Prebiotic Chemistry and Atmospheric Warming of Early Earth By An Active Young Sun

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Nitrogen is a critical ingredient of complex biological molecules [1]. Molecular nitrogen, however, which was outgassed into the Earth's early atmosphere [2], is relatively chemically inert and nitrogen fixation into more chemically reactive compounds requires high temperatures. Possible mechanisms of nitrogen fixation include lightning, atmospheric shock heating by meteorites, and solar ultraviolet radiation [3,4]. Here we show that nitrogen fixation in the early terrestrial atmosphere can be explained by frequent and powerful coronal mass ejection events from the young Sun - so-called superflares. Using magnetohydrodynamic (MHD) simulations constrained by Kepler space telescope observations, we find that successive superflare ejections produce shocks that accelerate energetic particles, which would have compressed the early Earth's magnetosphere. The resulting extended polar cap openings provide pathways for energetic particles to penetrate into the atmosphere and, according to our atmospheric chemistry simulations, initiate reactions converting molecular nitrogen, carbon dioxide and methane to the potent greenhouse gas nitrous oxide as well as hydrogen cyanide, an essential compound for life.

Furthermore, the destruction of N_2, CO_2 and CH_4 suggests that these greenhouse gases cannot explain the stability of liquid water on the early Earth. Instead, we propose that the efficient formation of nitrous oxide could explain a warm early Earth.

MAIN TEXT

Here we develop a new concept of the rise of prebiotic chemistry on early Earth that suggests abiotic nitrogen fixation mediated by the energy flux from paleo solar eruptive events. The flare statistics of *Kepler* data suggests that the frequency of occurrence of superflares with energies > 5 x 10^{34} erg observed on G-type dwarfs follows a power-law distribution with spectral index between ($\alpha = - 2.0$), which is comparable to those observed on dMe stars and the Sun [5,6]. If the occurrence rate of superflares on young solar-like ~ 0.1 events/day [6], then, the frequency of super Carrington-type flare events with E ~ 10^{33} ergs on the early Sun (≤ 0.5 Gyr) is expected to be ~ 250 events per day! Current data suggest that powerful solar flares (over X5 type) are usually associated with fast (≥ 1000 km s^{-1}) wide ($\theta > 100°$) coronal mass ejections (CMEs) and high-fluence solar energetic particle (SEP) events with kinetic energies up to 10^{33} ergs [7-9]. Tree ring data have recently provided evidence in favor of past superflares from the Sun [10,11]. Their energy is a factor of 2-3 greater than that suggested for the famous Carrington-type CME event [12]. Recent direct measurements of surface longitudinal magnetic fields on young solar-type stars imply that our young Sun had generated at least 10 times greater magnetic flux than that observed in the current Sun [13]. The stronger magnetic flux produces frequent and energetic flares, fast and wide coned CMEs and associated energetic SEP events with energies up to 10^{36} ergs. Our calculations suggest that the probability of CME striking the Earth is about 5% [14]. In the "perfect" magnetospheric storm, when the incoming cloud magnetic field, B_z component is sheared with respect to the Earth's magnetic field, the frequency of CME impacts is > 1 event per day! To model a CME event and its effects on the Earth's magnetosphere, we used the Space Weather Modeling Framework (SWMF) available through the Community Coordinated Modeling Center (CCMC) (see Supplementary Material). We assumed a steady state paleo solar wind at 0.7 Gyr with the mass loss rate of 1.7 x 10^{-12} M_{sun}/yr and the wind speed of 700 km/s as obtained from the 3D MHD young Sun's wind model [15] and a Carrington-type CME cloud propagating at the radial speed of 1800 km/s with the total energy of 2 x 10^{33} erg [12]. Figure 1 presents a 2D map of the steady-state plasma density superimposed by magnetic field lines for the magnetospheric configuration in the Y=0 plane corresponding to the initial 30 minutes of the simulations, when the Earth's magnetosphere was driven only by dynamic pressure from the paleo-solar wind. The left panel of Figure 1 shows the steady state paleo solar wind compresses the Earth's magnetosphere to ~ 9 R_E. The right panel of Figure 1 shows the state of the magnetosphere two hours later when the CME cloud hits the Earth's magnetosphere (also see the movies in Supplementary Material). At this time, the solar wind dynamic pressure and the magnetic reconnection between the southward directed CME's cloud magnetic field and northward Earth's dipole field pushing the dayside magnetosphere earthward reducing the magnetopause stand-off distance from 9 to ~1.5 Earth's radii. The CME drives large field aligned current distributions and produces significant disturbance of the magnetospheric field shifting the boundary of the open-closed field shifts to 36° in latitude and producing a polar cap opening to 70% of the Earth's dipole magnetic field. In the current version, we used the dipole magnetic field of the current Earth, however paleomagnetic studies of the Earth's ancient rocks suggest that the field was weaker [16]. This suggests that the fraction of the open field used in our model represent only a lower bound. Energetic particles accelerated in shocks driven by successive flare/CME events (see for example [17]) can then efficiently penetrate the early terrestrial atmosphere through the expended polar cap region.

We applied the Aeroplanet model [18] to simulate the atmospheric chemistry of the nitrogen-dominated (80% N_2, 20% CO_2 and 0.03% CH_4) primitive Earth's atmosphere [19]. The upper boundary of the atmosphere at 100 km is exposed to the steady state XUV flux with the spectrum reconstructed for the early Sun at 0.7 Gyr [20] and to energetic protons with the energy flux of 5 x 10^{11} protons/cm^2/MeV at 0.1 MeV with the spectral index of the energy spectrum of -2.15 representative of the Jan 20, 2005 SEP event and the energy range within 1 GeV [21]. The model calculates photoabsorption of the EUV-XUV flux from the early Sun (see Figure 2) and particle (electron and proton) fluxes to compute the corresponding fluxes at the atmospheric altitudes between 200 km and the surface. These fluxes are used to calculate the photo and particle impact ionization/dissociation rates of the atmospheric species producing secondary electrons due to ionization processes. Then, using the photon flux and the photoionization-excitation-dissociation cross-sections, the model calculates the production of ionized and excited state species and as a result, photoelectrons. In our steady-state model of the early Earth's atmosphere, energetic precipitating protons from an SEP event impacted the middle and low atmosphere and produce ionizations, dissociations, dissociative ionizations, and excitations of atmospheric species and as a result, secondary electrons. The model includes 117 neutral chemical reactions. The destruction of N_2 into reactive nitrogen, $N(^2D)$ and $N(^4S)$ and the subsequent destruction of CO_2 and CH_4 produces NO, CO, CH and NH in the polar regions of the atmosphere as shown in Figure 3 (see Supplementary Material).

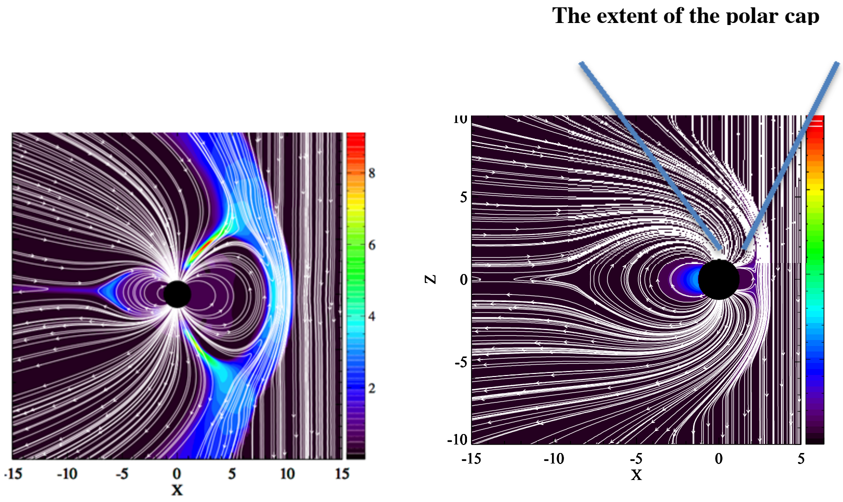
Our model predicts the formation of abundant NO and NH molecules and efficient formation of N_2O through $NO + NH \rightarrow N_2O + H$ with the major sink through the reaction $N_2O + H \rightarrow OH + N_2$ (see the pathway diagram in Figure 3). Photolysis of N_2O via the reaction pathway $N_2O + h\nu \rightarrow N_2+O(^1D)$ is not an efficient loss channel for N_2O, because of absorption of solar flux shorter than 2300 Å by CH_4. Atmospheric N_2O steady-state density reaches a concentration with the mixing ratio of 2 and 20 ppbv at 30 km in the 1 PAL (present atmospheric level) atmosphere with 100% (solid line) and 10% (dashed line) of the maximum photochemical destruction rate, as shown in Figure 4a. The derived value at 100% of the photodestruction rate should be considered as a lower bound, because our model does not account for a number of factors including the eddy diffusion and convection effects, the effects of Rayleigh scattering of solar EUV radiation in the atmosphere and formation of hazes that significantly reduces the photo-destruction rate of nitrous oxide, and therefore increases the production of N_2O. Thus, the model with 10% of the maximum photo-destruction rate probably better represents the density profiles when all factors are accounted for. The steady-state density of N_2O reaches 20 to 3000 ppbv in the 2 PAL model with 100% (solid line) and 10% (dashed line) of the maximum photochemical destruction rate, as shown in Figure 4b. The choice of 2 PAL in Figure 4b is consistent with compelling evidence that the atmospheric pressure of early Earth was enhanced by a factor of 2-3 [22]. Another factor affecting the equilibrium mixing ratios of Figure 4 is the representative energy of SEP events, which could be greater than that assumed in the model. Laboratory experiments report the production of nitrogen oxides and N_2O when N_2-CO_2 mixture that simulates the early Earth atmosphere was exposed by lightning and coronae discharges [23]. Enhanced production of nitrous oxide in the lighting experiments are caused by energetic electrons accelerated in the discharge and UV emission. Other evidence for the role of energetic particles in N_2O production comes from direct observations of its enhancement by 3% associated with thunderstorm events [24].

The efficient production of N_2O in our model offers a solution to warming the early

Earth. The 0.7 Gyr old Sun was 25-30% fainter than the present-day Sun [25], which would be insufficient to support liquid water on the early Earth contrary to geological evidence of that time [26]. Current models of atmospheric warming offer solutions of this problem, commonly known as Faint Young Sun (FYS) paradox due to a large atmospheric concentration of CO_2, H_2O, CH_4 or N_2 and H_2 [27]. However, as our model implies, these molecules will be efficiently dissociated due to photo-collisional processes driven by SEPs from the young Sun, which is consistent with the recent mineralogical data [28]. Instead, the production of CH, NH and NO sets stage for the formation of N_2O, HCN and other N-containing species in the lower parts of the atmosphere. HCN concentration reaches up to tens ppmv in the lower atmosphere. The calculated production rate of HCN in the low atmosphere is driven by the following major reactions: $NO + CH \rightarrow HCN + O$, $CH_2 + N(^4S) \rightarrow HCN + H$, $CH_3 + N(^4S) \rightarrow HCN + H + H$, $CH + CN \rightarrow HCN + H$, $N_2O + CH \rightarrow HCN + NO$. Organic molecules may subsequently rain out into surface reservoirs and engage in higher order chemistry producing more complex organics. For example, further HCN polymerization is known to produce various amino acids, the building blocks of proteins [29]. Production of other types of soluble N-containing species (NH_3, HNO, NO) by particles may have provided a massive dose of nitrogen “fertilizer” to early surface biology on terrestrial planets.

Thus, our concept implies that early Sun’s activity provided a window of opportunity for prebiotic life on Earth. The proposed model also redefines the conditions of habitability not just in terms of a “liquid water zone”, but as a biogenic zone (BZ), within which the stellar energy fluxes are high enough to ignite reactive chemistry that produces complex molecules crucial for life. As a by-product, this chemistry forms greenhouse gasses that may efficiently keep the atmosphere warm for liquid water to exist. The model predictions can tested by observing broad and deep molecular absorption lines of N_2O at 4.5 μm and 7.9 μm and HCN absorption features at 3 and 14.3 μm using James Webb Space Telescope NIRSpec and MIRI observations of primitive terrestrial-type atmospheres around active stars.

FIGURES



a. *b.*

Figure 1. The initial (panel a) and the final state (panel b) magnetic field lines in white) and the plasma pressure (in color) of the Earth's magnetosphere due to the CME event (Airapetian et al. 2015)

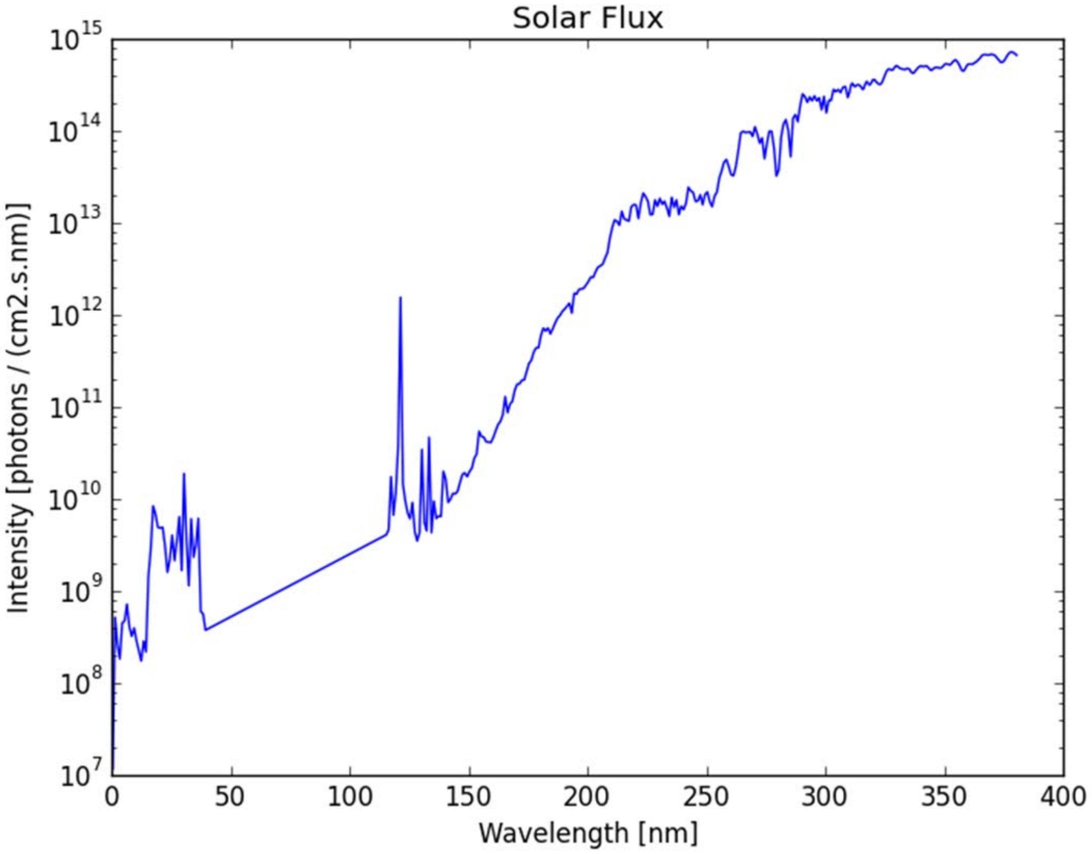


Figure 2. Spectrum of the young Sun's XUV flux at 0.7 Gyr [20]

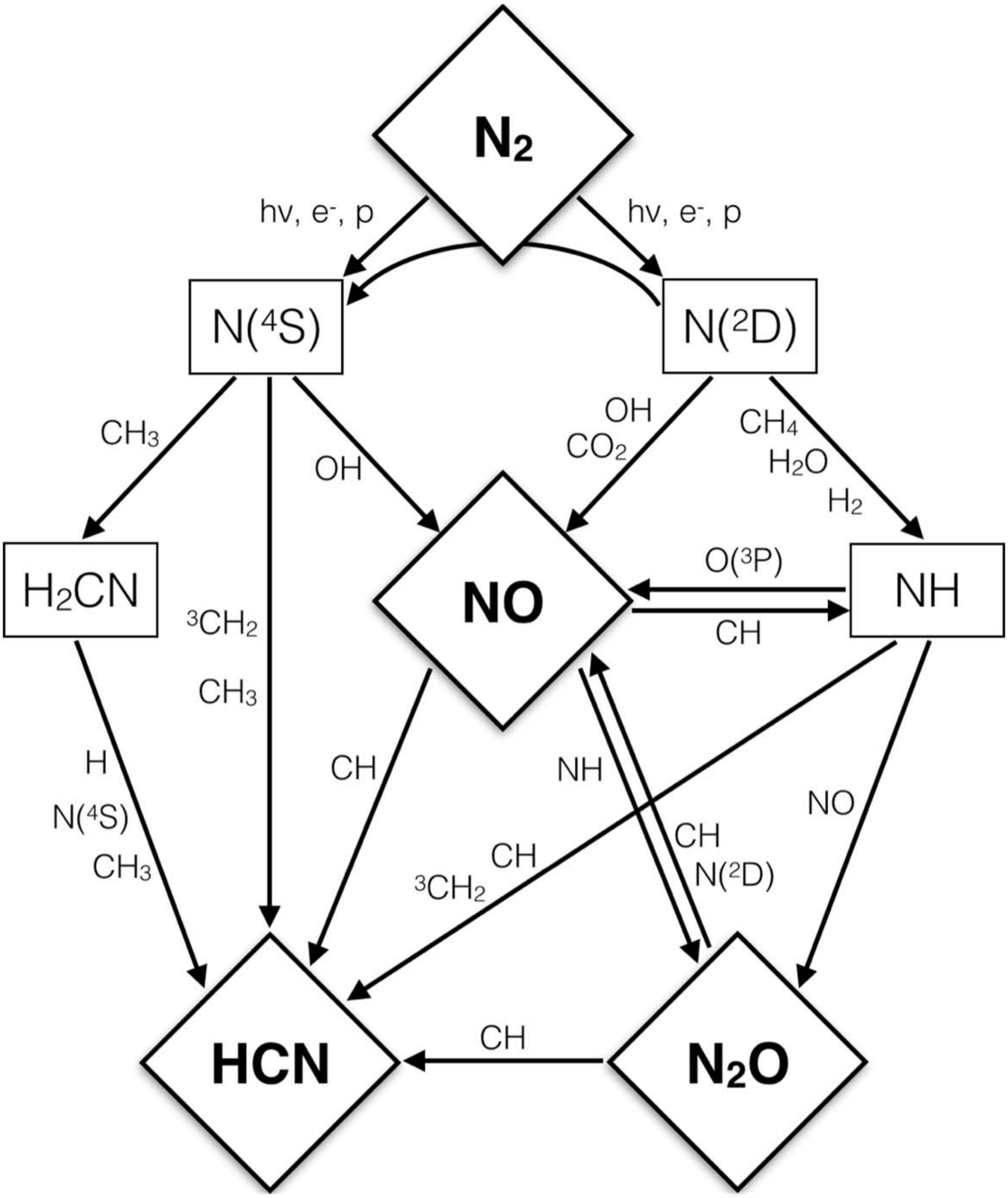
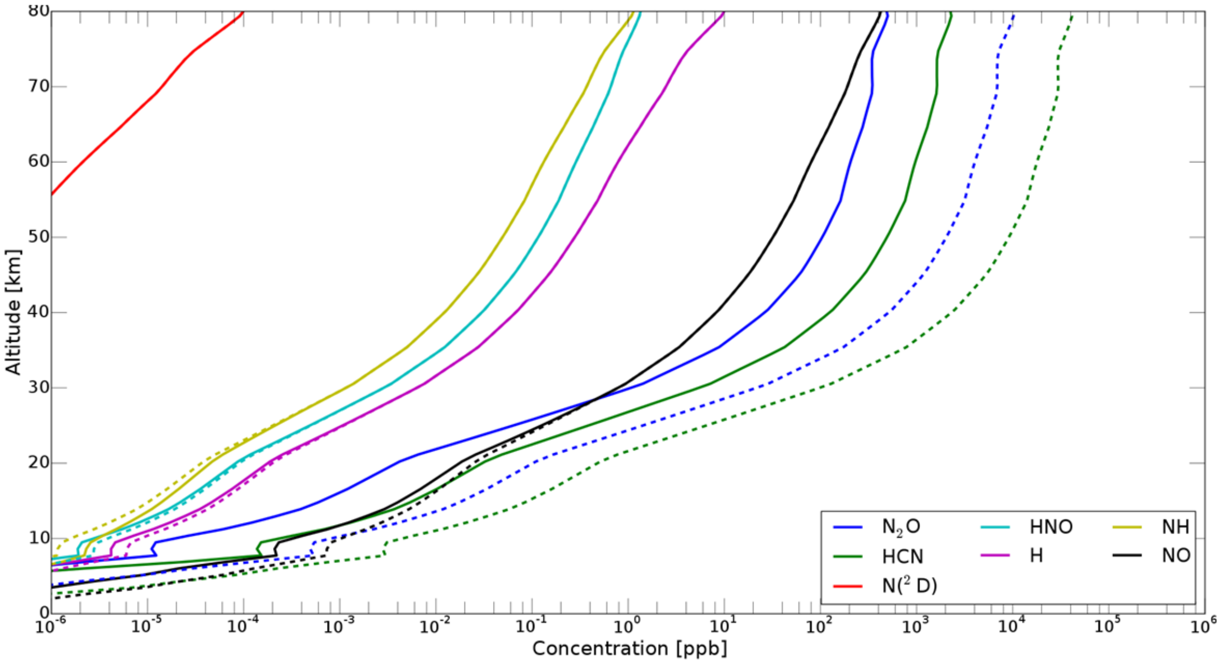
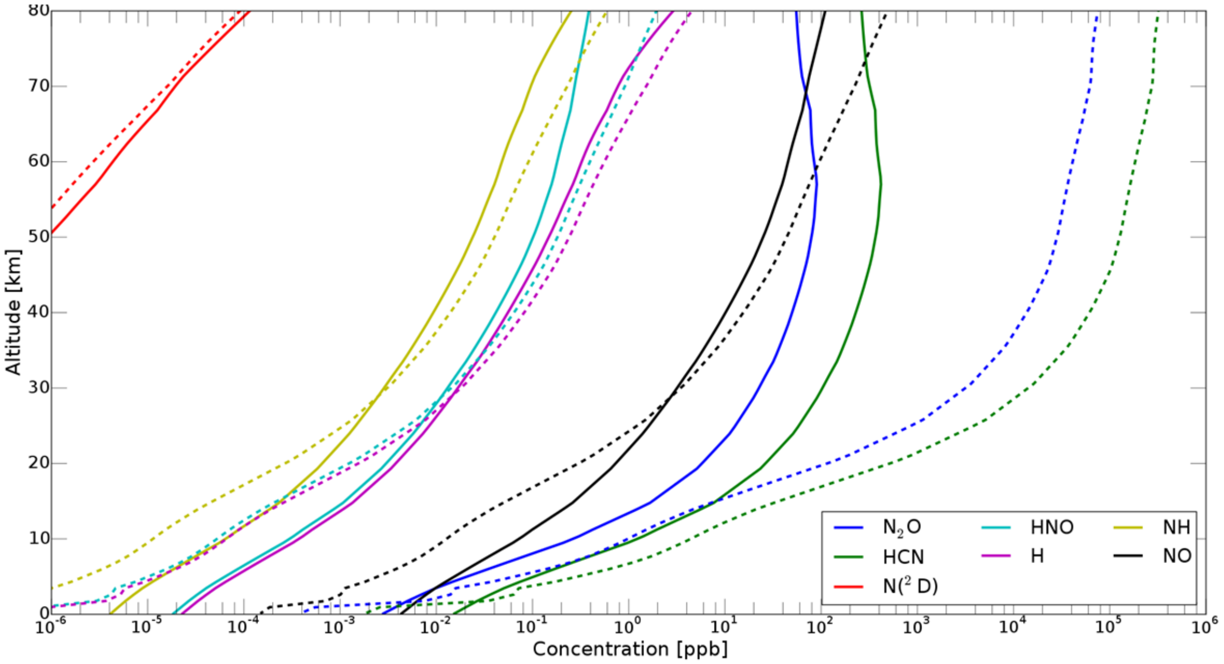

N$_2$
hv, e$^-$, p
hv, e$^-$, p
N(^{4}S)
N(^{2}D)
CH$_3$
OH
OH
CO$_2$
CH$_4$
H$_2$O
H$_2$
H$_2$CN
^{3}CH$_2$
CH$_3$
NO
O(^{3}P)
CH
NH
H
N(^{4}S)
CH$_3$
CH
NH
CH
N(^{2}D)
NO
CH
^{3}CH$_2$
HCN
CH
N$_2$O

Figure 3. The pathway diagram of abiotic production of odd nitrogen and nitrogen-bearing compounds including nitrous oxide and hydrogen cyanide due to photo and collisional dissociation and ionizations caused by XUV solar flux and SEP particle flux.



a.



b.

Figure 4. Radial profiles of the steady-state mixing ratios of various species produced by incoming flux of primary protons and secondary electrons for 10% (dotted lines) and 100% (solid lines) of the maximum photo-destruction rate at 1 PAL (top figure, a) and at 2 PAL (bottom figure, b).

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AUTHOR CONTRIBUTIONS:

V. Airapetian conceived and designed the numerical models, analyzed the data, contributed materials and wrote the manuscript. A. Glocer and G. Gronoff contributed to the development and execution of codes and data analysis. E. Hébrard contributed to the chemistry model and data analysis, W. Danchi contributed to data analysis and proofreading of the paper.

Competing financial interests.

The authors declare no competing financial interests.

FIGURE CAPTIONS.

Figure 1. The initial (left panel, a) and the final state (right panel, b) magnetic field lines in white) and the plasma pressure (in color) of the Earth's magnetosphere due to the CME event [14].

Figure 2. XUV flux of the young Sun at 0.7 Gyr [20].

Figure 3. The pathway diagram of abiotic production of odd nitrogen and nitrogen-bearing compounds including nitrous oxide and hydrogen cyanide due to photo and collisional dissociation and ionizations caused by XUV solar flux and SEP particle flux.

Figure 4. Radial profiles of the steady-state mixing ratios of various species produced by incoming flux of primary protons and secondary electrons for 10% (dotted lines) and 100% (solid lines) of the maximum photo-destruction rate at 1 PAL (top figure, 4a) and at 2 PAL (bottom figure, 4b).

METHODS

1. SWMF DESCRIPTION

In this paper, we utilized the Space Weather Modeling Framework (SWMF) available at Community Coordinated Modeling Center (CCMC) at NASA Goddard Space Flight Center (see at http://ccmc.gsfc.nasa.gov). A single-fluid, time dependent fully non-linear 3D magnetohydrodynamic (MHD) code BATS-R-US (Block-Adaptive-Tree Solar-wind Roe-type Upwind Scheme) is a part of SWMF and was developed at the University of Michigan Center of Space Environment Modeling (CSEM). The spine of the SWMF is the BATS-R-US code [30,31], which is coupled to Rice Convection Model (RCM, [31] to model a propagation and interaction of a model SCME with a magnetosphere and ionosphere of a young Earth. The MHD part of the code calculates the dynamic response of the large-scale magnetospheric plasma to varying solar wind conditions in a self consistent manner by using the block-adaptive wind Roe-type upwind scheme global MHD code [30]. The dynamics of the magnetosphere is described in a Cartesian geometry by using resistive MHD equations. The electromagnetic coupling of the magnetosphere to a conducting ionosphere is handled in a standard way [32]. Specifically, the magnetospheric currents near the inner boundary of the MHD simulation are mapped to the ionosphere where. A potential solver is then used which combines these currents with a conductance map of the ionosphere (including solar and auroral contributions) to produce the electric potential in the ionosphere. That potential is then used to set the electric field and corresponding drift at the magnetospheric simulations inner boundary.

The MHD approximation does not provide an adequate description of the inner magnetosphere because energy dependent particle drifts and ring current evolution become important. Here we use the Rice Convection Model, embedded in the MHD simulation, to model this important region [31]. The RCM code is a kinetic plasma model that couples plasma motions in the inner magnetosphere and calculates the energy dependent particle drifts and ring current evolution in the inner magnetosphere. The ring current carries the most of the energy density during magnetic storms and is essential to modeling strong storms. This coupling is crucial for description of solar wind effects on a magnetosphere, because the ionosphere provides closure of magnetospheric currents, which is needed for realistic description of magnetospheric convection and associated electric fields. Thus, we apply a dedicated inner magnetospheric model that is fully coupled to the MHD code for the treatment of the inner magnetosphere. We simulate the magnetospheric cavity (outer and inner magnetosphere) in a computational box defined by the following dimensions $-224R_E < x < 224R_E$, $-128R_E < y < 128R_E$, $-128R_E < z < 128R_E$, where R_E is the radius of the Earth placed at the center of the computational box. The dipole tilt is neglected in this problem. The simulations were carried out using a block adaptive high-resolution grid with the minimum cell size of 1/16 R_E.

The inner boundary is set at 1.25 R_E with a density of 100 cm^{-3}. The velocity at the inner body is set to the $\vec{E} \times \vec{B}$ velocity, where $\vec{E}$ is determined from the ionospheric potential and B is the Earth's magnetic field. The pressure is set to float. The magnetic field is set in a way that the radial component is the Earth's dipole and the tangential components are allowed to float. The simulation is initialized with a dipole everywhere in the computational domain and a small density, zero velocity, and a finite pressure. The solar wind conditions are set at the upstream boundary and some period of local time stepping is used to get an initial steady state solution. We assume the solar wind input parameters including the three components of interplanetary magnetic field, B_X, B_Y and B_Z, the plasma density and the wind velocity, V_X, using the physical conditions associated with a Carrington- type event as discussed by [33] and [14], see Figure 1. The time evolution of the plasma pressure (in nPa) and current density (in microAmps/m^2) during the extreme CME event are presented in the attached Movie 1.

2. AEROPLANETS MODEL DESCRIPTION

We used our sophisticated Aeroplanets model with enhanced chemistry [18] to model the upper atmospheric region (up to 200 km) in response to young Sun's XUV (X-ray and EUV) emission from and precipitating electrons and protons due to an SEP event. The model calculates the photo and collisional (due to protons) dissociation, ionization and photoexcitation processes in the Earth's atmosphere. The primary photoelectrons are then transported along a magnetic field line, and the electron impact is computed solving the stationary kinetic Boltzmann equation. This results in the dissociation, ionization and excitation of the different atmospheric species. The Aeroplanets code incorporates 117 chemical reactions with the rates presented in Table 1.

To converge to steady state chemical solution for the early Earth atmosphere described in the Main section was reached after running the code for 6 months of physical time.

Table 1. List of Chemical Reactions Used in Our Model

Reaction	**Reaction rate (in cgs units)**
H + CH -> C + H2	0.124E-09 * (T / 300) ** (0.260E+00)
H + CH2 -> CH + H2	0.220E-09 * (T / 300) ** (0.320E+00)

H + e3CH2 -> CH + H2	0.220E-09 * (T / 300) ** (0.320E+00)
H + CH3 -> e3CH2 + H2	0.100E-09 * exp(-0.760E+04 / T)
H + CH4 -> CH3 + H2	0.589E-12 * (T / 300) ** (0.300E+01) * exp(-0.404E+04 / T)
CH + H2 -> e3CH2 + H	0.310E-09 * exp(-0.165E+04 / T)
CH + CH -> C2H + H	2.00E-10
CH + CH -> e3CH2 + C	2.00E-11
CH + e3CH2 -> C2H2 + H	2.00E-10
CH + CH3 -> C2H3 + H	1.00E-11
CH + CH3 -> C2H2 + H + H	1.00E-10
CH + CH4 -> C2H4 + H	0.105E-09 * (T / 300) ** (-0.104E+01) * exp(-0.361E+02 / T)
CH2 + H2 -> CH3 + H	0.880E-10 * (T / 300) ** (0.350E+00)
CH2 + CH4 -> e3CH2 + CH4	0.310E-11 * exp(0.250E+03 / T)
CH2 + CH4 -> CH3 + CH3	0.279E-10 * exp(0.250E+03 / T)
CH2 + C2H2 -> e3CH2 + C2H2	2.30E-10
CH2 + C2H2 -> C3H3 + H	0.760E-10 * (T / 300) ** (-0.300E+00)

CH2 + N2 -> e3CH2 + N2	0.110E-10 * (T / 300) ** (0.810E+00)
e3CH2 + H2 -> CH3 + H	0.800E-11 * exp(-0.450E+04 / T)
e3CH2 + CH4 -> CH3 + CH3	0.713E-11 * exp(-0.505E+04 / T)
CH3 + H2 -> CH4 + H	0.245E-13 * (T / 300) ** (0.288E+01) * exp(-0.460E+04 / T)
N(4S) + CH -> CN + H	0.140E-09 * (T / 300) ** (0.410E+00)
N(4S) + e3CH2 -> HCN + H	0.500E-10 * (T / 300) ** (0.170E+00)
N(4S) + e3CH2 -> HNC + H	0.300E-10 * (T / 300) ** (0.170E+00)
N(4S) + CH3 -> H2CN + H	5.60E-11
N(4S) + CH3 -> HCN + H + H	6.00E-12
N(4S) + NH -> N2 + H	0.250E-10 * (T / 300) ** (0.170E+00)
N(4S) + CN -> C + N2	0.900E-10 * (T / 300) ** (0.420E+00)
N(4S) + H2CN -> N2 + e3CH2	4.00E-11
N(4S) + H2CN -> HCN + NH	5.00E-12
N(2D) -> N(4S)	2.30E-05
N(2D) + H2 -> NH + H	0.420E-10 * exp(-0.880E+03 / T)
N(2D) + CH4 -> NH + CH3	0.130E-10 * exp(-0.755E+03 / T)

N(2D) + CH4 -> CH2NH + H	0.350E-10 * exp(-0.755E+03 / T)
N(2D) + N2 -> N(4S) + N2	0.100E-12 * exp(-0.520E+03 / T)
N(2D) + NH3 -> N2H2 + H	5.00E-11
N(2D) + HCN -> CH + N2	5.00E-11
N(2D) + HNC -> CN2 + H	2.00E-11
N(2D) + HNC -> CH + N2	2.00E-11
NH + H -> N(4S) + H2	0.220E-11 * (T / 300) ** (0.155E+01) * exp(-0.103E+03 / T)
NH + CH -> HCN + H	5.00E-11
NH + CH -> HNC + H	5.00E-11
NH + e3CH2 -> H2CN + H	3.00E-11
NH + e3CH2 -> HCN + H + H	3.00E-11
NH + e3CH2 -> HNC + H2	5.00E-12
NH + CH3 -> CH2NH + H	0.130E-09 * (T / 300) ** (0.170E+00)
NH + NH -> N2 + H + H	2.00E-10
NH + NH2 -> N2H2 + H	0.100E-09 * (T / 300) ** (0.170E+00)
NH + CN -> CN2 + H	1.00E-10

NH + CN -> N2 + CH	1.00E-10
NH2 + H2 -> NH3 + H	0.209E-11 * exp(-0.428E+04 / T)
NH2 + H -> NH + H2	0.200E-10 * exp(-0.240E+04 / T)
NH2 + CH4 -> NH3 + CH3	0.399E-13 * (T / 300) ** (0.359E+01) * exp(-0.454E+04 / T)
NH2 + C2H2 -> NH3 + C2H	0.111E-12 * exp(-0.185E+04 / T)
NH2 + C2H3 -> NH3 + C2H2	2.00E-11
NH2 + C2H3 -> SOOTN + H	8.00E-11
NH2 + H2CN -> HCN + NH3	0.540E-10 * (T / 300) ** (-0.110E+01) * exp(-0.600E+02 / T)
NH3 + H -> NH2 + H2	0.423E-13 * (T / 300) ** (0.393E+01) * exp(-0.406E+04 / T)
NH3 + CH -> CH2NH + H	0.169E-09 * (T / 300) ** (-0.560E+00) * exp(-0.280E+02 / T)
NH3 + CH3 -> NH2 + CH4	0.510E-13 * (T / 300) ** (0.286E+01) * exp(-0.734E+04 / T)
CN + H2 -> HCN + H	0.412E-12 * (T / 300) ** (0.287E+01) * exp(-0.820E+03 / T)
CN + CH -> HCN + C	0.100E-09 * (T / 300) ** (-0.170E+00)
CN + e3CH2 -> HCN + CH	5.00E-11

CN + e3CH2 -> CHCN + H	5.00E-11
CN + e3CH2 -> C2N + H2	5.00E-11
CN + CH3 -> CH2CN + H	1.00E-10
CN + CH4 -> HCN + CH3	0.620E-11 * exp(-0.721E+03 / T)
CN + NH3 -> HCN + NH2	0.277E-10 * (T / 300) ** (-0.114E+01)
CN + HCN -> C2N2 + H	0.430E-12 * (T / 300) ** (0.171E+01) * exp(-0.770E+03 / T)
CN + HNC -> C2N2 + H	2.00E-10
HCN + CH -> CHCN + H	0.140E-09 * (T / 300) ** (-0.170E+00) * exp(-0.0 / T)
HCN + CH -> C2N + H2	0.140E-09 * (T / 300) ** (-0.170E+00) * exp(-0.0 / T)
HCN + 1C2 -> C3N + H	0.200E-09 * (T / 300) ** (0.170E+00) * exp(-0.0 / T)
HNC + H -> HCN + H	0.300E-10 * exp(-0.800E+03 / T)
H2CN + H -> HCN + H2	6.00E-11
H2CN + CH3 -> CH4 + HCN	3.00E-11
O(3P) + CH2 -> HCO + H	1.00E-11
O(3P) + CH2 -> CO + H + H	5.00E-11
O(3P) + CH2 -> CO + H2	6.00E-11

O(3P) + e3CH2 -> HCO + H	1.00E-11
O(3P) + e3CH2 -> CO + H + H	5.00E-11
O(3P) + e3CH2 -> CO + H2	6.00E-11
O(3P) + CH3 -> CO + H2 + H	2.90E-11
O(3P) + CH3 -> H2CO + H	1.10E-10
O(3P) + NH -> NO + H	6.60E-11
O(3P) + HNO -> OH + NO	3.80E-11
O(1D) + H2 -> OH + H	1.10E-10
O(1D) + CH4 -> OH + CH3	1.05E-10
O(1D) + CH4 -> CH3O + H	3.50E-11
O(1D) + CH4 -> H2CO + H2	7.50E-12
O(1D) + N2 -> O(3P) + N2	2.15E-11
OH + H2 -> H2O + H	0.280E-11 * exp(-0.180E+04 / T)
OH + CH4 -> H2O + CH3	0.185E-11 * exp(-0.169E+04 / T)
OH + N(4S) -> NO + H	4.50E-11
OH + N(2D) -> NO + H	4.50E-11

OH + CO -> CO2 + H	1.30E-13
H2O + CH -> H2CO + H	0.280E-10 * (T / 300) ** (-0.122E+01) * exp(-0.120E+02 / T)
H2O + N(2D) -> OH + NH	4.50E-11
H2O + N(2D) -> HNO + H	5.00E-12
CO2 + N(2D) -> CO + NO	0.100E-10 * exp(-0.100E+04 / T)
NO + CH -> HCN + O(3P)	0.100E-09 * (T / 300) ** (-0.130E+00)
NO + CH -> NCO + H	0.300E-10 * (T / 300) ** (-0.130E+00)
NO + CH -> CO + NH	0.300E-10 * (T / 300) ** (-0.130E+00)
NO + CH -> OH + CN	0.100E-10 * (T / 300) ** (-0.130E+00)
NO + e3CH2 -> HNCO + H	0.210E-11 * exp(0.554E+03 / T)
NO + e3CH2 -> CO + NH2	0.300E-12 * exp(0.554E+03 / T)
NO + N(4S) -> O(3P) + N2	0.400E-10 * (T / 300)
NO + N(2D) -> O(3P) + N2	0.600E-10 * (T / 300)
NO + NH -> N2O + H	0.290E-10 * (T / 300) ** (-0.300E+00) * exp(0.770E+02 / T)
NO + NH -> OH + N2	0.120E-10 * (T / 300) ** (-0.300E+00) * exp(0.770E+02 / T)

HNO + H -> NO + H2	0.310E-10 * exp(-0.500E+03 / T)
HNO + N(2D) -> NO + NH	5.00E-11
N2O + CH -> NO + HCN	0.150E-10 * exp(0.257E+03 / T)
N2O + N(2D) -> N2 + NO	0.150E-10 * exp(-0.570E+03 / T)
H + H -> H2	(0.914E-32 * (T / 300) ** (-0.600E+00) * exp(-0.0 / T))* [M] / (1 + (0.914E-32 * (T / 300) ** (-0.600E+00) * exp(-0.0 / T))* [M] / (0.100E-09 * exp(-0.0 / T)))
H + CH3 -> CH4	(0.890E-28 * (T / 300) ** (-0.180E+01) * exp(-31.8 / T))* [M] / (1 + (0.890E-28 * (T / 300) ** (-0.180E+01) * exp(-31.8 / T))* [M] / (0.320E-09 * (T / 300) ** (0.133E+00) * exp(-2.54 / T)))
HCN + H -> H2CN	(0.100E-33 * exp(-0.0 / T))* [M] / (1 + (0.100E-33 * exp(-0.0 / T))* [M] / (0.980E-11 * exp(-2080.0 / T)))

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Code availability. BATS-R-US code as a part of SWMF used to generate the scenario shown in Figure 1 can be accessed through GSFC's CCMC run-on-request web site at http://ccmc.gsfc.nasa.gov. We have opted not to make the computer code, Aeroplanets, associated with this paper available because we are currently in the phase of adopting it for free access at Exoplanetary part of CCMC's web site. The authors declare that model data supporting the findings of this study are available within the article and its supplementary information. Other model related data will be available on request from the authors.