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Refractive indices of Early Earth organic aerosol analogs

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Abstract

Organic aerosols in the early Earth atmosphere are hypothesized to provide additional shielding to solar radiation. We simulate the conditions of this primitive atmosphere by adding CO_2 to a N_2:CH_4 plasma mixture. We produce aerosol analogs (named *tholins*) in plasmas with CO_2 / CH_4 = 1 and 4. For the latter ratio, the production of tholins decreases significantly. We measured the thin organic films via ellipsometry and modeled this data to obtain the thickness, optical band gap, and refractive indices from 1 to 5.5 eV. These absorption coefficients vary with the inclusion of CO_2, where the maximum blueshifts as the CO_2 concentration is increased. Such measurements reveal how organic aerosols in the early Earth atmosphere preferentially absorb photons of shorter wavelengths than typical Titan tholins, suggesting a coolant role in the early Earth. The refractive indices of such materials can further improve climate models of the early Earth.

1. Introduction

CO_2 is considered to be the dominant greenhouse gas offsetting the early Sun that could have kept the early Earth unfrozen. The partial pressure of CO_2 is expected to be more abundant in the Archean eon than in the modern Earth, and even more abundant in the Hadean. Modeling work expects CO_2 abundances of 3% to sustain a global average surface temperature of 273 K in the Late Archean and 10% to sustain a temperature of 288 K in the Early Archean [1, 6]. However, CO_2 can be removed by the flow of carbon into the mantle via the subduction of carbonatized seafloor [4], diminishing the atmospheric reservoir and decreasing its warming effect on the Archean climate. In addition, photochemistry of CO_2 in the early atmosphere could lead to formation of hazes which, depending on their optical properties, could induce early atmospheric warming or cooling. The aim of this work is to experimentally simulate the hypothetical composition of the early and late Archean, and to understand the impact of CO_2 in the production and optical properties of organic hazes.

2. Methods

Tholins, complex amorphous organic solids, were produced using the PAMPRE setup, a low pressure (0.95 mbar) radiofrequency (R.F.) plasma reactor [5]. This setup allows the simulation of the complex organic chemistry initiated by VUV solar photons in the ionosphere of the early Earth and Titan [2]. A 13.56 MHz R.F. power source tuned at 30 W generates a capacitively coupled plasma (CCP) fed by a gas mixture. Two different gas mixtures were used N_2:CH_4:CO_2 at 90:2:8 and 90:5:5 ratios N_2:CH_4 at 95:5 ratios. The plasma was produced within a vertical cylindrical cage. Bare silicon substrates were placed on the bottom electrode. The plasma is turned on until a thin film is deposited on the substrates.

Table 1: Early Earth tholins.

N_2:CH_4:CO_2	CO_2/CH_4	Yield [nm / hour]
90:2:8	4	8 ± 3
90:5:5	1	180 ± 8
95:5:0	0	425 ± 15

3. Analysis

Ellipsometric measurements were performed for the three different tholin samples produced with and without CO_2. The measured Ψ and Δ parameters result from the interaction between the light with both the organic film and the Si substrate. We model a multilayer system consisting of the substrate, the organic material and a roughness layer, combining the optical constants of the organic layer and air. The tholin is modeled via a Tauc-Lorentz oscillator, applicable to amorphous organic films [3]. From these models, we note that the

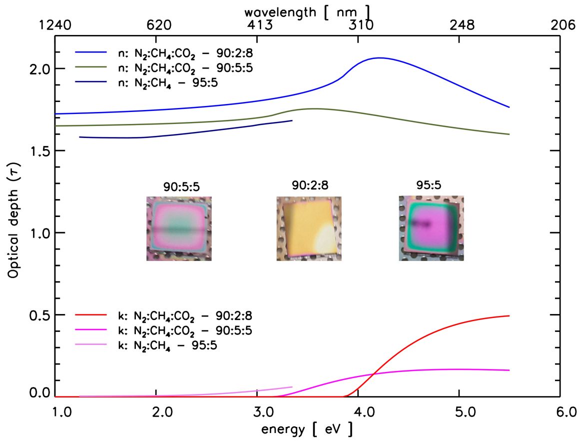

Figure 1: Refractive indices modeled for tholins prepared with different mixtures of N_2:CH_4:CO_2.

center of the main ultraviolet band is blueshifted for CO_2 / CH_4 = 4 with respect to CO_2 / CH_4 = 1, suggesting that the presence of CO_2 leads to organics absorbing UV photons at higher energies.

4. Conclusions

Our experiments show that even at high concentrations of CO_2/CH_4, organic aerosols can still be produced. This suggests that even if the atmosphere of the primitive Earth was oxidized, photochemical organic aerosols could still be produced. However, as the CO_2 concentration increases, the aerosol yield significantly decreases due to the intermediate plasma production of H_2O, among other reactants [2], consequently implying a reduced aerosol yield in the Hadean and early Archean.

We modeled the refractive indices of these tholins from 1 to 5.5 eV (225 - 1000 nm). The far UV shielding properties of the most oxidized tholins (with a maximum absorption peak at 318 nm) makes this organic haze essentially a coolant, particularly if considering the blueshifted spectrum of a young Sun. As the amount of CO_2/CH_4 decreases, the production of organic aerosols is more efficient, but they are optically less absorbing than those produced at higher CO_2 partial pressures, absorbing UV photons shortward of 413 nm. When CO_2 is removed, as in the case of Titan's reducing atmosphere, the tholin production yield is greatest, absorbing UV photons shortward of 518 nm.

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References

[1] Feulner, G. Reviews of Geophysics, 50, RG2006, 2012.

[2] Fleury, B., Carrasco, N., Marcq, E., et al. The Astrophysical Journal Letters, 807, 2, 2015.

[3] Mahjoub, A., Carrasco, N., Dahoo, P.-R., et al. Icarus, 221, 670, 2012.

[4] Sleep, N. H. & Zahnle, K. Journal of Geophysical Research, 106, 1373, 2001.

[5] Szopa, C., Cernogora, G., Boufendi, L., et al. Planetary and Space Science, 54, 394, 2006.

[6] von Paris, P., Rauer, H., Lee Grenfell, J., et al. Planetary and Space Science, 56, 1244, 2008.