

Final Report for NASA Grant NAG5-11474
Influence of nucleation mechanisms on the radiative properties of deep convective clouds
and subvisible cirrus in CRYSTAL/FACE

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During the past few years we have conducted work on several different topics, as reflected by our publications listed below.

As one of the Co-Project scientists for CRYSTAL FACE we worked to help design the mission and then conduct it in the field. We worked on an overview document for EOS (Jensen et al., 2004), and presented a summary talk for the meeting at the Spring AGU meeting in France. We also prepared an overview for Nature of one of the more interesting observations during CYRSTAL, that of dust over the Florida Peninsula (Toon, 2003). Our proposal before the CRYSTAL FACE project noted that such dust events were likely and would lead to an opportunity to test our knowledge of dust/cloud interactions. As we originally proposed to do, we forecast this would occur just before the event and notified the experimenters that dust was likely that day.

Another major activity during the past two years has been to pull together various groups to formulate plans for follow on missions to CRYSTAL FACE. We organized a workshop at the University of Colorado during the summer of 2003 to assess the best locations for future missions. Working with a group of about 10 scientists from around the country we prepared a science-planning document (Tropical Composition, Cloud and Climate Coupling Experiment (TC⁴)) that outlined the rationale, locations, strategy to accomplish the goals, and possible payloads for a set of three tropical missions. We also prepared background materials for various NRAs being prepared at NASA Headquarters for missions in Costa Rica, Darwin and Guam.

In conjunction with the group at NASA Ames we have helped build a new numerical model for deep convection and have applied that model to simulate the CRYSTAL data. Our goal in particular has been to better understand how convection distributes water vapor isotopes. CRYSTAL observations of water isotopes are very different from those suggested by previous workers who assumed the isotopes would obey Rayleigh fractionation. The water isotope study has several implications. First it is a check on the realism of the deep convection model. Second, the isotopes are a measure of the precipitation removal in the atmosphere. Hence they provide a constraint on a parameter that is difficult to otherwise measure. Finally it has been suggested that isotopes may be the key to unraveling the water transport into the stratosphere and upper troposphere. Such transport is critical both for the radiation balance and for stratospheric chemistry. Ours is the first model that is able to treat this transport. Our initial results have just been submitted to Geophys. Res. Lett (Smith et al., 2005). Essentially we are able to explain the vertical profiles of isotopes in the tropical tropopause transition layer. We are also able to account for stratospheric humidity and isotope abundances with this model.

We have also been heavily involved in trying to improve our understanding of nitric acid condensation on ice. Gao et al (2004) have shown that water supersaturations above ice occur when the atmosphere is supersaturated with respect to nitric acid trihydrate. As one of the co-authors of that work, we suggested the mechanism that may explain why this is occurring. Essentially, ice does not like to grow near unit supersaturation, but does so because the water molecules can find sites on the ice surface to attach themselves to

before they fly off the ice surface. This phenomena was well known in the 1960s when it was a source of debate about whether condensation and evaporation coefficients for ice would be the same. Evaporation does not require any molecular orientation, while condensation does, so it was possible that the coefficients would differ. They don't differ because the water molecules rapidly move across the surface and find places to attach. Nitric acid may be occupying these preferred sites and therefore the water molecules can't find a desirable place to attach. We anticipate that this research will be the subject of laboratory work during the coming few years. Another possibility that has been suggested is that cubic ice is forming in clouds. We have measured the vapor pressure of cubic ice, and plan to publish that result in the next few months.

We have also been working on additional aspects of the condensation of nitric acid on ice. With Y. Kondo we studied the condensation of NO_y on ice using the SOLVE data. Gamblin et al have continued this work. The CRYSTAL NO_y and HNO₃ groups have shown that their data can be fit using standard Langmuir isotherms as suggested in some, but not all, laboratory studies. We have found in the SOLVE data set that this is not the case. Moreover some laboratory studies show there are important kinetic effects that may be occurring in the atmosphere limiting the transfer of nitric acid to the ice. The SOLVE data seem consistent with these studies. We are currently re-analyzing the CRYSTAL data to look for these kinetic effects. There are a number of implications of these studies. One of the more interesting is that the nitric acid coating on ice can be used as a cloud clock to determine how long the cloud parcel has been in existence.

We have also been involved with several laboratory studies. We have worked to improve the database on ice optical constants, which are critical for remote sensing. We have also studied the ways in which ice nucleates on clays. We suspect now that the standard theories used for depositional ice nucleation are completely incorrect. Further work will be needed to develop a new theory.

Publications related to this grant:

1. "The Role of Deep Convection in Establishing the Isotopic Composition of Water Vapor in the Tropical Transition Layer", (Jamison A. Smith, Andrew S. Ackerman, Eric J. Jensen, and Owen B. Toon, *Geophys. Res. Lett.*, Submitted, (2005).
2. "Condensation of nitric acid on ice: I Non-HNO₃ constituent of NO_y condensing on Low temperature upper Tropospheric Cirrus Cloud Particles", (B. Gamblin, O. B. Toon et al.) *J. Geophys. Res.* submitted (2005).
3. "Condensation of nitric acid on ice: II kinetic limitations a possible clock for cloud parcel lifetimes", (B. Gamblin, O. B. Toon, M. Tolbert, P. Hudson, et al.) *J. Geophys. Res.* submitted (2005).
4. "Measurement of the temperature-dependent optical constants of water ice in the 15-200 μ m wavelength region, (B. Rajaram, D. B. Curtis, O. B. Toon, and M. A. Tolbert), *Appl Optics*, in press, (2005).
5. "Infrared Characterization of Water Uptake by Low Temperature Na-Montmorillonite: Implications for Earth and Mars", (Frinak, E., C Mashburn, O. F. Toon and M. Tolbert) *J. Geophys. Res.* Vol. 110, No. D9, D0930810.1029/2004JD005647, (2005).

6. "Mission Investigates Tropical Cirrus clouds" (E. Jensen, D. Starr, O.B. Toon) EOS Trans. AGU, 85,45, (2004)
7. "Evidence that Nitric Acid Increases Relative Humidity in Low-Temperature Cirrus Clouds"(R. S. Gao, P. J. Popp, D. W. Fahey, T. P. Marcy, R. L. Herman, E. M. Weinstock, D. G. Baumgardner, T. J. Garrett, K. H. Rosenlof, T. L. Thompson, P. T. Bui, B. A. Ridley, S. C. Wofsy, O. B. Toon, M. A. Tolbert, B. Kärcher, Th. Peter, P. K. Hudson, A. J. Weinheimer, A. J. Heymsfield, *Science* 303 (5657): 516-520, 2004.
8. "Atmospheric Science, African dust in Florida clouds" (O. B. Toon), *Nature*, 424, (6949): 62-624, (2003).
9. "Uptake of nitric acid on cirrus cloud particles in the upper troposphere and lowermost stratosphere", (Y. Kondo, O. B. Toon, H. Irie, B. Gamblin, M. Koike, N. Takegawa, M. A. Tolbert, P. K. Hudson, A. A. Viggiano, L. M. Avallone, A. G. Haller, B. E. Anderson, G. W. Sachse, S. Vay, D. E. Hunton, J. O. Ballenthin, and T. M. Miller), *Geophys. Res. Lett.*, 30 (4): Art. No. 1154, (2003).
10. "Uptake of nitric acid on ice at tropospheric temperatures: Implications for cirrus clouds" (P. K Hudson, J. E. Shilling, M. A. Tolbert, and Owen B. Toon), *J. Phys. Chem. A*, 106, 9874-9882, (2002).