

## Particle Production near Marine Clouds: Sulfuric Acid and Predictions from Classical Binary Nucleation

A.D. Clarke,<sup>1</sup> V. N. Kapustin,<sup>1</sup> F. L. Eisele,<sup>2</sup> R. J. Weber,<sup>3</sup> P. H. McMurry<sup>4</sup>

**Abstract.** Recent experiments demonstrate that cloud processes in the free troposphere, and at times in the marine boundary layer (MBL), can result in the production of new aerosol particles linked to sulfuric acid production that is photochemically driven. Here we provide observational evidence from the tropics and mid-latitudes indicating that this nucleation is often in accord with predictions of classical binary nucleation theory when it is applied to the high humidity environment near evaporating clouds edges located above the MBL. Coupled with suitable models for the relevant chemical species and conditions, these observations suggest a means for modeling natural particle production in these regions.

### Introduction

Substantial efforts are currently underway to improve our understanding of both anthropogenic and natural aerosol because of their potential to affect global climate through the direct scattering of sunlight back to space (direct radiative forcing) and alteration of cloud reflectivity through an increase of cloud condensation nuclei (CCN) and associated cloud droplet number (indirect radiative forcing) [NRC Report, 1996]. Aerosol sulfates are important because they constitute a major aerosol species that can dominate aerosol number, aerosol optical properties and those particles active as CCN. Recent progress has been made in linking sulfur mass emissions to measured concentrations and modeled aerosol burdens on global scales [Benkovitz and Schwartz, 1997]. However, the nonlinear processes that govern aerosol formation and evolution have limited similar assessments for aerosol number. This is needed to model processes that link their formation and evolution to CCN and their possible climatic effects.

Relatively stable nuclei concentrations observed over extended regions of the remote oceans [Covert *et al.*, 1996; Clarke *et al.*, 1987] imply that new particles are required to sustain these concentrations against removal via precipitation. While sea salt particles generally dominate marine aerosol mass [Woodcock, 1953], the smaller sulfate usually dominates aerosol number and CCN [Clarke *et al.*, 1987]. The major natural oceanic sulfur source is dimethylsulfide (DMS) [Bonsang *et al.*, 1980] but evidence for new particle formation in the MBL that might sustain sulfate aerosol number has been

limited and ambiguous [Hegg *et al.*, 1990; Covert *et al.*, 1992]. However, high concentrations of small particles in the free troposphere (FT) near deep convective clouds [Clarke, 1993; Perry and Hobbs, 1994; Hoppel *et al.*, 1994; Clarke *et al.*, 1998a] suggested conditions aloft could promote the nucleation of new particles that can later subside and mix into the MBL [Raes, 1995]. Recent experiments [Clarke *et al.*, 1998a; Weber *et al.*, 1999] confirmed that clouds can vent gas phase precursors aloft where photochemistry resulted in elevated H<sub>2</sub>SO<sub>4</sub>(g) concentrations associated with new particles.

Here we compare data from diverse flights with related values predicted from classical binary nucleation theory. We follow the treatment of Wexler *et al.* [1994]. Here the H<sub>2</sub>SO<sub>4</sub>(g)/water system are the presumed nucleating species, and approximations to classical binary nucleation theory lead to an expression for the critical concentration of H<sub>2</sub>SO<sub>4</sub>(g), C<sub>crit</sub>, required for a nucleation rate of  $J = 1 \text{ cm}^{-3}\text{s}^{-1}$ . This expression depends only on ambient temperature  $T$  (K) and relative humidity RH (0-1) and has this form:

$$C_{\text{crit}} = (\text{Const.}) \exp(0.1T - 3.5 \text{ RH} - 27.7) \quad (1)$$

Values obtained from this expression can be compared to ambient H<sub>2</sub>SO<sub>4</sub>(g) concentrations, C<sub>s</sub>, measured during both campaigns using a selected-ion chemical-ionization mass spectrometer [Mauldin *et al.*, 1999]. When C<sub>crit</sub> = C<sub>s</sub>, nucleation is expected. The classical nucleation model of Doyle [1961] is often used and is the basis for the calculations of C<sub>crit</sub> although the appropriate formulation remains controversial. An alternative model [Wilemski, 1984], which corrects for a thermodynamic inconsistency in the Doyle model, predicts significantly lower atmospheric nucleation rates [Kulmala *et al.*, 1998]. However, both models make simplifying assumptions for the hydration of H<sub>2</sub>SO<sub>4</sub>(g) vapor. Comparisons to laboratory measurements suggest that these assumptions may result in under-predicting binary nucleation rates [McGraw and Weber, 1998]. A study of two isolated clouds during the First Aerosol Characterization Experiment (ACE1) revealed that conditions present for nucleation fell between those predicted by the two models [Weber *et al.*, 1999]. One must view the current prediction of binary nucleation rates as uncertain; however, because C<sub>crit</sub> is less sensitive to these uncertainties than predicted nucleation rates, it can provide useful insights into conditions for the onset of binary nucleation.

We have shown previously that during photochemically active periods the regions near cloud outflow can be the source of elevated sulfuric acid and prompt the nucleation of particles [Clarke *et al.*, 1998a; Weber *et al.*, 1999]. These were evident even when RH values were reduced to 50% by dilution with adjacent dry air having much lower particle concentrations. Our hypothesis here is that if most of the elevated nuclei concentrations found aloft during ACE1 and the Pacific Exploratory Mission – Tropics A (PEMT) originate in cloud outflow, then RH will have been near 95% early in this process. Associated near-cloud H<sub>2</sub>SO<sub>4</sub>(g) concentrations can be

<sup>1</sup>School of Ocean and Earth Science and Technology, University of Hawaii, Honolulu, Hawaii

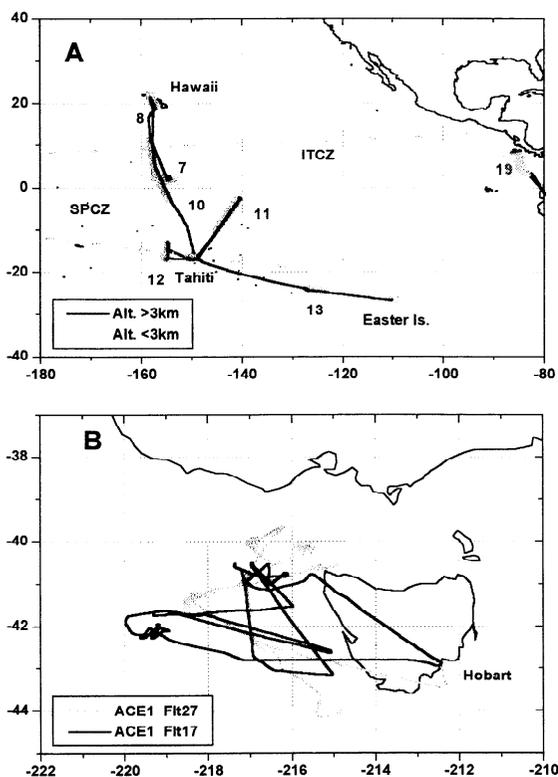
<sup>2</sup>National Center for Atmospheric Research, Boulder, Colorado and Georgia Institute of Technology, Atlanta, Georgia

<sup>3</sup>School of Earth and Atmosphere Sciences, Georgia Institute of Technology, Atlanta, Georgia

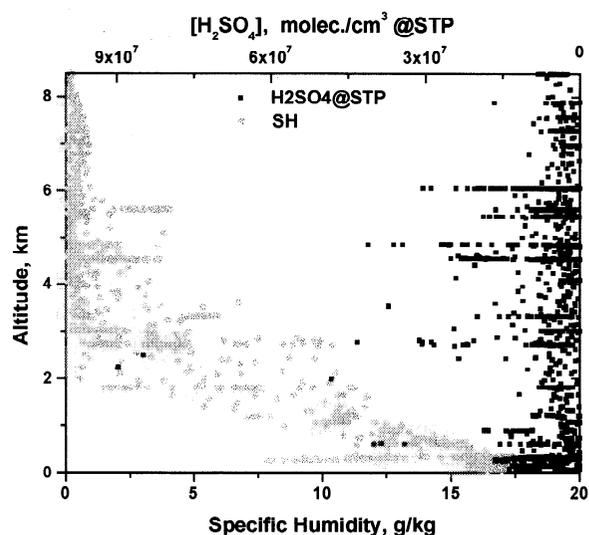
<sup>4</sup>Particle Technology Laboratory, University of Minnesota, Minneapolis, Minnesota

relatively high during the day since the high actinic flux near and above clouds can increase the production of OH by more than a factor of two [Mauldin *et al.*, 1999], which in turn produces more  $\text{H}_2\text{SO}_4(\text{g})$ . Also, OH concentrations are enhanced by increased  $\text{H}_2\text{O}$  near clouds. Subsequent mixing with FT is expected to reduce both RH and  $\text{H}_2\text{SO}_4(\text{g})$  but we assume temperatures to change far less.

Equation 1 involves ambient  $T$  and RH measured coincident with the  $\text{H}_2\text{SO}_4(\text{g})$  and nuclei measurements. However, in keeping with our hypothesis, we define a new parameter,  $C_{\text{crit}95}$ , that is given by Eq. (1) when calculated at 95% RH, a value arbitrarily selected for the vicinity of recently evaporated cloud during initial mixing with the drier FT environment. It is low enough to ensure that most cloud drops are evaporated so that remaining particle surface areas are low, but it is high enough so that mixing and a dilution with dry FT air is also limited. Use of some other similarly high RH will not significantly influence our interpretation. This “corrects” Eq. 1 to RH conditions near cloud outflow, assuming temperatures are the same. However, the same mixing/dilution with FT air that lowers RH will also tend to lower concentrations of  $\text{H}_2\text{SO}_4(\text{g})$ . At the same time FT air often has lower aerosol surface area thus reducing the  $\text{H}_2\text{SO}_4(\text{g})$  loss rate. This compensates for reduced production and suggests that variations in measured  $\text{H}_2\text{SO}_4$  should track variations in  $\text{H}_2\text{SO}_4$  that occurred at 95% RH. Here, we have not tried to “correct” the measured concentrations to near cloud conditions but expect them to be generally higher than those measured.



**Figure 1.** (A) PEMT (1996) flights (7) in equatorial zone. Altitude segments below 3 km are shaded. Higher altitudes include portions where high nuclei counts were encountered that appeared associated with earlier cloud processes. (B) The two ACE1 (1995) missions in and near cloud outflow.

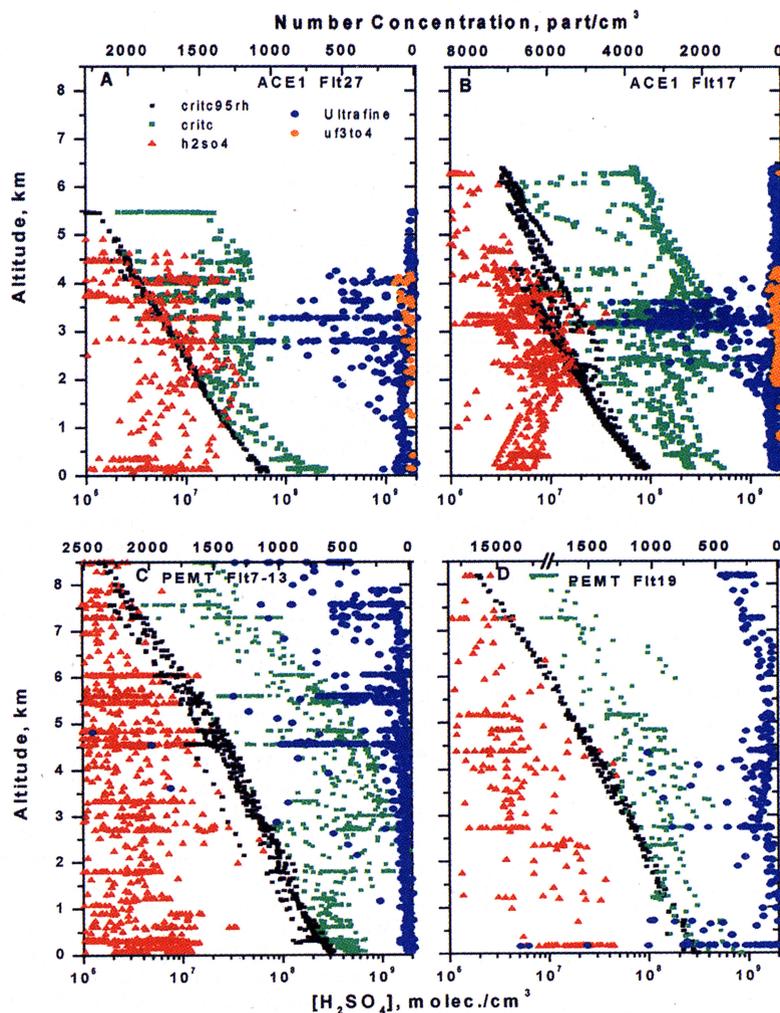


**Figure 2.** Water vapor mixing ratio and  $\text{H}_2\text{SO}_4(\text{g})$  (note variable values for constant altitude legs) for 6 PEM-T flights (7-13) (Figure 1A). Values for  $\text{H}_2\text{SO}_4(\text{g})$  (molecules/cm<sup>3</sup>) are at STP and on a linear scale so vertical variations are more readily apparent.

## Observations

The data presented here were from flights from the PEMT and ACE1 experiments (Figure 1). Previous papers [Clarke *et al.*, 1998a, b] have described the environmental conditions and observations associated with many of these flights. The influence of cloud-driven mixing is supported by the vertical structure in measurements of the water vapor mixing ratio and  $\text{H}_2\text{SO}_4(\text{g})$  from the 7 PEMT flights shown in Figure 2. The  $\text{H}_2\text{SO}_4(\text{g})$  concentrations are highly variable but show moderately high values in the marine boundary layer (MBL), where most convective clouds have their roots, and lowest values in the FT. The intermediate region from 2-6 km that is influenced by cloud-driven air clearly includes most of the highest concentrations observed for both water vapor and  $\text{H}_2\text{SO}_4(\text{g})$ . When nucleation is evident and if classical binary nucleation theory is relevant then measured  $\text{H}_2\text{SO}_4(\text{g})$  concentrations should approach  $C_{\text{crit}95}$  in these and similar regions.

Aerosol nuclei concentrations (15-s averages) indicative of recent nucleation are those in the 3-10 nm range and identified by differences in the TSI 3025CN counter [Stoltzenberg and McMurry, 1991] (detection limit of ~3 nm) and the TSI 3010 condensation nuclei counter (detection limit of ~10 nm), hereafter referred to as “ultrafine” CN. More limited data for concentrations of particles in the 3-4 nm range and averaged over 1 min. were also obtained during ACE1 [Weber *et al.*, 1998]. These data are combined in Figure 3 and shown with the measured  $\text{H}_2\text{SO}_4(\text{g})$  concentrations, the value of  $C_{\text{crit}}$  and  $C_{\text{crit}95}$  defined above. For the ACE1 cloud cases (Figures 3a,b),  $\text{H}_2\text{SO}_4(\text{g})$  concentrations equal or exceed near surface values until about 4.5 km, corresponding to the maximum altitude of clouds observed during these flights. Above 4.5 km  $\text{H}_2\text{SO}_4(\text{g})$  drops by about an order of magnitude and “ultrafine” particles drop to within the uncertainty of the difference measurement. Ultrafine CN and  $\text{H}_2\text{SO}_4(\text{g})$  concentrations are greatest in cloud outflow regions from 2 to 4 km, as are the smallest nuclei (3 to 4 nm range) indicative of recent nucleation. Here  $\text{H}_2\text{SO}_4(\text{g})$  concentrations are generally below  $C_{\text{crit}}$  but above  $C_{\text{crit}95}$ , indicating that classical binary nucleation



**Figure 3.** Vertical profiles of in-situ  $\text{H}_2\text{SO}_4(\text{g})$  concentrations (red dots),  $C_{\text{crit}}$  (green dots) and  $C_{\text{crit}95}$  (black dots) in units of molecules  $\text{cm}^{-3}$  (not at STP). Ultrafine concentrations of particles in the 3–10 nm range (blue dots) and smallest nuclei in the 3–4 nm range that exceed  $10 \text{ cm}^{-3}$  (orange dots-ACE1 only) are also shown. (A) ACE1 flight 27, near-cloud afternoon active photochemistry; (B) ACE1 flight 17, exploratory cloud outflow study; (C) six PEMT equatorial flights showing enhanced ultrafine nuclei where  $\text{H}_2\text{SO}_4(\text{g})$  concentrations approach  $C_{\text{crit}95}$ ; (D) PEMT flight 19 (Figure 1A) with very high  $\text{H}_2\text{SO}_4(\text{g})$  at surface and high RH and low aerosol surface area due to recent MBL precipitation. This resulted in dramatic near surface nucleation (note scale change) as well as evidence of nucleation aloft (2–4 km).

theory would predict nucleation if it had occurred at high RH near cloud edges.  $\text{H}_2\text{SO}_4(\text{g})$  concentrations are frequently higher on flight 27 and, unlike flight 17, values of  $C_{\text{crit}}$  and  $C_{\text{crit}95}$  are often similar because of the high RH measured near cloud. Below the inversion near 1.5 km,  $\text{H}_2\text{SO}_4(\text{g})$  concentrations are much lower and less than both  $C_{\text{crit}}$  and  $C_{\text{crit}95}$ , making binary nucleation unlikely there.

A similar plot (Figure 3b) includes 6 PEMT flights (Figure 1a) near equatorial regions but not near clouds. Here deep convection can feed the FT with cloud-pumped air on either side of the inter-tropical convergence zone (ITCZ). Over this extensive region (latitude 20N–20S, longitude 140–160W, and up to 8.5 km) the  $\text{H}_2\text{SO}_4(\text{g})$  concentrations vary markedly but are in the range of near-surface values. High near-surface DMS concentrations lead to greater net production of  $\text{H}_2\text{SO}_4(\text{g})$  in the MBL than aloft [Clarke *et al.*, 1998b]. However, aerosol surface areas in the MBL usually exceed  $30 \mu\text{m}^2$

$\text{cm}^{-3}$  (dry) compared to less than  $3 \mu\text{m}^2 \text{ cm}^{-3}$  aloft resulting in order-of-magnitude greater loss rates in the MBL that tend to keep  $\text{H}_2\text{SO}_4(\text{g})$  concentrations low. Elevated ultrafine CN are most pronounced between about 4 to 8.5 km and associated with locations where  $\text{H}_2\text{SO}_4(\text{g})$  values approach or exceed  $C_{\text{crit}95}$ . Here  $C_{\text{crit}}$  and  $C_{\text{crit}95}$  often differ by an order of magnitude, due to the low measured RH away from recent cloud outflow. As discussed earlier, post-cloud mixing that lowers RH will also lower  $\text{H}_2\text{SO}_4(\text{g})$  concentrations such that many observed PEMT values can be expected to lie below  $C_{\text{crit}95}$  when compared to near-cloud ACE1 data in Figures 3a, b.

It is of interest to compare these typical cases to an unusual observation of nucleation in the MBL [Clarke *et al.*, 1998b] made on flight 19 of PEMT (Figure 1a). This occurred under high RH in the MBL associated with recent precipitation scavenging that reduced measured ambient “wet” aerosol surface areas to below  $7 \mu\text{m}^2/\text{cm}^3$  and created near-surface condi-

tions similar to cloud outflow. Even though near-surface  $\text{H}_2\text{SO}_4(\text{g})$  is much higher than all other cases observed, it is about an order of magnitude below  $C_{\text{crit}95}$ . The very high, near-surface ultrafine concentrations observed appear inconsistent with classical binary nucleation theory and suggest other mechanisms such as ternary nucleation involving ammonia [Weber *et al.*, 1998] or enhanced ion concentrations (high lightning frequency was observed) may be involved.

These data indicate that nucleation near evaporating cloud boundaries in both mid-latitude and equatorial marine environments is consistent with classical nucleation theory. Measured and modeled [Davis *et al.*, 1999] photochemical production of  $\text{H}_2\text{SO}_4(\text{g})$  concentrations near levels expected from classical binary nucleation are in accord with precursor species, enhanced actinic flux, elevated water vapor, and low surface areas (about  $5 \mu\text{m}^2/\text{cm}^3$ ) in this cloud-scavenged air. We note that these observations do not confirm the validity of this formalism but they do support its use as a predictive tool. Hence, knowledge of the distribution of precursor species such as DMS, OH, or  $\text{SO}_2$  and a parameterization of convection and ambient lapse rate could be used with an appropriate chemical model to predict plausible  $\text{H}_2\text{SO}_4(\text{g})$  concentrations possible in cloud outflow regions. In conjunction with the application of  $C_{\text{crit}95}$  this may allow prediction of the location, altitude and time of day where such nucleation could occur and lead to improved models for the genesis and cycling of aerosol number in the remote atmosphere.

**Acknowledgments.** This work was supported primarily under grants NASA grant NAG-1-1764 and NSF grant ATM-9419475. SOEST Contribution no. 4823.

## References

- Bonsang, B., B. C. Nguyen, A. Gaudry, G. Lambert, Sulfate enrichment in marine aerosols owing to biogenic gaseous sulfur compounds, *J. Geophys. Res.*, **85**, 7410, 1980.
- Benkowitz, C. M., and S. Schwartz, Evaluation of modeled sulfate  $\text{SO}_2$  over North America and Europe for four seasonal months in 1986-1987, *Geophys. Res.*, **102**, 25,305-25,338, 1997.
- Clarke, A. D., Atmospheric nuclei in the Pacific midtroposphere: their nature, concentration, and evolution, *J. Geophys. Res.*, **98**, 20,633-20,647, 1993.
- Clarke, A. D., N. C. Ahlquist, and D. C. Covert, The Pacific marine aerosol: Evidence for natural acid sulfates, *J. Geophys. Res.*, **92**, 4179-4190, 1987.
- Clarke, A. D., J. L. Varner, F. Eisele, R. Mauldin, and D. Tanner, Particle production in the remote marine atmosphere: Cloud outflow and subsidence during ACE 1, *J. Geophys. Res.*, **103**, 16,397, 1998a.
- Clarke, A. D., D. Davis, V. N. Kapustin, F. Eisele, G. Chen, I. Paluch, D. Lenschow, A. R. Bandy, D. Thornton, K. Moore, L. Mauldin, D. Tanner, M. Litchy, M. A. Carroll, J. Collins, G. Albercook, Particle Nucleation in the Tropical Boundary Layer and its Coupling to Marine Sulfur Sources, *Science*, **282**, 89-92, 1998b.
- Covert, D. S., V. N. Kapustin, T. S. Bates, and P. K. Quinn, Physical properties of marine boundary layer aerosol particles of the mid-Pacific in relation to sources and meteorological transport, *J. Geophys. Res.*, **101**, 6919-6930, 1996.
- Covert, D. S., V. N. Kapustin, P. K. Quinn, and T. S. Bates, New particle formation in the marine boundary layer, *J. Geophys. Res.*, **97**, 20,581-20,589, 1992.
- Doyle, G. J., Self-nucleation in the sulfuric acid-water system, *J. Chem. Phys.*, **35**, 795-799, 1961.
- Hegg, D. A., L. F. Radke, and P. V. Hobbs, Particle production associated with marine clouds, *J. Geophys. Res.*, **95**, 13,917-13,926, 1990.
- Hoppel, W. A., G. M. Frick, J. W. Fitzgerald, and R. E. Larson, Marine boundary layer measurements of new particle formation and the effects that non-precipitating clouds have on the size distribution, *J. Geophys. Res.*, **99**, 14,443-14,459, 1994.
- Kulmala, M., A. Laaksonen, and L. Pirjola, Parametrizations for sulfuric acid/water nucleation rates, *J. Geophys. Res.*, **103**, 8301-8307, 1998.
- Mauldin, L. III, D. J. Tanner, J. A. Heath, B. J. Huebert, and F. L. Eisele, Observations of  $\text{H}_2\text{SO}_4$  and MSA during PEM-Tropics-A, *J. Geophys. Res.*, **104**, 5801-5816, 1999.
- McGraw, R., and R. J. Weber, Hydrates in binary sulfuric acid-water vapor: Comparison of CIMS measurements with the liquid-drop model, *Geophys. Res. Lett.*, **25**, 3143-3146, 1998.
- NRC Report, Aerosol Radiative Forcing and Climate Change, p. 48, National Academy Press, 1996.
- Perry, K. D., and P. V. Hobbs, Further evidence for particle nucleation in clear air adjacent to marine cumulus clouds, *J. Geophys. Res.*, **99**, 22,803-22,818, 1994.
- Raes, F., Entrainment of free-tropospheric aerosol as a regulating mechanism for cloud condensation nuclei in the remote marine boundary layer, *J. Geophys. Res.*, **100**, 2893, 1995.
- Stolzenburg, M. R., and P. H. McMurry, An ultrafine aerosol condensation nucleus counter, *Aerosol Sci. Tech.*, **14**, 48-65, 1991.
- Weber, R. J., P. H. McMurry, L. Mauldin, D. J. Tanner, F. L. Eisele, F. J. Brechtell, S. M. Kreidenweis, G. L. Kok, R. D. Schillawski, and D. Baumgardner, A study of new particle formation and growth involving biogenic trace gas species measured during ACE 1, *J. Geophys. Res.*, **103**, 16,385-16,396, 1998.
- Weber, R. J., P. H. McMurry, R. L. Mauldin III, D. J. Tanner, F. L. Eisele, A. D. Clarke, and V. N. Kapustin, New particle formation in the remote troposphere: A comparison of observations at various sites, *Geophys. Res. Lett.*, **26**, 307-310, 1999.
- Wexler, A. S., F. W. Lurmann, and J. H. Seinfeld, Modeling urban and regional aerosols, 1, Model development, *Atmos. Env.*, **28**, 531, 1994.
- Woodcock, A. H., Salt nuclei in marine air as a function of altitude and wind force, *J. Meteorol.*, **10**, 362, 1953.
- Wilenski, G., Composition of the critical nucleus in multi-component vapor nucleation, *J. Chem. Phys.*, **80**, 1370-1372, 1984.
- A. D. Clarke, V. N. Kapustin, School of Ocean and Earth Science and Technology, University of Hawaii, Honolulu, HI, 96822. (E-mail: tclarke@soest.hawaii.edu)
- F. L. Eisele, National Center for Atmospheric Research, Boulder, CO, 80303
- P. H. McMurry, Particle Technology Laboratory, University of Minnesota, Minneapolis, MN, 55455
- R. J. Weber, School of Earth and Atmosphere Sciences, Georgia Institute of Technology, Atlanta, GA, 30322

(Received: December 3, 1998; revised April 29, 1999; accepted May 5, 1999)