Frequent ozone depletion resulting from impacts of asteroids and comets

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Abstract

The impact with the Earth's oceans of a relatively small meteoroid, ≈260-300 m diameter, having a mean density of $2,500 \text{ kg/m}^3$ and mean velocity of 17.8 km/s, would vaporize and loft sufficient seawater to increase the global stratospheric content of chlorine by 3 ppbv and possibly cause an Antarctic "ozone hole." Meteoroids of this size or comets having equivalent kinetic energies are estimated to strike the Earth's oceans about once every 6,000-9,000 years. A large, globally distributed ozone depletion is predicted to occur about two to four times less frequently, resulting from the a combination of increased chlorine content (10 ppby chlorine every 15,000-22,000 yr), increased NO_v content (10 ppbv every 16,000-38,000 yr), and increased water vapor content (4 ppmv every 14,000-19,000 yr). The meteoroid diameter required to cause a large globally distributed ozone depletion is in the range 500-600 m for an average impact velocity of 17.8 km/s. These hypothesized ozone depletions are predicted to occur with sufficient frequency that it may be possible to detect past asteroid impacts by examining the UV damage to DNA of pollen grains retrieved from ice cores dating back ≈200,000 years. Model calculations using the Thermosphere-Ionosphere-Mesosphere-Electrodynamics General Circulation Model (TIME-GCM) to simulate coupled dynamics and chemistry in the altitude range 30-500 km confirm that oxides of nitrogen and water vapor lofted to altitudes above 70 km are rapidly dispersed horizontally. These simulations show that a large fraction of the injected NO and H₂O survives the photochemistry of the upper mesosphere and thermosphere and is transported to the stratosphere, with maximum ozone depletions occurring about three months after the impact.

1 Introduction

The fossil record reveals that the evolution of life on Earth has been punctuated by a number of catastrophic events, of which one of the most devastating occurred at the end of the Cretaceous, approximately 66 million years ago. The postulate introduced in 1980 by Alvarez et al. (1980) that the collision of an approximately 10 km diameter asteroid with the Earth caused the

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extinction of the dinosaurs along with about half of all plant and animal species, has resulted in a greatly expanded research efforts in the area of catastrophic events (Alvarez et al. 1980).

Large events such as the C-T impact, which may have thrown up enough debris to block most of the incoming solar radiation for months to years (Toon et al. 1982), produced enough nitric acid to reduce the pH of rainfall to phytotoxic levels (Lewis et al. 1982; Prinn and Fegley 1987), and/or injected enough water vapor (Emiliani et al. 1981) or carbon dioxide into the atmosphere to cause a global warming (O'Keefe and Ahrens 1989) are estimated to occur with extremely low frequency -- perhaps once every hundred million years or longer. Although not as devastating as the C-T impact, impacts of much smaller objects, which occur much more frequently, could have serious consequences for humanity and the ecosystems on which we depend. Here we postulate that the method of harming the global biosphere with the least amount of impact energy is to deplete the stratospheric ozone layer, thereby allowing enhanced levels of UV radiation to reach the Earth's surface. Both terrestrial and aquatic plants, at the base of the food chain, are highly sensitive to UV radiation (Nachtway et al. 1975). Model calculations presented here indicate large stratospheric ozone depletions occurring as often as once every few tens of thousands of years.

2 Physical interactions with the atmosphere

Here we consider the impacts of asteroids of having diameters =150 m. Objects of this size pass through the atmosphere with only minimal (approximately 5.8% for a 150 m stoney meteoroid) loss of energy to the atmospheric shock wave that they produce (Melosh 1989). The energy of impact, $1/2 \text{ mv}^2$, is given by

$$E = \frac{1}{6} \boldsymbol{p} D^3 v^2 \tag{E1}$$

where *D* is the diameter of the asteroid and ? is its density. The minimum impact velocity, *v*, is the Earth's escape velocity, 11.2 km/s, while the maximum velocity is 72.8 km/s, corresponding to the sum of the Earth's escape velocity, orbital velocity about the sun and the velocity of an object just barely bound to the sun at the Earth's orbital position (Melosh 1989). For all calculations made below, the impact velocity is assumed to be 17.8 km/s, the mean impact velocity with the Earth, and the density is assumed to be 2,500 kg/m³, characteristic of stoney

meteoroids. The amounts of energy released in the impact, $1/2 \text{ mv}^2$, are 400 Mt, 2,100 Mt and 6,200 Mt for 200 m, 350 m and 500 m diameter asteroids, respectively. Upon impact, this energy will be released in the form of a strong shock wave that heats the surrounding medium to temperatures of a few tens of thousands of degrees, producing in the atmosphere what in military parlance is termed a "fireball."

The hemispherical fireball expands until its internal pressure matches that of the surrounding atmosphere. For relatively small impacts, the radius of the fireball, R_{f} , may be calculated assuming adiabatic expansion as (Melosh 1989)

$$R_{f} = [(3V_{j}/2?)/(P_{j}/P_{0})^{1/?}]^{1/3}$$
(E2)

where P_i and V_i are the initial pressure and volume of the gas, P_o is the pressure after expansion, and ? is the ratio of heat capacities, C_p/C_v , and is approximately 1.4 for air. This simplifies to

$$R_{\rm f} = 0.009 \ {\rm E_d}^{1/3} \tag{E3}$$

when E_d , the energy deposited in the fireball, is known (Melosh 1989). Calculations using this equation with the assumption that one-half the impact energy is deposited in the fireball predicts radii of 8.5 km, 14.8 km and 21.1 km for 200 m, 350 m and 500 m diameter meteoroids, respectively. For meteoroids slightly larger than 165 m in diameter, the calculated radius of the initial fireball is greater than the scale height (\approx 7 km) of the atmosphere. Under such conditions, equations E2 and E3 no longer apply; instead, detailed computer models indicate that the phenomenon of "blowout" or "backfire" will occur in which the hot fireball of vaporized material rises rapidly, partially funnelled by the "vacuum straw" formed during passage through the atmosphere, and spills into the near vacuum of the mesosphere and above (Melosh 1982, 1989; Jones and Kodis 1982). Under such conditions, the contents of the fireball are expected to be distributed nearly uniformly across the globe.

3 Chemical perturbations of the upper atmosphere

Upon impact of a meteoroid with the solid Earth or its oceans, stratospheric ozone depletion could result from the injection of large quantities of 1) nitric oxide produced in the shock-heated air, 2) water vaporized and injected high into the upper atmosphere, and 3) halogens chemically activated from sea salt contained in vaporized seawater. Our calculations show that all three

effects may be important on times scales of $\approx 15,000-40,000$ years, although the effect of halogens, which are the most effective catalysts for ozone destruction, is speculative and requires further laboratory data and modeling to be confirmed.

3.1 Nitric oxide production

In air heated to high temperatures, nitric oxide is in equilibrium with N₂ and O₂:

$$N_2 + O_2 = 2 NO \tag{R1}$$

This equilibrium is rapidly established at the initially high temperature of a few thousand degrees in the shock wave as the bolide enters the atmosphere, in the shock-heated air produced by the high-velocity ejecta plume, and within the fireball itself. The equilibrium given by the stoichiometric reaction R1 is maintained by the following forward and reverse elementary chemical reactions:

$$O_2 + M = O + O + M \tag{R2}$$

$$O + N_2 = NO + N \tag{R3}$$

$$N + O_2 = NO + O \tag{R4}$$

$$NO + M = N + O + M \tag{R5}$$

where *M* represents any air molecule. These reactions have large activation energies, with the result that as air cools a "freeze out" temperature is reached where the time constant associated with maintaining equilibrium becomes long in comparison to the cooling rate. In the production of NO within the fireballs of nuclear explosions, for example, the cooling time is of the order of a few seconds, and the freeze out temperature is about 2,000 K (Foley and Ruderman 1973; Johnston et al. 1973; Gilmore 1975). At this temperature approximately 0.7% of the air molecules are present as NO. For lightning discharges, the cooling time of the shock wave is of the order of 2.5 ms and the freeze out temperature is about 2,660 K where the equilibrium mole fraction of NO is about 2.9% (Chameides 1986).

The problem of nitric oxide production upon impact of a meteoroid or comet with the Earth has been treated by Prinn and Fegley (1987). They estimate NO production from two terms as follows:

$$P = [\boldsymbol{e}_1 Y_1 + (1 - \boldsymbol{e}_1) \boldsymbol{e}_2 Y_2] E_k$$
(E4)

where \mathbf{e}_{2} is the fraction of kinetic energy of the bolide, E_{k} , transferred to the atmospheric shock wave during passage through the atmosphere and \mathbf{e}_{2} is the fraction of energy coupled to the atmosphere by the impact fireball. Y_{1} and Y_{2} are yields of NO for the two processes in molecules/J. The value of \mathbf{e}_{2} is estimated as the energy required to accelerate laterally the intercepted mass of air to the incoming bolide velocity and is given by

$$\boldsymbol{e}_{1} = \frac{\boldsymbol{p}D^{2}P_{s}}{4mg\cos\boldsymbol{f}}$$
(E5)

where *m* is the bolide mass, P_s is the surface pressure of one atmosphere, and *f* is the angle of impact, assumed here to be 45°. The calculated value of e_2 varies from 0.058 to 0.018 for 150 m and 500 m diameter meteoroids, respectively. A production factor, $P_1 = 1 \times 10^{17}$ molec/J, characteristic of NO production by lightning (Chameides 1986), was adopted by Prinn and Fegley (1987) for NO production during passage through the atmosphere. Based partly on the work of Emiliani et al. (1981), Prinn and Fegley (1987) estimate e_2 , the fraction of impact energy coupled to the atmosphere, to be 0.125. For P_2 , they assumed a value of 2 x 10¹⁶ molec/J as characteristic of NO production in nuclear explosions. In a careful analysis, Gilmore (1975) estimates a central value of 2.4 x 10¹⁶ molec/J for NO production factor most commonly adopted for studies of the effects of nuclear warfare on the ozone layer (NRC 1975; Whitten et al. 1975; Crutzen and Birks 1975; Turco et al. 1983; NRC 1985; SCOPE 1985). An important difference, however, is that nuclear fireballs lose about one-third of their energy to radiative emission while impact fireballs do not. For this reason, we assume a value of 3.6 x 10¹⁶ molec/J for P_2 .

For the range of bolide diameters and energies considered here, the two terms in equation E4 make comparable contributions to the amount of NO produced. However, as discussed above, the radius of the impact fireball is larger than the scale height of the atmosphere, and as a result nearly all of the NO produced during entry through the atmosphere will be raised to high temperature again and brought back into thermal equilibrium with N_2 and O_2 . Therefore, the amount of NO ultimately produced is solely determined by shock-wave heating following the impact. For this reason, we consider only the second term in equation E4 for production of NO

(i.e. we set $P_1 = 0$), while adopting the higher emission factor for P_2 with its associated uncertainty of ±50%. Thus, our NO emission factor is 3.6×10^{16} molecules/J or 1.5×10^{29} molecules/Mt. In past work, no differentiation has been made for NO production during land vs. ocean impacts. There is strong shock heating of the atmosphere in both cases, and we assume identical emission factors. However, additional theoretical studies are required to better estimate NO emissions for both types of impacts.

3.2 Lofting of water

An enormous amount of liquid water is ejected into the atmosphere upon collision of a meteoroid with the oceans. However, the altitude of injection of liquid water is well below the tropopause and will be removed rapidly from the atmosphere as rain (Emiliani et al. 1981). Of great significance, however, is water vaporized by the impact. Croft (1982) estimated the amount of water vaporized in an ocean impact by means of the Gamma model of shock wave heating and vaporization. The Gamma model is semi-empirical in that some features are derived from fundamental physics, while others are generalizations of the results obtained by computer code calculations of shock wave propagation. Croft (1982) calculated the number of projectile volumes of liquid water that would be vaporized for impacts of gabbroic anorthosite $(? \neq 2,936)$ kg/m^3 , a mineral simulating stony meteoroids) with the ocean in the velocity range 5-80 km/s. For an average impact velocity of 17.8 km/s, a third-order polynomial interpolation of their results predicts a total water vapor volume of 27.6-44.2 projectile volumes (for values of the semi-empirical parameter γ in the range 2.4-2.0). Since their assumed meteoroid density (2,936) kg/m^3) is slightly larger than ours (2,500 kg/m³), we reduce the volume of vapor to 23.5-37.6 projectile volumes, which amounts to assuming that the mass of water vaporized varies linearly with impact energy for a given velocity. For impact velocities between 15 and 20 km/s, the Gamma model predicts that 36.5% of the water vapor is present in the isobaric core produced by the shock wave and the remaining 63.5% is intimately mixed with an approximately equal volume of liquid water at its boiling point in a region of "incipient" vaporization. As discussed below, it is likely that all of the water contained in the region of insipient vaporization, both vapor and liquid, will be injected to altitudes well above the stratosphere, and we therefore take 38.4-61.5 projectile volumes as the amount of water vapor ultimately reaching the stratosphere and affecting the chemistry there.

The sea salt contained in the region of incipient vaporization will all be partitioned into the liquid phase. When this water evaporates in the upper atmosphere, salt particles having diameters of 100- μ m or larger will be formed and will rapidly settle out of the atmosphere, as discussed below. Thus, for calculations of the amount of sea salt contributing to perturbations in stratospheric chemistry, we consider only the water vapor in the isobaric core, which amounts to 8.6-13.7 projectile volumes.

A small downward correction (?6% for 150 m meteoroids and decreasing with increasing bolide diameter) is made for all injection volumes to account for loss of kinetic energy during transit of the meteoroid or comet through the atmosphere. Gamma Model calculations indicate that ocean impacts of comets (ice of density 0.917) vaporize approximately the same amount of seawater as meteoroids of the same mass (Croft 1982).

As discussed above, for meteoroids having diameters greater than about 150 m (impact energies \cong 165 Mt) the atmosphere offers little resistance to the expanding vapor plume. The asymptotic limit (t? 8 for the vertical component of the root-mean-square velocity, v_8 , of the supersonic expansion of the impact "fireball" into the near vacuum above the stratosphere is given by (Zel'dovich and Raizer 1968)

$$v_{\infty} = \sqrt{\frac{2E_k}{m}} \cos \boldsymbol{q} \tag{E6}$$

where E_k is the kinetic energy of the material, m is its mass, and q is the ejection angle with respect to normal. The mean altitude reached is given by

$$h = \frac{E_k}{mg} \cos \boldsymbol{q} \tag{E7}$$

For an average ejection angle of 45°, it requires partitioning of only 2% of the total impact energy into kinetic energy in order to loft the water vapor within the strongly shocked isobaric zone to an altitude of 66 km. Besides the initial kinetic energy, additional lofting can result from conversion of latent heat of vaporization to kinetic energy as the water vapor condenses. The latent heat within this strongly shocked isobaric zone amounts to \approx 7% of the total impact energy. The much less strongly shocked region of insipient vaporization is probably lofted to high altitudes as well. The mass of vapor and liquid is \approx 4.5 times greater, so the maximum altitude reached is \approx 4.5 times less for the same amount of kinetic energy. There is sufficient latent heat alone, however, to loft this mass of water to an altitude of ≈ 90 km. Numerical solutions of the shock wave equations for a wide range of kinetic energies and projectile and target compositions show that the vaporized bolide is typically injected well above the stratosphere and to altitudes of up to several hundred kilometers (O'Keefe and Ahrens 1982).

3.3 Fate of salt particles

Ozone depletion caused by halogens critically depends on the fate of the salt contained in the vaporized seawater. Sea salt and meteoroid vapor would be the first material to begin to condense as adiabatic expansion and work done against the Earth's gravitational field causes the temperature to decline in the rising fireball. The size distribution of salt particles produced is not possible to calculate but may be estimated from results of high-temperature combustion of materials containing salts or other low-vapor pressure substances. Condensation from the hot vapor results in primary particles, or Aitken nuclei, that is typically in the 0.005 to 0.1 μ m diameter range (Finlayson-Pitts and Pitts 1986). Once the gas-phase molecules are consumed, these particles may grow further by agglomeration. If the particles grow to sizes of a few microns, they will rapidly settle out of the atmosphere and have no effect on stratospheric ozone. Rapid agglomeration of salt particles most likely are prevented, however, since those particles serve as condensation nuclei for water vapor in the near vacuum of the mesosphere and above where within a few minutes from the time of impact water will condense, probably directly to ice, onto the salt particles. The size distribution of the salt/ice particles is determined by the size distribution of the salt particles initially formed. Given 3.5 wt-% salt in seawater, and taking into account the relative densities of salt and ice, the salt/ice particles will have diameters ≈5 times as large as the salt condensation nuclei, i.e. diameters $=0.5 \mu m$. The diameters may actually be less due to free fall of particles through the vapor cloud before condensation is complete. The time to free fall, $(2 \Delta z/g)^{1/2}$, from 300 km to 150 km, for example, is only 175 s, at which point the velocity, $(2 \text{ g } \Delta z)^{1/2}$, of the particle is 1.7 km/s. At about 150 km, the particles will reach terminal velocity where the gravitational force is balanced by frictional drag, and as these salt/ice particles settle through denser regions of the atmosphere they will begin to evaporate due to frictional heating. Any water that remains will be completely removed as the particles pass through the \approx 44-66 km region where the static pressure is less than the vapor pressure of water (List 1984). Considering the measured rate of sublimation of ice as a function of temperature (Haynes 1992),

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the time for complete removal of water from the salt/ice particles is only a fraction of a second as particles settle through the \approx 44-66 km region. These relatively dry, sub-micron salt particles will be transported primarily by vertical mixing through the 65-50 km region and into the upper stratosphere within a few days to weeks. Because of the "backfire" nature of the impact event, the particles will be fairly uniformly distributed in both zonal and meridional directions.

Water vapor also will be slowly transported downward to the stratosphere. A small fraction of the injected water will be photolyzed to form H and OH (and ultimately H_2 and O_2 through subsequent thermal reactions), but this fraction will be small since the characteristic time for vertical transport by eddy diffusion is shorter than the photolysis lifetime by about and order of magnitude at 65 km (Brasseur and Solomon 1984).

3.4 Activation of halogens from sea salt particles

Chloride, bromide and iodide ions contained in the sub-micron-sized salt particles settling through the stratosphere may be oxidized to form catalytically active species by several processes. Considering their relative abundances in seawater and relative catalytic efficiencies, only chlorine and bromine species will have a significant impact, with chlorine being by far the most important. Therefore, the following discussion will focus on chlorine even though bromide and iodide are much more easily oxidized. The amount of chloride converted to catalytically active species is limited by the NO_y concentration in the stratosphere, where NO_y is defined here as the sum NO + NO₂ + NO₃ + 2 N_2O_5 + HNO₂ + HNO₃ + HNO₄ + ClONO₂. The presence of these species, either directly or indirectly, will result in the oxidation of chloride, with some of the most important heterogeneous reactions being (Finlayson-Pitts et al. 1989; Timonen et al. 1994; Livingston and Finlayson-Pitts 1991):

$$ClONO_2 + NaCl(s)$$
? $Cl_2 + NaNO_3(s)$ (R6)

$$N_2O_5 + NaCl(s)$$
? $CINO_2 + NaNO_3$ (s) (R7)

$$HNO_3 + NaCl(s)$$
? $HCl + NaNO_3(s)$ (R8)

The key to "activation" of halide ions is replacement of the CI or other halide ions in the salt particle with another anion; for NO_y activation that anion is nitrate, NO_3^- . Sufuric acid also activates chloride by substituting sulfate for the chloride ion (Finlayson-Pitts and Pitts, 1986):

$$H_2SO_4(l) + 2 \operatorname{NaCl}(s) ? 2HCl + \operatorname{Na}_2SO_4(s)$$
(R9)

In the absence of acids or acid gases (e.g., NO_y species), the halogens will remain in inactive salt forms. However, the natural stratosphere contains approximately 10 ppbv of NO_y available for halogen activation (Brasseur and Solomon 1984). Small amounts of sulfuric acid aerosol are naturally present in the lower stratosphere with highly elevated levels during periods of volcanic activity (Junge et al. 1961; Brasseur et al. 1999). Because chlorine and other halogens catalyze ozone depletion at a much faster rate than oxides of nitrogen, replacement of the NO_y species with halogen species is expected to result in large ozone depletion. Thus, ozone depletion resulting from sea salt injection does not necessarily require additional input of NO_y from the asteroid impact. In fact, higher levels of ozone depletion might occur in the case where the amount of sea salt exceeds the NO_y content so that chlorine sequestered in the form of CIONO₂ becomes activated via reaction R6; a situation analogous to what occurs during formation of the Antarctic "ozone hole" where the polar stratosphere becomes "denitrified" (Brasseur et al. 1999).

3.5 Catalytic cycles for ozone depletion

Catalytic destruction of ozone based on reactions involving hydrogen oxides (HO_x) derived from water (Bates and Nicolet 1950), nitrogen oxides (NO_x) derived from naturally occurring N₂O (Crutzen 1970) and potentially from aircraft engine exhaust (Crutzen 1970; Johnston 1971), and chlorine oxides (ClO_x) derived from chlorofluorocarbons (Molina and Rowland 1974) is well known. At mid-latitudes the most important reaction cycles for catalytic ozone destruction based on HO_x, NO_x and ClO_x are:

| Net: 2 O_3 ? 3 O_2 | Net: 2 O_3 ? + 3 O_2 | Net: 2 O_3 ? + 3 O_2 |
|---------------------------------|---------------------------------|--------------------------------|
| | | |
| $HO_2 + O_3$? $OH + O_2$ (R11) | $NO_2 + O$? $NO + O_2$ (R14) | $ClO + O ? Cl + O_2 (R16)$ |
| $OH + O_3$? $HO_2 + O_2$ (R10) | $O_3 + h\nu + O_2 + O$ (R13) | $O_3 + h\nu + O_2 + O$ (R13) |
| | $NO + O_3$? $NO_2 + O_2$ (R12) | $Cl + O_3$? $ClO + O_2$ (R15) |

Other catalytic cycles also contribute, especially in polar regions where it is well established that chlorine derived from CFCs currently results in a seasonal "ozone hole" with typically more than half of the ozone column depleted over Antarctica each austral spring. Because the catalytic

species are regenerated in the cycles of reactions, part-per-billion levels of HO_x , NO_x and CIO_x can destroy ozone at three orders of magnitude higher concentration.

3.6 Estimates of asteroid impact and ozone depletion frequency

For our studies, we estimate the frequency of impacts similar to that done by Ward and Asphaug (2000) in their risk assessment for tsunamis. The cumulative impact rate is assumed to obey the power law

$$f_{impact} = aD^b \tag{E6}$$

where f_{impact} is the frequency of impacts of objects having a diameter greater than *D*, and *a* and *b* are fitting parameters. At the large end, the equation is fit to the estimate by Shoemaker et al. (1990) that a 1 km diameter or larger object strikes the Earth on average once every 100,000 years, and at the smaller end it is fit to the observation by Nemtchinov et al. (1997) that approximately 25 exploding meteors strike the Earth each year in the energy range 0.25-4 kt TNT (0.75 m < R < 1.19 m for V = 20 km/s and density of 3 g/cm³). Expressed as the period t_{impact} (i.e. average time between impacts having a diameter greater *D*), equation E6 may be rewritten as

$$t_{impact} = 1.0 \times 10^{-2} D^{7/3}$$
(E7)

where *D* is in units of meters. This expression predicts objects having diameters larger than 200, 350 and 500 m impact once every 2,300, 8,600 and 20,000 years, respectively. There is a large uncertainty in this estimate; for example, Toon et al. (1994) estimate that a 1-km object impacts only once every 300,000 years. For estimates of ozone depletion requiring impacts with the oceans (i.e. depletions resulting from injection of water vapor and sea salt into the upper atmosphere), the time between impacts is increased by a factor of 1.4 to account for the fact that oceans cover only 71% of Earth's surface.

Table 1 summarizes the calculated lower and upper limits for contributions to the stratospheric mixing ratios of chlorine, bromine, water vapor, and NO_y for impacts of meteoroids having diameters in the range 150-1,000 m. Also given is the mean time between ocean impacts. Mixing ratios are calculated for illustrative purposes assuming a constant mixing ratio for each species throughout the entire stratosphere containing 1.3×10^{43} molecules.

Estimates of the frequency of stratospheric ozone depletion resulting from asteroid and comet impacts are shown in Fig. 2. Here we assume that an approximate doubling of the natural level of water vapor (4 ppmv) or NO_y mixing ratio (10 ppbv) in the stratosphere will result in a major ozone depletion at mid latitudes. For NO_x this occurs about once every 16,000 to 38,000 years, where account has been taken of the fact that NO is produced in collisions with both land and ocean. Doubling of the natural water vapor mixing ratio in the stratosphere could occur as often as every 14,000-19,000 years. Similarly, an increase in the chlorine content of the stratosphere to 10 ppbv is predicted to occur about once every 15,000-22,000 years. Within error, the frequency of ozone depletion by any one of these effects is about the same. Any of these effects acting alone would be expected to have a large effect on stratospheric ozone; however, because of the complexity of the chemistry of the stratosphere, the effects are not additive, and detailed model calculations, such as those discussed below, are required to account for the various synergisms involved. Overall, we estimate that large stratospheric ozone depletions probably occur about once every 15,000-40,000 years as a result perturbations of stratospheric chemistry resulting from impacts of asteroids and comets.

Antarctic ozone holes may occur much more frequently. Assuming that the sea salt vaporized by ocean impacts becomes activated in the stratosphere to release chlorine and bromine, levels of \approx 3 ppbv of chlorine (and 2.9 pptv of bromine), which we now know is sufficient to cause an Antarctic ozone hole with loss of greater than 50% the ozone column in the austral spring, will occur with an average time between impacts of about 6,000-9,000 years.

3.7 Model of coupled chemistry and dynamics of the upper atmosphere

The Thermosphere-Ionosphere-Mesosphere-Electrodynamics General Circulation Model (TIME-GCM) was used to explore the effects on the upper atmosphere of nitric oxide and water vapor injected by an asteroid impact. This model has been described in detail by Roble and Ridley (1994) and Roble (2000). The model extends between 30 and 500 km altitude with a vertical resolution of four grid points per scale height and a horizontal resolution of 5° latitude and longitude. The model includes interactive chemistry and dynamics at each time step and is self-consistent, requiring only the specification of solar flux, auroral heat and momentum forcings from the solar wind parameters and dynamical and chemical forcings at the 30 km lower

boundary. The model is hydrostatic and thus cannot model the initial phase of the impact, but for an assumed initial distribution of constituents, it can calculate the transport of chemical constituents and their transformations as a function of time and determine the effects of those species on stratospheric ozone down to about 30 km. This model was chosen for our initial work because it allows us to evaluate the effects of the chemical inputs on atmospheric dynamics and chemistry immediately after the impact event. Results from this model can be used as inputs to more detailed models of the stratosphere to more accurately evaluate levels of ozone depletion. As discussed in the model results below, it is critical to determine what fraction of the NO produced in the impact event survives chemical reactions in the mesosphere and thermosphere that act to destroy NO.

3.8 Model results for injections of nitric oxide and water vapor

We have simulated the effects on the upper atmosphere for three different cases corresponding to impacts of $\approx 1,200$ m (large), ≈ 560 m (medium), and ≈ 260 m (small) diameter asteroids having impact energies of $\approx 87,000$, $\approx 8,700$ and ≈ 870 Mt, respectively. Based on the previous discussion, it is estimated that the largest impact injects 1.3×10^{39} molecules of H₂O and 1.3×10^{36} molecules of NO. The medium-sized impact injects 10% as much NO and H₂O, and the small impact injects 1% as much. For the large impact, this corresponds to about 100 ppbv of NO and 100 ppmv of H₂O if uniformly distributed over the globe and above the tropopause at constant mixing ratio. However, the injection was made within the boundaries of a single grid point and at constant mixing ratio at and above 70 km, well above the stratosphere. It was assumed that the impact occurred in the vicinity of the Yucatan Peninsula of Mexico on January 10 of a hypothetical year with present day chemical and dynamical structure. Goals of the simulation were to determine 1) how fast the H₂O and NO is redistributed, 2) how the injection affects the temperature structure and dynamics of the upper atmosphere, 3) what fractions of the NO and H₂O survive photochemical decomposition at such high altitudes and is transported downward to the stratosphere and 4) the combined effects of NO and H₂O on ozone in the upper stratosphere.

Figure 2 shows the horizontal and vertical distributions of NO_x ($NO_x = NO + NO_2$) and H_2O injection 10 days following the large impact. By this time the plume already has spread approximately 30° in latitude and 60° in longitude, and its lower boundary has descended nearly 10 km. This rapid dispersion continues over the next weeks to months, driven by the seasonal

winds and by the intense heating that results from absorption of solar radiation by NO, NO₂ and H₂O. Figure 3 shows the global average temperature changes that occur as a function of altitude during the first year following the impact for the high, medium and small impact cases. For the large case, increases in temperature by up to several hundred $^{\circ}$ C in the region 100-200 km destroys the mesosphere as a separate atmospheric layer, with temperature increasing rather than decreasing above what is normally the stratopause. Increased absorption of incoming radiation at higher altitudes causes the upper stratosphere to cool by as much as 40 $^{\circ}$ C for the large impact case. Heating of the lower thermosphere by several hundred degrees occurs in the medium case as well, with a globally averaged cooling in the stratosphere by as much as 10 $^{\circ}$ C. Temperature effects on the upper atmosphere are relatively minor for the small impact case, with a maximum heating near 110 km of 10-20 $^{\circ}$ C and cooling of the stratosphere by only about 5 $^{\circ}$ C.

Both water vapor and NO_x are rapidly transported downward to the stratosphere for all three impact cases. Figure 4 shows changes in the vertical distribution of these species during the first 50 days following large, medium small impacts; the results for NO_x and water vapor are extended to one year in Fig. 5. Large fractions of both water vapor and NO_x have descended below 50 km (height of the normal stratospause), with concentrations peaking in the stratosphere after only three months. Changes in ozone concentrations are shown in Fig. 6 for all three cases out to day 50, and ozone depletions for the large impact are simulated for the first full year following impact in Fig. 5. For the large impact case, injection of NO and H₂O causes large ozone depletions in the upper stratosphere that persist through the first year. Ozone depletions are summarized in Fig. 7 for the large, medium and small impact cases. By day 50 ozone depletion of the globally integrated ozone column (above 30 km) has been depleted by 58%, 9% and 1% for the large and medium impact cases. Local depletions within the hemisphere of impact are much larger. Stratospheric ozone levels are expected to recover over a period of 2-3 years as water vapor and NO_y are slowly removed to the troposphere.

Of particular interest is the degree to which NO is destroyed by the "cannibalistic" reactions of NO that occur in the mesosphere and above. This destruction of NO can reduce the effect on stratospheric ozone. Nitric oxide is destroyed by nitrogen atoms derived from the photolysis of NO:

$$NO + hv? N + O$$
(R17)

$$N + NO ? N_2 + O \tag{R18}$$

Net: 2 NO ? $N_2 + 2 O$

At high NO concentrations the rate-limiting step for this cycle of reactions is the photolysis of NO (reaction R17), which has a lifetime of only about 3 days. However, at high concentrations of NO in the upper atmosphere becomes optically thick in NO, so that the rate of NO destruction is limited by the solar flux, and, as a result, the lifetime of NO is greatly increased. Thus, we expect the fraction of NO that survives destruction in the mesosphere and thermosphere to increase with the impact size. For the high, medium, and low impact cases, we found that xx, xx and xx% of the injected NO is still present as NO_x at 50 days following the impact event.

In conclusion, we find that the medium case, corresponding to the impact of a \approx 560 m asteroid with the oceans, would result in a very significant ozone depletion that would have serious implications for the biosphere. These calculations do not take into account the additional ozone-destruction chemistry made possible by activation of chlorine and bromine in the sea salt vaporized and deposited at high altitudes, which could further reduce the size of asteroid required to produce a major ozone depletion. Despite the many uncertainties, it appears likely that the size threshold for asteroids producing a major ozone depletion that would seriously damage the global biosphere is in the range 500-600 m.

3.9 Possible test of the impact-induced ozone depletion hypothesis

Ice cores dating back to 200,000 B.P. contain pollen grains that may serve as tiny UV-B dosimeters. When exposed to UV-B radiation, adjacent pyrimidine bases of the pollen DNA photodimerize to produce thymine-thymine (T-T), cytosine-thymine (C-T) and cytosine-cytosine (C-C) photodimers (Setlow and Carrier 1966; Witkin 1969; Hall and Mount 1981). Thus, the degree of pyrimidine photodimer formation may serve as a proxy for UV-B radiation. Monoclonal antibodies have been developed against T-T dimers (Wani et al. 1987; Mori et al. 1991; Lee and Yeung 1992), and capillary electrophoresis has been used in conjunction with laser-induced fluorescence detection to analyze for molecules in single cells (50). Thus, the technology currently exists to test the hypothesis presented here that asteroid and comet impacts result in large ozone depletion every few tens of thousands of years on average.

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Figure and table legend

 Table 1 Impact-Induced Changes in Stratospheric Composition for Meteoroid and Comet Impacts with the Earth's Oceans

| Meteoroid | Comet | Ocean | Chlorine | Bromine | Water | NO |
|-------------|-------------|--------------|-----------|-----------|-----------|-----------|
| Diameter, m | Diameter, m | Impact | Ppbv | pptv | Ppmv | ppbv |
| | | Interval, yr | | | | |
| 150 | 200 | 1700 | 0.35-0.55 | 0.53-0.84 | 0.16-0.26 | 0.11-0.33 |
| 200 | 270 | 3300 | 0.84-1.3 | 1.3-2.0 | 0.40-0.64 | 0.27-0.81 |
| 250 | 340 | 5500 | 1.7-2.7 | 2.5-4.0 | 0.79-1.3 | 0.53-1.6 |
| 300 | 410 | 8500 | 2.9-4.6 | 4.4-7.0 | 1.4-2.2 | 0.93-2.8 |
| 350 | 480 | 12000 | 4.6-7.4 | 7.0-11.2 | 2.2-3.5 | 1.5-4.5 |
| 400 | 540 | 17000 | 6.9-11 | 11-17 | 3.1-4.9 | 2.2-6.7 |

| 450 | 610 | 22000 | 9.09-16 | 15-24 | 4.7-7.5 | 3.2-9.6 |
|------|------|--------|---------|---------|---------|---------|
| 500 | 680 | 28000 | 14-22 | 21-33 | 6.5-10 | 4.4-13 |
| 600 | 810 | 43000 | 24-38 | 36-57 | 11-18 | 7.6-23 |
| 700 | 950 | 61000 | 37-60 | 57-91 | 18-29 | 12-36 |
| 800 | 1090 | 84000 | 56-90 | 85-140 | 27-43 | 18-54 |
| 900 | 1220 | 110000 | 80-130 | 120-190 | 38-61 | 26-77 |
| 1000 | 1360 | 141000 | 110-180 | 170-270 | 52-84 | 35-106 |

^a As noted in the text, we assume that the same amount of NO is produced for ocean impacts as for land impacts. Therefore, for consideration of ozone depletion by NO production alone, multiply the impact interval by 0.71 to give

the mean time between impacts with either land or ocean



Fig. 1 Estimated upper and lower limits to frequencies of asteroid and comet impacts that result in large ozone depletions due to increases in the stratospheric mixing ratio of NO_y of 10 ppbv (upper), H₂O by 4 ppbv (center) and ClOx by 10 ppbv (lower). These estimates do not take into account any loss of NO to cannabalistic reactions in the mesosphere and above



Fig. 2 Horizontal and vertical distributions of H_2O (left) and NO_x (right) 10 days following the large simulated impact



Fig. 3 Globally averaged atmospheric temperature as a function of altitude and time following the simu lated large, medium and small impacts



Fig. 4 Simulated increases in water vapor (left) and NO_x (NOx = NO + NO₂, right) concentration as a function of altitude and time following the simulated large, medium and small impacts



Fig. 5 Model results for the globally averaged concentrations of water vapor (upper), NOx (middle) and ozone (lower) as a function of altitude and time for the first year following a large impact



Fig. 6 Changes in globally averaged ozone concentration as a function of altitude and time following the simulated large, medium and small impacts



Fig. 7 Calculated depletions of the globally integrated ozone column for the large (red), medium (green) and small (blue) impacts as a function of time following impact