase transition. The grey shade
background indicates the time period
analysed in Fig.2, 3.
The x-axis will begin from 0.

Figure 2. Mixed phase cloud, phase transition period (Run #1291.16). The uncertainty in sizing is in the order of the size bin width (Table S2). The error of the polarisation ratio and asphericity is approximately 20 %. (a) CASPOL particle size distribution, (b) CASPOL PBP aspherical fraction, (c) CASPOL measured water and ice concentrations derived from asphericity compared to ACPIM.

Comment [L.N50]: As mentioned previously, how is the diameter defined here? The colour maps are different to those used in the other concentration contour plots; these should be unified i possible. Remove the blue background from 2b, an increase in the size of the d points would also assist the reader. Add size uncertainty bars to 2b (with associated discussion of their derivation the text).

Reply: The optical diameter is defined based on calibration and binning of the forward scattered intensity (comment 31442.8).
Addition of size uncertainty bars to all data points in Fig.2b produces an uncle phase transition and overloads the plot the uncertainty will be described in the caption.

- Colour maps unified
- Fig.2B background removed, size of data points increased

Figure 3. Cluster analysis (Run #1291.16). K in the title indicates the number of clusters found with best silhouette value. Each cluster appears with a percentage of particles in it. The centres of clusters are marked by centroids ⊙. (a) 1 s averaged data, whole size range and all concentration, (b) particle by particle data clustering for selected size range and concentration thresholds,. , (c) particle by particle data clustering plotted in a space comparable to Glen and Brooks (2013).

Comment [L.N51]: Refine size of pl
and size of text to make full use of colu
width. The symbol for the cluster centr
in the caption is incorrect.
Changed to larger figure, different centroid in the caption

Figure 4. Images of ice particles in CLOUD captured by 3VCPI with 2 μm resolution. Most of the particles are smaller than 100 μm (scale on the left).

Figure 5. SOA growth over a 10 h period, 1 Hz sampling rate (Run #1516). CASPOL and UHSAS overlapped size measurements. Black lines – particles measured with UHSAS, instrument's cut-off is at 1000 nm. Blue lines – particles measured with CASPOL. Red lines indicate that CASPOL has passed the saturation threshold and the measurements may be subject to coincidence errors.

Figure 6. Polarisation scatter-plots of SOA growth and liquefaction measured by CASPOL in four experiments. Ratio of perpendicularly polarised backscatter intensity to total backscatter intensity ($Dpol/Bck$) vs. ratio of perpendicularly polarised backscatter to forward scatter intensity ($Dpol/Fwd$), 1 s averaged run periods where the concentration was below 1300 cm^{-3}, colour is concentration $dN/dlogD_p$ [cm^{-3}], (a) Run #1513, (b) Run #1514, (c) Run #1515, (d) Run #1516.

Comment [L.N52]: Refine size of pl and size of text to make full use of colu width.
Reply:
Instructions will be given to the publish to make full use of column width

Figure 7. CASPOL polarisation ratio (blue line) increases as RH (black dotted line) decreases during the cooling period after a SOA experiment (Run #1515.16).

Figure 8**.** Large dry particles decrease in size. Smaller frame: illustration of the hypothesised transition sequence from CASPOL and SMPS measurements (liquid to viscous and dried further).

Figure 9. Atmospheric particle classification map for CLOUD data. The dimensions of the coloured rectangular boxes represent the space of measurements error and data points' distribution. Additional CASPOL data points from aircraft measurements are presented for comparison (Johnson et al., 2012).

Comment [L.N53]: The labels are almost illegibly small. Several colours (especially the dark blues) are too simil
Changed:
Colours changed, labels slightly bigger

Supplementary materials

The CLOUD Chamber

The CLOUD chamber is a 3 m-diameter electropolished stainless-steel cylinder (26.1 m^3). An insulated thermal housing surrounds the chamber. The temperature is controlled by precisely regulating the temperature of the air circulating in the space between the chamber and the thermal housing. Experimental runs can be performed at highly stable temperatures (near 0.01 ^{0}C) between +40 ^{0}C and -70 ^{0}C. Ultra-pure synthetic air is obtained from the evaporation of cryogenic liquid N_2 and liquid O_2, mixed in the ratio 79:21 (Fig. S1), respectively. The air is humidified using ultra-pure water from a filtered re-circulation system. Ozone is added to the chamber by UV irradiation of a small inlet flow of dry air. Magnetically coupled stainless steel fans on both manhole covers serve to mix the fresh gases and beam ions, and ensure uniformity inside the chamber (Voigtlander et al., 2012). Volatile trace gases such as SO_2 or NH_3 are supplied from concentrated gas cylinders pressurised with N_2 carrier gas. The trace gas mixtures are highly diluted using synthetic air before injection into the chamber. Less volatile trace gases such as alpha-pinene ($C_{10}H_{16}$) are supplied from temperature-controlled stainless steel evaporators using ultrapure N_2 carrier gas. In order to compensate for sampling losses, there is a continuous flow of fresh gases into the chamber of about 150-250 L/min, resulting in a dilution lifetime of 2-3 h. The chamber and gas system are designed to operate at up to +220 mb relative pressure and to make controlled adiabatic expansions down to +5 mb. In this way, starting from relative humidity near 100 %, the chamber can be operated as a classical Wilson cloud chamber for studies of ion-aerosol interactions with cloud droplets and ice particles. The chamber can be evacuated from +200 mb to +5 mb over any chosen time interval above 10 sec, in order to simulate the adiabatic cooling in ascending air masses that form clouds. Multistep programmed variations of pressure drop are available for cloud lifetime extension or regrowth. Two 60 cm in diameter fans rotating at speeds up to 400 RPM are responsible for uniform mixing in the chamber. (For more details see Duplissy et al., 2015, and Kirkby et al., 2011)

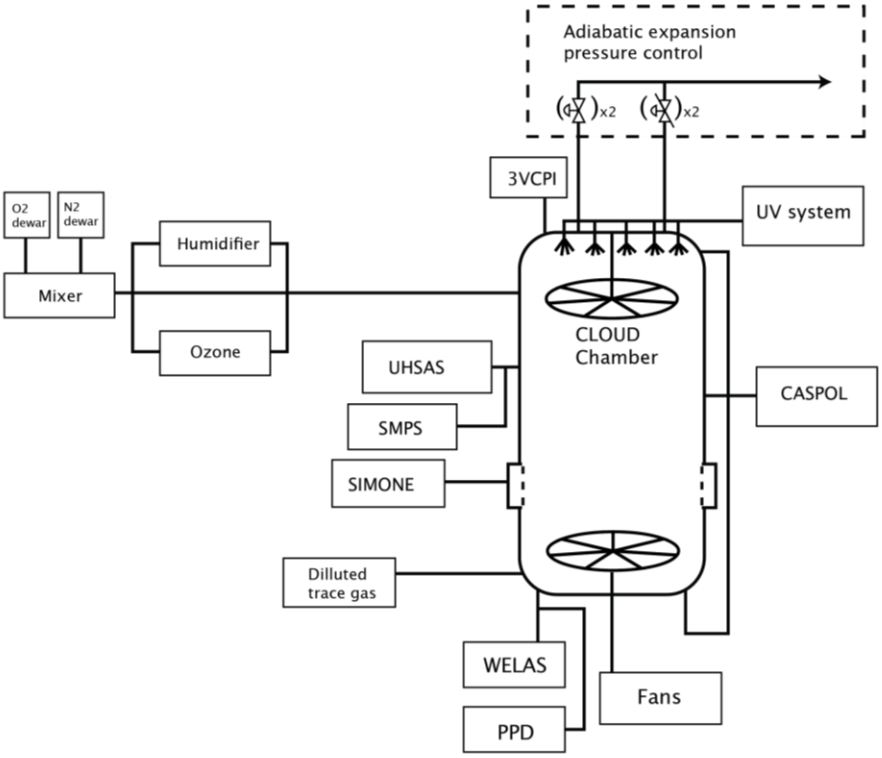


Fig. S1 Simplified diagram of the CLOUD chamber.

Table S2. Lower and upper size bin thresholds in CASPOL.

Bin number	Bin lower threshold	Bin upper threshold
1	0.51	0.61
2	0.61	0.68
3	0.68	0.75
4	0.75	0.82
5	0.82	0.89
6	0.89	0.96
7	0.96	1.03
8	1.03	1.10
9	1.10	1.17
10	1.17	1.25
11	1.25	1.5
12	1.5	2
13	2	2.5
14	2.5	3
15	3	3.5
16	3.5	4
17	4	5
18	5	6.5
19	6.5	7.2
20	7.2	7.9

Bin number	Bin lower threshold	Bin upper threshold
21	7.9	10.2
22	10.2	12.5
23	12.5	15
24	15	20
25	20	25
26	25	30
27	30	35
28	35	40
29	40	45
30	45	50

Table ~~S2~~S3. CASPOL detectors have 3 gain stages in the forward scattering direction and 2 in the backward. Signal to size conversion requires the adjusted linearly scaled reading of PBP data. Corrections to the Forward, Backward and the Dpol signals are summarized.

Forward signal	Adjusted Forward scattering signal
$20 - 3071$	$20 - 3071$
$3072 - 6143$	$([Forward\ Size] - 3071)\ x\ 22 + 3072$
$6143 - 9216$	$([Forward\ Size] - 6143)\ x\ 506 + (6143 - 3071)\ x\ 22 + 3072$

Backward signal	Adjusted Backward scattering signal
$0 - 2000$	$0 - 1536$
$2001 - 3071$	$([Backward\ Signal] - 2000)\ x\ 22 + 3072$

Dpol signal	Adjusted Dpol signal
> 2730	$([Dpol\ signal] - 2730)\ x\ 22 + 2731$

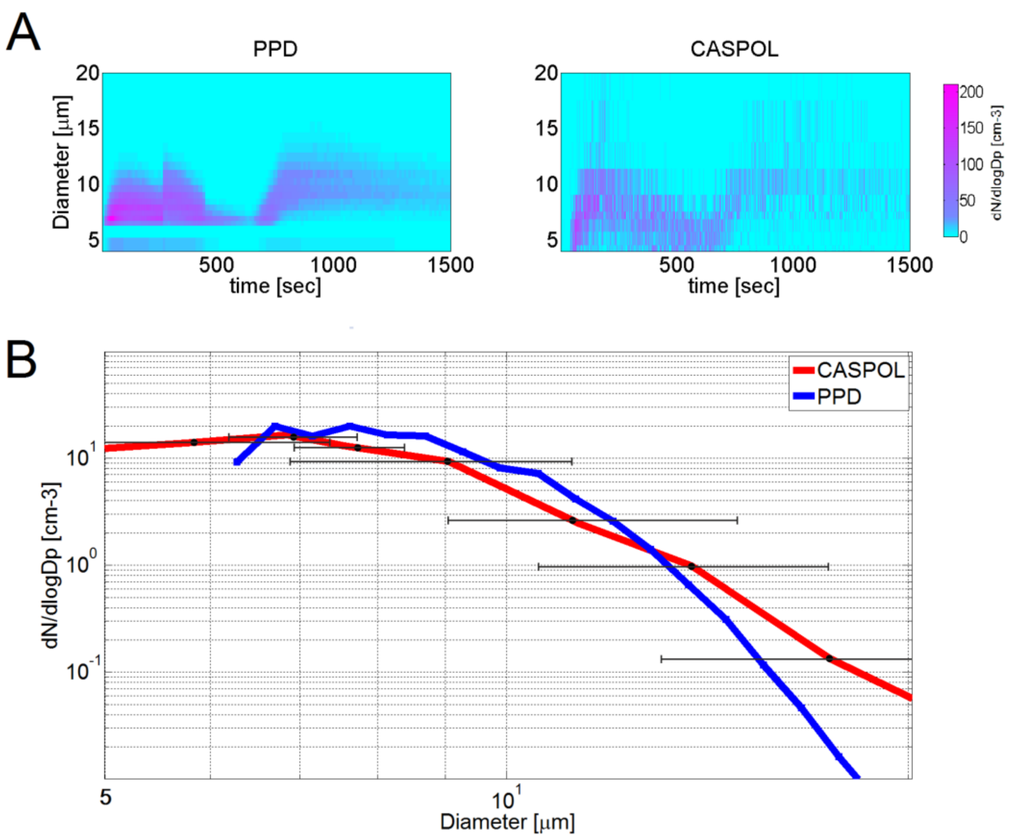


Fig. ~~S3~~ S4 Ice measurements (-50^{0}C) PPD-CASPOL comparison (Run # 1298.20), Represented as 'Ice - CLOUD 8' in Fig. 8 (A) PSD plots: PPD, CASPOL. (B) Total PSD for the whole run.

Comment [L.N54]: Add uncertainti to PSD in S3b. Improve axis labels so tha there is more than a single number on t x-axis.

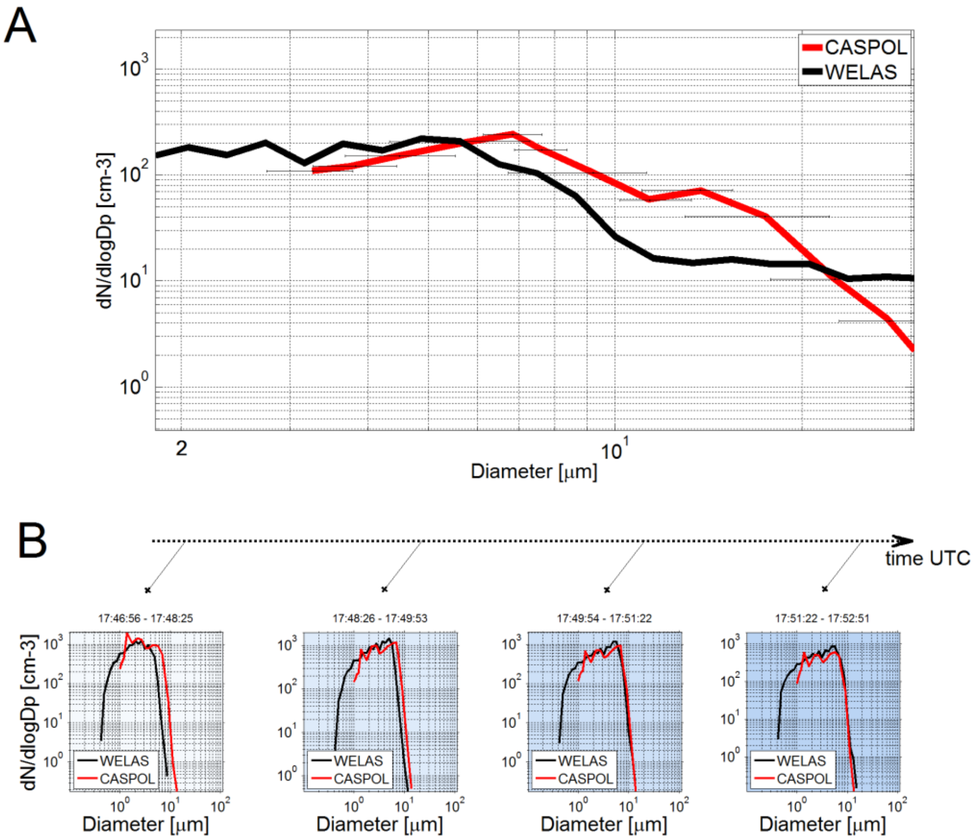


Fig. ~~S4~~ S5 Super-cooled water droplets (-10^{0}C) (Run # 1311.03). Represented as 'Supercooled, frozen droplets – CLOUD 8' in Fig. 8 (A) CASPOL WELAS, total PSD comparison for the whole run (B) Comparison of sequential time frames.

Comment [L.N55]: Add uncertainti to PSD in S4a. Improve axis labels so tha there is more than a single number on t x-axis.

References

Duplissy J., Merikanto J., Franchin A., Tsagkogeorgas G., Kangasluoma J., Wimmer D., Vuollekoski H., Schobesberger S., Lehtipalo K., Flagan R.C., Brus D., Donahue N.M., Vehkämäki H., Almeida J., Amorim A., Barmet P., Bianchi F., Breitenlechner M., Dunne E.M., Guida R., Henschel H., Junninen H., Kirkby J., Kürten A., Kupc A., Määttänen A., Makhmutov V., Mathot S. , Nieminen T., Onnela A., Praplan A.P., Riccobono F., Rondo L., Steiner G., Tome A., Walther H., Baltensperger U., Carslaw K.S., Dommen J., Hansel A., Petäjä T., Sipilä M., Stratmann F., Vrtala A., Wagner P.E., Worsnop D.R., Curtius J. and Kulmala M.: Effect of ions on sulfuric acid-water binary particle formation II: Experimental data and comparison with QC-normalized classical nucleation theory., J. Geophys. Res. Atmos, Accepted, 2015.

Kirkby, J., Curtius, J., Almeida, J., Dunne, E., Duplissy, J., Ehrhart, S., Franchin, A., Gagne, S., Ickes, L., Kurten, A., Kupc, A., Metzger, A., Riccobono, F., Rondo, L., Schobesberger, S., Tsagkogeorgas, G., Wimmer, D., Amorim, A., Bianchi, F., Breitenlechner, M., David, A., Dommen, J., Downard, A., Ehn, M., Flagan, R. C., Haider, S., Hansel, A., Hauser, D., Jud, W., Junninen, H., Kreissl, F., Kvashin, A., Laaksonen, A., Lehtipalo, K., Lima, J., Lovejoy, E. R., Makhmutov, V., Mathot, S., Mikkila, J., Minginette, P., Mogo, S., Nieminen, T., Onnela, A., Pereira, P., Petaja, T., Schnitzhofer, R., Seinfeld, J. H., Sipila, M., Stozhkov, Y., Stratmann, F., Tome, A., Vanhanen, J., Viisanen, Y., Vrtala, A., Wagner, P. E., Walther, H., Weingartner, E., Wex, H., Winkler, P. M., Carslaw, K. S., Worsnop, D. R., Baltensperger, U., and Kulmala, M.: Role of sulphuric acid, ammonia and galactic cosmic rays in atmospheric aerosol nucleation, Nature, 476, 429-433, http://www.nature.com/nature/journal/v476/n7361/abs/nature10343.html#supplementary-information, 2011.

Voigtländer, J., Duplissy, J., Rondo, L., Kürten, A., and Stratmann, F.: Numerical simulations of mixing conditions and aerosol dynamics in the CERN CLOUD chamber, Atmos. Chem. Phys., 12, 2205-2214, 10.5194/acp-12-2205-2012, 2012.