2013

Chemical Consequences of Chicxulub Impact Ejecta Reentry

Devon Donald Parkos

Purdue University, devo324@gmail.com

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For the degree of Master of Science in Aeronautics and Astronautics

Is approved by the final examining committee:
Alina Alexeenko
Chair
Henry J. Melosh
Gregory Blaisdell

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Approved by Major Professor(s): Alina Alexeenko

Approved by: Weinong Chen 12/2/13

Head of the Graduate Program Date
CHEMICAL CONSEQUENCES OF
CHICXULUB IMPACT EJECTA REENTRY

A Thesis
Submitted to the Faculty
of
Purdue University
by
Devon Parkos

In Partial Fulfillment of the
Requirements for the Degree
of
Master of Science in Aeronautics & Astronautics

December 2013
Purdue University
West Lafayette, Indiana
Dedicated to my friends and family,
who have supported me thus far.
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## SYMBOLS

- $c_p$: Constant Pressure Specific Heat
- $d$: Spherule Diameter
- $h$: Altitude
- $k_B$: Boltzmann constant
- $n$: Number Density
- $\bar{u}$: Mean Flow Velocity
- $u_t$: Characteristic Turbulent Velocity
- $D$: Diffusion Coefficient
- $E_a$: Activation Energy
- $K$: Reaction Rate
- $Kn$: Knudsen number
- $L$: Characteristic Length
- $M$: Molecular Mass
- $N_A$: Avogadro’s Number
- $NO_x$: Mixture of NO and NO$_2$
- $P$: Pressure
- $T$: Temperature

### Greek Symbols
- $\beta_R$: Rosseland-Mean Extinction Coefficient
- $\lambda$: Mean Free Path
- $\mu$: Viscosity
- $\rho$: Density

### Subscripts
- $a$: activation
- $f$: forward
m  molecular
r  reverse
t  turbulent
trn translational mode
## ABBREVIATIONS

<table>
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<tr>
<td>DSMC</td>
<td>direct simulation Monte Carlo</td>
</tr>
<tr>
<td>gPC</td>
<td>generalized Polynomial Chaos</td>
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<tr>
<td>K-Pg</td>
<td>Cretaceous-Paleogene</td>
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<tr>
<td>SMILE</td>
<td>Statistical Modeling In Low-density Environments</td>
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<td>TCE</td>
<td>Total Collision Energy</td>
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ABSTRACT

Devon Parkos M.S.A.A., Purdue University, December 2013. Chemical Consequences of Chicxulub Impact Ejecta Reentry. Major Professor: Alina A. Alexeenko.

The Chicxulub impact 66.0 million years ago initiated the second biggest extinction in the Phanerozoic Eon. The global reentry of material ejected by the impact generated a strong pulse of thermal radiation that wiped out much of the terrestrial biota. The cause of the marine extinction, however, has remained elusive. This report shows that reentering ejecta produces enough NO\textsubscript{x} to acidify the upper ocean and cause a massive marine extinction. Using non-equilibrium chemically reacting flow simulations coupled with atmospheric transport modeling, it is determined that enough NO\textsubscript{x} reached the stratosphere and precipitated to overpower the carbonate buffer and acidify the upper ocean down to a pH of 6.7, causing most organisms to perish.
1. Introduction

Scarring the Yucatán peninsula 66.0 million years ago, the Chicxulub impact heralded the end of the Cretaceous Period [1, 2]. The Cretaceous-Paleogene (K-Pg) boundary layer was the first indication that the impact of a 10 km diameter asteroid caused the second largest mass extinction in the Phanerozoic Eon [3, 4]. This ∼3 mm thick global layer is composed of sub-millimeter spherules, which were ejected as part of a massive vapor plume or fireball [5–8]. The global reentry of these spherules produced a thermal radiation pulse that wiped out much of the terrestrial biota [9–11]. However, it remains unlikely that transient elevated radiation can explain the concurrent loss of ocean life. Indeed, recent geologic observations [12] suggest that ocean acidification is responsible for the marine extinctions, which selectively targeted calcifying species. Here I report that Chicxulub impact ejecta generates enough NO\textsubscript{x} to acidify the upper ocean and cause a mass marine extinction. Nonequilibrium chemically reacting flow simulations coupled with atmospheric transport modeling yields $8 \times 10^{16}$ moles of NO\textsubscript{x}. Upon reaching the stratosphere and precipitating into the oceans, the nitric acid overpowers the carbonate buffer in the upper ocean. I find that the pH of the upper ocean drops below 6.7 long enough to trigger widespread marine extinctions.

Geologic observations of the K-Pg boundary layer show that approximately $10^{23}$ spherules reentered the atmosphere following the Chicxulub impact [7, 10]. These spherules have a combined cross-sectional area of $5 \times 10^9$ km$^2$, a value that is 8 orders of magnitude larger than the area of the original impactor, assuming a 10 km diameter impactor. Consequently, the reentry of the dispersed spherules induces far more chemical activity in the upper atmosphere than the impacting asteroid itself.

Previous work computed the NO yield from the impact energy using estimates of nitric oxide production versus energy of lightning, meteors, and thermonuclear explosions [13]. An alternative approach presumed that chemical equilibrium prevailed
in the shock-heated air flowing around the ejecta particles [14]. For realistic impact energies and upper estimates of oceanic buffering capability, the predicted amount of nitric oxide was about 100 times too small for global acidification and ocean extinctions [15, 16]. Because the target material at the Chicxulub site contains large amounts of anhydrite, ocean acidification by release of sulfuric acid has also been proposed [12, 17, 18]. Existing impact estimates predict the release of \(2.0 \times 10^{14}\) to \(1.3 \times 10^{17}\) moles of sulfuric acid [15]. However, \(\text{H}_2\text{SO}_4\) droplets persist as aerosols for decades [19], thus oceanic mixing and replenishment of the carbonate buffer could prevent significant acidification.

Spherules initially ejected into space begin their reentry under rarefied gas conditions, where the mean distance between collisions of air molecules is at least one tenth of the spherule diameter. Under such conditions, the assumption of local thermal equilibrium is invalid. Additionally, spherules reenter the atmosphere with an average velocity of \(\sim 8\) km/s, and at these hypersonic velocities the typical convection time of air molecules across the spherules is comparable to molecular excitation and reaction times. The flow around the reentering spherules is thus not in chemical equilibrium. I use the direct simulation Monte Carlo (DSMC) method to model the spherule reentry flow because it captures both thermal and chemical nonequilibrium effects [20]. Finally, I consider additional reaction pathways that dominate in high temperature flows. Our modeling shows that nonequilibrium hypersonic conditions greatly increase the O and N production, ultimately leading to much more \(\text{NO}_x\).

I estimate the amount of nitric acid that the reentering spherules produce by first calculating chemical species production rates for a single 250 micron diameter spherule at different altitudes and velocities. I do not vary the spherule diameter, because geologic observations of the global fireball layer indicate that spherule size is independent of distance from the crater [5]. The reentry of the mass of spherules compresses and heats the upper atmosphere, raising its ambient temperature and density [9]. To account for this effect, I assume that the majority of the spherules ex-
perience the conditions occurring during the maximum spherule mass flux [9]. Figure 1.1 indicates the atmospheric temperature and density at this time.

![Figure 1.1](image)

Figure 1.1. The temperature and density profiles of the heated and compressed upper atmosphere during the spherule reentry event, shown with the Knudsen number for a 250 µm diameter spherule.

16 different DSMC calculations for altitudes between 66 and 134 km and spherule velocities ranging from 5.5 and 11.5 km/s represent the flow conditions, chosen using collocation points from generalized Polynomial Chaos (gPC) theory. I extract the spherule drag coefficient and the generation rate of NO, O, and N from each case. Higher velocities and densities favor NO production due to the increase in dissociation of O2 and N2. Figures 1.2 and 1.3 show the resulting temperature and NO densities for several cases. I determine the NO production for a representative spherule by interpolating the drag coefficient and the NO generation rate between the 16 DSMC calculations. The initial velocity is 8 km/s, angled 45° downward from horizontal.
I integrate the reaction product generation rates with respect to time along this trajectory and multiply by the number of reentering spherules to produce an initial distribution of N, O, and NO [21].

Figure 1.2. The translational temperature around a spherule at 65 km altitude (top) and 113 km altitude (bottom) is shown for two velocities.
Figure 1.3. The resulting number density of nitric oxide is shown in (top) and (bottom), respectively. Note the different scale for the density in each flowfield.
The upper atmosphere cools by radiation shortly after the spherule reentry ceases, restoring the atmospheric temperature profile to its original state. As the atmosphere cools, I model the global atmospheric chemical reactions using the same rate-dependent reaction set [22, 23] implemented in the DSMC simulations. Additionally, I include reactions for generating NO₂ and NO₃, which become more stable at lower temperatures. This resulting distribution of chemical species then becomes the initial condition for an atmospheric transport calculation.

Turbulent diffusion transports NOₓ to lower altitudes after the atmosphere cools. The horizontal momentum of the obliquely falling spherules initially generates supersonic winds in the upper atmosphere, which induce strong turbulent mixing and erase the atmospheres normal stratification [9]. I estimate the turbulent diffusion coefficient using the standard equations for homogeneous turbulence [24], in which the characteristic eddy length scale is proportional to the scale height at each altitude. The NO produced by the spherules mixes downward, diffusing along concentration gradients. The distribution of NO at several different times is shown in Fig. 1.4.

I estimate the rate of conversion of NOₓ into nitric acid in the troposphere. Previous work [16] examines post reentry NOₓ production in the atmosphere via the reaction pathway
\[ 2NO + O₂ \rightleftharpoons 2NO₂. \] (1.1)

However, the presence of free radicals from non-equilibrium air dissociation makes the reactions
\[ NO + O \rightleftharpoons NO₂, \] (1.2)
\[ NO₂ + O \rightleftharpoons NO₃ \] (1.3)
far more important. The inclusion of these reactions vastly increases the quantity of NOₓ compounds that persist down to lower altitudes.

Upon reaching the troposphere, cloud water absorbs NOₓ during the condensation process and ultimately precipitates into the ocean. I estimate the rate of absorption as a function [25] of the local atmospheric conditions and the availability of water vapor
Figure 1.4. The NO density profile in the atmosphere at several instances, where time begins at the end of the spherule reentry event. The oscillatory behavior of the initial distribution is an artifact of the DSMC interpolation scheme.
and NO\textsubscript{x} compounds. I assume that the absorbed NO\textsubscript{x} is spread evenly among water droplets suspended in the cloud layer. I use a constant, globally averaged rainfall rate of 1.12 m/year [26].

I assume that this acid rain mixes only into the upper 100 m of water, because the time scale for mixing of this layer with the deep ocean is typically decades, whereas the timescale for atmospheric diffusion and rainout is on the order of weeks [16]. By definition, the oceanic carbonate buffer tends to keep pH stable. However, once the concentration of nitric acid in the ocean increases sufficiently to overpower the effect of the buffer, the pH begins to drop rapidly. I estimate the carbonate buffering capacity of the upper ocean using an effective initial carbonate ion concentration of 1.1 to 2.3 mmol/kg [13, 15], which accounts for the atmosphere's ability to extend oceanic buffering.

The upper oceans pH reaches a minimum of 4.9 and 6.7, corresponding to the 1.1 and 2.3 mmol/kg buffer estimates respectively. The resulting time history for the pH of the upper 100 meters of the ocean is shown in Fig. 1.5. After pH reaches the minimum value, the acidity of the rain begins to decline. In the following decades oceanic mixing will return the pH to normal levels and replenish the carbonate buffer.

Nitric acid rainout as the lead cause of marine extinctions is consistent with the N isotope enrichment observed in K-Pg boundary sites. Observations show a 20-fold increase in nitrogen isotopic concentrations in a marine K-Pg site in New Zealand [27], as well as Tunguska fallout [28], with the abundance of N closely paralleling that of Ir and C. A similar nitrogen isotopic anomaly is reported in a non-marine K-Pg site in Canada [29] and suggests shock production of HNO\textsubscript{2} and HNO\textsubscript{3} as the underlying cause. Moreover, calcifying plankton and ammonites, which were disproportionately extinguished, are particularly vulnerable to removal of the carbonate buffer and ocean acidification [12]. Thus, I conclude that NO\textsubscript{x} produced by reentering ejecta and the subsequent acidification of the upper ocean is an adequate cause of the end Cretaceous marine extinctions.
Figure 1.5. Resulting time history of the pH of the upper 100 m of the ocean for buffer values of 0, 1.1, and 2.3 mmol/kg [13, 15]
2. Process Overview

The Chicxulub impact had several catastrophic longterm effects on the environment and life, both marine and terrestrial (Fig. 2.1). The process for modeling these effects begins from geological observations of the spherule layer and the original impact crater. Using these measurements, the spherule reentry event is simulated. By using nonequilibrium chemistry models in conjunction with the direct simulation Monte Carlo (DSMC) method, the aerothermodynamic properties of the spherules are determined. Using flux calculations from the simulated flowfields, I produced an estimate for the production rate of nitric oxide and monoatomic species of interest.

These produced chemical species are then used as inputs for a finite rate chemistry calculation that tracks the reactions that occur during the cooldown of the atmosphere. The resulting species are allowed to diffuse into the lower atmosphere, eventually reaching the cloud layer. I use an estimate for the absorption rates into
the cloud water vapor and the resulting rainout process. A time history of the pH of the upper ocean is determined assuming a fixed initial concentration of buffer species. The acidified upper ocean water will eventually mix with the remaining ocean, restoring the pH of the upper layer to its original level. An overview of this overall process is provided in Fig. 2.2.

Figure 2.2. Acidification process overview.
3. Direct Simulation Monte Carlo Method

3.1 Reaction Rates

The direction simulation Monte Carlo method [20], intended for flows with a high Knudsen number, emulates the motion and interaction of gas molecules. Simulation particles, representing a large number of molecules, move through physical space and collide with other molecules and solid surfaces in a probabilistic manner. Reaction probabilities during collisions are determined using a total collision energy (TCE) model with modified Arrhenius rates.

To generate the DSMC results presented in the paper, I used the Statistical Modeling in Low-density Environment (SMILE) code [30]. The reaction rate coefficients, listed in Table 3.1, are from Hassan and Hash [22]. The reaction rates corresponding to the table data for the forward and reverse reactions are of the form

\[ K_f = A_T^b \exp(-E_a/k_B T), \quad \text{and} \]

\[ K_r = A_r T^{b_r} \exp(-E_{a,r}/k_B T). \]

(3.1)\hspace{1cm} (3.2)

The coefficients for these reaction rates are typically generated using high enthalpy shock tubes or other ground based testing facilities, due to the difficulty in recreating high enthalpy flight conditions. Consequently the coefficients can have high degrees of uncertainty. However, the extreme difference in rates for different reactions, typically several orders of magnitude, mitigates the relative error imposed by these uncertainties.

To determine the relevant range of velocities to consider for production of NO, consider the required energy to dissociate diatomic nitrogen. Figure 3.1 illustrates the reaction probability for dissociation of N\(_2\) (Equations 3.3 and 3.4), shown with
Table 3.1 Reaction rate coefficients for the modified Arrhenius equation.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$E_a$</th>
<th>$A$</th>
<th>$b$</th>
<th>$E_{a,r}$</th>
<th>$A_r$</th>
<th>$b_r$</th>
</tr>
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<tbody>
<tr>
<td>O + N$_2$ → O + N + N</td>
<td>1.56E-18</td>
<td>4.09E-11</td>
<td>-1</td>
<td>5.24E-19</td>
<td>2.49E-12</td>
<td>-1</td>
</tr>
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<td>N + N$_2$ → N + N + N</td>
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<td>-1</td>
<td>1.56E-18</td>
<td>2.49E-12</td>
<td>-1</td>
</tr>
<tr>
<td>O + NO → O + N + O</td>
<td>1.04E-18</td>
<td>6.79E-12</td>
<td>-1</td>
<td>2.69E-19</td>
<td>5.81E-12</td>
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<tr>
<td>N + NO → N + N + O</td>
<td>1.04E-18</td>
<td>6.79E-12</td>
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</tr>
<tr>
<td>O$_2$ + NO → O$_2$ + N + O</td>
<td>1.04E-18</td>
<td>6.79E-12</td>
<td>-1</td>
<td>1.04E-18</td>
<td>5.81E-12</td>
<td>-1</td>
</tr>
<tr>
<td>N$_2$ + NO → N$_2$ + N + O</td>
<td>1.04E-18</td>
<td>6.79E-12</td>
<td>-1</td>
<td>1.04E-18</td>
<td>5.81E-12</td>
<td>-1</td>
</tr>
<tr>
<td>NO + NO → NO + N + O</td>
<td>1.04E-18</td>
<td>6.79E-12</td>
<td>-1</td>
<td>1.04E-18</td>
<td>5.81E-12</td>
<td>-1</td>
</tr>
<tr>
<td>O + O$_2$ → O + O + O</td>
<td>8.20E-19</td>
<td>1.50E-11</td>
<td>-1</td>
<td>8.20E-19</td>
<td>1.49E-14</td>
<td>-0.5</td>
</tr>
<tr>
<td>N + O$_2$ → N + O + O</td>
<td>8.20E-19</td>
<td>1.50E-11</td>
<td>-1</td>
<td>1.00E-27</td>
<td>1.49E-14</td>
<td>-0.5</td>
</tr>
<tr>
<td>O$_2$ + O$_2$ → O$_2$ + O + O</td>
<td>8.20E-19</td>
<td>1.50E-11</td>
<td>-1</td>
<td>8.20E-19</td>
<td>1.49E-14</td>
<td>-0.5</td>
</tr>
<tr>
<td>N$_2$ + O$_2$ → N$_2$ + O + O</td>
<td>8.20E-19</td>
<td>1.50E-11</td>
<td>-1</td>
<td>8.20E-19</td>
<td>1.49E-14</td>
<td>-0.5</td>
</tr>
<tr>
<td>NO + O$_2$ → NO + O + O</td>
<td>8.20E-19</td>
<td>1.50E-11</td>
<td>-1</td>
<td>8.20E-19</td>
<td>1.49E-14</td>
<td>-0.5</td>
</tr>
<tr>
<td>O + N$_2$ → NO + N</td>
<td>5.24E-19</td>
<td>1.22E-18</td>
<td>0.5</td>
<td>5.24E-19</td>
<td>0.00E+00</td>
<td>0</td>
</tr>
<tr>
<td>O + NO → O$_2$ + N</td>
<td>2.69E-19</td>
<td>4.95E-19</td>
<td>0.5</td>
<td>2.69E-19</td>
<td>0.00E+00</td>
<td>0</td>
</tr>
<tr>
<td>N + NO → N$_2$ + O</td>
<td>0.00E+00</td>
<td>2.66E-19</td>
<td>0.5</td>
<td>0.00E+00</td>
<td>0.00E+00</td>
<td>0</td>
</tr>
<tr>
<td>N + O$_2$ → NO + O</td>
<td>0.00E+00</td>
<td>1.58E-20</td>
<td>1</td>
<td>0.00E+00</td>
<td>0.00E+00</td>
<td>0</td>
</tr>
</tbody>
</table>
the energy distribution function at the stagnation point for flow around a spherule at several velocities.

\[ N_2 + O_2 \rightleftharpoons 2N + O_2. \tag{3.3} \]

\[ N_2 + N_2 \rightleftharpoons 2N + N_2. \tag{3.4} \]

As seen in the figure, below 5 km/s, no significant fraction of particles will exceed the dissociation probability. This lower limit is applied during the spherule trajectory integration and provides the minimum velocity to consider for the DSMC cases. The upper limit considered corresponds to the escape velocity for Earth.

![Figure 3.1. Reaction probability of diatomic nitrogen dissociation in air shown with the collision energy distribution functions at the stagnation point for various spherule velocities [31].](image)
3.2 Case Selection

I modeled 16 DSMC cases in order to generate a response surface for the drag force and generation of O, N, and NO. Aerodynamic forces were compared to theory [32]. The cases consist of all combinations of the altitudes and velocities listed in Table 3.2. These node locations were chosen based on a 3rd order generalized polynomial chaos fit. The initial temperature distribution and density for each case are listed in Table 3.3. The corresponding mole fractions for each species, based on equilibrium conditions, are shown in Fig. 3.2.

![Initial mole fraction based on equilibrium chemistry, assuming the elevated temperature profile extracted from Goldin and Melosh [9].]

Figure 3.2. Initial mole fraction based on equilibrium chemistry, assuming the elevated temperature profile extracted from Goldin and Melosh [9].

Ambient atmospheric conditions are needed to find the production rates from the hypersonic chemosynthesis. Using data from Goldin and Melosh [9] for atmospheric conditions during the spherule reentry event, I determined the equilibrium concen-
Table 3.2 Simulated particles per cell and sampling information for each altitude used for generating the drag and production response surfaces.

<table>
<thead>
<tr>
<th>Altitude [km]</th>
<th>Particles Per Cell</th>
<th>NO Particles Per Cell</th>
<th>Time Step [s]</th>
<th>Sampled Steps</th>
<th>Samples Per Cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>134.45</td>
<td>4.3482</td>
<td>3.97034</td>
<td>1.00E-09</td>
<td>1,500,000</td>
<td>5.956E+06</td>
</tr>
<tr>
<td>113.60</td>
<td>6.0114</td>
<td>5.98520</td>
<td>1.00E-09</td>
<td>1,500,000</td>
<td>8.978E+06</td>
</tr>
<tr>
<td>86.40</td>
<td>6.8898</td>
<td>7.68804</td>
<td>1.00E-10</td>
<td>1,500,000</td>
<td>1.153E+07</td>
</tr>
<tr>
<td>65.56</td>
<td>10.544</td>
<td>10.99103</td>
<td>4.00E-11</td>
<td>1,500,000</td>
<td>1.649E+07</td>
</tr>
</tbody>
</table>

Table 3.3 Free-stream temperature and density information for each altitude used for generating the drag and production response surfaces.

<table>
<thead>
<tr>
<th>Altitude [km]</th>
<th>Temperature [K]</th>
<th>Number Density [molecules/m³]</th>
<th>Mole Fractions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>N2</td>
</tr>
<tr>
<td>134.45</td>
<td>3698</td>
<td>5.00E+19</td>
<td>0.526</td>
</tr>
<tr>
<td>113.60</td>
<td>3285</td>
<td>8.30E+19</td>
<td>0.641</td>
</tr>
<tr>
<td>86.40</td>
<td>2225</td>
<td>3.17E+20</td>
<td>0.741</td>
</tr>
<tr>
<td>65.56</td>
<td>534</td>
<td>4.85E+21</td>
<td>0.789</td>
</tr>
</tbody>
</table>
trations of O, N, O₂, N₂, and NO that would naturally occur. The reentry of the spherules produces enough thermal energy to heat the entire upper atmosphere thousands of degrees Kelvin. Due to the elevated ambient temperature (Fig. 1.1), more O₂ and N₂ dissociates [31] at equilibrium than is typical in Earth’s atmosphere. These adjusted equilibrium concentrations and the elevated ambient temperature are used to determine incoming flow properties for the spherule aerodynamics and consequent reaction rates. For the DSMC simulations, the spherules are assumed to remain cool and do not ablate, due to their high emissivity.

3.3 Simulation Results

Figure 3.3 indicates the regions used for integration when determining the desired macroscopic output values. The surface pressure acting on the spherule is integrated and converted to the drag coefficient shown in Fig. 3.4. The overall flux of particles around the entire edge of the domain is integrated and converted to a production or destruction rate for the trace species. The number density flowfields for two trace species are shown in Figs. 3.5 amd 3.6. The rate for NO production at each DSMC point is shown in Fig. 3.7. The flowfield temperature around the spherule is shown in Fig. 3.8.
Figure 3.3. Schematic of flowfield for sample spherule reentry. Pressure data is for reentering spherule at 65 km altitude and 11 km/s velocity.

Figure 3.4. The drag coefficient predicted by the SMILE simulations compared to the model provided by Crowe [32].
Figure 3.5. Nitric oxide number density for a reentering spherule at 65 km altitude.

Figure 3.6. Monoatomic nitrogen number density for a reentering spherule at 65 km altitude.
Figure 3.7. The production rate predicted by the SMILE simulations.
Figure 3.8. The translational temperature for a reentering spherule at 65 km altitude.
4. Spherule Trajectory Integration

To determine the overall effect of the spherules on the atmosphere, I calculated a the trajectory for a reference spherule. I chose an initial velocity of 8 km/s acting 45° downward from the horizontal, representative of average conditions for a spherule. This trajectory was propagated using a forth order Runge-Kutta scheme.

To determine the aerodynamic drag force and the production rates at each time step, I generated response surfaces for each property based on the the DSMC cases. Integration of the flux of each species across the computational domain boundary determines the overall production or destruction rates for each DSMC case. To determine the drag coefficient of the spherule at each DSMC point, I integrate the aerodynamic surface forces. The surface for drag is shown in Fig. 4.1 and the surface for the NO production rate is shown in Fig. 4.2.

![Drag Surface](image.png)

Figure 4.1. Response surface for drag force acting on spherule.
By integrating the production rate divided by the velocity and the altitude dependent surface area across which it is spread, the altitude dependent density contribution due to the reentry of one spherule is obtained, given by the expression

\[ n_i = \frac{\dot{N}}{v} \frac{1}{4\pi (r_e + h)^2}, \]  

(4.1)

where \( N \) is the number of particles, \( v \) is the spherule velocity, \( r_e \) is the radius of the earth, and \( h \) is altitude.

Using these properties, the trajectory was propagated forward in time, resulting the velocity profile shown in Fig. 4.4 and the NO production given in Fig. 4.6. My multiplying the concentrations by the number of spherules, I determined the initial concentrations for the finite rate chemistry process during the atmospheric cooldown. The total production profiles for each trace species due to all the spherules are shown in Fig. 4.7.
Figure 4.3. Trajectory of reference spherule.

Figure 4.4. Velocity history of reference spherule.
Figure 4.5. Acceleration load history of reference spherule.

Figure 4.6. Profile of generated NO from reference spherule.
Figure 4.7. Profile of generated trace species from all spherules.
5. Atmospheric Cooldown and Chemistry

To estimate the effect of these chemicals on the environment, this work includes the subsequent reactions as the atmosphere cools and the transport of the toxins via turbulent diffusion. The atmosphere decreases in temperature after the spherule reentry event terminates. I modeled the reactions during this cooldown phase using the same reaction set [22,23] used for the DSMC simulations. The resulting distribution of produced chemicals becomes the initial conditions for the atmospheric transport calculations.

To determine the rate of the atmospheric cooldown, the atmosphere was discretized vertically into layers. The heat flux between the layers was determined by assuming the layers were optically thick, and using the Rosseland-mean extinction coefficient [9]

$$\beta_R = (1.2 \times 10^5 + 0.031T^2).$$  \hspace{1cm} (5.1)

For an optically thick layer, the effective radiative heat transfer coefficient [33] becomes

$$k_R = \frac{16n^2\sigma T^3}{3\beta_R}.$$  \hspace{1cm} (5.2)

This heat transfer coefficient formulation was then implemented in a finite volume scheme with an adaptive time step that iterated until reaching thermodynamic equilibrium. The atmospheric temperature profiles for several instances are shown in Fig. 5.1. The upper portion of the atmosphere cools more quickly, due to less of the emitted radiation being locally absorbed before reaching the edge of the atmosphere. To ensure the stability of the time integration scheme, the time step was limited such that Eq. 5.3 was satisfied for each volume.

$$\frac{\partial T}{\partial t}\frac{\Delta t}{\Delta h} = \frac{k_R\Delta t}{\rho c_p\Delta h^2} \leq 1.$$  \hspace{1cm} (5.3)
Figure 5.1. Temperature history of atmosphere during cooldown. The initial time corresponds to the end of the spherule reentry phase.
6. Ice Formation

As the previous section shows, the initial heat radiates away significantly faster than the species diffuse. Therefore, the equilibrium temperature distribution will resemble the current day temperature distribution during the majority of the atmospheric transport. The Chicxulub impact would vaporize a considerable amount of water, which could be present in the upper atmosphere during the resulting transport process. Altitudes above 33.2 km have pressures below the triple point for water (611.7 Pa). Consequently, to fully consider the transport and reactions of the trace species, one must consider ice deposition (desublimation) above 33.2 km in addition to condensation in the cloud layer.

![Modern Day Temperature Distribution](image)

Figure 6.1. Modern day temperature distribution.
The deposition rate can be calculated in a manner similar to sublimation. The number of particles striking a unit area per unit time is given by

\[ J = \frac{1}{4} n \sqrt{\frac{8k_b T}{\pi m}}. \]  

(6.1)

Assuming ideal gas behavior and a ice crystal surface temperature similar to the ambient temperature, the expression the net exchange of particles is then given by

\[ \dot{N} = \sqrt{\frac{1}{2\pi mk_b T_{\infty}}} (P_\infty - P_v), \]  

(6.2)

where \( P_v \) is the vapor pressure for the solid species of interest. To get the actual rate, one must consider a time averaged surface area during crystal production (Available for various temperatures from paper by K. Libbrecht).

The vapor pressure can be found using Clausius Clapeyron relation,

\[ \frac{dP}{dT} = \frac{L}{T\Delta v}. \]  

(6.3)

Information is available for water, but further information is needed for less common species. Use the Antoine equation,

\[ \log_{10}(P_v) = A - \frac{B}{T + C}. \]  

(6.4)

Coefficients are empirically fit from experimentation and available for many species (including NO\(_2\) and NH\(_3\)) in the NIST database.

Plotting the rate indicates that ice will only be produced for a limited range of altitudes. Ice formation can be introduced into code for finding the transfer between various species. One must now consider the transport of denser species (H\(_2\)O, NO\(_2\), and NO\(_3\)) to lower altitudes and determine dominant transport phenomenon (e.g. Diffusion, Turbulence, Virga).

Major reactions for NO\(_x\) related species with liquid water and ice can now be accounted for. Ice formation will only play a major role for a limited range of altitudes (and possibly during descent of water). One must now determine dominant methods of species transport and determine the characteristic time for the descent. Liquid water and potentially acid rain clouds could start forming once the species descend below 33.2 km.
Figure 6.2. Ice production flux for region of atmosphere where the rate is positive.
7. Atmospheric Transport Modeling

7.1 Turbulence Model

To determine the time scale for the spread of species produced in the upper atmosphere, one must consider and compare the diffusion rate for both turbulent and molecular diffusion. The mass flux due to diffusion is given by Fick’s law,

$$\rho_i \ddot{u}_i = -\rho D \nabla \left( \frac{\rho_i}{\rho} \right),$$  \hspace{1cm} (7.1)

where $D$ is the diffusion coefficient and the subscript $i$ denotes the value for a specific species. The molecular diffusion coefficient is set by the species of interest and the local temperature and pressure. Cussler [34] suggested the following correlation.

$$D_{m,P1} \rho_{P1} = D_{m,P2} \rho_{P2},$$ \hspace{1cm} (7.2)

where $P1$ and $P2$ denote two different pressure conditions. Values for the diffusion coefficient in air at sea level pressure are widely available.

For the turbulent diffusion coefficient, Tennekes and Lumley [24] suggest

$$D_t \propto u_t L_t \propto \bar{u} L_t,$$ \hspace{1cm} (7.3)

where $u_t$ is the characteristic velocity of the turbulence and $L_t$ is the characteristic length. For flows with a mean velocity, the characteristic turbulence velocity can be estimated to be 1/30 of the mean flow velocity, $\bar{u}$ [24]. The characteristic length for atmospheric turbulence can be estimated [24] by

$$L_t = \frac{1}{4} \bar{u} T,$$ \hspace{1cm} (7.4)
where $T$ is the period for the turbulence, approximately $10^4$ seconds for most atmospheric turbulent flows. By combining these expressions, it is apparent that molecular diffusion will be negligible.

To characteristic length of a fluid flow is given by

$$L = \frac{P}{\left(\frac{\partial P}{\partial x}\right)}$$

(7.5)

where $P$ is a property of interest for the flow (in this case pressure). Performing this calculation for the atmosphere yields an expression identical to the atmospheric scaling height:

$$L = \frac{k_B T}{M g}$$

(7.6)

This expression can be used to calculate the turbulent diffusion coefficient for a known turbulent velocity, assuming the characteristic eddy size is proportional to the characteristic length. The model can be scaled to match existing atmospheric data.
The initial bulk flow velocity profile was determined by allowing the momentum imparted by the spherules diffuse through the entire atmosphere, and is assumed to relax to a modern day average velocity profile.

The stratified diffusion coefficient profile can be extracted from empirical measurements [35]. The diffusion coefficient for a destratified atmosphere is directly proportional to the bulk flow velocity and the turbulent length scale.

![Diffusion Coefficient](image)

**Figure 7.2.** Diffusion coefficient for both stratified and destratified conditions.

Once mass fluxes are known, the overall rate of change at each altitude can be calculated. From the conservation of mass,

\[
\frac{\partial \rho}{\partial t} = -\vec{V}(\rho \vec{u}).
\] (7.7)

Therefore the rate of change of number density will be

\[
\frac{\partial n_i}{\partial t} = \frac{\partial}{\partial y} \left( n_D \frac{\partial}{\partial y} \left( \frac{n_i}{n} \right) \right) + \dot{n}_{i,rxns},
\] (7.8)
where the first term on the LHS represents the flux due to the overall flow, the second term represents diffusion, and the third term represents the species generation and destruction due to chemical reactions.

Convert Eq. 7.8 to be in terms of the non-dimensional mole fraction. Let \( x \) represent the mole fraction for species \( i \).

\[
\frac{\partial x}{\partial t} = \frac{1}{n} \frac{\partial}{\partial y} \left( nD \frac{\partial x}{\partial y} \right) + \frac{n_{i,rxns}}{n} \tag{7.9}
\]

To ensure that the FVE will be unconditionally consistent and preserve mass, leave the first term on the RHS in strong conservation form. Assume uniform grid spacing and approximate the diffusion flux at the boundaries of the \( j \)th cell using central differencing.

\[
\left( nD \frac{\partial x}{\partial y} \right)_{j \pm 1/2} = \frac{1}{2} [(nD)_{j+1} + (nD)_{j}] \frac{x_{i \pm 1} - x_i}{\pm \Delta y} \tag{7.10}
\]

Using the flux in the non-dimensional expression for the time derivative at time step \( k \) and again using central differencing yields

\[
\left( \frac{\partial x}{\partial t} \right)_j^k = \frac{1}{n_j \Delta y} \left[ \left( nD \frac{\partial x}{\partial y} \right)_{j+1/2}^k - \left( nD \frac{\partial x}{\partial y} \right)_{j-1/2}^k \right] + \frac{n_{i,rxns,j}^k}{n_j}, \tag{7.11}
\]

where the flux terms at time step \( k \) are

\[
\left( nD \frac{\partial x}{\partial y} \right)_{j \pm 1/2}^k = \frac{1}{2} [(nD)_{j \pm 1} + (nD)_{j}] \frac{x_{i \pm 1}^k - x_i^k}{\pm \Delta y}. \tag{7.12}
\]

These two expressions can be used for explicit or implicit integration schemes.

Application of Fourier stability analysis to the previously shown integration scheme indicates that the following inequalities must be satisfied.

\[
\Delta t \leq \frac{\Delta y^2}{2D} \tag{7.13}
\]

\[
\Delta t \leq \frac{n \Delta y}{D} \left| \frac{\partial n}{\partial y} \right|^{-1} \tag{7.14}
\]
These conditions are analogous to a CFL number corresponding to the flux due to diffusion instead of a bulk flow velocity. Due to large time scale needed for the reactions to occur in significant quantities, the spatial grid spacing should not be made larger than necessary, $O(100m)$.

### 7.2 Transport Results

![Figure 7.3. Mole fraction of surplus monatomic oxygen.](image)
Figure 7.4. Number density of surplus monatomic oxygen.

Figure 7.5. Mole fraction of surplus monatomic nitrogen.
Figure 7.6. Number density of surplus monatomic nitrogen.

Figure 7.7. Mole fraction of nitric oxide.
Figure 7.8. Number density of nitric oxide.
8. Cloud Absorption and Rainout Rate

The pH of the ocean is initially constant as the produced NO diffuses downward. Upon reaching the cloud layer, NO begins to be absorbed into the cloud water vapor and precipitate into the ocean. I assume the primary mechanisms for absorption occur from the following reactions.

\[
2NO_2(g) + H_2O(l) \rightarrow 2H^+ + NO_3^- + NO_2^- \quad (8.1)
\]

\[
NO(g) + NO_2(g) + H_2O(l) \rightarrow 2H^+ + 2NO_2^- \quad (8.2)
\]

\[
3NO_2(g) + H_2O(l) \rightarrow 2H^+ + 2NO_3^- + NO(g) \quad (8.3)
\]

I estimated the rate of absorption using an expression from [25], dependent on the local atmospheric conditions and the availability of water vapor and NO\textsubscript{x} compounds. The rate is for the dominant mechanism, Eq. 8.1, reducing to

\[
R_1 = k_1H^2NO_2p^2NO_2. \quad (8.4)
\]

I assumed that the acid rain has a molarity equivalent to the moisture in the clouds. I then approximated the rainout rate to be 1.12 m/year [26], spread evenly across the planet and averaged across an entire year.
Figure 8.1. Mole fraction of aqueous HNO\textsubscript{2}.

Figure 8.2. Number density of aqueous HNO\textsubscript{2}.
Figure 8.3. Total NO molecules remaining in atmosphere.

Figure 8.4. Total HNO$_2$ molecules absorbed by clouds.
Figure 8.5. Fraction of initial NO molecules converted into HNO$_2$. 
9. Oceanic Buffering and pH Level

The ocean maintains a natural carbonate (CO$_3^{2-}$) and bicarbonate (HCO$_3^-$) buffer, which can absorb 2 and 1 hydrogen ions, respectively. This naturally occurring carbonate concentration is crucial for the survival of calcifying species. The corresponding buffer reactions are

$$H^+(aq) + CO_3^{2-}(aq) \rightleftharpoons HCO_3^-(aq) \quad (9.1)$$
$$H^+(aq) + HCO_3^-(aq) \rightleftharpoons H_2CO_3(aq), \quad (9.2)$$

which have known equilibrium constants for a given temperature and pressure.

The buffering byproduct (H$_2$CO$_3$) decomposes into water and carbon dioxide (Eq. 9.3). In the timescale of years, the atmosphere can absorb a limited amount of CO$_2$, thus allowing more buffering to take place before reaching equilibrium (Eq. 9.4).

$$H_2CO_3(aq) \rightleftharpoons H_2O(l) + CO_2(aq) \quad (9.3)$$
$$CO_2(aq) \rightleftharpoons CO_2(g) \quad (9.4)$$

In equilibrium, the addition of hydrogen ions will remove the naturally occurring carbonate concentration crucial for the survival of calcifying species.

To estimate the effect of carbonate buffering, I included an initial carbonate ion concentrations of 1.1-2.3 mmol/kg [15] to account for the equivalent atmospheric CO$_2$ equilibration. The pH drop is determined via

$$pH = -\log_{10} \left( \frac{\Delta n_{H^+}}{N_A} + 10^{-8.14} \right). \quad (9.5)$$

This assumes the initial pH of the upper ocean is 8.14 [16]. The hydrogen ions initially added to the upper ocean are quickly removed by the buffer, resulting a delay in the pH drop. Ultimately, the acidification overcomes the buffer, resulting in the significant pH decrease seen in Fig. 9.1.
Figure 9.1. pH level of upper ocean.
10. Comparison with Primary Impact

The detailed numerical modeling of the Chixculub impact structure implies that an impact energy of $2.8 \times 10^{23} \text{ J}$ was required to make the structure [36]. The presence of a fossilized meteorite fragment in the K-Pg boundary layer is evidence that the Chixculub impactor was an asteroid [37]. Assuming an impact velocity, $v_{\text{imp}} = 20 \text{ km/s}$, typical for asteroids striking the Earth [38], and an impactor density, $\rho_{\text{imp}} = 2680 \text{ kg/m}^3$, then the Chixculub crater was made by roughly 10 km diameter object.

Prinn and Fegley [13] produced the following equation to estimate the amount of NO produced by a given impact.

$$ P = \left[ \epsilon_1 Y_1 + (1 - \epsilon_1) \epsilon_2 Y_2 \right] \frac{1}{2} m_{\text{imp}} v_{\text{imp}}^2, \quad (10.1) $$

where $\epsilon_1$ is the fraction of the impact energy that get transferred to the atmosphere during initial entry of the impactor (before it hits the Earths surface), given by

$$ \epsilon_1 = \frac{\pi r_{\text{imp}}^2 (10^5 \text{ Pa})}{m_{\text{imp}} g \cos(\phi)} = 0.0008 \quad (10.2) $$

The impact angle $\phi$ is assumed to be 45 degrees. $Y_1 = 10^{17} \text{ molecules/J}$ is the yield of NO expected from this initial entry into the atmosphere. $\epsilon_2 = 0.125$ is a rough estimate of the amount of impact energy that gets transferred to the atmosphere by material ejected by the impact and $Y_2 = 2 \times 10^{16} \text{ molecules/J}$ is the expected yield from this process. Using these values and the impact energy of $2.8 \times 10^{23} \text{ J}$, then the total NO production predicted by Prinn and Fegley’s [13] method is $P = 1.2 \times 10^{15} \text{ mol}$ and 97% of the estimated NO production is caused by interactions between the atmosphere and material ejected by the impact.
11. Conclusion

The Chicxulub impact triggered the end of the Cretaceous Period [1, 2], ejecting enough sub-millimeter spherules to cover the Earth in a ∼3 mm thick layer [5–8]. The global reentry of these spherules produced a thermal radiation pulse that wiped out much of the terrestrial biota [9–11], however, this transient elevated radiation cannot explain the concurrent loss of ocean life. Recent geologic observations [12] suggest that ocean acidification is responsible for the marine extinctions, which selectively targeted calcifying species. Here I conclude that Chicxulub impact ejecta generates enough NO$_x$ to acidify the upper ocean and cause a mass marine extinction. Nonequilibrium chemically reacting flow simulations coupled with atmospheric transport modeling yields $8 \times 10^{16}$ moles of NO$_x$. Upon reaching the stratosphere and precipitating into the oceans, the nitric acid overpowers the carbonate buffer in the upper ocean. I find that the pH of the upper ocean drops below 6.7 long enough to trigger widespread marine extinctions. Thus, I conclude that NO$_x$ produced by reentering ejecta and the subsequent acidification of the upper ocean is an possible cause of the end Cretaceous marine extinctions.
12. Future Work

12.1 Ocean Acidification Model Generalization

1. Add oceanic mixing to determine timeframe for pH restoration and provide a minimum pH.

2. Determine the amount of ejecta and size/velocity distribution produced for a given impactor size/energy. Use historical impacts to determine relevant range for study.

3. Examine effect of spherule size on production rates.
   - Determine if non-dimensionalization of response surface input parameters permits elimination of diameter input in favor of Knudsen number dependency.

4. Use trajectory code to produce a fit of the initial distribution of produced chemical species as a function of ejecta conditions (and consequently impactor conditions).

5. Run atmospheric transport code and determine minimum pH (and response/recovery times) as a function of impactor conditions.

12.2 Other Scenarios to Consider

- Other produced species that may affect life
  - Other potential toxic chemicals
  - Precursors such as HCN
  - Catalyzed breakdown of CO$_2$
• Consider other atmospheric/gravitational conditions
  
  – Early earth atmosphere
  
  – Effect of great oxidation event on chemical byproducts
  
  – Martian and Venusian impacts
    
    * Atmospheric composition effect on chemistry
    
    * Escape velocity effect on spherule size/velocity distribution
    
    * Gravity/radius effect on spherule entry angle distribution
    
    * Gravity/atmospheric density effects on spherule trajectories

12.3 Overall Code Improvements

• Improve cooldown process accuracy
  
  – Include convective heat transfer.
  
  – Improve transparency implementation as temperature cools.
  
  – Improve surface heat flux boundary condition.

• Append finite rate reaction set with larger/more complex species.

• Sensitivity analysis
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