**IMPACT OF MOLECULAR OXYGEN ON ION CHEMISTRY AND ARCHEAN EARTH HAZE.** M. S. Ugelow[1,2], J. L. Berry[1,2], E. C. Browne[1,2], and M. A. Tolbert[1,2], [1]Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO, 80309, USA, Melissa.Ugelow@colorado.edu; [2]Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO, 80309, USA, Jennifer.L.Berry@colorado.edu.

**Introduction:** Life on Earth is thought to have arisen during the Archean, with the oldest microfossils aged at 3.5 Ga [1]. However, the atmospheric conditions during this time are quite uncertain. To maintain liquid water with a faint young sun, models typically include methane and carbon dioxide as greenhouse gases. However, the estimated atmospheric methane and carbon dioxide concentrations needed to warm the planet could have led to the formation of an organic haze in the atmosphere of the ancient Earth [2-9]. While the amounts of these gases varied during the Archean, previous laboratory studies have shown that haze can exist with $CO_2$:$CH_4$ ratios as high as 10:1 [7], supporting the existence of a haze during much of Earth's ancient history. The presence of an atmospheric haze, and understanding how it forms, is important to consider when examining the evolution of life since haze can be composed of prebiotic molecules [10] and can also modulate surface temperatures, and thus the presence of surface liquid water [11].

Much of what is understood about the formation of planetary organic hazes is from Saturn's moon Titan. In Titan's atmosphere, haze production begins in the upper atmosphere through ion-neutral chemistry [12-16]. As ions react with neutrals and oppositely charged ions in the ionosphere, they will ultimately become aerosol [16]. Using Titan as an analog for the Archean Earth, it is possible that an Archean haze could have formed by ion-neutral chemistry as well. However, unlike Titan, the Archean Earth would have contained $CO_2$ and laboratory studies have demonstrated that a haze that forms in a $CO_2/CH_4/N_2$ atmosphere would be chemically distinct from a haze that forms in the absence of any major oxygenated species [4, 17, 18].

In addition to $CO_2$ influencing haze formation chemistry, it could have also lead to the synthesis of molecular $O_2$ when photolyzed. While $O_2$ levels during the Archean are uncertain, theoretical studies suggest that a planet with 0.2 bars $CO_2$ could contain up to tenths of a percent of stratospheric $O_2$ due to $CO_2$ photolysis [19, 20]. It has also been suggested that up to 63 ppm of atmospheric $O_2$ may have existed as long as 3 Ga [21]. The presence of $O_2$ could alter haze formation chemistry since oxygen is believed to terminate haze production by initiating reactions that oxidize the gas species before they polymerize into haze [22]. Here we examine the effect of molecular oxygen on the formation of Archean Earth haze analogs, the relationship between ion chemistry and haze analog formation, and the effect of molecular oxygen on the ion chemistry.

**Experimental Methods:**

*Haze analog formation*. Haze analogs were produced with 0.1% $CO_2$ and 0.1% $CH_4$ in $N_2$ with 0, 2, 20, 200 and 2000 ppmv $O_2$. The gases $CO_2$, $CH_4$, $O_2$ and $N_2$ were flowed into a mixing chamber and mixed for at least 8 hours. Then, a mass flow controller flowed the gas mixture into the UV reaction cell at a rate of 100 sccm. One side of the reaction cell has a deuterium continuum lamp that outputs light between 115 and 400 nm, peaking between 115 and 165 nm. Haze formation chemistry is initiated, and the resulting haze particles and gas phase neutrals and ions were flowed to a Scanning Mobility Particle Sizer (SMPS) or an Atmosphere Pressure interface High-Resolution Time-of-Flight Mass Spectrometer (APi-HR-ToF-MS).

*Instrumentation.* An SMPS is the combination of a differential mobility analyzer (DMA) and a condensation particle counter (CPC) and is used to quantify the number of haze particles produced. An APi-HR-ToF-MS uses no ionization source and thus only naturally charged species are detected. Here, it measures the composition of ions produced during haze analog formation. This instrument can be operated in both positive and negative ion mode, and measures ions between m/z = 1 and m/z = 1000 with extremely high mass resolution (up to M/ΔM = 10,000). Therefore, ions with the same nominal mass can be identified exactly.

**Results:** During the formation of the different haze analogs in this study, ion chemistry is initiated at the same time as aerosol formation, i.e. when the UV lamp is turned on. Figure 1 shows that the total negative ion

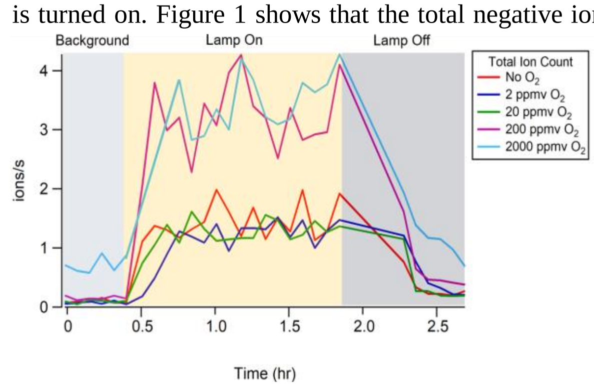


*Figure 1. Negative ion chemistry is initiated by the UV lamp*

count increases once the lamp is turned on and returns to background levels after it is turned off. Additionally, the total number of negative ions that form when the UV lamp is turned on increases for the analogs produced with the largest concentrations of precursor $O_2$.

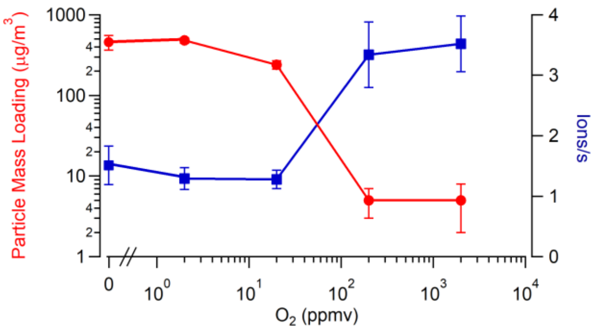


*Figure 2. Negative ion concentration and haze particle mass loading for each haze analog as a function of precursor $O_2$. Mass loadings are calculated from the SMPS measured number density and effective density values from [23].*

The total negative ion count during aerosol formation was compared to the aerosol mass loading for each haze analog in this study. Figure 2 shows that there is an inverse relationship between the concentration of negative ions and haze, with a transition between 20 and 200 ppmv precursor $O_2$. The inverse relationship between ion concentration and haze particle mass loading follows what is observed in Titan's atmosphere where haze forms by the reaction of ions. When more haze particles are produced, there are less ions because they have reacted with other ions, neutrals and/or aerosol and turned into haze particles. However, when less haze is produced, there are more ions because they have not reacted to form haze particles. Also noteworthy, while there is a steep drop off in haze analog production after 20 ppmv $O_2$, haze analogs can still form in the presence of 2000 ppmv $O_2$.

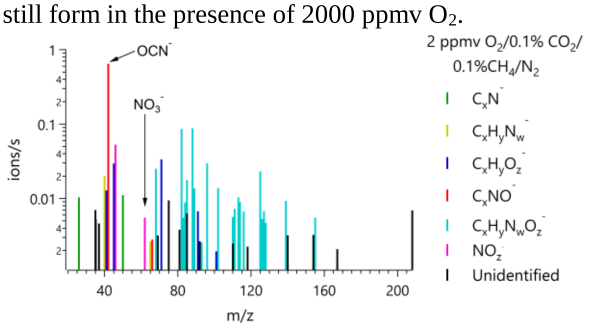


*Figure 3. An example mass spectrum of the negative ions detected during haze analog formation*

Figure 3 includes an example mass spectrum obtained by the APi-HR-ToF-MS when the UV lamp was turned on to produce haze analogs from 2 ppmv $O_2$/0.1% $CO_2$/0.1% $CH_4$ in $N_2$. Negative ions are colored according to chemical composition. Most of the negative ions produced during Archean haze analog formation contain both nitrogen and oxygen.

When following the types of negative ions produced during Archean Earth haze analog formation, the most noticeable feature is the transition in the type of chemistry that follows the decline of particle mass loading. When haze analogs are formed in the absence of, or with small amounts of $O_2$, the ions mostly contain organic nitrogen, with the most intense ion peak being $OCN^-$. However, with 200 ppmv $O_2$ and greater, the ions contain mostly inorganic nitrogen and the most intense ion peak is $NO_3^-$. The growth of the nitrate ion signal with precursor $O_2$ could be relevant to early life. Being a potential source of fixed nitrogen, atmospheric $NO_3^-$ produced during haze formation could be an important nutrient for the rise and/or evolution of life.

**Conclusion:** Similar to what is observed in Titan's atmosphere, ion chemistry is likely related to early Earth haze analog formation. Additionally, ion composition and the ability to form a thick organic haze is related to the amount of precursor $O_2$, with a transition observed between 20 and 200 ppmv precursor $O_2$. The transition from $OCN^-$ to $NO_3^-$ with increasing $O_2$ could have been important for the evolution of early life, with atmospheric $NO_3^-$ produced during haze formation being a potential source of fixed nitrogen.

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