LETTER

Solution coating around ice particles of incipient cirrus clouds

Kuhs et al. (1) report on the nanometer-scale roughness on the surface of laboratory vapor-deposited cubic ice, I_c, and state that such roughness on the surface of cirrus I_c ice particles can influence the surface reactivity, radiative properties, and water vapor uptake coefficient of incipient cirrus clouds. This assumes that the ice surface of cirrus particles is exposed to air. However, this is not the case when cirrus particles are formed by freezing aqueous aerosol drops. Freezing of aqueous drops with ~20–40 wt% of solute is the mechanism discussed in literature studies mentioned by Kuhs et al., i.e., their refs. 20, 55, 58, and 59.

Fig. 1 demonstrates that ice formed by freezing micrometer-scale drops is enveloped by a residual freeze-concentrated solution (FCS) that is formed by the expulsion of solute molecules (ions) from the ice lattice during the nucleation and growth of ice (2). Fig. 1 *A* and *B* were taken from the same H_2SO_4/H_2O drop at two temperatures. At 214 K, the viscosity of FCS is less than that at 183 K, and therefore a single ice particle surrounded by the FCS is seen (3). Other images were taken on warming from drops investigated in refs. 20, 55, 58, and 59. Fig. 1*C* demonstrates that a branched ice structure is immersed into a partly melted FCS of $(NH_4)HSO_4/H_2O$. Fig. 1*D* was taken after the eutectic melting of the FCS of $(NH_4)_3H(SO_4)_2/H_2O$, and therefore, ice particles are clearly visible. The images of frozen $(NH_4)_2SO_4/H_2O$ drops (data not shown) are similar to Fig. 1 *C* and *D*. Fig. 1*E* shows that a single ice particle is surrounded by the FCS of citric acid/H_2O. Earlier we showed that mixed-phase particles in which the ice core is coated with FCS are formed by freezing $HNO_3/H_2SO_4/H_2O$ drops with access to HNO_3 (4). Ref. 20 reported that HNO_3/H_2O drops produced I_c.

Although our laboratory drops are larger than atmospheric aerosol drops (1–3 μm in diameter), they give a clear picture of how the freezing process proceeds in the atmosphere. Being much smaller than their laboratory counterparts, the atmospheric aerosol drops would likely produce a single ice crystal instead of the branched ice structure coated by a viscous FCS (5).Thus, independently of whether I_c or hexagonal ice, I_h, is formed by freezing atmospheric aerosol drops, the cirrus ice particles will necessarily be coated with the FCS, which ultimately determines the surface reactivity, radiative properties, and water vapor uptake coefficient of cirrus clouds at the very beginning of their development (3). Kuhs et al. (1) would be on firmer ground in their assumption about the role of I_c in cirrus clouds, if there was evidence for I_c formation by vapor deposition on dry atmospheric surfaces.

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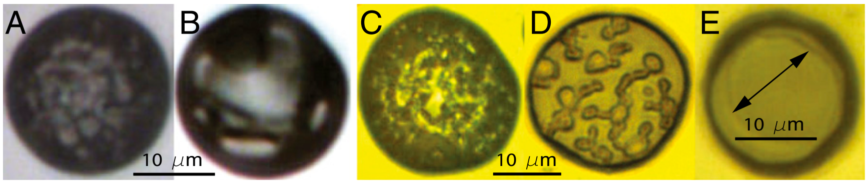

Fig. 1. Optical microscope images of (*A* and *B*) 20 wt% H_2SO_4 drop at 183 and 214 K, respectively, (*C*) 25 wt% $(NH_4)HSO_4$ at 243 K, (*D*) 35 wt% $(NH_4)_3H(SO_4)_2$ at 257 K, and (*E*) 20 wt% citric acid at 218 K. The arrows show the border of ice core.

1 Kuhs WF, Sippel C, Falenty A, Hansen TC (2012) Extent and relevance of stacking disorder in "ice I_c". *Proc Natl Acad Sci USA* 109(52):21259–21264.

2 Bogdan A, Molina MJ (2009) Why does large relative humidity with respect to ice persist in cirrus ice clouds? *J Phys Chem A* 113(51): 14123–14130.

3 Bogdan A, Molina MJ, Sassen K, Kulmala M (2006) Formation of low-temperature cirrus from H_2SO_4/H_2O aerosol droplets. *J Phys Chem A* 110(46):12541–12542.

4 Bogdan A, Molina MJ, Tenhu H, Mayer E, Loerting T (2010) Formation of mixed-phase particles during the freezing of polar stratospheric ice clouds. *Nat Chem* 2(3):197–201.

5 Bogdan A, Molina MJ (2010) Aqueous aerosol may build up an elevated upper tropospheric ice supersaturation and form mixed-phase particles after freezing. *J Phys Chem A* 114(8):2821–2829.

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The authors declare no conflict of interest.

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