Fractal Organic Hazes Provided an Ultraviolet Shield for Early Earth

E. T. Wolf, *et al.*

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Fractal Organic Hazes Provided an Ultraviolet Shield for Early Earth

E. T. Wolf and O. B. Toon

The Archean Earth (3.8 to 2.5 billion years ago) was probably enshrouded by a photochemical haze composed of fractal aggregate hydrocarbon aerosols. The fractal structure of the aerosols would have had a strong effect on the radiative properties of the haze. In this study, a fractal aggregate haze was found to be optically thick in the ultraviolet wavelengths while remaining relatively transparent in the mid-visible wavelengths. At an annual production rate of 10^{14} grams per year and an average monomer radius of 50 nanometers, the haze would have provided a strong shield against ultraviolet light while causing only minimal antigreenhouse cooling.

The atmosphere of the Archean Earth (3.8 to 2.5 billion years ago) was much different from the present one. The prevailing view of the Archean atmosphere is that it consisted primarily of N_2 with lesser amounts of CO_2, CH_4, H_2, and H_2O. Solar evolutionary models predict that the young Sun was up to ~30% less luminous than now (*1*), but the lack of evidence of glaciation combined with positive evidence of primitive life indicates that Archean surface temperatures were generally as warm or warmer than today (*2*, *3*). Resolving this paradox is important for understanding the environment of Earth at the time of the origin of life. Although a dense CO_2 atmosphere could theoretically have warmed the early Earth, the absence of siderite in fossil weathering profiles constrains the amount of CO_2 present in the young atmosphere (*4*). Combined greenhouse warming from CO_2, CH_4, NH_3, and other less abundant gases is typically invoked to resolve this apparent paradox. Past studies indicate that N_2-CH_4 photochemistry produces an organic haze at high altitudes that could cool the planet, offsetting any greenhouse warming (*5*, *6*). In contrast, we show here that the haze would be optically thin at visible wavelengths and therefore have little cooling effect on climate, but would be optically thick at ultraviolet (UV) wavelengths and thus could shield reduced gases from photolysis. The key is to consider the fractal nature of the haze particles.

Atmospheric conditions similar to those that prevailed on the young Earth exist currently on Titan, a moon of Saturn. Titan's atmosphere is strongly reducing, consisting of 98.4% N_2 along with 1.6% CH_4 and other hydrocarbons. Photochemical production of organic aerosols on Titan produces an optically thick haze that has been much studied (*7*). Similar organic aerosols are observed to form readily even in weakly reducing early–Earth-like laboratory gas mixtures having CO_2:CH_4 ratios as high as 10:1 (*8*). A Titan-like photochemical haze should have formed high in the Archean atmosphere as well. Sagan and Chyba (*9*) argued that an organic haze may have provided a strong UV shield, protecting underlying constituents and primitive organisms from photochemical destruction. It is of particular interest that if NH_3 is protected by a strongly UV-absorbing haze and allowed to accumulate, a surface mixing ratio of 10^{-5} could alone provide sufficient greenhouse warming to keep Archean surface temperatures above freezing (*1*). However, recent modeling studies have suggested that the haze would be of a similar optical thickness in both the UV and visible wavelengths (*5*, *6*). Thus, any increase in UV shielding is accompanied by a thickening at visible wavelengths, which would cause intense antigreenhouse cooling and freeze the planet.

Previous models of the Archean haze have inaccurately made the simplifying assumption of particle sphericity. Hydrocarbon aerosols have long been known to form fluffy aggregates that exhibit fractal structure (*10*). This fractal structure affects both the microphysical and radiative properties of the haze. Given the expected chemical and microphysical similarities between Titan and early Earth, we simulated haze particles as fractal aggregates (*11*), using a scheme introduced by Cabane *et al.* (*12*) and later used by Rannou *et al.* (*13*–*15*), to model fractal aggregate hazes in Titan's atmosphere. The fractal model is successful in reproducing the scattering properties of Titan's haze (*7*).

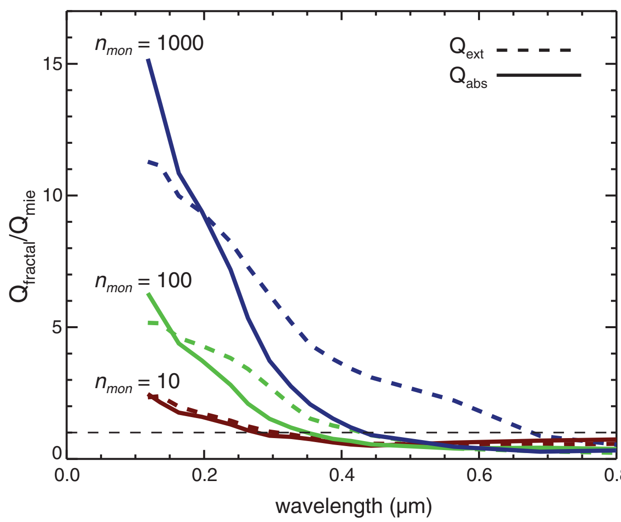

Fig. 1. The ratio of absorption (Q_{abs}, solid line) and extinction (Q_{ext}, dashed line) efficiencies calculated for fractal aggregate particles ($Q_{fractal}$) to those calculated for Mie particles of equal mass (Q_{mie}). A value of unity indicates that the aggregate particle is radiatively indistinguishable from the Mie particle. The particles illustrated have $D_f = 2$, $r_{mon} = 50$ nm, and n_{mon} = 10, 100, and 1000, corresponding to fractal radii of 0.16, 0.5 and 1.6 μm, respectively (Eq. 1). We assume refractive indices for Titan analogs (*19*). Fractal aggregate particles are an order of magnitude more absorbing in the UV while being slightly less absorbing in the visible than are Mie particles of equal mass. The gradient increases for larger aggregates containing more monomers.

Department of Atmospheric and Oceanic Sciences, Laboratory for Atmospheric and Space Physics, University of Colorado, Boulder, CO 80309–0311, USA.

A fractal aggregate is formed by the coagulation of many primary spherical particles (henceforth called monomers) into a larger complex structure. Although the shape of each individual aggregate can appear complicated, fractal objects have the unifying property of self-similarity. The structural properties of fractal aggregates can be quantified to a first approximation by a single parameter, the fractal dimension, denoted D_f. The fractal dimension describes the morphological dimension of the aggregate: $D_f = 3$ describes a compact spherical particle, whereas $D_f = 1$ describes a linear chain. When $D_f < 3$, the particle radius is not so easily defined. Fractal geometry provides the needed mathematical framework to proceed. The radius of a fractal aggregate, R_f, is defined by the equation

$$n_{mon} = \alpha \left(\frac{R_f}{r_{mon}} \right)^{D_f} \quad (1)$$

where n_{mon} is the number of monomers contained in the aggregate, α is a dimensionless constant (taken here to be unity), and r_{mon} is the average monomer radius (*16*).

Fractal particles behave optically like a bimodal distribution of spherical particles. Monomers contained within the aggregate interact strongly with shortwave radiation, whereas the bulk size of the aggregate affects longer wavelengths. Considerable work has been done on the theory of scattering and absorption by fractal aggregate particles. Here we adopt the mean-field approximation of Mie scattering by fractal aggregates of identical spheres proposed by Botet *et al.* (*17*, *18*). In this method, fractal aggregates are considered to be composed of n_{mon} identical spherical monomers of radius r_{mon}, each acting as a Mie particle. The total scattered electric field from an aggregate is the sum of the scattered fields from each monomer contained within the aggregate. We assume refractive indices for Titan-analog hazes (*19*). The incorporation of oxygenated species into early-Earth hazes would probably have altered their refractive indices; however, wavelength-dependent data for oxygenated hazes are not currently available. As illustrated in Fig. 1, fractal aggregates are considerably more absorbing in the UV while being slightly more transparent in the visible and near-infrared than are Mie particles of equal mass. This trend becomes more pronounced as n_{mon} increases and is attributed to the inherent bimodal nature of fractal aggregates (*20*).

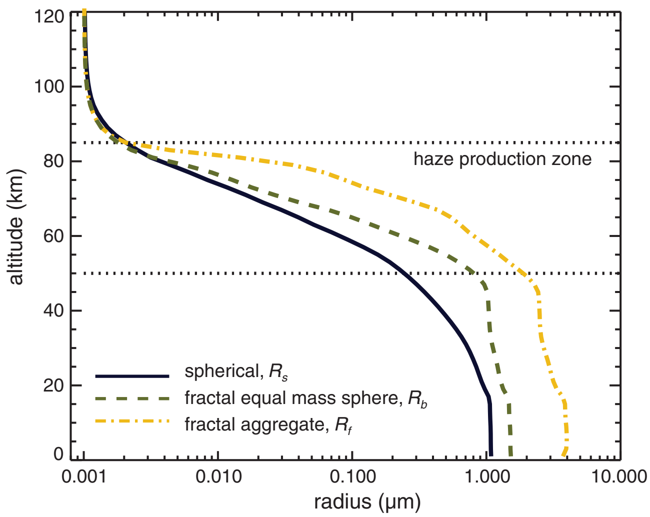

Fig. 2. The globally and annually averaged effective radii for spherical particles (solid line), equal-mass sphere effective radii calculated for aggregate particles (dashed line), and the effective fractal radii (dash-dotted line) are shown for a haze production rate of 10^{14} g year^{-1} and r_{mon} = 50 nm. Fractal aggregates grow both more massive and geometrically larger than spherical particles.

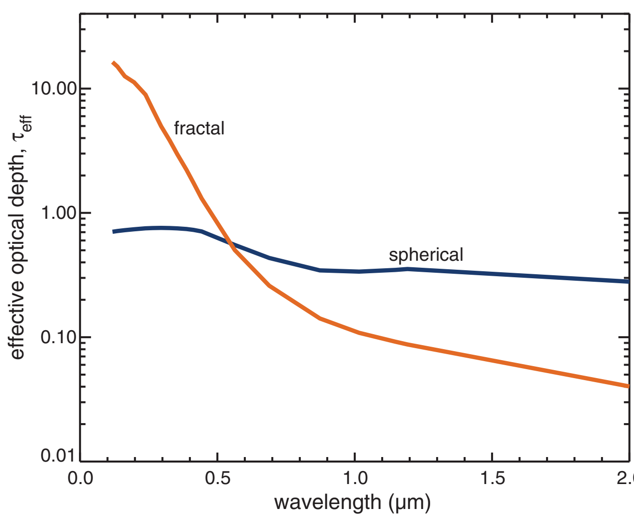

Fig. 3. The globally and annually averaged effective optical depth (τ_{eff}) plotted for both spherical and fractal models for a haze production rate of 10^{14} g year^{-1} and r_{mon} = 50. Fractal aggregate particles (orange line) provide strong UV shielding while remaining thin at visible wavelengths. A steep gradient is exhibited at wavelengths below 0.8 μm. A spherical haze (blue line) exhibits no such gradient, shielding all wavelengths more or less equally.

In this study, we focused on an annual haze production rate of 10^{14} g year^{-1} because it presents the most interesting ramifications for the Archean climate and is also a median value predicted for the production rate of early-Earth hazes (*8*). For comparison, the current rate of mass production in the global S cycle is about 1 × 10^{14} g year^{-1} to 2 × 10^{14} g year^{-1} (*21*), whereas the current rates of organic C burial and of CH_4 production are of the same order of magnitude (*5*). Measurements of the phase function and polarization of Titan fractal aggregate hazes constrain monomer radii to be no larger than 50 nm (*7*). We used the canonical value of r_{mon} = 50. Simulations were conducted using both the fractal and spherical models.

Using a size-resolved aerosol model in a three-dimensional global climate model (*11*), we are able to predict the global distribution of the particle optical and microphysical properties. Particle effective radii reach micrometer sizes in the lower atmosphere in these simulations; such sizes are similar to those that occur in the atmosphere of Titan (Fig. 2). The effective radii of equal-mass spheres, R_b, are an indicator of the mass per aggregate rather than its true geometric size. In the troposphere, R_b is larger than the effective radii of spherical particles, R_s, by a factor of 1.5, indicating that fractal aggregates grow more massive than do spherical particles. This trend is attributed to the increased geometric cross section of aggregates, which both reduces sedimentation velocities and enhances coagulation. The effective fractal radius, R_f, describes geometrical information about fractal aggregates. In the troposphere, $R_f > R_s$ by a factor of 4 and is more than double R_b. Our results indicate that fractal aggregates grow to significantly greater geometric sizes while remaining only slightly more massive than spherical particles, thus reflecting the fluffy nature of fractal aggregates. We find that early-Earth haze particles typically would have contained ~10^4 monomers (*11*). For comparison, Titan aerosols are estimated to contain ~3000 monomers per aggregate in its stratosphere; however, estimates are not well constrained because of uncertainties in the fractal dimension, average monomer size, and haze optical constants, all of which are required to determine n_{mon} from observations (*7*).

The global mean effective optical depth (τ_{eff}) was calculated using both spherical and fractal models (*22*). The spherical simulation predicts that the early-Earth haze would have been too thin in the UV (τ_{UV} = 0.73) to provide effective shielding, but sufficiently thick in the visible (τ_{vis} = 0.55) to initiate mild antigreenhouse cooling. The ratio of the effective optical depth in the UV to that in the visible is $\tau_{UV}/\tau_{vis} \approx 1.3$. In this case, the young Earth would be cooled by the haze while not benefiting from a substantial accumulation of photolytically shielded greenhouse gases. This result agrees with previous studies that assumed particle sphericity (*5*, *6*).

The fractal simulation indicates that the haze could have been a highly effective UV shield. Organic aerosols produced at a rate of 10^{14} g year^{-1} would have sustained a haze that was optically thick in the UV while remaining optically thin in the mid-visible (Fig. 3). For r_{mon} = 50 nm, $\tau_{UV} = 11.23$ and $\tau_{vis} = 0.50$, thus the ratio of effective optical depths is $\tau_{UV}/\tau_{vis} \approx 22.4$. A fractal aggregate haze is optically thinner in the mid-visible and infrared while being more than an order of magnitude thicker in the UV when compared to the spherical particle model. Sensitivity tests indicate that τ_{UV}/τ_{vis} remains large for all feasible haze production rates; however, a haze production rate near 10^{14} g year^{-1} is required to maintain a haze that is both sufficiently thick in the UV to protect reduced gases from photolysis and sufficiently thin in the visible as to not cause substantial antigreenhouse cooling (*11*). Additional sensitivity tests indicate that our results are largely independent of the choice of r_{mon}, D_f, and optical constants (*11*). This work marks an important result in the study of the Archean climate, because it suggests a viable means of creating a UV shield that would allow the buildup of reduced gases without causing strong antigreenhouse cooling.

The mass independent fractionation of S isotopes found in Archean sediments is cited as evidence against the presence of a high-altitude UV shield (*23*). We do not believe this poses a serious contradiction, because a fractal aggregate haze will shield only the lower atmosphere (altitudes less than 20 km). Photolysis of SO_2 above the haze may produce the observed S isotopic signatures.

This work revitalizes the Miller-Urey hypothesis that the early Earth was home to a strongly reducing atmosphere (*24*). In particular, the presence of NH_3 is of dual importance. As previously mentioned, NH_3 mixing ratios of 10^{-5} or more added to the Archean atmosphere could alone resolve the faint young Sun paradox (*1*). However, without UV shielding, an ammonia mixing ratio of 10^{-5} would be irreversibly converted into N_2 in less than 10 years (*25*). Ammonia resupply rates during the Archean could not have supported an ammonia mixing ratio above 10^{-8} without a strong UV shield (*26*).

Sagan and Chyba estimated the atmospheric lifetime of NH_3 by

$$t_{NH_3} = \frac{t'_{NH_3}}{e^{-\tau_{UV}\sec\theta}} \qquad (2)$$

where t_{NH_3} is the atmospheric lifetime of NH_3 in the presence of an overlying haze, t'_{NH_3} is the atmospheric lifetime of NH_3 in the absence of haze, τ_{UV} is the haze optical depth at 200 nm, and θ is the solar zenith angle, taken here to be 45° (*9*). In this work, the haze effective optical depth at 200 nm is found to be ~11. In this case for $[NH_3] \sim 10^{-5}$, the atmospheric lifetime is extended to 7×10^7 years; thus, ammonia could feasibly accumulate to high concentrations and persist throughout much of the Archean period even if sources were small. Granted, this number is probably an overestimation of the true lifetime of ammonia, because the calculation assumes that all NH_3 lies beneath the UV shield. One-dimensional photochemical modeling indicates that for $[NH_3] \sim 10^{-5}$, the altitude of peak photolysis occurs near 30 km (*25*), whereas in this study the haze is most absorbing near 20 km. The altitude of peak photolysis is critically dependent on the chosen eddy diffusion profile (*27*). Past models have assumed contemporary values for the eddy diffusion coefficient; however, a strongly absorbing haze may stabilize the upper troposphere/lower stratosphere, reducing the vertical transport of constituents to above the haze. Ammonia may have additional sinks, such as removal in rainfall, that we do not consider here but may ultimately control its lifetime.

Ammonia plays an important role in prebiotic synthesis. Reducing atmospheres produce amino acids and other organic molecules in spark discharge experiments (*24*). More-oxidizing atmospheres are not conducive to prebiotic synthesis of complex organics. In the view of this work, the strong UV shielding characteristics of a fractal aggregate haze would allow the young atmosphere to remain reducing while not causing substantial antigreenhouse cooling, thus making the atmosphere/ocean system a favorable environment for prebiotic synthesis. The degree to which the Archean atmosphere was reducing is dependent on the redox state of the young mantle, which is not well constrained but is believed to have been more reduced than today (*28*). The haze itself would be composed of complex organic molecules that would precipitate down into the primordial oceans, providing a source of organics to the surface comparable to current carbon burial rates. A strongly UV-shielding haze is also desirable because it would protect young organisms from the intense high-frequency radiation of the young Sun. A fractal aggregate haze elegantly provides a solution to the faint young Sun paradox through the UV shielding of reduced gases while itself creating a large source of biological precursors.

The work presented here demonstrates the ability of a Titan-like haze to act as an effective UV shield on the early Earth. The haze as described in this work would surely allow the buildup photolytically unstable reduced gases in the atmosphere, but the extent to which the constituents and chemistry of the atmosphere would change is not precisely known. A complete analysis of the Archean haze and its impacts on the faint young Sun paradox requires the use of a fully coupled climate model linking atmospheric chemistry, aerosol microphysics, and radiative transfer.

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Supporting Online Material

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