

Interactive comment on “Ice nucleation by surrogates for atmospheric mineral dust and mineral dust/sulfate particles at cirrus temperatures” by C. M. Archuleta et al.

C. M. Archuleta et al.

Received and published: 23 July 2005

General comment: We appreciate Scot Martin's assessment of the utility of this paper and his comprehensive set of comments. We address his specific concerns below.

Specific responses:

1. *...particles appear to be agglomerates, which is supported by the TEM image shown in Figure 2. Should the authors consider addressing how the nonsphericity affects the interpretation of results? In several places in the analysis, spherical particles are assumed.*

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This is a good point that was also raised by other reviewers. Although we had considered including such discussion in the original paper, we deemed then and continue to believe that there is insufficient information to discern the exact direction or magnitude of impact on nucleation rate interpretations. Nevertheless, it is important to qualify the presented results, so we now include some discussion of the potential impacts of non-sphericity effects in the revised paper. Figure 2 actually presents the “worst” case of agglomerate configuration (chain configuration and three dimensional), for the largest particles generated (200 nm DMA size) from powders. A range of agglomerate configurations were present and some were also much more compact than shown in Figure 2. Smaller particles of all types contain fewer agglomerates, as borne out by TEM images that are not presented. We also wish to note that the natural mineral dusts did not possess this agglomerate structure and may wish to include an image in the revised paper.

2. The authors appear to conclude that the results of the noncoated particles are difficult to interpret. Should these results then be omitted from the paper? What added value do these results provide given the uncertainty in their interpretation?

We believe that the added value is to indicate the uncertainty in activation characteristics when particles are less coated with contaminants. We disagree with the conventional wisdom that all mineral dust particles in the atmosphere are fully coated and do not believe that this topic has been explored to the extent necessary to make overreaching statements.

3. Shouldn't the Asian dust particles also be coated? The methods section describes that these Asian dust particles are obtained freshly from collected soils, whereas the Asian dust particles over the Pacific and arriving in the USA are coated by sulfates and nitrates. Dust from northern Africa is similarly coated. At the least, if no more experiments are to be done, should these issues be discussed in the paper?

Following from the previous comment, we are not entirely sure what preponderance

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of evidence the reviewer might be referring to in making blanket statements on the general nature of African and Asian dust particles reaching the United States. We will add some review of this topic (present in Archuleta's thesis) to the final article, noting studies that emphasize a coated nature versus others that do not, especially those that isolated mineral dusts as natural ice nuclei (already noted on page 3394). We definitely agree that coating the natural dusts would provide an interesting series of experiments, one that we are presently pursuing.

4. The quantitative agreement in j values of this manuscript and those of Hung et al. is actually very, very good...

True. We have modified our description of these comparisons to remove any context of apparent negativity. We have corrected Figure 8 and now consider the potential impact of agglomeration on J values (see next comment), which we estimate to make uncertain those calculated on the assumption of a single spherical particle by perhaps a factor of 3 to 5. Thus, the results correspond within less than two orders of magnitude, quite good for nucleation studies. We will also offer alternate hypotheses as promoted separately by the commenter.

5. ...comparison of their results with those of Hung et al. One point that is not explicitly considered is the effect of nonspherical agglomerated particles versus spherical particles (i.e., those of Hung et al.). Do the authors want to mention this point and possible implications, too? For example, agglomerated particles may also provide additional active sites in concave dimensions, which could increase j values.

The impact of agglomerated particles on ice nucleation is quite difficult to quantify. The impact on nucleation rates could be in either direction depending on the history of the particle. To explain this, we need to provide additional information on the particle collections as represented within Figure 2. This image is of a particle remaining after melting and evaporation of an ice crystal nucleated on a generated particle that grew in the CFDC and then was impacted onto a TEM grid. At impactation, the particle had

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grown to in excess of 2 microns in size (impactor "cut" size), and so by mass was mostly water. Melting and evaporation may have rearranged the particle morphology from that present prior to nucleation. The exact morphology of the particle in a "dry" state prior to nucleation was not assessed and the effect of increasing water uptake (due to coating) on this morphology is also unknown. Thus, although the particle may have been quite compact prior to ice nucleation, melting and evaporation may have released the unit particles and then rearranged them in a manner that was not representative of the initial particle. One can only guess at the exposed surface area prior to ice nucleation, the nature of the coating morphology and the effects of active sites of concave dimensions. An estimate of the maximum surface area for nucleation can be obtained by decomposing agglomerates such as shown in Figure 2 into their individual particle components. For example, a "200 nm" agglomerate containing unit particles of 100 nm (2), 50 nm (3) and 25 nm (5) spherical components would have an exposed surface area about 2.5 times that of a single spherical particle. One can imagine another agglomerate configuration sized at 200 nm that possesses less surface area than a perfectly spherical single particle. Thus, we conservatively estimate an uncertainty of 3 to 5 in either direction. We will also duly note, with reference, that the agglomerate structure could explain enhanced ice nucleation activity versus the single particles used by Hung and Martin.

6. *Do the authors want to cite Hung and Martin (2001)?*

We can definitely offer this reference as a prior example of the utility and need for the types of calculations we make in this paper. Nevertheless, it is clear from our conference presentations and publications that we have already been motivated to present rate calculations from such studies for a number of years.

7. *...comparisons to homogeneous freezing of pure sulfate particles. My first question is if the comparison is based upon the volume-equivalent of the sulfate layer or on the volume-equivalent of the entire particle. Does either answer to the first question make sense as a comparison point to heterogeneous freezing? It seems to me that a*

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full parcel model with initialization conditions of a scenario (similar to what the authors have done in the past) is necessary to make any meaningful comparison between homogeneous and heterogeneous nucleation. Can the authors clarify these points?

We are happy to clarify these points. We will revisit our description of these calculations to assure that our intent is clear. On the left side of Figure 3 (untreated particles), the homogeneous freezing curves for sulfate particles are based on the volume equivalent of a pure sulfate particle. On the right side (coated particles), the freezing conditions are based on the volume nucleation rate of the sulfate solution present on spherical particle, but also considering Kelvin (curvature) effects on equilibrium composition (or water activity) due to the solution being distributed over an insoluble core particle. We have presented such calculations in the literature previously (e.g., DeMott et al., 1997). We think this presentation offers a simplistic, but effective comparison of the onset conditions required for the different freezing mechanisms. A parcel model exercise such as presented by DeMott et al. (1997) but incorporating nucleation rate data could offer more insight, but that prior reference already indicates the sense of the impact of heterogeneous nucleation on cirrus formation. Such an exercise would further lengthen the present paper, so might be more appropriate as part of a focused paper on cirrus cloud impacts, one that might also have to consider the impacts within the context of cloud dynamics. We will mention these things within a revised conclusion section.

8. ...any information on the dispersion in CCN activities? If so, does this dispersion have implications on the interpretation of the IN results?

For static type thermal diffusion chambers such as employed in this study, the spread in fractional activation versus supersaturation evident in Figure 2 may not simply caused by a range of true activation properties. There are instrumental factors involved and they may vary from device to device. For example, the "peak" concentration signal for a single set-point supersaturation may sometimes depend on the dynamics of particle activation, growth and sedimentation in the re-established supersaturation field following sample ingestion, and these things may depend on the range of supersaturations

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where activation begins. This may be one reason that most studies emphasize the 50

9. *Page 3405: Should ΔT_{hf} be ΔT_{hetf} ?*

No. Equation (1) is stated for the homogeneous nucleation condition. The discussion in this section is intended to provide the analogy for heterogeneous freezing. In doing so, ΔT_{hf} must be replaced by ΔT_{hetf} . As a minimum, we will add words to this effect in the appropriate place on page 3406 and we will consider listing the modified equation.

10. *Page 3405, line 19-21. I do not understand this sentence. Can it be re-phrased or explained differently?*

The proportionality constant was evaluated based on studies of median freezing temperatures. Sassen and Dodd (1988) considered that this constant was also valid at any temperature so that the defined effective freezing temperature could be used within nucleation rate expressions and therefore be applied over a continuum of nucleation rates, not just to define a homogeneous freezing condition. We will rephrase this statement accordingly.

11. *Page 3406, line 10. Should the functional relationship for J_{hetf} include λ inside the parentheses?*

No, λ is already included via Θ_{etf0} . That is, Θ_{etf0} is warmer than the actual temperature T by the factor $\lambda \Delta T_m$. Clearly, we need to add equations for heterogeneous nucleation that rephrase homogeneous equations (1) and (2).

12. *Page 3409, eq 4. Should J_{hetf} be $J_{hetf}(A)$ since page 3408 makes the point that the number of active sites and hence J_{hetf} depends on A ?*

Perhaps the confusion here relates to the difference between nucleation rates per unit surface area (J) and nucleation rates per particle (j). We assume a uniform distribution of active sites regardless of area in the present treatment. Thus, the probability of nucleation is given by $P = 1 - \exp(-J_{hetf} A \Delta t)$, where the terms $J_{hetf} A$ are equal to

jhetf.

13. *Page 3410, lines 15-18. a 5-fold difference in observation time would not seem to explain the >1000-fold difference in activation fraction. An alternative interpretation is that a small fraction of the particles have high activity (i.e., $j_{hetf}(A)$), in which case the Hung et al. measurement should capture higher nucleation rates than this manuscript's measurements. The observations are in opposite of this explanation, unless the possibility exists that the particles of this manuscript are different than those of Hung et al. because of the difference between agglomeration and single particles. In this case, the agglomerates would nucleate faster than the single particles, which could explain the differences described on page 3410. Should the authors consider this line of thinking?*

We address this issue in response to H. Hung. Prof. Martin offers another possibility. While we do not favor offering too much speculation, we will now offer a few alternate hypotheses to explain the differences in results.

14. *Table 1. Should the authors consider the effect of water (i.e., equilibration with ambient relative humidity) on coating thickness?*

Particles were processed quite dry (<5percent RH) prior to coating and then immediate sampling by the CCN counter. We don't expect that much of the coating reflects water.

15. *Figure 2. Can the dispersion in CCN activity be represented on the figure?*

See response to point 8. This is already evident in the figure, although the source of the rise to total activation is not clearly due to physical factors. We add a few words regarding this now.

16. *Figure 6. Should the "bulk freezing" line instead be called the "bulk melting" line?*

Yes.

17. *Figure 8. Why are there two sets of diamonds?*

This error has been corrected and the figure now correctly includes four data points at

each inferred water activity, corresponding to the four mode sizes used by Hung and Martin.

18. *Figure 10. Should squares and triangles be distinguished in the figure caption?*

Yes. We also note the meaning of the contact parameter m to distinguish it from its common use as slope of linear regressions.

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 3391, 2005.

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