OPTICAL GROWTH MEASUREMENTS OF TITAN AND EARLY EARTH ORGANIC AEROSOL ANALOGS. C. A. Hasenkopf[1, 2] , M. R. Beaver[2, 3], M. A. Freedman[2], M. A. Tolbert[2, 3], and O.B. Toon[1, 2] [1]Department of Atmospheric and Oceanic Sciences, University of Colorado, Boulder, CO 80309, [2]Cooperative Institute for Research in the Environmental Sciences, CIRES, University of Colorado, Boulder, CO 80309, [3]Department of Chemistry, University of Colorado, Boulder, CO 80309, Christa.Hasenkopf@colorado.edu, Melinda.Beaver@colorado.edu, Miriam.Freedman@colorado.edu, Margaret.Tolbert@colorado.edu, Brian.Toon@lasp.colorado.edu

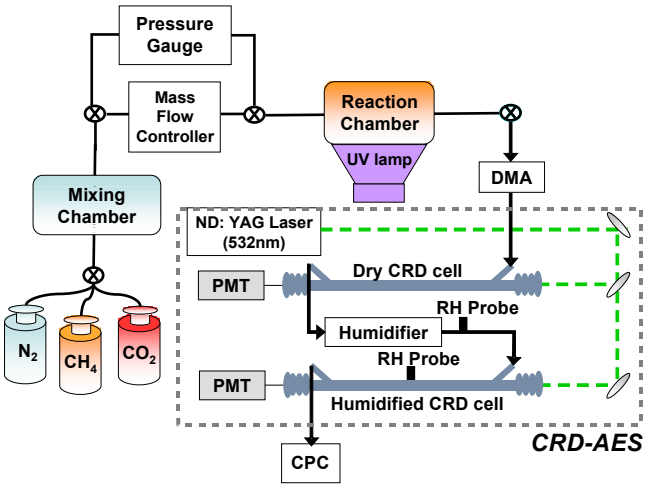
Introduction: Organic haze is known to be ubiquitous throughout Titan's atmosphere [1],[2], and a similar aerosol may have been present in Archean Earth's atmosphere, as well [3], [4]. On Titan, the haze generated from the photolytic dissociation of methane (CH_4) and nitrogen (N_2) has a profound effect on the radiative balance of its atmosphere and surface temperature. The haze acts as an anti-greenhouse agent by blocking incoming solar radiation and keeps the surface 10% cooler than it would be without its presence [5]. The strong impact of this organic haze on Titan begs the question of how a similar aerosol layer may have influenced the climate of the Earth 3 billion years ago, as early life was evolving. For example, depending on the optical properties of such a haze, it may have served as an ultraviolet shield in a time before the ozone layer was present [3], or perhaps it may have been so opaque that the temperature of the surface was drastically reduced as it is on Titan [6].

In order to understand the magnitude of an organic aerosol's influence on the radiative balance of early Earth, both how the aerosol directly interacts with radiation and how it indirectly affects the formation and optical properties of clouds must be considered [7]. One way to assess both of these effects is by measuring the optical growth of analog particles upon humidification. Using the novel technique of cavity-ringdown spectroscopy, we report optical growth factors at a relative humidity (RH) of 80% and an incident wavelength of 532 nm for Titan and early Earth organic aerosol at several sizes.

Experimental Technique: Fig. 1 shows the experimental setup.

Aerosol generation. Aerosols are generated from UV photolysis of either a Titan or an early Earth atmospheric analog. Our Titan analog atmosphere consists of 0.1% CH_4 in a background of N_2. This composition, when photolyzed with UV light, produces aerosol that are chemically and physically identical to analog aerosol generated from a more stratospheric Titan-like gas mixture of 2% CH_4 in N_2, yet provides higher signal for our main analysis instrument than other CH_4-N_2 mixtures [8]. The early Earth analog consists of 0.1% CH_4 and 0.1% CO_2 in N_2. This mixture has a C/O ratio

Fig. 1: Experimental setup.



of 1 and is considered to be a plausible early Earth analog atmosphere [9]. Additionally, highest production of particles is found at this concentration, and this mixture lends itself well to comparison with the particles generated from the Titan analog gas mixture.

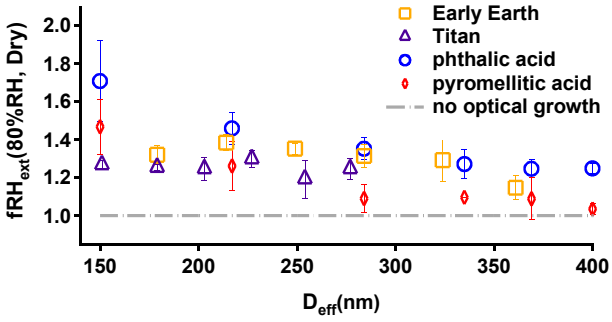
Cavity-ringdown system. Once generated, particles enter a differential mobility analyzer (DMA) in order to create a monodisperse aerosol population. The size-selected flow enters the cavity-ringdown aerosol extinction spectrometer (CRD-AES), shown in Fig. 1. A detailed description of the CRD system used in this study can be found in [10]. The aerosol first enters the the dry cell (RH <15%), where the extinction coefficient of the dry particles, $b_{ext\text{-}dry}$ (cm^{-1}), is measured. The aerosol flow then enters a humidification chamber in which it is conditioned to an RH of 80 ± 3%. The extinction of the humidified particles, $b_{ext\text{-}wet,}$, is then measured in the wet cell. By determining these two extinction coefficients, the optical growth f(RH) of the humidified particles can be calculated:

$$f(RH) = \frac{b_{ext\text{-}wet}}{b_{ext\text{-}dry}}$$

Results & Discussion: Fig. 2 shows f(RH) of the Titan and early Earth analog aerosols as a function of particle diameter. The f(RH) of both analogs is significantly above unity. For the size range measured, the average extinction enhancement of the humidified particles is 124 ± 3% and 131 ± 7% for Titan and early

Earth aerosols, respectively. The optical growth of these aerosols is similar to known slightly-soluble organic acids, such as phthalic and pyromellitic acids. The optical growth of the early Earth analog was slightly larger than the Titan analog at all sizes. This is not surprising since earlier work in our laboratory shows incorporation of oxygen in the early Earth analog aerosol [8], which should make them slightly more water soluble than the Titan analog aerosol. Two interesting implications arise from these results. (1) The significant departure of the optical growth factors from unity of the early Earth analog indicates that it is important for radiative balance models of the Archean atmosphere to account for optical growth of organic aerosol. (2) The fact that the early Earth analog takes up any water at all mark it as a possible cloud condensation nuclei (CCN) candidate. This is intriguing since it is not know what types of CCN existed on early Earth. The majority of CCN today are generated through biogenic processes [11] that would not have been relevant in an anoxic atmosphere. Work is being done to connect the optical growth properties of the hazes with their ability to act as CCN.

Fig. 2: Optical growth f(RH) for the Titan analog aerosol (triangles), the early Earth analog aerosol (squares), and several other organic aerosols (phtalic acid-circles, pyrometallic acid-diamonds). The dashed line indicates no optical growth. The phtalic and pyromellitc acid data is from [10].



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