

# Bolide impacts, acid rain, and biospheric traumas at the Cretaceous-Tertiary boundary

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Large projectiles impacting the Earth will cause severe shock heating and chemical reprocessing of the Earth's atmosphere. This occurs during atmospheric entry and, more importantly, as a result of the supersonic plume ejected on impact. In particular, very large amounts of nitric oxide would result from the impact of the putative Cretaceous-Tertiary bolide(s). We present models of the shock chemistry, the conversion of NO to NO<sub>2</sub> and thence to nitrous and nitric acids, and the global dispersion of the NO<sub>2</sub> and acids. Two plausible projectiles are considered: an ice-rich long-period comet and a much smaller rock-metal asteroid. The comet produces semi-global atmospheric NO<sub>2</sub> mixing ratios of 0.1% while the asteroid produces these high mixing ratios only in the immediate region of the impact. The comet produces concentrated nitrous and nitric acid rain with a pH ≈ 0–1.5 globally. The asteroid produces rain with a pH ≈ 0–1 near the impact and ≈ 4–5 globally. Immediate environmental effects of these nitrogen species include inhibition of photosynthesis due to extinction of solar radiation by NO<sub>2</sub>, foliage damage due to exposure to NO<sub>2</sub> and HNO<sub>3</sub>, toxicosis resulting from massive mobilization of soil trace metals, and respiratory damage due to exposure to NO<sub>2</sub>. The acid rain decreases the pH of the oceanic mixed layer affecting the stability of calcite with important implications for the survival of calcareous-shelled organisms and for exhalation of CO<sub>2</sub> from the mixed layer to the atmosphere. Longer-term environmental effects perhaps ≈ 1000 years in duration include a global warming due to the sudden CO<sub>2</sub> injection and the simultaneous extinction of the ocean micro-organisms which normally help remove CO<sub>2</sub> from the atmosphere-mixed layer system. Havens for survival include carbonate-buffered lakes and burrows. This acid rain theory therefore serves to explain the peculiar selectivity of the extinctions seen at the Cretaceous-Tertiary boundary. The first few years of acid rain will lead to massive weathering rates of continental soils characterized by large ratios of the relatively insoluble metals (e.g. Be<sup>2+</sup>, Al<sup>3+</sup>, Hg<sup>2+</sup>, Cu<sup>+</sup>, Fe<sup>2+</sup>, Fe<sup>3+</sup>, Ti<sup>3+</sup>, Pb<sup>2+</sup>, Cd<sup>2+</sup>, Mn<sup>2+</sup>, Sr<sup>2+</sup>) to the more soluble metals (Ca<sup>2+</sup>, Mg<sup>2+</sup>) which should have left a clear signal in the fossils of neritic organisms and in unperturbed neritic sediments near river deltas if such sediments still exist for the Cretaceous-Tertiary time frame.

## 1. Introduction

In 1980 Alvarez et al. [1] proposed that the very large Ir and Os enrichments seen in the thin clay-rich layer separating the Cretaceous and Tertiary carbonate-rich sediments were due to the impact of an ≈ 10 km diameter asteroid on the Earth 65 million years ago. They also proposed that the massive extinctions which occurred at the Cretaceous-Tertiary boundary resulted from the large amount of dust injected into the atmosphere which suppressed photosynthesis. Emiliani et al. [2] examined this hypothesis further and concluded that the impact was probably oceanic and that water injected into the atmosphere may have led to a global warming sufficient to traumatize the biosphere. The geological, paleontological, bio-

logical, chemical, and physical effects of impacts have been widely discussed and debated (see Silver and Shultz [3] and 48 papers therein).

The extinctions observed at the Cretaceous-Tertiary boundary indicate a curious selectivity [4,5]. Evidently siliceous pelagic organisms (e.g. diatoms, radiolarians), terrestrial higher plants, terrestrial mammals, and limnetic organisms (bony fishes, gastropods, amphibians) suffered far less extinctions than calcareous pelagic micro-organisms (e.g. coccoliths, foraminifers), nektonic marine organisms (e.g. calcareous ammonites and belemnites, bony fishes, plesiosaurs), neritic marine organisms (e.g. sponges, corals, gastropods, bivalve shellfish), and (perhaps) the great terrestrial reptiles.

Lewis et al. [6] proposed in 1982 that a com-

etary or asteroidal impact comparable to that which (putatively) terminated the Cretaceous era must have severely shock-heated the atmosphere producing large amounts of nitrogen oxides and (subsequently) acid rain over the globe. The amount of acid consequently added to the mixed layer of the ocean was sufficient in the comet case (but not in the asteroid case) to destroy all calcium-carbonate shelled organisms but not silicate-based organisms in the mixed layer thus explaining a major aspect of the selectivity in extinctions noted above.

Lewis et al. [6] assumed that massive comets break up upon entry at near-grazing angles leading to direct deposition of 10% of their total energy in the atmosphere. In retrospect, this is a dubious assumption. Even with an impact at  $75^\circ$  from the vertical a large long-period comet ( $10^{16}$  kg mass, 65 km/s velocity, 13 km radius) encounters only 0.2% of its mass of air on entry and takes only 6 seconds to traverse the atmosphere between the turbopause and the surface. For this comet to encounter 10% of its mass of air during entry it would need to drastically disintegrate (e.g. into  $(10/0.2)^3 = 125,000$  equal mass fragments) upon impacting the atmosphere. Assuming the sound speed in the cometary material is  $2 \times 10^3$  m/s even the weak shock of the comet occurring at the turbopause will not have penetrated to the center of the comet before it hits the surface so such disintegration is extremely unlikely.

In this paper we revisit the proposal addressed by Lewis et al. [6]. We will show that while the impacting projectiles themselves do not shock heat the atmosphere very extensively, the supersonic plume of water vapor and rock produced on impact does shock the atmosphere up to global scales and the shock is of sufficient intensity to produce abundant nitric oxide. We also address a number of subjects not addressed in the original Lewis et al. [6] report. The fraction of the atmosphere shock heated, the global circulation of the nitrogen oxides, the effects of the ejecta plume water on the acid rain predictions, the effects of the acid rain on continental soils, the relationship between acid rain production rates and the total amount of acid needed to acidify the surface oceans, and finally the longevity of the oceanic acidity event and the exhaled  $\text{CO}_2$  event and their implications for the environment in the first millenia or so after the impact are specifically discussed.

## 2. Shock production of nitric oxide

Nitric oxide yields  $Y$  in shock-heated air have been extensively investigated both theoretically and experimentally due to the importance of thermonuclear explosions, meteors, and lightning in producing nitrogen oxides in the present-day atmosphere. The reactions producing and removing NO in the shock-heated air are summarized in Table 1. As the shock-heated air cools, the NO mixing ratios decrease until we reach the quench temperature where the time constant for NO removal exceeds the time constant for cooling. For thermonuclear explosions  $Y \approx (0.4-5) \times 10^{16}$  molecule/J [7-9], for the Tunguska meteor  $Y \approx 15 \times 10^{16}$  molecule/J [10], and for lightning  $Y \approx (2-30) \times 10^{16}$  molecule/J [11]. The quench temperature ranges from  $\approx 2000$  K in thermonuclear explosions to  $\approx 2700$  K in lightning [7-10].

The total NO production ( $P$ ) from the bolide is estimated from

$$P = [\epsilon_1 Y_1 + (1 - \epsilon_1) \epsilon_2 Y_2] \frac{1}{2} m v^2 \quad (1)$$

where  $\epsilon_1$  is the fraction of the incoming bolide kinetic energy deposited during entry into the atmosphere and  $Y_1$  is the corresponding NO yield,  $\epsilon_2$  is the fraction of the bolide kinetic energy at surface impact which is returned to the atmosphere as kinetic energy in the high-velocity ejecta plume and  $Y_2$  is the corresponding NO yield,  $m$  is the bolide mass, and  $v$  the bolide speed. We will consider two plausible but somewhat extreme identities for the bolide: an ice-rich new long-period comet with  $m = 1.25 \times 10^{16}$  kg, radius  $r = 14 \times 10^3$  m,  $v = 65 \times 10^3$  m/s, and impact angle  $\phi = 75^\circ$ ; and, a rock-metal (e.g. chondritic or stony-iron) asteroid with  $m = 5 \times 10^{14}$  kg,  $r = 3 \times 10^3$  m,  $v = 20 \times 10^3$  m/s, and  $\phi = 45^\circ$ . Using the formulae which we will present here the reader may scale our results to other masses, impact velocities, and impact angles as desired. Since the majority of the comet mass is C-, N-, and O-bearing ices, both bolides would contain approximately the amounts of Ir, Os, etc., needed to explain the Cretaceous-Tertiary boundary-layer enrichments [1].

To a first approximation the total energy deposited during entry into the atmosphere can be equated to the energy required to accelerate (laterally) the intercepted mass of air to the incoming

TABLE 1

Reactions which produce and remove NO in shock-heated air

Reaction	Role
$O_2 \rightarrow O + O$	NO source in shock
$O + N_2 \rightarrow NO + N$	NO source in shock
$N + O_2 \rightarrow NO + O$	NO source in shock
$NO \rightarrow N + O$	NO sink in shock
$NO + N \rightarrow N_2 + O$	NO sink in shock
$NO + O \rightarrow N + O_2$	NO sink in shock
$NO + NO \rightarrow N_2O + O$	NO sink in shock
$NO + NO + O_2 \rightarrow 2NO_2$	oxidation of shock-produced NO
$NO_2 + NO_2 + M \rightleftharpoons N_2O_4 + M$	gas-phase $NO_x$ chemistry
$NO + NO_2 + O_2 \rightleftharpoons NO_2 + NO_3$	gas-phase $NO_x$ chemistry
$NO_2 + NO_3 + M \rightleftharpoons N_2O_5 + M$	gas-phase $NO_x$ chemistry
$NO + NO_3 \rightarrow 2NO_2$	gas-phase $NO_x$ chemistry
$2NO_2 + H_2O(l) \rightarrow HNO_3(aq) + HNO_2(aq)$	nitric and nitrous acid formation
$NO_2 + NO_3 + H_2O(l) \rightarrow 2HNO_3(aq)$	nitric and nitrous acid formation
$N_2O_4 + H_2O(l) \rightarrow HNO_3(aq) + HNO_2(aq)$	nitric and nitrous acid formation
$N_2O_5 + H_2O(l) \rightarrow 2HNO_3(aq)$	nitric and nitrous acid formation
$3HNO_2(aq) \rightarrow HNO_3(aq) + H_2O(l) + 2NO$	nitric and nitrous acid formation

bolide velocity since deceleration of the bolide by the intercepted air is negligible. Thus if  $P_s$  is surface pressure and  $g$  the gravitational acceleration then:

$$\epsilon_1 \approx \frac{\pi r^2 P_s}{mg \cos \phi} \quad (2)$$

yielding  $\epsilon_1 = 0.002$  (comet) and 0.0008 (asteroid) respectively. The initial average energy per unit mass ( $0.5 v^2$ ) added to the air impacting the bolide is  $2 \times 10^9$  J/kg (comet) and  $2 \times 10^8$  J/kg (asteroid). Using the Hugoniot shock relation in an ideal polytropic gas (see Courant and Friedrichs [11]) the temperature  $T_s$  of the shocked air is related to that of the pre-shocked air  $T_0$  by:

$$T_s = T_0 \left[ \mu^2 (M_s^2 - 1) + M_s^2 \right] \times \left[ \mu^2 (M_s^2 - 1) + 1 \right] / M_s^2 \quad (3)$$

where  $M_s$  is the Mach number of the shock front (relative to pre-shocked air),  $\mu^2 = (C_p - C_v)/(C_p + C_v) \approx 0.17$  for air,  $T_0$  is the pre-shock air temperature (about 263 K at the average atmospheric pressure of 500 mbar in the present-day atmosphere), and  $C_p$  and  $C_v$  are the heat capacities of air at constant pressure and constant volume respectively. The (probably detached) shock front will move at a Mach number somewhat greater than that of the bolide ( $v/c$ ). To a sufficient

approximation we will take  $M_s$  as simply equal to the bolide Mach number (62 for the asteroid and 200 for the comet). Thus  $T_s = 2 \times 10^6$  K for the comet and  $2 \times 10^5$  K for the asteroid. For a real gas in such strong shocks the shock temperatures will be a factor of a few to several times less than these ideal values but there is no doubt that the shock heating in both cases will be extremely intense. The heating should be analogous to that for the Tunguska meteor and for lightning and based on the yields discussed earlier we will assume therefore that  $Y_1 = 10 \times 10^{16}$  molecule/J.

The lack of evidence for a continental crater of the appropriate size and age favors an oceanic impact. Various investigators [2,12] have addressed the complex task of determining the energy added to the atmosphere by the high velocity steam and rock (solid, liquid, vapor) ejected by an oceanic impact. Emiliani et al. [2] consider a bolide with  $m = 2.5 \times 10^{15}$  kg,  $r = 7 \times 10^3$  m,  $v = 20 \times 10^3$  m/s, and  $\phi = 45^\circ$  (our bolides have kinetic energies 53 times greater and five times less than this). The plume mass is  $\approx 1.1 \times 10^{17}$  kg with 16% being steam and 84% being rock. The plume energy per unit mass including initial internal energy (sensible plus latent heat) is  $\approx 2.8 \times 10^6$  J/kg with 45% being kinetic energy and 55% being internal energy. The average speed of the plume material is  $\approx 1600$  m/s producing shock fronts

with Mach numbers  $\approx 5$  with respect to pre-shocked air. Both the plume energy and the plume mass are proportional approximately to the total kinetic energy of the incoming bolide [2]. Thus the energy density and speed of the plume for our comet and asteroid are expected to be similar to the values for the Emiliani et al. [2] bolide.

Using equation (3) with  $M_s = 5$  and  $T_0 = 263$  K gives an initial temperature  $T_s(1)$  for ideal shocked air of 1554 K. At this low Mach number deviation of real air from ideal behaviour will be small. However, the plume material has a wide range of Mach numbers about the average [12]. The outer part of the expanding plume has  $M_s \gg 5$  producing shock temperatures  $\gg 1554$  K. Also, the later-arriving inner plume material can cause the already-shocked air to be shocked again. For  $n$  shocks with  $M_s = 5$  in rapid succession the shock temperature  $T_s(n)$  will be  $T_0(T_s(1)/T_0)^n$  yielding  $T_s(2) = 9182$  K,  $T_s(3) = 54,255$  K, and so on. Not long after being shocked one or more times the air will be mixed with the hot particles and steam in the plume. The above plume internal energy density corresponds to an initial plume temperature of only 1000 K if we take into account the fact that the latent heat in the steam is not available until water condensation occurs at low temperatures unimportant for NO production. In addition, because the initial gas pressure in the plume is extremely high (14 kbar for the Emiliani et al. [2] bolide), the potential temperature of the  $H_2O$  in the plume is much lower than 1000 K, so by the time the  $H_2O$  in the plume has expanded to displace an equi-molar volume of air (a process which takes about 7 minutes for the asteroid plume and about 2 hours for the comet plume) it will have an actual temperature probably not much different than the normal pre-impact air temperatures. Thus mixing of the plume rock (at 1000 K) and the plume  $H_2O$  (at  $< 1000$  K) with the  $\gg 1554$  K shocked air will cool the air rather than heat it (this acceleration in cooling rates should however improve NO yields). Of course, the expanding plume  $H_2O$  will do work on the air but this work cannot exceed the initial internal energy content of the  $H_2O$  which is  $0.16 \times 0.55 \times 2.8 \times 10^6 = 2.5 \times 10^5$  J/kg. Transferring this energy totally to air isobarically at 1554 K would yield a temperature rise of only  $2.5 \times 10^5 / C_p = 200$  K.

From the above discussion it is apparent that

shock heating of the air by the plume produces maximum temperatures  $> 2000$  K but less than those produced by the incoming bolide itself. The temperatures achieved in the air shocked by the plume are similar to those in thermonuclear explosions. For this reason we will assume that the plume NO yield  $Y_2$  is  $2 \times 10^{16}$  molecule/J (a typical value in nuclear explosions) which is significantly less than  $Y_1$ . Note that other than assuming this similarity in  $Y$  values, we claim no analogy between the nuclear and bolide-plume events.

The total energy imparted to the atmosphere by the plume is much greater than that imparted by the bolide; that is  $\epsilon_2 \gg \epsilon_1$  [12]. Emiliani et al. [2] estimate that about 0.25 of the incoming bolide energy appears as kinetic energy in the plume. This provides an upper limit to  $\epsilon_2$  since not all of this kinetic energy is imparted to the air ( $N_2$  plus  $O_2$ ). Some is returned to the surface as high velocity condensed material and some of the condensed material causes heating of the plume vapor rather than the air. For the solid part of the plume, those fragments large enough that they encounter much less than their own mass of gas (air or plume water) while airborne will have roughly drag-free ballistic trajectories and will return much of their kinetic energy to the surface. Since the plume velocity  $V_p$  is on the average much less than the planetary escape velocity (about 11.2 km/s) the ballistic fragments will have a horizontal range  $R_h \approx V_p^2 \sin^2 \theta / g \leq 261$  km and a vertical range  $R_v \approx V_p^2 \sin^2 \theta / 2g \leq 131$  km where  $\theta$  is the elevation angle of fragment ejection. For an average  $\theta = 45^\circ$  the mass of gas encountered is roughly  $4.5\pi a^2 P_s / g$  where  $a$  is the radius of the fragment. Thus for a rock density of  $3.5$  g/cm<sup>3</sup> a fragment with  $a = 10$  m will barely encounter its own mass of air. Fragments with  $a > 10$  m will travel no further than 261 km and return most of their kinetic energy to the surface.

Smaller plume fragments will experience significant drag as they fall relative to the supersonic plume vapor flow and thus travel horizontally further. For a horizontal velocity  $= V_p \cos \theta$  and average sedimentation velocity  $w$  the particle will traverse after apogee a horizontal distance  $= V_p \cos \theta R_v / w = 1460$  km for  $\theta = 45^\circ$  and  $w = 50$  m/s (this  $w$  is appropriate for a dust particle with  $a = 0.33$  mm). Thus the smaller plume fragments

(i.e. the dust) are expected to travel significant distances and give up most of their kinetic energy to the air and plume vapor.

The supersonic plume water vapor itself will expand hydrodynamically until it displaces roughly its own mass of air (which happens some 6600 km (comet) and 420 km (asteroid) from the impact point). In doing so it will deliver essentially all of its kinetic energy to the air.

The fraction of the plume mass in fragments with  $a > 10$  m is expected to be  $\ll 0.5$  [12]. The fraction of the kinetic energy in fragments with  $a < 10$  m which is imparted to plume water vapor rather than the air is also expected to be  $< 0.5$ . We will assume here that only 50% of the kinetic energy in the plume as estimated by Emiliani et al. [2] is imparted to the air with the remainder imparted either to the plume vapor or returned to the surface; that is  $\epsilon_2 = 0.5 \times 0.25 = 0.125$ . This may appear overly conservative based on the above discussion but the Emiliani et al. [2] estimate itself was considered by those authors as an upper bound. We also note that O'Keefe and Ahrens [12] deduce a similar  $\epsilon_2$  value to ours using an independent approach.

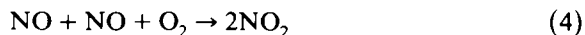
From equation (1) the total NO production  $P$  from shock heating of the air by the incoming bolide plus the ejecta plume is therefore  $7 \times 10^{40}$  molecules for the comet and  $3 \times 10^{38}$  molecules for the asteroid. For both bolides the ejecta plume shockwave is the dominant producer of NO. For the record, for our comet to produce  $7 \times 10^{40}$  NO molecules due to the bolide entry shock alone, it would need to furcate into about 2550 equal mass fragments each of which would give up  $\approx 2.6\%$  of its kinetic energy to the atmosphere. We note parenthetically that the NO resulting from both the bolide shock and the plume shock is produced largely in the dense lower atmosphere. We reject the unsubstantiated assertion by Kasting and Ackerman [13] that the NO is produced primarily in the upper atmosphere for the Cretaceous-Tertiary bolide.

At the instant of impact the ocean water which provides the H<sub>2</sub>O in the plume is also shock heated but the amounts of H<sub>2</sub> and O<sub>2</sub> produced are negligible. It is important to note that the H<sub>2</sub>O in the plume and the air in the atmosphere are shocked in separate events. Thus the H<sub>2</sub>O concentrations in the pre-shock air are those ap-

propriate to normal atmospheric conditions (H<sub>2</sub>O mixing ratios  $<$  few percent) and not to the H<sub>2</sub>O-rich air produced after the shocked plume H<sub>2</sub>O and the shocked air are mixed.

### 3. Atmospheric chemistry and circulation

The reaction sequence in the initial shock-heated NO-rich region can be summarized as follows. The ozone layer disappears due to reaction of O<sub>3</sub> with NO [6,14]. The bulk of the tropospheric NO is converted to NO<sub>2</sub> on a time scale of minutes to hours [6] by the reaction:



This thermochemical reaction essentially is irreversible since the rapid ultraviolet photodissociation of NO<sub>2</sub> which occurs in the present-day troposphere is precluded through ultraviolet shielding by the overlying high altitude NO<sub>2</sub>. Other relevant gas-phase reactions are summarized in Table 1.

For present tropospheric NO<sub>x</sub> (NO plus NO<sub>2</sub> plus NO<sub>3</sub> plus twice N<sub>2</sub>O<sub>4</sub> plus twice N<sub>2</sub>O<sub>5</sub>) mixing ratios ( $\approx 3 \times 10^{-11}$ ), removal is dominated by reaction of NO<sub>2</sub> with OH forming HNO<sub>3</sub> which rains out on a time scale of about a week [15]. This mechanism is not operative in the impact-perturbed atmosphere because the high NO<sub>2</sub> opacity prevents penetration of the ultraviolet light required for OH formation. Instead (as outlined in Table 1) NO<sub>2</sub>, NO<sub>3</sub>, N<sub>2</sub>O<sub>4</sub>, and N<sub>2</sub>O<sub>5</sub> dissolve directly in cloud and surface water forming nitrous and nitric acids [6,16]. Removal of nitrogen oxides from the atmosphere by these reactions at high nitrogen oxide levels has been considered by Kasting and Ackerman [13]. For NO<sub>x</sub> mixing ratios of  $10^{-6}$  they compute NO<sub>x</sub> lifetimes  $t_{\text{chem}}$  of 1.6–45 months (the range represents uncertainties in the calculations). At higher NO<sub>x</sub> mixing ratios the lifetimes are likely to be shorter than these due to the second order dependence of the rates of several reactions in Table 1 on NO<sub>x</sub>. Simple vertical transport considerations however preclude average lifetimes for tropospheric NO<sub>x</sub> less than about 1 month. In this paper we will not attempt to define  $t_{\text{chem}}$  precisely but instead illustrate the results obtained assuming a wide range of plausible  $t_{\text{chem}}$  values (specifically 1, 3, 6, 12, 24 and 48 months). In all cases nitrous and nitric acid are

the immediate products of  $\text{NO}_x$  removal.

The local downward flux of nitrous and nitric acids  $\phi_A$  is determined from the local areal rate of chemical removal of  $\text{NO}_x$  by:

$$\begin{aligned}\phi_A &= -\frac{d}{dt} \left( \int [\text{NO}_x] dz \right) \\ &= \int ([\text{NO}_x]/t_{\text{chem}}) dz\end{aligned}\quad (5)$$

We must distinguish between two rainout events: immediate rainout of the water in the ejecta plume and subsequent rainfall associated with the usual hydrologic cycle. In the usual hydrologic cycle the rainfall flux is constrained strongly by the solar energy input flux and is unlikely to differ much from its present-day value. The concentration  $C$  of the acid after the plume water has rained out is therefore computed assuming the rainfall flux  $\phi_R$  is the same as its global average value today (namely 0.099 liter/cm<sup>2</sup> y). Thus  $C = \phi_A/\phi_R$ .

The water in the ejecta plume as it is mixed with the shocked air will however enhance considerably the initial removal rates of  $\text{NO}_x$  (and dust) in comparison to their values after the plume rainout. Following Emiliani et al. [2], we estimate the mass of water in our comet-produced plume to be about  $9.3 \times 10^{17}$  kg ( $3 \times 10^{43}$  molecules) and in our asteroid-produced plume to be about  $3.5 \times 10^{15}$  kg ( $1.2 \times 10^{41}$  molecules). Essentially all of this water will condense out by the time the plume has expanded to ambient pressures and temperatures (263 K, 500 mbar on average). The atmosphere contains  $1.1 \times 10^{44}$  molecules so the equivalent volume fraction of the global atmosphere occupied by the plume water at this ambient stage is roughly  $3 \times 10^{43}/1.1 \times 10^{44} = 0.27$  (comet) and  $1.2 \times 10^{41}/1.1 \times 10^{44} = 0.001$  (asteroid). The actual fractions filled with plume water will be somewhat larger than these due to mixing of the plume with the shocked air. Since the shock-heated air is warmer than the plume water, this mixing process when it occurs will tend to suppress further water condensation.

Using the total  $\text{NO}_x$  yields discussed in section 2 and an initial shock-produced  $\text{NO}_x$  mixing ratio of  $10^{-2}$  (conversant with a quench temperature of 2000 K appropriate for thermonuclear explosions), the fractions  $F$  of the global atmospheric mass  $M$

( $5.2 \times 10^{18}$  kg) contained in the chemically-relevant strongly shocked region are  $100 \times 7 \times 10^{40}/1.1 \times 10^{44} = 0.064$  (comet) and  $100 \times 3 \times 10^{38}/1.1 \times 10^{44} = 0.00027$  (asteroid). These  $F$  values are easily conversant with upper limits set by the need to accelerate shocked air from rest to at least sound speed  $c$  (325 m/s at 263 K), namely:

$$F < \epsilon_2 \frac{mv^2}{Mc^2}\quad (6)$$

yielding  $F < 12$  (icy comet) and  $F < 0.05$  (stony-iron asteroid). They are also conversant with upper limits set by the need to heat shocked air from  $T_0$  to at least 2000 K, namely:

$$F < \frac{\epsilon_2 \frac{1}{2} mv^2}{MC_c(2000 - T_0)}\quad (7)$$

yielding  $F < 0.38$  (comet) and  $F < 0.0016$  (asteroid).

The strongly shocked air comprising 0.027–6.4% of the global atmosphere will be very rapidly mixed with less strongly shocked air and with some of the plume water vapor due to turbulence associated with the impact itself. We will conveniently define the end of this mixing process as occurring when the strongly shocked air has been diluted into a ten times greater molar amount of air in which  $\text{NO}_x$  then has a mixing ratio of  $10^{-3}$ . At this latter mixing ratio, simple physical dissolution of  $\text{NO}_2$  under average atmospheric conditions (263 K, 500 mbar) would (by Henry's law [16]) give about  $10^{37}$  molecules  $\text{NO}_x$  (comet) and  $4 \times 10^{34}$  molecules  $\text{NO}_x$  (asteroid) dissolved in and thus removed by plume water. These values correspond to only 0.015% (comet) and 0.013% (asteroid) of the total impact-produced  $\text{NO}_x$ . These are lower limits since  $\text{NO}_x$  reacts with water by reactions shown in Table 1. If the plume water mixes with and totally removes by these reactions the  $\text{NO}_x$  from an equi-molar amount of air containing 1 part in  $10^3$  of  $\text{NO}_x$  this would consume  $3 \times 10^{40}$  molecules  $\text{NO}_x$  (comet) and  $1.2 \times 10^{38}$  molecules  $\text{NO}_x$  (asteroid). These values correspond to about 40% of the total impact-produced  $\text{NO}_x$  for both bolides and should be regarded as upper limits. Note also that some neutralization of the  $\text{HNO}_3$  by sedimentary carbonates in the plume particles is possible but the effect is probably small. The rock (mainly basaltic but some sedimentary) in our comet-derived plume corresponds

to a hemispherical excavation of radius about 87 km. The oceanic sediment column contains about  $1.4 \times 10^5$  g/cm<sup>2</sup> of CaCO<sub>3</sub> so the plume will contain about  $3.3 \times 10^{16}$  kg ( $6.6 \times 10^{17}$  equivalents) of CaCO<sub>3</sub>. However, O'Keefe and Ahrens [12] estimate that 99% of the plume particulate mass is contained in particles with diameters > 0.1 mm and since the atmospheric residence time of these large particles is only a few minutes to hours they will fall back in the impact region without reacting and be re-mixed into the turbulent post-impact ocean. If we assume that all of the CaCO<sub>3</sub> in the remaining 1% is completely reacted it would neutralize only 5.5% of the  $1.2 \times 10^{17}$  equivalents of HNO<sub>3</sub> produced in the comet case (a similar result applies in the asteroid case).

Based on the above discussion we assume that in a matter of days after the impact the NO<sub>x</sub> in the shocked air is diluted by a factor of 10 by mixing and 20% of the total NO<sub>x</sub> produced is removed as nitrous and nitric acid by the plume rainout and neutralization processes. Thus the post-impact initial states will consist of either 64% of the atmosphere with a NO<sub>x</sub> mixing ratio  $\chi(0)$  of  $0.8 \times 10^{-3}$  (comet) or 0.27% of the atmosphere with a NO<sub>x</sub> mixing ratio  $\chi(0)$  of  $0.8 \times 10^{-3}$  (asteroid). The shocked air will be distinctly reddish-brown in color at these mixing ratios.

A detailed three-dimensional model for the global dispersion of these initial shock-produced NO<sub>x</sub> "clouds" is complicated by the fact that the global circulation itself is expected to be perturbed both by the immediate shock heating and by the longer-term changes in the radiation budget caused by impact-produced dust [17], soot [18], and NO<sub>2</sub> [6,13]. However, we require here only an approximate simulation of the effects of dilution of the NO<sub>x</sub> cloud to global scales and for this purpose such a detailed model is not necessary. We have specifically assumed a roughly pancake-shaped NO<sub>x</sub> cloud centered at the impact point and occupying a fraction  $F(0)$  of the global atmosphere which is vertically and horizontally well-mixed by the turbulence associated with the impact itself. This cloud then disperses horizontally with its two horizontal Gaussian widths both being proportional to  $t^{1/2}$  where  $t$  is time after the NO<sub>x</sub> cloud formation. This model, which is conversant with Prandtl mixing length theory [19] is equivalent simply to assuming that the mass fraction of

the global atmosphere occupied by the cloud equals  $F(0) + [1 - F(0)] t/t_{\text{mix}}$  where  $t_{\text{mix}}$  is the time for global-scale dispersion. This is clearly a qualitative model but it is sufficient for our purposes.

With the above model the average NO<sub>x</sub> mixing ratio  $\chi(t)$  in the cloud for  $t < t_{\text{mix}}$  is given by

$$\chi(t) = \frac{\chi(0) \exp[-t/t_{\text{chem}}] F(0)}{F(0) + [1 - F(0)] t/t_{\text{mix}}} \quad (8)$$

If  $t_{\text{mix}}^*$  is the global mixing time for an initially very small cloud (i.e.  $F(0) \ll 1$ ) then  $t_{\text{mix}} \approx [1 - F(0)] t_{\text{mix}}^*$ . From a three-dimensional general circulation model study of the observed global dispersion of chlorofluoromethanes [20],  $t_{\text{mix}}^* \approx 2$  years in the present atmosphere. Thus  $t_{\text{mix}}$  is about 9 months (comet) and 24 months (asteroid) if present-day mixing rates are applicable (in the post-impact-perturbed atmosphere  $t_{\text{mix}}$  could conceivably be double or half these values).

In Figs. 1 and 2 we summarize for the comet and asteroid cases our calculations of the NO<sub>x</sub> mixing ratio  $\chi(t)$  using (8) and the concentration

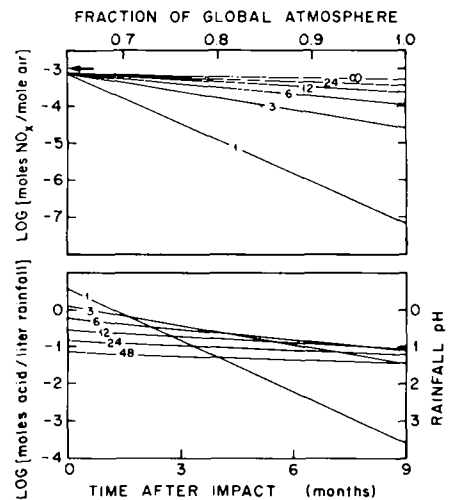


Fig. 1. NO<sub>x</sub> mixing ratios (upper graph) and concentrations of nitric plus nitrous acid in rainfall (lower graph) as a function of time after the ice-rich comet impact for assumed NO<sub>x</sub> lifetimes  $t_{\text{chem}} = 1, 3, 6, 12, 24, 48, \infty$  months. The curves for  $t_{\text{chem}} = 6$  months are considered most appropriate for the range of NO<sub>x</sub> levels shown. The arrow denotes the NO<sub>x</sub> mixing ratio prior to removal of 20% of the NO<sub>x</sub> by rainout of plume water. Over the 9 month time period shown the NO<sub>x</sub> cloud and acid rain expands from 64% to 100% of the global atmosphere. The rainfall pH scale assumes the acids are fully ionized.

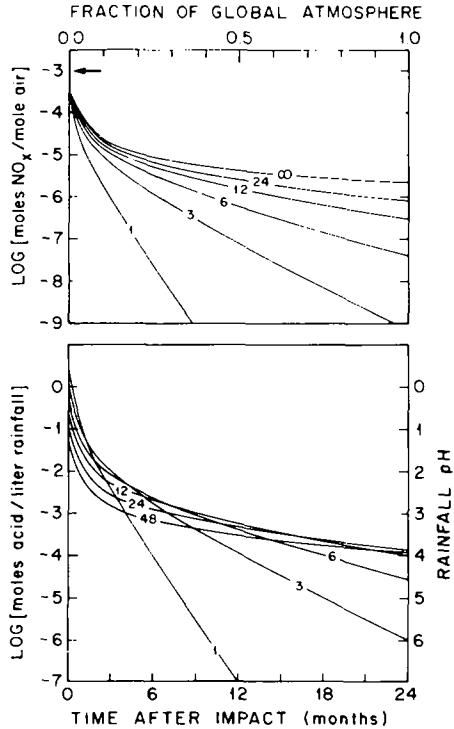


Fig. 2. As in Fig. 1 but for the stony-iron asteroid impact. The  $\text{NO}_x$  cloud and acid rain initially occupies  $\ll 1\%$  of the atmosphere and spreads to global scale in 24 months. The curves for  $t_{\text{chem}} = 12$  months are considered most appropriate for the range of  $\text{NO}_x$  levels shown.

of nitrous plus nitric acid in rainwater  $C(t)$  using:

$$C(t) = \frac{\chi(t) P_s}{t_{\text{chem}} \bar{m} g \phi_R} \quad (9)$$

which is derived from equation (5) assuming  $\text{NO}_x$  is vertically well mixed (in (9)  $\bar{m}$  is the average molecular weight of air molecules). The above figures illustrate the results only up to the time the  $\text{NO}_x$  cloud disperses to global scale. After this time the  $\text{NO}_x$  levels will decrease with an e-folding time equal to  $t_{\text{chem}}$ .

It is immediately clear from Figs. 1 and 2 that the atmosphere is severely perturbed chemically by the impacts. The comet produces atmospheric  $\text{NO}_x$  mixing ratios of  $10^{-4}$  to  $10^{-3}$  and concentrated nitrous and nitric acid rain with  $\text{pH} \approx 0-1.5$ ; these effects are semi-global immediately and global after 9 months. The asteroid produces  $\text{NO}_x$  mixing ratios of  $10^{-3}$  and acid rain with  $\text{pH} \approx 0-1$  at the point of impact. As the asteroid-produced  $\text{NO}_x$  cloud disperses globally and rains out

the  $\text{NO}_x$  mixing ratios decrease to  $\approx 10^{-7}-10^{-6}$  and the rain  $\text{pH}$  increases to  $\approx 4-5$ . For comparison, present-day stratospheric  $\text{NO}_x$  levels are  $\leq 10^{-8}$  [15] and present-day tropospheric  $\text{NO}_x$  levels are  $\leq 10^{-10}$  [8]. Present-day  $\text{pH}$  levels range from 3.5 to 6.5. Present-day levels of atmospheric  $\text{CO}_2$  in equilibrium with cloud droplets lead to  $\text{pH}$  levels in rainwater of about 5.7 [21].

The predicted very high initial atmospheric  $\text{NO}_x$  levels will significantly decrease solar heating of the surface and troposphere leading to a cooling of the lower atmosphere and heating of the upper atmosphere [6,13]. As  $\text{NO}_x$  mixing ratios fall to values  $\approx 10^{-8}-10^{-6}$  sunlight again penetrates to the surface and a warming of the lower atmosphere begins due to the greenhouse effects of  $\text{NO}_2$  [13]. These successive surface cooling and warming events will however be short-lived. For the comet case, global  $\text{NO}_2$  mixing ratios fall below  $10^{-8}$  within 3 years after impact if  $t_{\text{chem}} \approx 3$  months. For the asteroid case the same mixing ratio is reached within the first year if  $t_{\text{chem}} \leq 6$  months.

The severe depletion of the ozone layer caused by the  $\text{NO}_x$  will not be reversed until  $\text{NO}_x$  mixing ratios decrease below  $10^{-8}$ . However when  $\text{NO}_2$  mixing ratios exceed  $10^{-5}$  the  $\text{NO}_2$  itself provides an effective ultraviolet screen [6,13] so biologically-detrimental radiation at wavelengths  $< 300$  nm will penetrate to the surface only during the 1-2 year period when  $\text{NO}_x$  mixing ratios range from  $10^{-5}$  down to  $10^{-8}$ .

#### 4. Continental flora, fauna, soil, and water

The predicted  $\text{NO}_x$  levels will have serious effects on continental flora and fauna. For  $\text{NO}_2$  mixing ratios exceeding  $10^{-4}$  (which occur globally for the comet and at the impact site only for the asteroid), daylight levels are extremely low and photosynthesis essentially ceases [6]. The same  $\text{NO}_x$  mixing ratios combined with the predicted acid rain lead to defoliation of plants and to asphyxiation of lung-respiring animals. The dual effect of defoliation and cessation of photosynthesis will severely deplete the food supply for vegetarians; one would expect the largest animals to be affected the greatest. Only for the comet case are the effects global and therefore potential causal agents for extinction of species.

As noted earlier the high  $\text{NO}_x$  and low pH rain events last only a few years. Probably most of the continental flora survived these events in dormant or seed stages. Aquatic flora and fauna on the continents are also likely to survive these early traumas since some of the lakes will have sufficient carbonate rocks to buffer the acid rain and remove the dissolved  $\text{NO}_x$ . Faunal species hibernating in burrows and animals laying eggs in burrows are also likely to have survived the  $\text{NO}_x$  asphyxiation and acid rain. Clearly, the faunal species most likely to be extinguished are terrestrial vegetarians needing large food supplies, lacking the ability to hibernate for long periods, and laying eggs exposed to the elements. The transient surface cooling and heating and transient removal of the atmosphere's ultraviolet screen noted earlier will add further to the stress imposed on these terrestrial fauna.

The nitrous/nitric acid rain will weather severely the continental surface. In particular, when the concentrated acid rain first falls on the soil it will dissolve and mobilize normally insoluble and strongly bound metal ions. Detailed modelling of the resulting solubility equilibria, transport processes, and precipitation equilibria is difficult because of the wide range of soil compositions and because of unknown or unreliable data on solubility products, stability constants, activity coefficients, and dissolution kinetics. However, consideration of simple equilibria demonstrates that the weathering products will differ very significantly from those seen today (see, e.g., Stumm and Morgan [21]). Fig. 3 illustrates the calculated solubilities of several metal oxides in aqueous solution as a function of pH. These calculations, which were done by standard methods [21–23], also consider complex ion formation in aqueous solution. Thermodynamic data for these calculations and for additional solubility calculations summarized in Table 2 were taken from several sources [21–29].

Fig. 3 shows that Al, Fe, and trace metals, including some highly toxic elements such as Be, Hg, and Tl, will be mobilized by the concentrated acid rain. Furthermore, as the representative calculations for BeO suggest, even trace metals present in solid solution in more abundant phases will be mobilized at the predicted low pH levels. Table 2 shows that qualitatively similar effects are

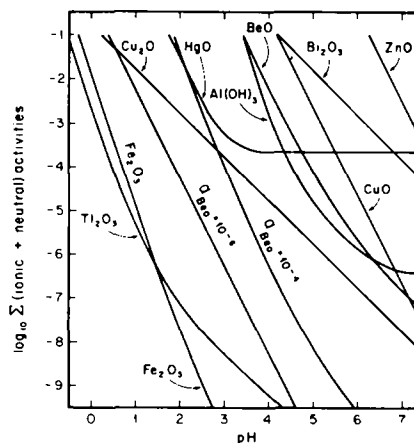


Fig. 3. The calculated solubilities in water of several pure oxides of Al, Fe, and trace metals found in continental soils as a function of pH. Curves are extended to activity values of  $10^{-1}$  to illustrate trends. Results for BeO at less than unit activity are also shown. Additional results for other oxides are given by Pourbaix [22].

predicted for metals present in carbonates and sulfides.

The results given in Fig. 3 and Table 2 and extensive literature calculations of mineral solubilities as a function of pH and redox potential [21–23] predict that many metal ions including  $\text{Hg}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Be}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cu}^+$ ,  $\text{Bi}^{3+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Sr}^{2+}$ , and  $\text{Tl}^{3+}$  will enter the highly acidic surface water streamlets with ratios to the most soluble metal ions (e.g.  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) far in excess of those seen in surface waters today. As these metal- and nitrate-rich surface run-off waters enter streams, lakes, and rivers the various organic complexing anions which serve to limit metal ion concentrations in present-day natural waters have much lower activities in the transiently acidic run-off waters so they are not nearly as effective as metal ion scavengers.

This point is illustrated in Table 2 by the ratios of free  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Cu}^{2+}$  ions to the respective metal humate complexes ( $\text{MA}_2$ ) formed by the reaction of the free metal ions ( $\text{M}^{2+}$ ) with a humic acid (HA). These calculations utilize data from Stevenson and coworkers [30–33] on metal humate stability complexes, peat humic acid pK values (i.e., dissociation constants), and organic acid concentration levels in soils. Similar results are obtained for metal humate complexes with soil

TABLE 2  
Calculated metal ion activities in aqueous solution <sup>a</sup>

Carbonates <sup>b</sup>	pH Value		
	10	8	6
BaCO <sub>3</sub>	-5.9	-1.9	» -1
CaCO <sub>3</sub>	-6.6	-2.6	» -1
CdCO <sub>3</sub>	-9.5	-5.5	-1.5
FeCO <sub>3</sub>	-8.8	-4.8	» -1
MgCO <sub>3</sub>	-6.6	-2.6	» -1
MnCO <sub>3</sub>	-8.8	-4.8	» -1
PbCO <sub>3</sub>	-11.2	-7.2	-3.2
SrCO <sub>3</sub>	-7.6	-3.6	» -1
Sulfides <sup>c</sup>	pH Value		
	7	5.6	1
CdS	-12.6	-9.8	> -1
CuS	-19.7	-16.9	-7.7
FeS	-2.6	> -1	» -1
NiS	-4.8	-2.0	» -1
PbS	-8.4	-5.6	» -1
ZnS	-8.3	-5.5	» -1
Oxalates <sup>d</sup>	pH Value		
	4	2.5	1
Ba <sup>2+</sup>	-6.5	-3.5	> -1
Ca <sup>2+</sup>	-8.2	-5.2	-2.2
Cd <sup>2+</sup>	-7.4	-4.4	-1.4
Cu <sup>2+</sup>	-8.9	-5.9	-2.9
Fe <sup>2+</sup>	-6.2	-3.2	» -1
Mn <sup>2+</sup>	-6.2	-3.2	» -1
Pb <sup>2+</sup>	-8.6	-5.6	-2.6
Sr <sup>2+</sup>	-6.8	-3.8	» -1
Humates <sup>e</sup>	pH Value		
	7	5.6	1
Cd <sup>2+</sup>	-3.2	0.4	8.8
Cu <sup>2+</sup>	-5.0	-2.3	6.9
Pb <sup>2+</sup>	-4.8	-2.1	7.1

<sup>a</sup> For carbonates, sulfides, and oxalates the values of log<sub>10</sub> metal ion activity are given. For humates values of log<sub>10</sub> [M<sup>2+</sup>]/[MA<sub>2</sub>] are given.

<sup>b</sup> The (present day) CO<sub>2</sub> partial pressure of 10<sup>-3.5</sup> bar is assumed. Solid solution of trace metals in more abundant carbonates will decrease the calculated metal ion activities at constant pH.

<sup>c</sup> A representative H<sub>2</sub>S partial pressure of 5 × 10<sup>-10</sup> bar is assumed.

<sup>d</sup> A representative oxalic acid activity of 10<sup>-3</sup> [33] is assumed and an overall pK = (pK<sub>1</sub> + pK<sub>2</sub>) = 5.42 was used.

<sup>e</sup> A humic acid activity of 10<sup>-4</sup> is assumed based on Stevenson and Ardakani [33]. Humate stability constants and peat humic acid pK values are from Stevenson [30-33].

humic acids [30-32] while metal ion complexes with fulvic acids have smaller stability constants [30,34].

Other simpler organic anions which are present in soils and their run-off waters will also tend to complex with and precipitate metal ions. Again Table 2 provides some representative calculations for several metal oxalates showing that metal oxalate formation is relatively inefficient for controlling metal ion activities at low pH values but will be more important for regulating metal ion activities as pH values increase.

Once the water pH exceeds 1 or 2 these organic acids will become more efficient metal ion scavengers. The defoliation of continental plants will produce an influx of dead organic material into rivers and lakes and these organic particles in addition to the organic acids will serve as further loss mechanisms for metals. Nevertheless, there will clearly be an increase in the concentrations of a large number of metal ions in the soil water tapped by plant roots, and in the stream, pond, lake, and river water utilized by animals. Many of the metals (e.g. Al, Be, Tl, Hg) are known to be highly toxic to plants and animals.

The total fresh water in lakes and rivers today is about 3.6 × 10<sup>17</sup> liters. About 30% of the total 7 × 10<sup>40</sup> molecules (1.2 × 10<sup>17</sup> moles) of acid produced by the comet impact will rain out on the continents and most of this rainout occurs in the first year. Since the global-average time constant for rivers to drain the water in lakes and rivers into the sea is 10 years, the average concentration of acid in lakes and rivers assuming no neutralization is 0.3 × 1.2 × 10<sup>17</sup> / 3.6 × 10<sup>17</sup> = 0.1 mole/liter (i.e. a pH of about 1) during the first year. This provides a lower limit for the pH of well-buffered lakes but it is a reasonable estimate for the pH of a poorly-buffered lake. Poorly-buffered lakes with average drainage will then increase their pH by 1 unit every 23 years assuming average rainfall and a drainage time of 10 years. Well-buffered lakes (i.e. lakes with greater than the 1.1 × 10<sup>-2</sup> mole/cm<sup>2</sup> of soluble carbonate or 18-34 g/cm<sup>2</sup> of smectite clay needed to neutralize the comet-derived acid) will experience much shorter-lived and much smaller excursions in their pH.

The above discussion refers only to hypothetical average continental conditions and may not apply precisely to any real drainage basin. Nevertheless, it is evident from this discussion for the comet case, that for 10 years or more the rivers

which drain carbonate-poor regions could have very low pH and high nitrate and metal ion concentrations. As this acidic water mixes with alkaline ocean water in delta regions massive precipitation of the metals will occur. The sediments formed will be characterized by extremely abnormal concentrations of insoluble metals as noted earlier. For a river water pH = 1, inspection of Fig. 3 and Table 2 indicates the possibility of increases in ratios such as  $\text{Be}^{2+}/\text{Ca}^{2+}$  by many orders of magnitude compared to present-day delta sediments. If unperturbed river delta sediments from the Cretaceous-Tertiary period exist (the chances seem slight indeed) they would provide a direct test of this prediction. Fossils of neritic organisms from the Cretaceous-Tertiary boundary would be particularly interesting to investigate because they would tend to concentrate trace metals in their tissues and skeletons.

Not all of the effects of the acid rain are detrimental. Plants which survive will find themselves in nitrate-rich soil and faunal survivors will be able to expand into ecological niches formerly occupied by extinguished species.

## 5. Oceanic biota and carbon dioxide exhalation

Lewis et al. [6] computed the change in the pH of the topmost 75 m (the wind-mixed layer) of the ocean for various amounts of added nitric acid. They assumed initial average mixed layer conditions based on present-day measurements (alkalinity = 2.3 meq/kg, total  $\text{CO}_2$  content = 2.0 meq/kg, temperature = 20°C, salinity = 35‰). They concluded that addition of a total of  $2 \times 10^{40}$  molecules of  $\text{HNO}_3$  uniformly dispersed over the world's oceans would suffice to lower the mixed layer pH to about 7.8 (corresponding to an alkalinity of about 1.1 meq/kg). This is sufficient to dissolve calcite with obvious catastrophic effects on all calcareous upper oceanic organisms.

The highly variable space and time dependence of the depths of the mixed layer and euphotic zone and of the rate of transport of trace species from the ocean surface down to the thermocline coupled with the fact that the particular ocean basin in which the bolide landed will be massively perturbed unfortunately make the problem of deducing pH changes far more complex than the above average calculations would imply.

The enormous tsunami produced by the impact will cause extensive mixing of deep and shallow ocean water in the relevant ocean basin. After the ocean basin returns to its former relatively quiescent state (a process which will take weeks) the mixed layer will contain large amounts of formerly bottom water undoubtedly with quite different chemical and physical properties (higher nutrient levels, lower temperatures) than the pre-impact mixed layer. This mixing in itself probably resulted in destruction of most of the photosynthetic micro-organisms in this basin; they would be mixed on the average to deep dark levels where they could not survive. Both the perturbed and unperturbed ocean mixed layers over the globe would then receive strong acid rain over a period of a year or so. Calcareous phytoplankton will be among the first organisms to be affected. They exist only in the euphotic zone (the top 30 m in clear coastal waters and the top 150 m in clear ocean waters) and their skeletons cannot survive pH levels too much less than 8. The neritic phytoplankton obviously will be particularly vulnerable. Their euphotic zone is shallow and they will receive acid through both rainout and river flows. Indeed in many river delta areas the pH may have been low enough to annihilate siliceous as well as calcareous organisms.

Taking the aforementioned number of 1.2 meq/kg of strong acid needed to be added to ocean surface water to decalcify calcareous organisms, we show in Fig. 4 the total amounts of impact-derived strong acid necessary to decalcify neritic and open ocean calcareous phytoplankton. We also show the time taken for the acid to be mixed down to the relevant ocean depths. For this latter purpose we assume vertical diffusivities of 1 and 10  $\text{cm}^2/\text{s}$  which are typical of the range of mixing rates in the near-surface ocean (see the review by Sundquist [35]). It is evident that destruction of calcareous phytoplankton to a depth of 30 m ocean-wide will require only about  $8 \times 10^{39}$  molecules of strong acid added to the ocean or  $1.1 \times 10^{40}$  molecules acid added globally. This acid will mix down to 30 m in less than 0.3 years. If we take into account the acid added to the neritic zone by acidic rivers the required global amount to affect the neritic zone is less. If 10% of the world's ocean area is considered neritic, phytoplankton decalcification in the neritic zone alone

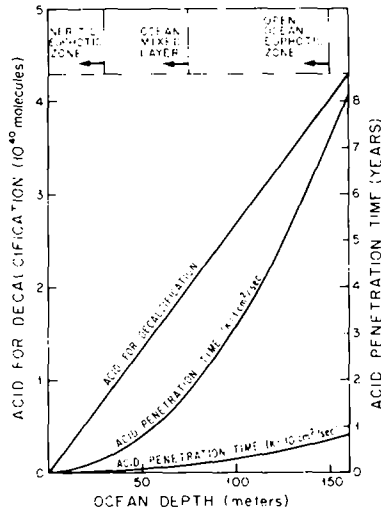


Fig. 4. Amount of added acid required to decrease the upper oceanic calcite saturation factor to unity down to the indicated ocean depths and the time for penetration of this acid down to these depths for two indicative values of the vertical ocean eddy diffusivity  $K$ . These amounts of acid are considered to be just sufficient to decalcify calcareous organisms. Typical depths of neritic and open ocean euphotic zones and of the mixed layer are indicated.

requires  $1.3 \times 10^{15}$  equivalents of strong acid. In 0.3 years global river flows with an average pH of  $\leq 1$  would deliver  $\leq 1.1 \times 10^{15}$  equivalents or  $\leq 85\%$  of the required acid.

In our comet case, about  $5 \times 10^{40}$  molecules of acid will fall on the oceans; most of it within one year after the impact. From Fig. 4 the acid will penetrate to a depth of 150 m in 1–8 years and be sufficient to annihilate globally all calcareous organisms (phytoplankton, corals, etc.) in the euphotic zone with subsequent deleterious effects on all their dependent zooplankton and nekton populations particularly in the euphotic, neritic, and shallower pelagic zones. A comet 1/7 of the mass we have assumed would be sufficient to cause these catastrophic effects down to a depth of 30 m including most of the world's neritic zone where oceanic productivity is heavily concentrated. Life in the neritic zone will be further perturbed by the toxic trace metals entering from rivers. These predicted effects of the impact-produced acid rain seem to go a long way toward explaining the peculiar selectivity of extinctions at the Cretaceous-Tertiary boundary discussed in the Introduction.

For the initial mixed layer conditions discussed above, the equilibrium  $\text{CO}_2$  mixing ratio in the atmosphere  $f_0 = 3.5 \times 10^{-4}$ . Addition of more than about 0.3 meq/kg of strong acid to the upper ocean will lead to significant exhalation of  $\text{CO}_2$  (about 0.3 meq/kg of added acid are used to convert  $\text{CO}_3^{2-}$  to  $\text{HCO}_3^-$  and  $\text{B(OH)}_4^-$  to  $\text{H}_3\text{BO}_3$  and the remainder converts  $\text{HCO}_3^-$  to  $\text{CO}_2$ ). We assume that total  $\text{CO}_2$  is conserved in the system comprising the global atmosphere and a mass  $M_{\text{sea}}$  of the upper ocean (in equilibrium with the atmosphere). Thus the mixing ratio  $f$  of  $\text{CO}_2$  in the post-impact atmosphere and the pH of the upper ocean are given approximately by:

$$f = \bar{m} \frac{M_{\text{sea}}}{M} (\Delta a - 0.3 \times 10^{-3}) + f_0 \quad (10)$$

$$\text{pH} \approx \log(2.3 \times 10^{-3} - \Delta a) + 7.4 - \log f \quad (11)$$

where  $\Delta a$  is the equivalents of strong acid added per kg of ocean water (these equations are valid only for  $2.3 > \Delta a > 0.3$  meq/kg). In the comet case for  $M_{\text{sea}} = 5.4 \times 10^{19}$  kg (i.e. the top 150 m) we have  $\Delta a = 5 \times 10^{40} / (6 \times 10^{23} \times 5.4 \times 10^{19}) = 1.5 \times 10^{-3}$  eq/kg,  $f = 7.1 \times 10^{-4}$  (i.e. the atmospheric  $\text{CO}_2$  mixing ratio is doubled!), and  $\text{pH} = 7.45$ . For addition of  $1.2 \times 10^{-3}$  eq/kg of strong acid (i.e. the amount needed to just destabilize calcite) to the top 30 m, 75 m, and 150 m of the ocean we obtain  $f = 4.1 \times 10^{-4}$ ,  $4.9 \times 10^{-4}$ , and  $6.3 \times 10^{-4}$  and  $\text{pH} = 7.83$ , 7.75, and 7.64 respectively. These latter three cases would occur for comet masses 0.16, 0.4, and 0.8 of the mass of our canonical comet.

This sudden exhalation of  $\text{CO}_2$  from the ocean to the atmosphere would lead to a significant warming trend in the post-impact atmosphere. The warming (and the instability of calcite) would be transient because the  $\text{CO}_2$  would be re-incorporated into the ocean as the upper oceanic alkalinity rises again due to physical mixing of the surface waters with the deeper ocean. The rate of this mixing in the present-day ocean has been determined using various tracers [36]. Sinking of cold polar water removes about  $50 \times 10^6 \text{ m}^3/\text{s}$  [35] of surface water which would transport the volume of water in the top 150 m to the bottom in 34 years. Diffusive transport across the thermocline (100–700 m) occurs with a vertical diffusivity of about  $1.6 \text{ cm}^2/\text{s}$  [37] corresponding to a diffusive time of 71 years. If such mixing times are in

any way relevant to the Cretaceous-Tertiary oceans they imply that the acid added to the surface oceans will be diluted ten-fold by mixing into the deeper ocean on a time-scale of about 120 years thus restoring the stability of calcite. In this same time frame the  $\text{CO}_2$  exhaled into the atmosphere will have been largely re-absorbed into the upper layers of the ocean.

The extinction of the carbonate shelled organisms will seriously disrupt the global carbon cycle and lead to probably the longest-lived effect of the bolide impact. At the present time the sedimentation of dead calcareous organisms is the major mechanism whereby carbon is removed from the upper ocean-atmosphere system. The  $\text{CO}_2$  added to this latter system by volcanoes and continental weathering will therefore be removed by sedimentation at only a fraction of the rate prior to the impact. This would lead to a steady increase in atmospheric  $\text{CO}_2$  concentrations for thousands of years until calcareous phytoplankton could again repopulate the world's oceans. Indeed Hsü and McKenzie [38] interpret the carbon isotope shift across the Cretaceous-Tertiary boundary as indicative of precisely such an event.

## 6. Volcanism and acid rain

Recently, Officer et al. [39] have suggested that acid rain produced from increased volcanic activity in the late Cretaceous and early Tertiary periods would have similar effects on the environment to those caused by the bolide-produced acid rain event discussed here. This was proposed as part of a general hypothesis that the Cretaceous-Tertiary extinctions were not caused by a bolide impact but by an epoch of unusually intense volcanism. They specifically predicted annual volcanic emissions of about  $1.1 \times 10^{13}$  eq of  $\text{H}_2\text{SO}_4$  and  $9.6 \times 10^{11}$  eq of HCl over a period of  $\geq 10,000$  years. For comparison, our comet and asteroid cases involved comparatively sudden injection of  $1.2 \times 10^{17}$  eq and  $5 \times 10^{14}$  eq respectively of  $\text{HNO}_3$  in about 1 year.

Although the total amount of acid postulated to be added by volcanism over a 10,000 year period is in fact comparable to the acid added in our comet case, the volcanic acid is added at far too slow a rate to cause any of the major effects on the ocean biota discussed in this paper. This is

because the relevant water above the thermocline of the ocean is (as discussed earlier) mixed with deeper intermediate and bottom water on a e-folding time scale of only 50 years or so. The top 150 m of the ocean has  $1.2 \times 10^{17}$  eq of alkalinity and is obviously strongly perturbed by addition of a comparable amount of acid but only provided this acid is added on a time frame less than 50 years. The total ocean contains  $3.5 \times 10^{18}$  eq of alkalinity; addition of  $1.2 \times 10^{17}$  eq of acid from volcanoes over 10,000 years will cause very little perturbation to the total ocean.

To be more specific the proposed volcanism would add about  $4.2 \times 10^{14}$  eq of acid to the oceans (and  $1.8 \times 10^{14}$  eq to the land) over a 50 year time frame. Added to the top 150 m of the ocean, this corresponds to  $\Delta a = 0.008$  meq/kg. Calcareous phytoplankton would be quite unaffected since calcite instability requires  $\Delta a \approx 1.2$  meq/kg. Also the atmospheric  $\text{CO}_2$  mixing ratio and the upper ocean pH will be similarly unaffected by the volcanic acid. These conclusions will clearly not be changed even if the volcanic acid input over the 50 year period is 10 times greater than the average postulated value.

## 7. Conclusions

An ice-rich long-period comet with a mass of  $1.25 \times 10^{16}$  kg and velocity of 65 km/s striking the earth would produce about  $7 \times 10^{40}$  molecules NO through shock-heating of the atmosphere by the high velocity ejecta plume fragments. This NO is converted to  $\text{NO}_2$  and then nitrous and nitric acid rain with a pH  $\approx 0-1.5$  globally. This  $\text{NO}_2$  and acid rain would traumatize the biosphere.

If the bolide were instead a much lower velocity short-period comet or a much less massive and lower velocity asteroid the nitrogen oxide and acid rain effects would be much less. Specifically a  $5 \times 10^{14}$  kg, 20 km/s asteroid collision would produce amounts of nitrogen oxides and acid rain which although traumatic in the region of impact would be relatively unimportant once spread to global scales.

The possible relics in the sedimentary record of a collision with a massive long-period comet would include:

- (1) a sudden annihilation of all calcareous

organisms in the top 150 m of the world's oceans including the phytoplankton as a result of acid raining directly on the oceans (a comet with a mass of 80% of the mass we have assumed would be sufficient for this purpose);

(2) annihilation of calcareous and other organisms in the neritic zone as a result of both the acid rain and the input of acid and many toxic metals from rivers;

(3) massive weathering of continental soils characterized by large ratios of relatively insoluble metals (e.g.  $\text{Be}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Cu}^+$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Tl}^{3+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Sr}^{2+}$ ) to the more soluble metals ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) which would be best recorded in fossils of neritic organisms and in minerals in unperturbed neritic sediments near river deltas (the chances of such sediments existing is unfortunately slim);

(4) low survival rates of large terrestrial herbivores due to  $\text{NO}_2$  asphyxiation and the defoliation of much of the continental vegetation by  $\text{NO}_2$  and acid rain;

(5) relatively high survival rates of deep ocean organisms and of upper ocean siliceous organisms whose skeletons would not be affected by the acid;

(6) relatively high survival rates of limnetic fauna since a not insignificant fraction of the world's lakes would be well-buffered by carbonate rocks;

(7) relatively high survival rates of animals living in or laying eggs in burrows in well-buffered continental soils;

(8) a disruption of the global carbon cycle resulting initially in a doubling of atmospheric  $\text{CO}_2$  due to exhalation of  $\text{CO}_2$  from the upper ocean and in the longer term (a few millenia perhaps) continued high  $\text{CO}_2$  levels due to temporary loss of the carbonate shell pump for removing  $\text{CO}_2$  from the atmosphere-upper ocean system.

A majority of these relics are evident in the sediments at the Cretaceous-Tertiary boundary and we regard this as evidence in favor of a massive cometary impact at that time with its associated production of nitric acid. We urge further study of this geologic boundary aimed at addressing relic (3) concerning the insoluble metals. Intense Cretaceous-Tertiary volcanism while it may indeed have occurred [39] cannot explain the selective nature of the Cretaceous-Ter-

tiary extinctions exemplified by relics (1) and (5); the production rate of acid is far too slow. We emphasize that the bolide impact may also be accompanied by: inhibition of photosynthesis and climate changes caused by the ejecta dust [1,17]; destruction of vegetation by wildfires and climate changes caused by soot and carbon dioxide production in wildfires [18]; and climate changes caused by the ejected water vapor [2]. Thus relics (4) and (8) in particular are not unique to our acid rain hypothesis.

Finally, we note that the Earth has been subject to large asteroidal and cometary impacts throughout its history [40], and that the impact rate during the early stages of its evolution [41,42] may have been much higher than the present impact rate of large ( $\approx 10$  km) objects. Such events would also cause chemical reprocessing of the Earth's atmosphere although the nature of the products formed is very different depending on the atmospheric composition [43] (e.g., HCN rather than NO in putative  $\text{CO}$ ,  $\text{N}_2$  ancient atmospheres [43]).

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