

Reply to interactive comment on „Ice nucleation properties of fine ash particles from the Eyjafjallajökull eruption in April 2010“ by B. Murray

First, we would like to thank B. Murray for thoroughly evaluating our manuscript and giving constructive feedback.

Referee comment 1:

The ice active surface site density was first employed by Connolly et al. But, it has its roots in Vali's work who expressed a comparable quantity in terms of per unit volume rather than per unit surface area (see references in Connolly). This should be mentioned. Also, in the list of papers making use of this model, Murray et al. (ACP, 11, 4191–4207, 2011) has also been omitted. (P17670, ln 1-5)

Reply to referee comment 1:

In section 3.3 we have now added a sentence referring to the singular hypothesis formulation brought up by Vali (1971) which afterwards has been developed further by Fletcher (1974) into an active site approach:

“A similar time-independent concept already has been proposed by Vali (1971) who described immersion freezing by an ice nuclei concentration $k(T)$, with $k(T)$ being the concentration of ice nuclei becoming active at a certain temperature. Taking up this idea, Fletcher (1974) then formulated a temperature-dependent expression for the ice nucleation sites per square centimeter of particles being immersed in a droplet.”

We will refer to the findings by Murray et al. (2011) at a later point in our paper (see reply to comment 12).

Referee comment 2:

Water saturation is not reached during the second experiment – the sentence as it is written implies it is. (P17673, ln 15,16)

Reply to referee comment 2:

We deleted part of the sentence which now reads: “First, from looking at the humidity data (1b and 2b) it can be seen that water saturation is only reached during the first experiment.”

Referee comment 3:

I think ‘droplet concentration’ is intended rather than ‘particle concentration’. (P17674, ln 1-2)

Reply to referee comment 3:

‘Particle concentration’ has been changed to ‘droplet concentration’.

Referee comment 4:

'Long run' what does this mean/refer to? (P17674, ln 15)

Reply to referee comment 4:

For clarification this sentence was changed and now reads: "In contrast, deposition nucleation is associated with an immediate growth of ice crystals at a certain supersaturation over ice (2d, 2e), which then leads to a significant temporary increase in depolarization while for immersion freezing and low ice crystal concentrations the depolarization is not influenced much by ice nucleation and ice crystal growth over the course of the experiment."

Referee comment 5:

How uncertain is the estimate of surface area based on the assumption of spherical particles. This is critical for the derivation of n_s values. The ESEM pictures clearly show non-spherical particles, how much larger might the actual surface area be? In other work researchers have used gas adsorption measurements to quantify ice surface area and then derive n_s values from this (Murray et al., ACP, 11, 4191–4207, 2011). This takes into account the non-spherical nature of particles. It is therefore important to quantify the uncertainty here in order to compare the data sets. (P17674, ln 25)

Reply to referee comment 5:

So far, we were able to conduct BET analyses of Eyjafjallajökull volcanic ash only for the bulk sample which gives $4.2 \text{ m}^2/\text{g}$ for the ash type that has been used in our experiments (comparable to a value measured by Gislason et al. (2011)). However, for our ice nucleation experiments, we used an impactor stage for eliminating particles larger than $\sim 5 \text{ }\mu\text{m}$ in the aerosol added to the AIDA chamber. This particle fraction corresponds to roughly 15% of the total bulk mass (Gislason et al., 2011). For this fraction of smaller particles there are currently no BET measurements available because the aerosol extraction on nuclepore filters during AIDA experiments does not allow for a collection of sufficiently enough sample material for BET analyses. However, with future additional experimental studies we plan to establish a better knowledge of possible deviations between BET measurements and our estimated aerosol surface in order to draw comparisons between the ice-active surface site densities that we measure at the AIDA chamber and other experimental studies such as Murray et al. (2011). Finally, in this context we would also like to point out that the surface area estimated from SMPS/APS measurements has been used in previous studies (Connolly et al, 2009; Niedermeier et al, 2010) and also in volcanic ash dispersion models (Emeis et al., 2011) and for the evaluation of atmospheric measurements (Stohl et al., 2011) volcanic ash particles are assumed to be spherical.

We added a remark with respect to this issue on p. 16: "Note that a factor that could have a major influence on the measurement uncertainty ΔA is that A is derived under the simplifying assumption of spherical particles which does not apply for volcanic ash particles. However, also in volcanic ash dispersion models (Emeis et al., 2011) and for the evaluation of atmospheric measurements (Stohl et al., 2011) volcanic ash particles are assumed to be spherical."

Referee comment 6:

What is the density based on? (P17676, ln 4)

Reply to referee comment 6:

This estimate of the density is based on the assumption that volcanic ash has a similar density compared to mineral dusts which also mainly consist of silicates. This information has been added to section 3.1.

Referee comment 7:

What is the physical state of the volcanic ash? Is it crystalline or amorphous? If crystalline then it may be comparable to mineral dusts from arid regions, but if amorphous then comparison with studies of ice nucleation on amorphous solids from the AIDA chamber would be relevant. According to the lattice match idea, amorphous solids wouldn't represent effective ice nuclei since they have no organised structure. (section 3.1)

Reply to referee comment 7:

According to a study by Gislason et al. (2011), the ash from Eyjafjallajökull is dominated by andesitic glass. However, they also found crystals of plagioclase, pyroxene and olivine (note added on p.9). As the composition of the volcanic ash probably changed over the eruption period, it is difficult to draw general conclusions.

Referee comment 8:

Uncertainty in RH with respect to water is discussed here, but in the figure RH with respect to ice is used. It would make more sense to stick to RH_{ice} . (P17677, ln 25)

Reply to referee comment 8:

We added a note that the correction with respect to water saturation is applied to RH_{wat} and RH_{ice} .

Referee comment 9:

This discussion would be helped by an example plot of f_{ice} vs T . (P17678, ln 10-15)

Reply to referee comment 9:

We made modifications to Fig. 5, so that it is easier to distinguish between freezing modes. We also added the freezing onset for immersion freezing where the ice fraction is smaller than 0.1%.

Referee comment 10:

Reference to an unpublished manuscript is unacceptable here. Justify why eq 1 is a good approximation for the determination of n_s or use the established method. The other authors who have used this (which are published) used a different set of equations. Are the values derived here really comparable? (P17679, ln 5-15)

Reply to referee comment 10:

We do agree that it might be problematic to reference to an unpublished article. However, the manuscript by Niemand et al. has been submitted and we will try to reference to the pre-print for the final version of our paper. Also, referencing to papers in preparation and under review is accepted in ACP. Furthermore, we think that the information given in our manuscript is sufficient to allow others to retrace and reproduce our analysis.

We used a linear approximation for the exponential function which is commonly used. This approximation can be used for small activated fractions ($f < 10\%$). The reason for using an approximation is that for the polydisperse aerosol population in our experiments the exact formulation cannot be solved analytically. We added a remark regarding this approximation on p. 15.

Referee comment 11:

The singular model is used here and it is stated that the time dependence is neglected. Some studies have shown that time dependence can be significant (e.g. Murray et al., ACP, 11, 4191–4207, 2011). What justification can be given to support the assumption for volcanic ash? (P17679)

Reply to referee comment 11:

We agree that heterogeneous ice nucleation is a stochastic process by nature, and thus describing the ice nucleation properties of volcanic ash with a contact angle distribution would also be possible. However, due to the varying ice nucleation properties of the individual ash particles, it could also be assumed – with AIDA experiments giving evidence – that this heterogeneity of sites with different activation energies (associated with a wide range of freezing probabilities at a certain temperature) masks the inherent stochastic nature of the ice nucleation process, which then justifies the application of the singular approach.

Referee comment 12:

There are two other studies which report n_s values in a form which can be compared to the present study, which have been omitted. Both of these studies were done with different instruments, and highlights the benefit of n_s values for comparison of different ice nucleating species from different studies. Niedermeier et al.(2010) report n_s values for ATD and Murray et al.(2011) report values for the single mineral kaolinite. These should be referred to. In fact, it may help the discussion on p. P17683 to include a comparison plot of n_s values from different experiments rather than simply discussing it in words. (P17681, In 5-10)

Reply to referee comment 12:

In the study by Niedermeier et al. (2010) ice-surface site densities for ATD are presented for immersion freezing ($235 \text{ K} < T < 239 \text{ K}$). However, we did not observe immersion freezing in the temperature range where ice nucleation was observed in the aforementioned study. Thus, we refrained from comparing those studies to our measurements. However, we included a comparison with the immersion freezing study by Murray et al. (2011) as suggested by the referee (p. 17).

For deposition nucleation there is a study by Wheeler et al. where ice-active surface site densities are presented for kaolinite and illite. However, the graphical comparison of n_s values from different studies is not straightforward because n_s depends on two parameters (T and RH_{ice}).

Technical point 1:

The referencing to the figures is incorrect throughout the manuscript.

Reply to technical point 1:

This has been corrected.

Technical point 2:

The term 'British Islands' refers to the United Kingdom of Great Britain, the channel islands and the isle of Mann. The terms British Isles which refers to the geographical region which includes Ireland might be more appropriate. For simplicity perhaps just say Northern and North Western Europe.

Reply to technical point 2:

We changed "British Islands" to "North Western Europe" as suggested.

Technical point 3:

I think it is helpful to create figures which can be read in black and white if possible. In Figures 5 and 7 this could be done by using different symbols as well as colours to distinguish between data.

Reply to technical point 3:

Fig. 5 and 7 can now be printed also in black and white.

References

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