

## ***Interactive comment on “Ice supersaturations exceeding 100% at the cold tropical tropopause: implications for cirrus formation and dehydration” by E. Jensen et al.***

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I find the observational data shown and the calculations presented in this paper to be very interesting. However, I had one problem with one of the hypothesis put forward to explain the high ice saturations, mainly the presence of an organic film to seal off the sulfate particles in the UT. How realistic is this hypothesis given what we know about the formation of aerosols in the atmosphere?

I guess we all have a pretty good understanding of how sulfate particles form, but how do soapy sulfated-particles form (transport) in a relatively pristine environment

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of the upper troposphere. What is the actual physical mechanism to produce these particles? The measurements show that organics are present in the UT aerosols, but is it reasonable to assume that the fraction of soup-type material is enough to seal off the sulfate to an extent to reduce the water uptake in the amounts suggested in this paper. I would think that most of the organics in the particles are phase separated from the solution, at least a fraction of the particles should have that type of an orientation, which makes it possible for the water soluble fraction to grow without much of a barrier. I guess what I am getting at here is that the calculations will give the obvious answer that the authors are after, but the question is how realistic is the physical assumption made. What organic compounds do the authors have in mind, and what type of a process could possibly produce such a unique size distribution with all the sulfate aerosols neatly sealed off with a strong surfactant layer.

It is also useful to keep in mind that if the surfactant material is present in a particle, in an amount larger than a monolayer, this layer often turns on itself and produces a miscel in the particle because the miscel formation reduces the free energy state of the mixed system. These micelles, if present in sufficient quantity, can nucleate to form organic matter in the aerosol (see many discussions on surfactant systems in the journal of Chemical Physics, the authors refer to surfactants as an organic film in the paper). Thus from the physics aspects of this problem (involving surface tension restrictions with surfactants), I find it hard to believe that such a distribution of sulfate particles, perfectly coated with a strong surfactant layer, is a likely occurrence in nature. If the particles are not sealed off, then the accommodation coefficient cannot be lowered to the extent suggested in this paper or else the authors have not shown calculations to indicate that partially sealed off particles can have low accommodation coefficients as well.

Alternative possibilities are perhaps the fact that nucleation process is highly sensitive to the surface tension of the “ice” nucleus formed, which is either against the solution or the air (Tabazadeh et al, PNAS, 2002). Any type of impurity, like organics, even if

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dissolved in small amounts in the aqueous solution could significantly change the rate of nucleation. For example, the importance of surface tension in activation of small aerosols to form cloud droplets has been known for many years (Kohler curve, see the paper right before yours at the ACPD site). The same idea, even more strongly, applies to ice activation from liquid solutions as well.

The new observations shown in this paper provide a new opportunity to reconsider the important role of surface tension in ice nucleation in general, whether it is in the lab or the atmosphere. In my view a model of any nucleation process should have a surface tension dependence to represent the actual physical process. One can experiment with the classical theory of nucleation by changing the value of surface tension slightly to see how that would affect the rate of nucleation or the critical ice saturation (the term used in this paper). One of the main problems that I see with this paper is a lack of consideration for the known effects of organics on surface tension of aqueous solutions. I believe this issue requires more discussion in the paper.

The main reason for me to doubt the explanation, regarding organic films, has to do with the fact that the physical system needed to make the problem work is somewhat unrealistic in my opinion. Unfortunately, nature likes disorder and these types of idealistic systems are hard to imagine. Personally, I could not think of any physical process that could form such a neat size distribution, but I sure like to learn of one if the authors have one in mind!

The authors may want to cite a new paper by Wise et al. In this study they show that some organics can in fact nucleate ice at a warmer temperature than sulfate at the same water activity (see Wise, JGR, 2004). These experiments show that it is not the water activity per se that controls the rate of nucleation (of course there is always a strong dependence on water activity because that is related to the critical ice saturation terms in the classical nucleation model), but perhaps the surface tension of the ice nuclei formed in the organic solution is somewhat different than the surface tension of the ice nuclei formed in a sulfate solution. The surface tension is the driver of any

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nucleation process, whether it is a gas to liquid formation or liquid to solid formation.

Overall, I believe the answer to the problem sought in this paper may involve organics, as pointed out by the authors, but probably the role that organics play in changing the surface tension of the ice nuclei and not the accommodation coefficient, which is emphasized in this paper. I encourage the authors to develop a discussion along a thermodynamic explanation as well and let the readers decide which one is more likely, a kinetic (the one presented in this paper) one or perhaps a thermodynamic one involving changes in surface tension. For example, I would guess that changing the surface tension in the free energy term of a classical model by just about 1 unit could give more ice saturation buildup in the air along the lines measured in the atmosphere. In my simple view of nature, I would see a small change in surface tension (because organics were in the aerosols) a more likely possibility with organics than a neat distribution of soapy sulfated-particles in the tropical upper troposphere.

Of course, the other extreme explanation is that the particles measured were much more pristine than those prepared in the laboratory. It is known that fresh sulfate particles nucleate on top of convective cumulus clouds and these particles may be much more pristine than the ones prepared in the laboratory. Even when sulfate particles are nucleated in the lab, they still have impurity on/in them (see Middle brook et al, AST, 1997), which may be absent in the real atmosphere particularly in the TTL. The authors look at the problem in the opposite direction from the onset, pure sulfate lab samples and impure atmospheric particles. In the case of the tropical troposphere and freshly nucleated particles, the situation, at least in some cases, may be the other way around. We argued a similar case for the differences in freezing rates observed in the atmosphere versus those measured in the lab for polar stratospheric clouds (Tabazadeh, ACP, 2003). The core of the argument relies on the fact that small amounts of impurity can slightly change the surface tension of the ice nuclei formed in the solution and small changes in surface tension can affect the rate process by orders of magnitude (or percentages in terms of critical ice saturation).

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