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A HYBRID MODEL OF THE CO_2 GEOCHEMICAL CYCLE AND ITS APPLICATION TO LARGE IMPACT EVENTS

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ABSTRACT. A hybrid model of the carbonate-silicate geochemical cycle is presented which is capable of calculating the partitioning of carbon dioxide between the atmosphere, ocean, and sedimentary rocks. The ocean is subdivided into a shallow, mixed layer, which remains in equilibrium with the atmosphere, and a massive, deep layer which does not. Gradients in dissolved carbon content are established between the mixed layer and the deep ocean as a consequence of downward fluxes of fecal matter and of dead planktonic organisms. The dissolved carbon content and alkalinity of the ocean as a whole are controlled by weathering and metamorphism of sedimentary rocks. Equilibrium solutions are derived for the preindustrial atmosphere/ocean system and for a system that may be similar to that existing during the Late Cretaceous Period.

The model is then used to determine how the modern and ancient marine biospheres might be affected by an oceanic impact of a large asteroid or comet. Such an event could perturb the carbon cycle in several different ways. Global darkening caused by a stratospheric dust veil could destroy most of the existing phytoplankton in a period of several weeks to several months. At the same time, dissolution of atmospheric NO_x compounds synthesized during the impact would lower the pH of ocean surface waters and release CO_2 into the atmosphere. Both effects might be enhanced by an influx of CO_2 released from upwelling of deep ocean water near the hot impact site, from oxidation of dead organic matter, and from the comet itself. The net result could be to raise surface temperatures by several degrees and to make the surface ocean uninhabitable by calcareous organisms for as much as 20 yrs (the time scale for mixing with the deep ocean). It appears unlikely, however, that an impact could create a "Strangelove ocean," in which surface waters remained corrosive to calcium carbonate for thousands or tens of thousands of years. Thus, disruption of the carbon cycle by an impact event cannot by itself explain the scarcity of calcium carbonate in sediments found within the first few centimeters above the K/T boundary.

I. INTRODUCTION

As interest has mounted concerning the buildup of fossil fuel carbon dioxide in the atmosphere, researchers have discovered that CO_2 levels may have fluctuated in the past in response to a variety of natural forcing mechanisms. Over periods of thousands to tens of thousands of years, CO_2 levels are thought to be controlled by changes in marine productivity (Broecker, 1982). Such changes, which may be caused by fluctuations in the supply of nutrients such as phosphorus (Broecker, 1982) or nitrogen

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(Knox and McElroy, 1985), are recorded by variations in the CO_2 content of air bubbles trapped in ice cores (Berner, Stauffer, and Oeschger,1979; Oeschger, Stauffer, Finkel, and Langway, 1985). Since these variations are driven by biological pumping of CO_2 from the surface to the deep ocean, the simplest models capable of describing them are so-called "two-box" ocean models like those of Broecker (1982) or Keir and Berger (1983) (henceforth, KB), in which the ocean is divided into a relatively shallow surface layer and a much thicker deep layer. Gradients in the concentrations of dissolved inorganic carbon species (H_2CO_3, HCO_3^-, and $CO_3^=$) are established between these layers as a consequence of the downward fluxes of fecal matter and of dead planktonic organisms. One noteworthy result of this biological pumping mechanism is that deep water contains roughly three times as much dissolved CO_2 per unit volume as does surface water (Broecker, 1982).

Over longer time periods (millions to tens of millions of years), the CO_2 content of the entire atmosphere/ocean system varies in response to changes in the rates of weathering and metamorphism of carbonate and silicate rocks (Berner, Lasaga, and Garrels, 1983, henceforth BLAG — see also Budyko and Ronov, 1979; Fischer, 1984; Mackenzie and Pigot, 1981; Holland, 1978). Increased rates of carbonate metamorphism 60 to 100 my (million years) ago (inferred from faster rates of seafloor spreading), coupled with smaller amounts of continental area exposed to weathering, could have caused Cretaceous CO_2 levels to be as much as 6 to 30 times higher than today (BLAG; Lasaga, Berner, and Garrels, 1985). CO_2 increases near the lower end of this range are consistent with those required by climate modelers (Barron and Washington, 1985) to explain the warm surface temperatures during that period. Modelers who have attempted to simulate this long-term carbonate-silicate geochemical cycle (BLAG; Lasaga, Berner, and Garrels, 1985) have thus far limited their consideration to "single-box" ocean models, in which the composition of the ocean is assumed to be uniform with depth. While useful for the long time scale simulations for which they were intended, these models are not capable of predicting more rapid CO_2 fluctuations, such as those mentioned in paragraph one.

Our present interest in the carbon cycle concerns its possible disruption by an impact event at the Cretaceous/Tertiary (K/T) boundary and its subsequent role in causing mass extinctions. Evidence for the impact of either an asteroid or a comet at this time includes high concentrations of iridium and other siderophile elements in both marine (Alvarez and others, 1980; Ganapathy, 1980; Smit and ten Kate, 1982; Brooks and others, 1984) and continental (Orth and others, 1981, 1982) boundary clays, "cosmic" isotopic signatures for Ir and Os (Smit and Hertogen, 1980; Luck and Turekian, 1983), and the presence of both sanidine (impact melt?) spherules and shocked quartz grains (Smit and Klaver, 1981; Bohor and others, 1984).

While the evidence for such an impact has become more and more convincing, the actual mechanism (or mechanisms) by which it could

have triggered mass extinctions is still a subject of debate. The hypothesis originally suggested by Alvarez and others (1980) and explored in greater detail by Toon and others (1982) and Pollack and others (1983) was that the dust injected into the atmosphere by such an impact would have blocked out most of the sun's rays for a period of several months, causing light levels to fall below the minimum intensity required to sustain photosynthesis. The marine food chain would have collapsed suddenly and dramatically; continental food chains would have been less severely affected because of the greater amount of available biomass and a longer time constant for its consumption (Milne and McKay, 1982; Toon and others, 1982; Pollack and others, 1983). Extinctions of organisms might also have been caused, however, by a variety of related environmental effects, including a sudden drop in temperature caused by the dust layer (Toon and others, 1982; Pollack and others, 1983), an inability to locate food in the dark (Toon and others; Pollack and others), decreases in stratospheric ozone, and concommitant increases in the intensity of the solar UV flux reaching the ground (Turco and others, 1981; Kasting and Ackerman, 1985), highly acidic rain caused by removal of NO_x compounds synthesized by the impact (Lewis and others, 1982; Kasting and Ackerman, 1985), greenhouse warming associated with increased stratospheric water vapor levels (Emiliani, Kraus, and Shoemaker, 1981), and poisoning by heavy metals (Hsu, 1980).

The physics of large impact events is sufficiently complex that it is difficult to confirm or rule out possible extinction mechanisms solely on the basis of theoretical models. The most fruitful approach to the problem must therefore be to determine the success of a given model in explaining the detailed pattern of extinctions and sedimentological anomalies. Besides the disappearance of the dinosaurs, the most pervasive changes observed at the K/T boundary are the drastic reduction in the calcium carbonate content of sediments lying immediately above the iridium anomaly (Hsu and others, 1982a,b; Smit, 1982; Perch-Nielson, McKenzie, and He, 1982) and the catastrophic reduction in the abundance and diversity of calcareous plankton at this time (Bramlette and Martini, 1964; Thierstein, 1981, and references therein). These observations have led several investigators (Tappan, 1968; Worsley, 1974; McLean, 1978; Hsu, 1980, 1985; Hsu and others, 1982a,b) to conjecture that the calcite compensation depth, or CCD (the depth at which the rate of calcite dissolution is exactly balanced by the downward flux of calcite particles from the surface ocean), may have risen from its usual depth of 5 to 6 km to within the photic zone. The suggested cause of this phenomenon is a sudden injection of CO_2 into the atmosphere and surface ocean. In the impact-hypothesis models, the suggested sources of this CO_2 are the comet itself (Hsu, 1980), the decay of vegetation killed off by the impact (Hsu and others, 1982a,b), and the deep ocean (Hsu, 1985). Such an addition of CO_2 would have lowered the carbonate ion concentration and the pH of surface waters by affecting the equilibrium reaction

$$CO_2 + CO_3^{=} + H_2O \longleftrightarrow 2\,HCO_3^{-} \qquad \text{(R1)}$$

An alternative mechanism for acidifying surface waters is the dissolution of atmospheric NO_x compounds synthesized by the impact (Lewis and others, 1982).

The occurrence of such a widespread calcite dissolution event is not universally accepted and cannot be the sole cause of marine extinctions, since siliceous plankton, such as diatoms and radiolaria, also experienced mass mortality at this time (Thierstein, 1982). Such an event might, however, help to explain the prolonged (10,000-30,000 yr) disappearance of calcium carbonate from marine sediments (Hsu, 1982a,b; Smit, 1982; Perch-Nielson, McKenzie, and He, 1982). If the biological CO_2 pump was turned off for an extended period (~1000 yrs), the surface ocean would have gradually approached the composition of deep water, which contains about 3 times less dissolved carbonate ion and 3 times more dissolved CO_2 (Broecker and Peng, 1982). This would not by itself drive the modern surface ocean below saturation, since surface water is presently supersaturated with respect to calcite by a factor of about 5 (Broecker and Peng, 1982). However, it is not clear that this same statement would have been true in the past, when the carbon cycle was quite different (BLAG). If an undersaturated surface layer was created by mixing with deep water, then it should have persisted until either the biological CO_2 pump was reestablished (presumably by non-calcareous organisms), or until the slow influx of dissolved carbon from the rock cycle raised the carbonate concentration of the entire ocean above saturation. The latter process would require on the order of 10,000 yrs or more (BLAG); thus, this type of long-lived dissolution event could account for the prolonged absence of calcite deposition.

Alternative explanations for the low abundance of calcium carbonate above the boundary involve rapid erosional processes in the early Tertiary (Thierstein, 1982) or simply a long biological time constant for the recovery of calcareous species after the (short-lived) extinction event. The latter hypothesis is unattractive, since the time constants involved in planktonic growth cycles are of the order of months or less (for example, Milne and McKay, 1982). Soil erosion might have been facilitated by widespread destruction of vegetation following the impact; if so, the time required to deposit the calcite-depleted layer could have been less than that predicted assuming a uniform sedimentation rate. Only a huge increase (a factor of 10-100) in sedimentation rate, however, would shorten the deposition time sufficiently to explain the disappearance of calcium carbonate. We therefore feel that it is worthwhile to explore the dissolution hypothesis in some detail to determine whether such a phenomenon is theoretically feasible.

From a modeling standpoint, a challenging aspect of simulating this event is that it involves both the short- and long-term CO_2 cycles. Any dramatic compositional changes resulting from the impact must have been confined to the surface ocean, since the deep ocean is far too massive to have been affected by the expected influx of nitric acid or by any readily available sources of CO_2 (see sec. IV). Thus, the model ocean must

necessarily be divided into a surface and a deep layer. The steady-state concentrations of dissolved carbonate species in these layers must, however, reflect the modified carbonate-silicate geochemical cycle which was probably operative during Cretaceous times. To address this problem, we have therefore developed a hybrid model of the CO_2 cycle, which combines elements of the BLAG geochemical model with the two-box ocean formulation employed by Keir and Berger (1983). The behavior of the model over long time scales is similar to that of the BLAG model, although the mechanics of its operation are quite different. The next section describes the physical assumptions and the mathematical framework upon which the model is based.

II. THE MODEL

A. *Mechanics.*—The ocean is divided into a 200 m thick mixed layer and a 3700 m thick deep ocean. The assumed mixed layer depth is to some extent arbitrary; it represents a compromise between the ~75 m thick layer which is well-stirred due to wind stress and the ~600 m thick layer which lies above the base of the thermocline. Fortunately, as discussed below, the steady-state results predicted by the model are relatively insensitive to the mixed layer depth, so the choice of this parameter is not critical for the equilibrium calculations that will be presented here.

The equations to be solved in the model are analogous to eqs (6) to (9) of KB. The alkalinity and total dissolved inorganic carbon content of the atmosphere/mixed layer and deep ocean reservoirs are assumed to obey the relations:

$$\frac{d\Sigma_T}{dt} = \frac{1}{\tau_m}(\Sigma_d - \Sigma_m) + \frac{1}{V_m}[(1+\nu_2)H_{CO_2} - (1+\nu_1)\,I_{carb} - E_{carb} - E_{org}] \quad (1)$$

$$\frac{dA_m}{dt} = \frac{1}{\tau_m}(A_d - A_m) + \frac{1}{V_m}[H_{Alk} - \nu_2\nu_0 H_{CO_2} - (2-\nu_1\nu_0)\,I_{carb} - 2\,E_{carb} + \nu_0\,E_{org}] \quad (2)$$

$$\frac{d\Sigma_d}{dt} = -\frac{1}{\tau_d}(\Sigma_d - \Sigma_m) + \frac{1}{V_d}[\nu_1\,I_{carb} + \xi - B_{org}] \quad (3)$$

$$\frac{dA_d}{dt} = -\frac{1}{\tau_d}(A_d - A_m) + \frac{1}{V_d}[2\xi - \nu_0\,(\nu_1\,I_{carb} - B_{org})] \quad (4)$$

Here

Σ_T = total dissolved inorganic carbon in the atmosphere and mixed layer per unit volume of mixed layer
Σ_m = concentration of dissolved inorganic carbon in mixed layer
Σ_d = concentration of dissolved inorganic carbon in the deep sea
A_m = alkalinity of mixed layer
A_d = alkalinity of deep sea
V_m = volume of mixed layer ($= 2/39 \times 1.37 \times 10^{21}$ l)

V_d = volume of deep sea (= $37/39 \times 1.37 \times 10^{21}$ l)
τ_d = residence time of water in deep sea (= 1000 yrs)
τ_m = residence time of water in mixed layer (= $\tau_d \times V_m/V_d$)
ν_2 = ratio of organic carbon burial rate to inorganic carbon burial rate (= 0.25)
ν_1 = ratio of organic carbon to carbonate carbon in particulate matter falling from mixed layer to deep sea (= 3.3)
ν_0 = ratio of alkalinity titrated to CO_2 produced by organic matter oxidation, due to production of NO_3 from organic N (= 0.17)
I_{carb} = rate of carbonate transfer by particulates falling from mixed layer to deep sea
E_{carb} = rate of carbonate burial on continental shelves or in shallow seas
H_{CO_2} = rate at which inorganic carbon is supplied to the atmosphere/mixed layer by weathering and metamorphism
H_{Alk} = rate at which alkalinity is supplied to the mixed layer by weathering
B_{org} = burial rate of organic carbon in deep ocean (= $\nu_2 H_{CO_2}$)
E_{org} = burial rate of organic carbon on continental shelves
ξ = rate of carbonate dissolution in the deep sea

In this formulation the atmosphere and mixed layer are assumed to remain in equilibrium. Thus, Σ_T and Σ_m are related by the expression

$$\Sigma_T = \Sigma_m + \gamma c_m \ , \tag{5}$$

where γ (= 76.39 for a 200 m thick mixed layer) is a dimensionless constant that depends on the mass of the atmosphere, the volume of the mixed layer, and the Henry's Law constant for CO_2, and c_m is the concentration of H_2CO_3. (See app. to KB.) For part of the discussion in section IV we assume a mixed layer depth z_m of 75 m, in which case γ must be multiplied by a factor of 200/75. As mentioned above, the equilibrium solution to eqs (1) to (4) is only weakly affected by the mixed layer depth. This is because both V_m and τ_m are proportional to z_m; thus, the steady-state concentration gradients between the shallow and deep ocean are unaltered by a change in z_m.

The terms Σ_m and Σ_d, representing total dissolved inorganic carbon, are defined by the relationship: $\Sigma \equiv [H_2CO_3] + [HCO_3^-] + [CO_3^=]$. The (titration) alkalinity terms A_m and A_d include contributions from the dissociation products of both carbonic and boric acids: $A = [HCO_3^-] + 2[CO_3^=] + [BO_3^-]$. Physically, the alkalinity is a measure of the net negative charge carried by anions which are capable of assuming different charge states, depending upon the ambient pH.

Eqs (1) to (4) are numerically integrated using subroutine DIFSUB from Gear (1971). The implicit nature of this algorithm allows the model to take very large time steps as the system approaches equilibrium. Thus, the amount of CPU time required on a CRAY-1 computer for a typical model run is only a fraction of a second.

The differences between our formulation and that of KB involve the source terms for total carbon and alkalinity. In the KB model the source of inorganic carbon was represented by H_{Riv}, which stood for the rate of supply of dissolved calcium carbonate by rivers. The source term for alkalinity was therefore equal to $2H_{Riv}$. This approximation was suitable for the relatively short (10^5 yr) simulations presented in their paper. Over longer time periods, however, the total carbon and alkalinity budgets are controlled by weathering and metamorphism of carbonate and silicate rocks (see BLAG) and, to a lesser extent, by the organic carbon cycle. We have incorporated the rock cycle into our model by adopting the inorganic carbon fluxes derived by BLAG. (We use the values that were modified to remove the effect of sulfate weathering.) The source term for total carbon (see eq 1) is $(1 + \nu_2)H_{CO_2}$. The source term for alkalinity (eq 2) is H_{alk}. In the notation of BLAG, these source terms may be written as

$$H_{CO_2} = F_{W_C} + 2F_{W_D} + 2F_{M_D} + F_{M_C} \tag{6}$$

$$H_{alk} = 2(F_{W_C} + 2F_{W_D} + F_{W_{CaSi}} + F_{W_{MgSi}} \tag{7}$$

where

F_{W_C} = weathering rate of calcite

F_{W_D} = weathering rate of dolomite

$F_{W_{CaSi}}$ = weathering rate of calcium silicate

$F_{W_{MgSi}}$ = weathering rate of magnesium silicate

F_{M_C} = rate of metamorphism of calcite

F_{M_D} = rate of metamorphism of dolomite

The present magnitudes of these fluxes (denoted by the superscript zero) in units of 10^{12} moles yr^{-1} are: $F^\circ_{W_C} = 7.84$, $F^\circ_{W_D} = 1.98$, $F^\circ_{W_{CaSi}} = 2.72$, $F^\circ_{W_{MgSi}} = 3.02$, $F^\circ_{M_C} = 2.86$, and $F^\circ_{M_D} = 1.44$ (see BLAG). Thus, $H^\circ_{CO_2} = 17.54$ and $H^\circ_{alk} = 2 \times 17.54$. A diagram showing the various fluxes and reservoirs involved in the rock cycle is presented in figure 1.

The terms B_{org} and E_{org} were not included in the original BLAG model. They represent an additional throughput of carbon which we know must exist based on the observation that the ratio of organic to carbonate carbon in sediments has remained close to the "Ronov ratio" ($\nu_2 = 0.25$) throughout most of geologic time (Schidlowski, Eichmann, and Junge, 1975). As a simple, first-order approximation, we have constrained our model by assuming that $E_{org} = \nu_2 E_{carb}$, and that $B_{org} + E_{org} = \nu_2 H_{CO_2}$. Consequently, an additional source term for CO_2, given by $\nu_2 H_{CO_2}$, must be added to the CO_2 source assumed by BLAG to balance the loss of carbon due to organic carbon burial. The organic carbon cycle has little effect on the results presented here, since we have assumed that ν_2 remains constant but can have a significant influence on CO_2 levels if this assumption is relaxed (Lasaga, Berner, and Garrels, 1985).

The internal mechanics of the model are as described in KB app. A and B. The relative amounts of dissolved $CO_3^=$, HCO_3^-, and H_2CO_3 and

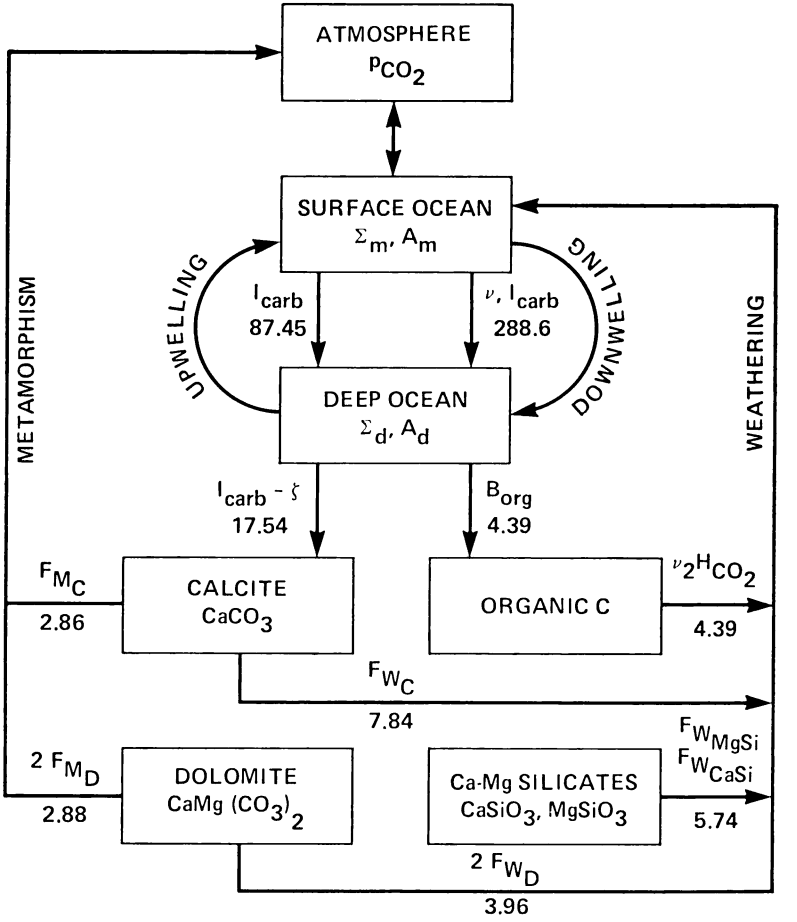

Fig. 1. Schematic diagram showing the present-day carbon fluxes assumed in the model. All fluxes are in units of 10^{12} moles yr^{-1}.

of atmospheric CO_2 in the atmospheric/mixed layer reservoir are determined by solving a system of two nonlinear equations for $[H_2CO_3]$ and $[CO_3^{=}]$, or c_m and y, respectively, in the notation of KB. The solution to this system is straightforward, except that one should be careful to use the corrected versions of KB eqs (A5) and (A12), as given in Keir and Berger (1985). Once c_m is known, the atmospheric CO_2 content may be calculated from:

$$pCO_2 = \frac{c_m}{\alpha}, \tag{8}$$

where the Henry's Law constant α has a value of 3.4×10^{-2} mole l^{-1} atm^{-1} at the assumed mixed layer temperature of 20°C. Since α increases by roughly 40 percent for each 10 degree of decrease in temperature (Broecker

and Peng, 1982, p. 151), there is in reality a continual flux of CO_2 out of the warm tropical ocean and into the cold polar oceans. We ignore this complication, along with changes in α or any of the other carbonate equilibrium constants caused by warmer ocean temperatures in the past.

The carbonate dissolution flux ξ is calculated from eqs (B1), (B5), and (B6) of KB. Since this is one of the primary differences between our model and the BLAG model, and since there are several important physical assumptions incorporated in these equations, it is worthwhile to go through their derivation in some detail. First, a nondimensional undersaturation factor S is defined by

$$S = 1 - [CO_3^{=}]_d/[CO_3^{=}]_d^{eq} \tag{9}$$

where $[CO_3^{=}]_d$ is the carbonate ion concentration in the deep ocean and $[CO_3^{=}]_d^{eq}$ (= 0.1055 mmole l^{-1}) is the carbonate ion concentration that would be expected in equilibrium with $CaCO_3$ at a depth of 5 km, assuming a present-day Ca^{++} concentration of 10.3 mmole l^{-1} (Broecker and Peng, 1982). One then defines a variable $F \equiv J/J_T$, where J and J_T are the carbonate fluxes out of and into the sediment, respectively, in units of mg cm^{-2} yr^{-1}. A fraction X_1 of the particulate carbonate entering the deep ocean from the surface is aragonite; this material is more soluble than calcite and is assumed to dissolve entirely on its way down to the bottom. We assume that $X_1 = 0.5$, based on recent data from sediment traps (Betzer and others, 1984; Byrne and others, 1984); this represents a significant departure from the model of KB, who assumed an aragonite fraction of 0.1. The remaining fraction $(1 - X_1)$ of the particulate carbonate is assumed to survive until it reaches the ocean floor. Thus,

$$J_T = (1 - X_1)\, I_{carb} z_{av}/V_{oc} \ , \tag{10}$$

where Z_{av} (= 3900 m) is the average depth of the ocean, and V_{oc} (= 1.37 $\times$ 10^{21} l) is the ocean volume. The total particulate carbonate flux I_{carb} for the present ocean is estimated to be 8.7 $\times$ 10^{13} mole s yr^{-1}, according to KB eq (11). Thus, J_T is presently equal to about 1.2 mg cm^{-2} yr^{-1}.

Given S and J_T, the value of F is found by solving the cubic equation

$$F^2(1 - X_o F) - \frac{\kappa S^{n+1}}{J_T^2} X_o(1 - F) = 0 \ . \tag{11}$$

This equation is a corrected version of KB eq (B5). (Their published equation contained a sign error.) Here, X_o (= 0.9) is the fractional amount of carbonate in the particulate matter reaching the sediment, κ (= 9776.4 mg^2 cm^{-4} yr^{-2}) is a rate constant that depends on the density and porosity of the sediment, and n (= 4.5) is an empirically-determined coefficient that reflects the dependence of calcite dissolution on the degree of undersaturation of the overlying bottom water. The flux of calcite out of the sediment is proportional to $S^{(n+1)/2}$ or $S^{2.75}$ (KB, eq B3); this strong dependence on S makes it unlikely that the degree of undersaturation of deep water has varied greatly with time (see sec. IV).

Finally, once F is known, the value of ξ is calculated from

$$\xi = [X_1 + (1 - X_1)F]\, I_{carb} \ . \tag{12}$$

Eq (12) reflects the assumption that the aragonitic debris dissolves entirely as it falls through the deep ocean.

An important aspect of the BLAG model which we have incorporated into our model is the variation in the carbonate-silicate geochemical cycle with respect to changes in surface temperature (through its effect on the amount of precipitation), land area (through its effect on the amount of continental area available for subaerial erosion), and seafloor spreading rates (as an indicator of the level of metamorphism and volcanism). BLAG proposed that the weathering rates F_{W_i} in eqs (6) and (7) should be proportional to a land-area correction factor $f_A(t)$ and a temperature/runoff correction factor $f_B(CO_2)$. Thus

$$F_{W_C} = f_A(t) f_B(CO_2) F^\circ_{W_C} \equiv f_A f_B F^\circ_{W_C} \ .$$

and similarly for the other weathering fluxes. The metamorphic/volcanic fluxes F_{M_i} were assumed to be proportional to a seafloor spreading rate factor $f_{SR}(t)$. The factors f_A and f_{SR} were set equal to unity for the present; their estimated values during the past 100 my are given in figures 2 and 4 of BLAG.

The temperature/runoff correction factor $f_B(CO_2)$, given by BLAG eq (32) and their figure 3, was derived by using results from the climate model of Manabe and Stouffer (1980) in conjunction with measurements of pCO_2 in air bubbles in Pleistocene glacial ice by Berner, Oeschger, and Stouffer (1980) and measurements of $[HCO_3^-]$ in ground water by Harmon and others (1975). The magnitude of f_B is related to the size of the atmospheric CO_2 reservoir, because of the coupling of pCO_2 and temperature and the relationship between temperature and precipitation. We have modified the BLAG formulation slightly by replacing this with the ratio of the partial pressure of atmospheric CO_2 in ppm (parts per million) compared to the preindustrial value of about 285 ppm. Thus

$$f_B(CO_2) = 1 + 0.252\, ln\left(\frac{pCO_2}{285}\right) + 0.0156\left[\, ln\left(\frac{pCO_2}{285}\right)\right]^2 \ . \tag{13}$$

As will be demonstrated shortly, the effect of this change is to ensure that pCO_2 relaxes to the preindustrial value when f_A and f_{SR} are set equal to unity. This seems to us to be more natural than having pCO_2 relax to the present value, which is known to have been perturbed by man's activities.

We have extended the reasoning of BLAG by assuming that the particulate carbonate flux is also proportional to the weathering factors f_A and f_B; thus, $I_{carb} = f_A f_B I^\circ_{carb}$, where I°_{carb} is the present-day flux. This assumption is based on the idea that I_{carb} should be related to the rate of primary marine productivity, which is thought to be limited by the availability of the nutrient phosphorus (Broecker and Peng, 1982). Dissolved phosphorus is derived mainly from continental weathering and ought, therefore, to be controlled by the same factors that affect weathering of carbonates and silicates.

B. *Steady-state solution.*—Much can be learned about the behavior of our model by examining the steady-state solution. In steady state the budgets of total inorganic carbon and of alkalinity for the ocean as a whole must be in balance. Setting the time derivatives equal to zero, multiplying eq (1) by V_m/V_d, and adding the result to eq (3) yields

$$H_{CO_2} = I_{carb} - \xi + E_{carb} \ . \tag{14}$$

This equation simply states that the source of inorganic carbon (excluding that needed to balance organic carbon burial) must be equal to the total burial rate of calcite. Following the same procedure with eqs (2) and (4) gives

$$H_{alk} = 2\,(I_{carb} - \xi + E_{carb}) \ . \tag{15}$$

Thus, it follows that $H_{alk} = 2\,H_{CO_2}$ or, using eqs (6) and (7):

$$F_{W_{CaSi}} + F_{W_{MgSi}} = 2\,F_{M_D} + F_{M_C} \ . \tag{16}$$

Eq (16) expresses the fact that the carbon budget can remain balanced over the long term only if the loss of CO_2 from weathering of silicate minerals is balanced by the production of CO_2 from metamorphism of dolomite and calcite. If we put the time-dependent correction factors into eq (16), we obtain

$$f_A f_B\,(F^\circ_{W_{CaSi}} + F^\circ_{W_{MgSi}}) = f_{SR}\,(2\,F^\circ_{M_D} + F^\circ_{M_C}) \ , \tag{17}$$

where the superscript zero indicates the present-day fluxes. Solving for f_B explicitly then yields

$$f_B(CO_2) = \frac{f_{SR}}{f_A}\left[\frac{2F^\circ_M + F^\circ_M}{F^\circ_{W_{CaSi}} + F^\circ_{W_{MgSi}}}\right] \ . \tag{18}$$

The bracketed expression in eq (18) is equal to unity, so the result reduces to: $f_B(CO_2) = f_{SR}/f_A$. This equation shows that the atmospheric CO_2 level is directly linked to other factors in the CO_2 geochemical cycle by its effect on temperature and weathering rates. This result is essentially the same as that derived by Kasting (1984) in his steady-state analysis of the BLAG model; the only difference is that we have not allowed for the possibility of changes in the reservoirs of dolomite and calcite.

An additional steady-state relationship can be derived by combining eqs (12) and (14) and eliminating ξ to get

$$X_1 = 1 - \frac{H_{CO_2} - E_{carb}}{I_{carb}(1 - F)} \ . \tag{19}$$

Since F must lie between 0 and 1, it follows that X_1 must be less than some maximum value. For the case described in the next section, in which E_{carb} is assumed to be zero and the ratio of $H_{CO_2}/I_{carb} \cong 0.2$, the fraction of aragonite in the particular matter reaching the deep ocean must be less than 0.8, in order for the model to achieve a steady state. This must be kept in mind when one looks at possible variations to the standard model.

Some comments on the comparison between our model and those of KB and BLAG are in order at this point. If we neglect organic carbon, the source of carbon in our model ($H_{CO_2} = 17.54 \times 10^{12}$ moles yr^{-1}) is only slightly greater than the carbon source assumed by KB ($H_{Riv} = 13.8 \times 10^{12}$ moles yr^{-1}). The KB model, however, does not contain sufficient information to define a unique steady-state solution; the values it yields on output depend upon the assumed initial values. Thus, the KB model has no useful predictive capability over time scales longer than the residence time of carbon in the ocean/atmosphere system ($\sim 2 \times 10^5$ yrs). Our model, however, converges to the same solution regardless of the assumed initial conditions. For example, if f_A and f_{SR} are both set equal to unity, eqs (13) and (18) ensure that the steady-state solution will correspond to $pCO_2 = 285$ ppm. This does not prove that the concentrations of dissolved carbon species in the surface and deep ocean are also unique; however, we have never encountered any multiple solutions in practice.

Since our model incorporates the same rock cycle fluxes as BLAG, its behavior over long time scales is very similar to that of the BLAG model. Thus, the atmospheric CO_2 levels it predicts are the same as predicted by BLAG for any time interval longer than about 10^5 yrs. The model is also subject to many of the same faults as the BLAG model. For example, if the model is used to try to predict the concentrations of Ca^{++} and Mg^{++} ions in the Cretaceous oceans, by including equations for the reservoirs of dolomite, calcite, and dissolved calcium and magnesium (see BLAG), it generates an unrealistically low $[Ca^{++}]/[HCO_3^-]$ ratio. The BLAG model has the same problem when the initial conditions are specified self-consistently (Kasting, 1984). The fundamental limitation to both models is that they ignore the effects of the oceanic sulfur cycle. This problem is remedied in the expanded geochemical model of Lasaga, Berner, and Garrels (1985), which includes both the sulfur cycle and that of organic carbon. Unfortunately, however, Lasaga, Berner, and Garrels have relied on the assumption that the dissolved sulfate concentration was the same at the beginning of their simulation (100 my ago) as it is today. By doing so, they ignore the possibility that changes in the reservoir of gypsum ($CaSO_4 \cdot 2H_2O$) could have caused corresponding changes in $[Ca^{++}]$ and $[SO_4^{=}]$. The sulfur cycle is treated self-consistently after this point, but the predicted species concentrations are suspect because of the arbitrary initial conditions. Since it is not a simple matter to correct this problem, we have chosen simply to ignore variations in dissolved calcium and magnesium. Sensitivity studies are presented in section III to illustrate the possible effect on our results.

Our method of estimating the calcite deposition flux into sediments ($F_{calcite} = I_{carb} - \xi$ in our model) is entirely different from the procedure adopted by BLAG. In their model, $F_{calcite}$ was computed from an expression based on the equilibrium reaction

$$CaCO_3 + CO_2 + H_2O \rightarrow Ca^{++} + 2\,HCO_3^-$$

(see BLAG, eq 47). The values of the "effective" equilibrium constant K_{eq} and a kinetic rate constant k_{prep} were adjusted so as to make their model

respond in a reasonable manner. The partitioning of carbon dioxide between the atmosphere and ocean was also computed using an "effective" equilibrium constant in the BLAG model. While clever, their approach does not account for the role that shelled organisms play in calcite deposition nor does it identify the important distinction between supersaturated surface waters and the undersaturated deep ocean.

By contrast, the KB approach we use in our model explicitly considers the downward flux of inorganic (carbonate) and organic particulate matter associated with dead organisms. Furthermore, the dissolution flux ξ depends upon several physically important variables, including the degree of undersaturation of the deep ocean, the ratio of calcite to aragonite in shells, and the percentage of calcium carbonate in the sediment. This added realism is not without its price, of course: using this model effectively requires that one be able to estimate how all these factors have varied with time. Thus, our model is not necessarily any more informative than the original BLAG model. It does, however, provide a mathematical parameterization of the CO_2 geochemical cycle which is particularly appropriate for investigating the transient response to large amplitude perturbations, such as impact events.

C. *Temperature calculations.*—Surface temperature calculations were performed using the one-dimensional radiative-convective model described by Kasting, Pollack, and Ackerman (1984), and Kasting, Pollack, and Crisp 1982). The parameterization of infrared absorption by CO_2 is based on an empirical fit to laboratory data developed by D. Crisp. Infrared absorption by H_2O is calculated by the method of Rodgers and Walshaw (1966). The model assumes fixed relative humidity, a moist adiabatic lapse rate in the troposphere, and no cloud albedo feedback. It predicts a warming of 2.2°C in response to doubling the concentration of CO_2 in the present atmosphere. Further details are given in the two previous papers by Kasting and others.

III. EQUILIBRIUM RESULTS

A. *Preindustrial ocean.*—The steady-state solution for the preindustrial ocean was obtained by integrating eqs (1) through (4) to equilibrium, under the assumptions that $f_A = f_{SR} = 1$, and $E_{carb} = 0$. The latter assumption is taken from the model of KB; it is based on the observation that the rate of carbonate burial on continental shelves has generally been less than 10 percent of the burial rate in the deep ocean since the close of the Miocene (Milliman, 1974). (This does not appear to be true for the present ocean — see below). The results are shown in figure 2. The predicted atmospheric CO_2 level is 285 ppm, as required by eqs (13) and (18). The corresponding surface temperature T_S is calculated to be 286.7 K using the radiative-convective model. This is about 0.8 K cooler than the surface temperature computed by the same model for a more modern CO_2 level of 330 ppm.

The predicted carbonate ion concentration in the mixed layer is 0.231 mmoles l^{-1}, which is equal to roughly 5 times the saturation concentra-

tion of $CO_3^=$ in surface waters ($[CO_3^=]_m^{eq}$ = 0.047 mmoles l^{-1}, Broecker and Peng, 1982). This high degree of supersaturation with respect to $CaCO_3$ reflects the kinetic difficulty in precipitating calcium carbonate and is consistent with observations of the present surface ocean, which show carbonate concentrations between 0.20 and 0.27 mmoles l^{-1} (Broecker and Peng, 1982, figs. 2-10 to 2-13). (We will henceforth use the terms "present ocean" and "preindustrial ocean" interchangeably, since the differences between the two are small compared to that between the present and the Cretaceous oceans.) The carbonate ion concentration in the deep ocean is found to be 0.087 mmoles l^{-1} or about 82 percent of the saturation value at 5 km depth. This value is again fairly representative of modern deep water, which has carbonate concentrations between 0.05 and 0.11 mmoles l^{-1} (Broecker and Peng).

The predicted deep ocean carbonate ion concentration is moderately sensitive to the ratio of calcite to aragonite in the particulate carbon flux from the surface. For our standard model, this ratio has been set equal to unity (that is, the aragonite fraction X_1 equals 0.5). For a low-aragonite

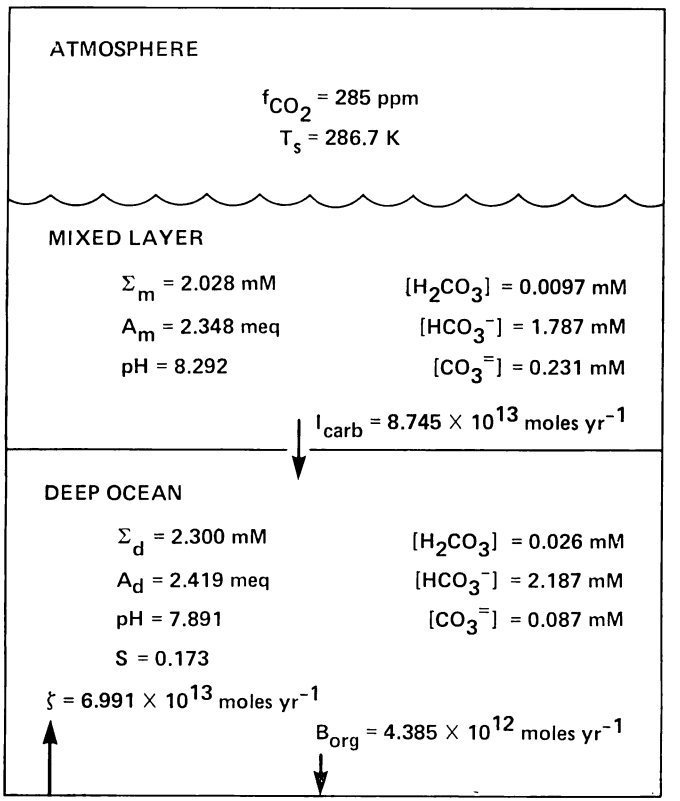

Fig. 2. Steady-state solution for the preindustrial atmosphere/ocean system. The surface temperature T_s is determined from our radiative-convective model.

model such as that of KB ($X_1 = 0.1$), the degree of calcite saturation drops to 76 percent; for a high-aragonite model ($X_1 = 0.75$), it increases to 91 percent. (Predicted species concentrations for these and other cases of interest are given in table 1.) Since the estimated calcite/aragonite ratio in falling particulate matter has undergone extensive revision only recently (Berner, 1977; Betzer and others, 1984; Byrne and others, 1984), the preferred value may well change as new data become available.

Also shown in figure 2 are the magnitudes of the particulate carbonate flux I_{carb} and the calcite dissolution flux ξ. The value of I_{carb} was determined by evaluating eq (11) in KB at time $t = 0$. (This equation provides an estimate for how I_{carb} has varied over the past 120,000 yrs, based on the ^{13}C isotopic record.) The calcite deposition flux ($I_{carb} - \xi$) has a value of 17.54×10^{12} moles yr^{-1}, which is equal to the magnitude of the inorganic carbon source H_{CO_2}, as required by eq (14). The gradients in ΣCO_2 and A between the surface and deep ocean are, of course, caused by the downward particulate fluxes of organic and inorganic carbon.

As indicated above, the assumption that $E_{carb} = 0$ is not valid for the present ocean. Milliman (1974) estimates that deposition of calcite on continental shelves and on reefs currently accounts for about 30 percent of the total $CaCO_3$ burial rate. We investigated the effect of such a change by performing a model experiment with $E_{carb} = 0.3H_{CO_2}$. As shown in table 1, this change causes only slight variations in our results.

B. *Cretaceous ocean.*—According to BLAG, the Cretaceous carbon cycle differed from the present cycle as a result of the smaller amount of continental area exposed to weathering and a faster rate of carbonate metamorphism, as inferred from faster seafloor spreading rates. The change in land surface area over the past 100 my is fairly well-documented (Barron, Sloan, and Harrison, 1980). For our land area correction factor f_A, we chose a typical mid-Cretaceous value of 0.83. Changes in seafloor spreading rates, on the other hand, are more difficult to estimate. The actual spreading rate in the mid- to late Cretaceous was somewhere be-

TABLE 1

Steady-state solutions

Case	Σ_T(mM)	Σ_m(mM)	A_m(meq)	Σ_d(mM)	A_d(meq)	D_m*	D_d**	pH_m
Preindustrial	2.768	2.028	2.348	2.300	2.419	4.91	0.82	8.292
$E_{carb} = 0.3H_{CO_2}$	2.746	2.006	2.322	2.284	2.400	4.82	0.81	8.288
$X_1 = 0.1$	2.718	1.978	2.287	2.250	2.357	4.70	0.76	8.282
$X_1 = 0.75$	2.826	2.086	2.421	2.359	2.491	5.17	0.91	8.303
Cretaceous	8.091	4.392	4.678	4.719	4.722	5.17	0.81	7.954
$2 \times I_{carb}$	9.058	5.359	5.726	6.033	5.927	7.56	0.73	8.036
$0.5 \times I_{carb}$	7.562	3.863	4.051	4.017	4.077	4.04	0.91	7.901
$2 \times \tau_d$	9.287	5.588	5.987	6.242	6.156	8.18	0.81	8.054
$0.5 \times \tau_d$	7.381	3.682	3.850	3.846	3.893	3.69	0.81	7.881
$2 \times Ca^{++}$	7.250	3.551	3.707	3.878	3.791	6.88	0.81	7.865
$0.5 \times Ca^{++}$	9.131	5.433	5.810	5.760	5.895	3.88	0.81	8.042
$E_{carb} = 0.5H_{CO_2}$	8.007	4.309	4.545	4.646	4.645	4.99	0.79	7.946
$E_{carb} = 0.9H_{CO_2}$	7.885	4.186	4.408	4.531	4.521	4.72	0.73	7.934

* $D_m = [CO_3^=]_m/[CO_3^=]_m^{eq} = [CO_3^=]_m/0.047$ mmoles l^{-1}

** $D_d = [CO_3^=]_d/[CO_3^=]_d^{eq} = [CO_3^=]_d/0.1055$ mmoles l^{-1}

tween 1 and 2 times the present rate (BLAG, fig. 4). We shall arbitrarily assume that $f_{SR} = 1.2$. This choice of f_{SR} and f_A corresponds to the parameters used by Kasting (1984) in his steady-state analysis of the BLAG model. As shown by eq (18), the physically most important quantity is actually the ratio f_{SR}/f_A, which in this case is equal to about 1.45. By the late Cretaceous this ratio may have decreased to about 1.25 (BLAG), in which case the prevailing CO_2 level at the time of the dinosaur extinctions would have been about half that assumed here.

The steady-state "Cretaceous" ocean which the model predicts given these correction factors is shown in figure 3. To facilitate comparison with the modern ocean, the shelf burial term E_{carb} has again been set equal to zero. (In reality, shelf burial of carbonates was probably important during the Cretaceous; however, the effect of shelf burial on our numerical results is relatively minor.) The predicted atmospheric CO_2 concentration is 1424 ppm, which is 5 times the preindustrial level, or 4.2 times the present CO_2 level. The corresponding mean surface temperature is 292.0 K or 4 degrees warmer than at present. The surface ocean is slightly more acidic than the present ocean (pH 7.95 versus 8.29 at present), but the

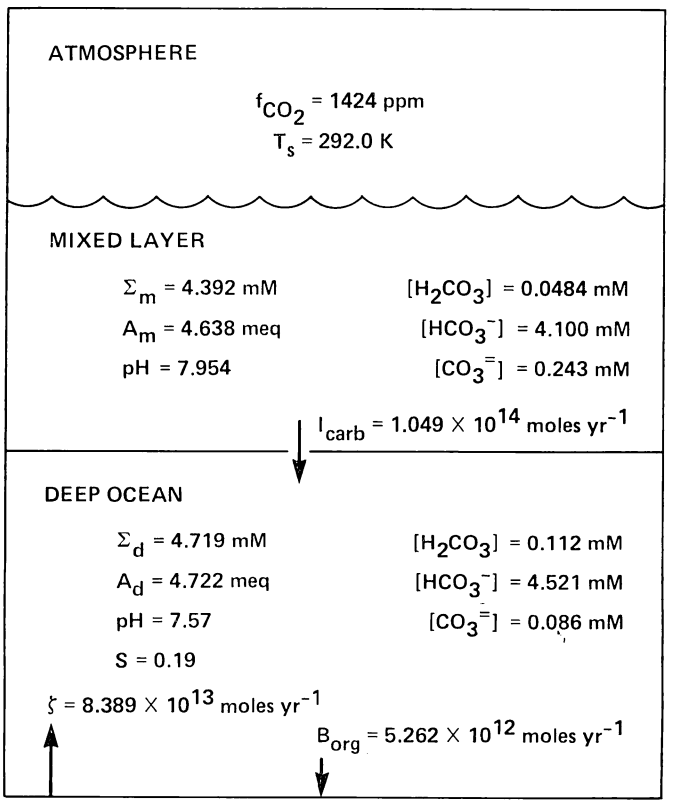

Fig. 3. Steady-state solution for the Cretaceous atmosphere/ocean system.

carbonate ion concentration (0.24 mmoles l^{-1}) is very nearly the same. The bicarbonate ion concentration, on the other hand, is higher than in the present ocean by roughly a factor of two. The carbonate ion concentration in deep water is almost identical to that in the present ocean, reflecting the relatively small change in the ratio of ξ/I_{carb} (see eq 12) and the strong dependence of ξ on S (see eqs 9 and 11).

The steady-state solution shown in figure 3 is, at best, only crudely representative of what the actual Cretaceous ocean may have been like. Its greatest merit is that the atmospheric CO_2 concentration it predicts (4.2 PAL) falls within the range of concentrations (4-6 PAL) required to explain the warm Cretaceous climate (Barron and Washington, 1985). Other factors besides f_A and f_{SR} could have varied in the past without changing the atmospheric CO_2 level (see eq 18). Frequent anoxic episodes in the deep ocean, marked by black shale deposition, imply either a longer turnover time for deep water during the Cretaceous or an enhanced rate of primary productivity in the surface ocean (Southam, Peterson, and Brass, 1982). Changes in oceanic mixing times could be related to the difficulty in forming deep water in the relatively warm polar regions of that time (Bralower and Thierstein, 1984). The rate of burial of carbonate sediments and organic matter on continental shelves or in inland seas could have been greater than at present because of widespread marine transgressions (Barron, Sloan, and Harrison, 1980). The dissolved Ca^{++} ion concentration could have varied because of changes in the geochemical cycles of carbon and sulfur (BLAG; Lasaga, Berner, and Garrels, 1985).

To illustrate the effect of such changes on our model, we performed a set of sensitivity studies, the results of which are shown in table 1. Two features of these experiments are worthy of note: First, the degree to which the deep ocean is undersaturated with respect to calcium carbonate remains relatively constant in all cases, a consequence (as mentioned earlier) of the strong dependence of the calcite dissolution flux on the undersaturation factor S. Second, the alkalinity and total inorganic carbon content of the mixed layer remain significantly higher than in the present ocean; this is forced by the need to maintain equilibrium with an atmospheric CO_2 level of 1424 ppm. Both these results have important implications for the cometary impact problem, as discussed in the next section.

IV. EFFECTS OF LARGE IMPACTS

A. *Short-term effects.*—In section I we reviewed the evidence that the surface ocean may have become undersaturated with respect to calcite as a result of an impact event at the end of the Cretaceous, some 65 my ago. The dissolution event should have been relatively short-lived (~20 yrs), if it resulted from an influx of nitric acid or CO_2 to the atmosphere/mixed layer, but it could have been longlived (>10,000 yrs) if caused by mixing with the deep ocean. Let us consider first the shorter time-scale phenomena. Lewis and others (1982) have analyzed the effects of an influx of nitric acid, and we shall follow their approach here. According to their

estimate, the amount of NO_x created by the (hypothetical) K/T impact could have ranged from $10^{36.1}$ NO molecules for a high-density, low-impact velocity, 10^{17} gm metallic asteroid to $10^{41.6}$ NO molecules for a low-density, high-impact velocity, 10^{19} gm ice-rich comet. (Both these events would bring in sufficient iridium to explain the observed Ir anomaly.) Their lower limit is probably too conservative, since it assumes that only 0.1 percent of the impact energy is transferred to the atmosphere. O'Keefe and Ahrens (1982) have estimated that as much as 40 percent of the impact energy would be transferred to the atmosphere, mostly through the interaction with small particles of molten ejecta. The upper limit of Lewis and others assumes a 10 percent atmospheric coupling efficiency and is therefore more realistic. Since only about one-tenth this many NO molecules are needed to produce a significant decrease in surface water pH, it is clear that this mechanism deserves serious consideration.

The NO synthesized during the impact would be oxidized rapidly to NO_2 (Lewis and others, 1982) and would dissolve in rainwater and surface waters following the reactions (Lee and Schwartz, 1981; Kasting and Ackerman, 1985)

$$NO_2(g) + NO_2(g) + H_2O(l) \longleftrightarrow NO_2^- + NO_3^- + 2\,H^+ \qquad (R2)$$

$$NO_2(g) + NO(g) + H_2O(l) \longleftrightarrow 2\,NO_2^- + 2\,H^+ \ . \qquad (R3)$$

The effect on the surface ocean would be equivalent to that of adding HNO_3: the alkalinity would decrease, causing corresponding decreases in pH and $[CO_3^=]$, and releasing gaseous CO_2 into the atmosphere.

We have simulated such an addition of nitric acid by using the numerical apparatus described in section II, modified to assume a mixed layer depth of 75 m, similar to that assumed by Lewis and others (1982). This shallower depth is more appropriate for this simulation than the 200 m value used previously, since it is the depth over which rapid mixing occurs. The effect of adding HNO_3 to our "preindustrial" ocean is shown in figure 4,A and B. (These are similar to figs. 4 and 5 of Lewis and others, 1982, except that the horizontal scale has been reversed). Each increment of 10^{40} HNO_3 molecules lowers A_m by 0.63 meq. As A_m decreases from 2.3 meq to 0.4 meq, the pH of the surface ocean drops from 8.3 to 7.4, and the atmospheric CO_2 mixing ratio f_{CO_2} rises from 285 to 510 ppm (fig. 4A). At the same time, the calcite saturation factor ($[CO_3^=]_m/[CO_3^=]_m^{eq}$) falls from 4.9 to 0.16 (fig. 4B). The number of HNO_3 molecules required to achieve a saturation factor of unity is about 2×10^{40}, in agreement with the prediction of Lewis and others (1982). Addition of more than this amount of nitric acid could make surface waters uninhabitable by calcareous organisms for as long as 20 yrs (the time required to mix with the deep ocean).

When this experiment is performed on our "Cretaceous" ocean, the results are qualitatively similar, but about twice as much HNO_3 must be added to produce the same effect (fig. 5A and B). The higher alkalinity of the Cretaceous model ocean gives it a greater buffering capacity, there-

by reducing the likelihood that the surface ocean could have become undersaturated with respect to calcite. The amount of HNO_3 required in this case is still within the upper limit estimated by Lewis and others (1982). Since the actual quantity of nitrogen oxides synthesized by the K/T impact may have been smaller than this, however, it is worthwhile to look for ways by which the required acid input might be reduced.

Some of the modified Cretaceous solutions (see table 1) have a lower surface alkalinity and would therefore be less strongly buffered. For ex-

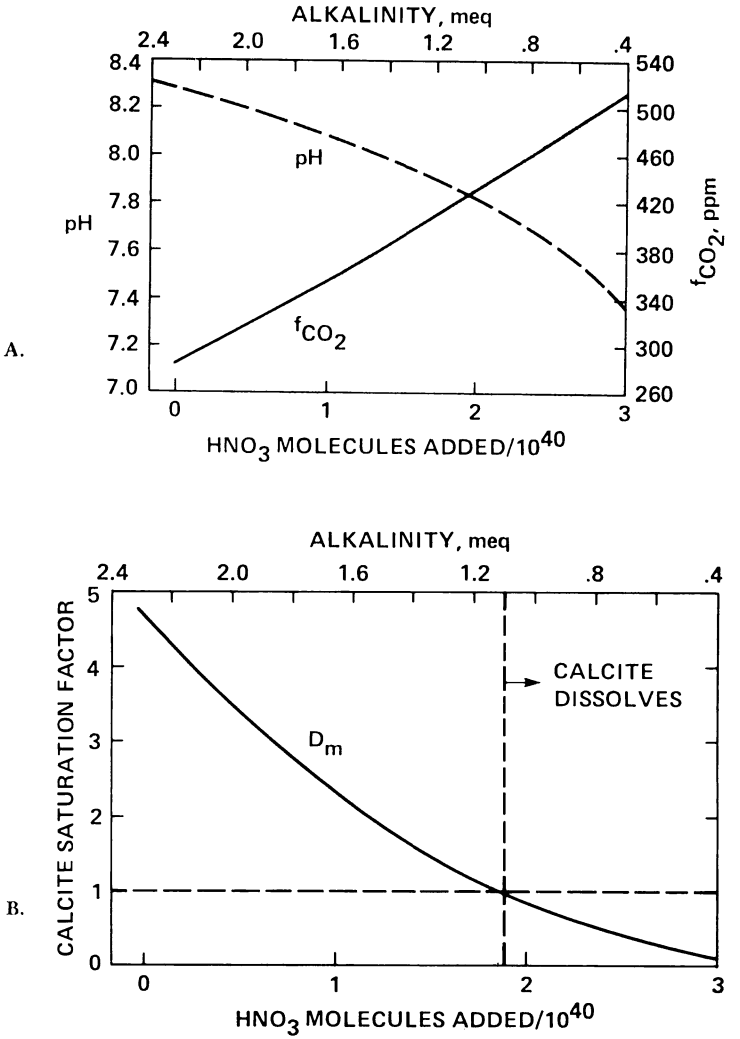

Fig. 4. Changes induced in the preindustrial surface ocean by the addition of HNO_3. The assumed depth of the mixed layer is 75 m. (A) Changes in CO_2 mixing ratio and in pH. (B) Change in the solubility of calcite.

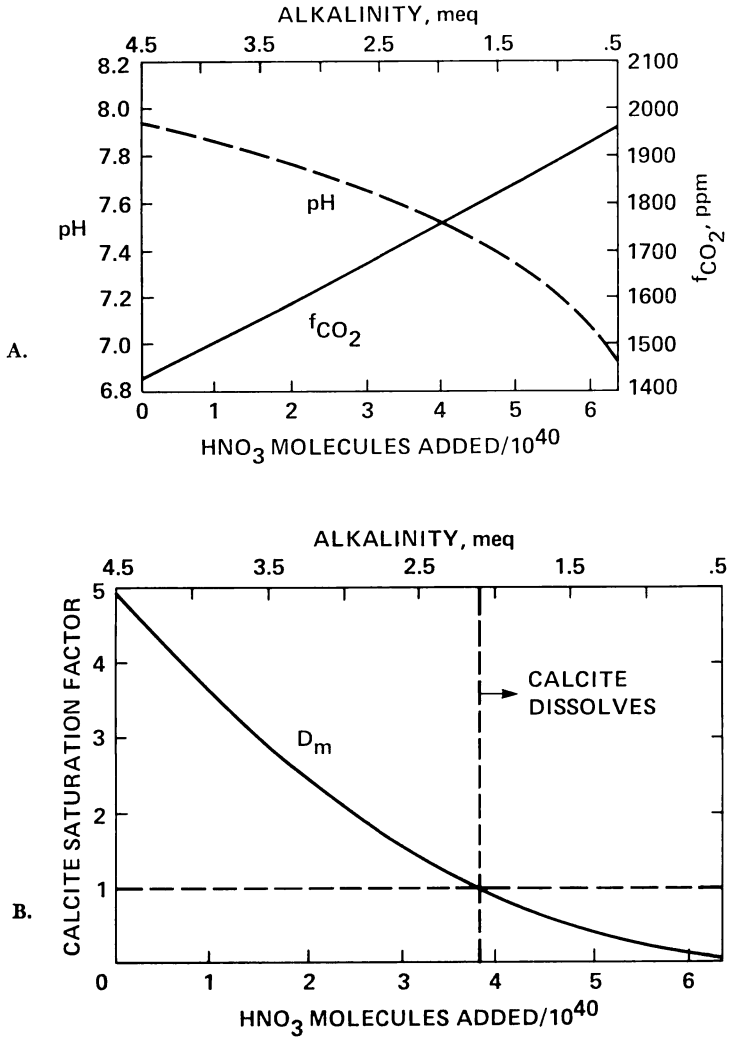

Fig. 5. Same as figure 4 for the Cretaceous surface ocean.

ample, the "$0.5 \times \tau_d$" case (for which $A_m \cong 3.8$) requires about 30 percent less HNO_3 to become undersaturated. This particular case, however, represents exactly the opposite of what is thought to have been true of Cretaceous mixing rates (Bralower and Thierstein, 1984); thus, an additional physical mechanism for lowering the pH may be needed. One promising possibility is that of a concurrent injection of CO_2 into the atmosphere and mixed layer. As discussed in section I, the most likely sources of CO_2 are the comet itself, the biosphere, and the deep ocean. Let us start off by considering the first two of these sources.

The amount of CO_2 in our preindustrial atmosphere is about 4.9×10^{16} moles, corresponding to 5.9×10^{17} gm(C). The total amount of dissolved inorganic carbon in the uppermost 75 m of the ocean is roughly the same. The impact of a 10^{19} gm comet containing 5 percent carbon by weight could (after oxidation) yield an amount of CO_2 equal to that present in the atmosphere, which would increase Σ_T (for the 75 m mixed layer) by about 50 percent. This CO_2 injection would be virtually instantaneous, since the carbonaceous component of the comet would presumably react rapidly with atmospheric oxygen.

The amount of CO_2 that could be derived from the biosphere can be estimated from the carbon cycle data given by Holland (1978, p. 262). The living biosphere contains 4.5×10^{17} gm(C) on the land and 7×10^{15} gm(C) in the oceans. The marine component is negligible, but the carbon content of the terrestrial biomass is comparable to that of the atmosphere. This carbon is returned to the atmosphere by decay and oxidation at a rate of 2.3×10^{16} gm(C) yr^{-1}; thus, the entire biosphere would be converted to CO_2 in about 20 yrs were decay not balanced by photosynthesis. If terrestrial vegetation were largely killed off by the effects of the impact, its breakdown could release an amount of CO_2 equal to that in the atmosphere over a time interval comparable to the mixing time of the surface ocean.

Another potential source of biospheric CO_2 is the oxidation of dead terrestrial and marine organic matter (Hsu and others, 1982a). These reservoirs contain 7×10^{17} gm(C) and 3×10^{18} gm(C), respectively, and are currently oxidized at a combined rate of 5.5×10^{16} gm(C) yr^{-1}. If production of new organic material were to cease, these additional fluxes could roughly triple the rate at which CO_2 was added to the atmosphere and surface ocean.

The effects of adding CO_2 to the atmosphere/mixed layer can be illustrated by the same type of diagrams shown for HNO_3. The results for the preindustrial ocean are shown in figure 6,A and B. The units on the horizontal axis represent the amount of CO_2 present in the steady-state preindustrial atmosphere (that is, 285 ppm or 5.9×10^{17} gm(C)). An injection of twice this much CO_2 would lower the surface pH from 8.3 to 7.8 (fig. 6A) and would reduce the calcite saturation factor to a value of approx 2 (fig. 6B). This would reduce the input of HNO_3 required to achieve undersaturation by about 30 percent. It seems unlikely that the addition of CO_2 could by itself produce undersaturation, since more than 6 times the amount of CO_2 in the modern atmosphere would be required to accomplish this (fig. 6B).

The effect of adding CO_2 to the Cretaceous atmosphere and surface ocean is less dramatic (fig. 7,A and B) because of the much larger amount of CO_2 already present. As in the case of the nitric acid injection, the Cretaceous ocean is better buffered against changes in pH or in $[CO_3^=]$. To get a large effect in this case, one must look for CO_2 sources other than the two that have been considered thus far.

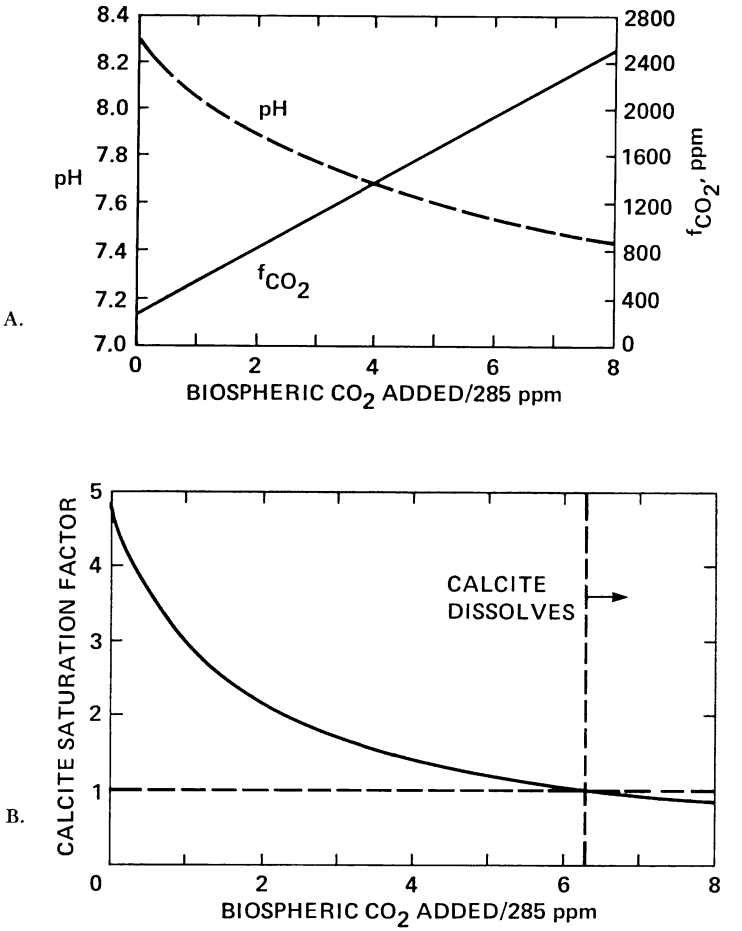

Fig. 6. Changes induced in the preindustrial surface ocean by the addition of CO_2. The units on the horizontal scale represent the amount of CO_2 present in the preindustrial atmosphere (285 ppm, or 4.9×16^{16} molcs). (A) Changes in CO_2 mixing ratio and in pH. (B) Change in the solubility of calcite.

An additional potential source of CO_2 is the deep ocean. Deep water is known to be enriched in dissolved CO_2 as a result of the downward fluxes of calcite and organic matter from the surface (section I). Deep water brought to the surface "isochemically" (that is, undergoing no reactions with external material during the process) would be in equilibrium with a pCO_2 level about three times higher than the present value (Broecker and Peng, 1982). Thus, if all life in the oceans were to die off suddenly (Broecker's "Strangelove" scenario), and if sufficient time were allowed for the deep ocean to mix upward and to equilibrate with the atmosphere, the CO_2 partial pressure would approximately triple. Normally, about 1000 yrs would be required for the deep ocean to overturn and

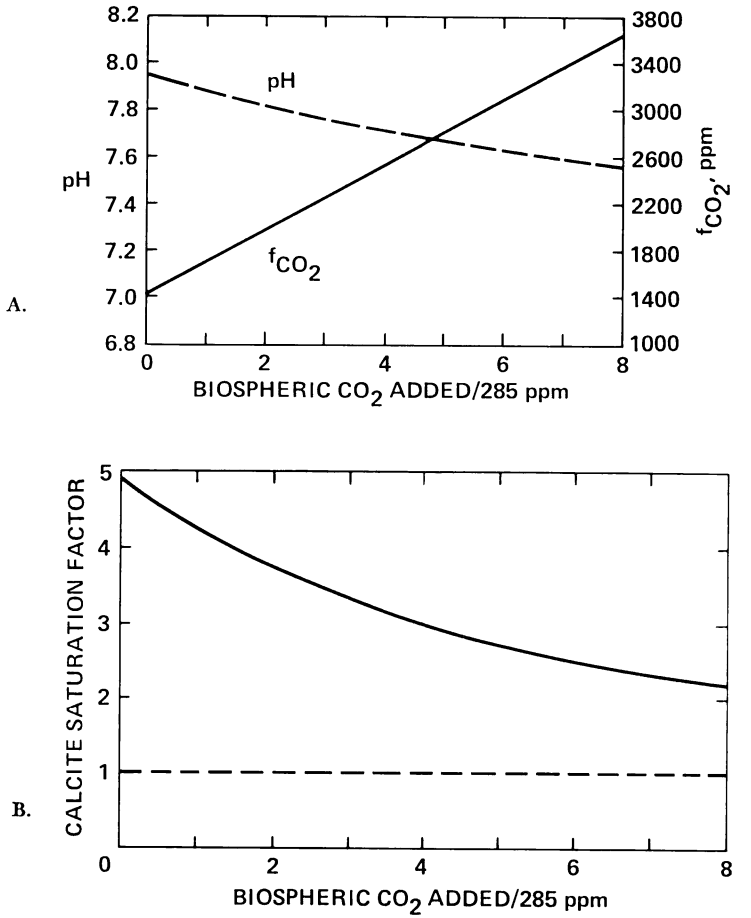

Fig. 7. Same as figure 6 for the Cretaceous surface ocean.

release its CO_2, but the mixing process could conceivably have been greatly accelerated by mechanical stirring provided by the impacting bolide (Gault and Sonett, 1982) and by continued upwelling of water around the hot impact site (Hsu, 1980).

The effect of ocean mixing is different from that of simply adding CO_2, because deep water differs from surface water in both its total carbon content and its alkalinity. One can illustrate this effect by calculating "homogenized" values for Σ and A and then using the model to derive new values for pCO_2 and for the concentrations of dissolved carbonate species. The result of performing this calculation for the preindustrial ocean is shown in figure 8. The CO_2 mixing ratio increases from 285 to 843 ppm; this change would produce a 3.6 degree rise in surface temperature according to our 1-D climate model. The carbonate ion concentration

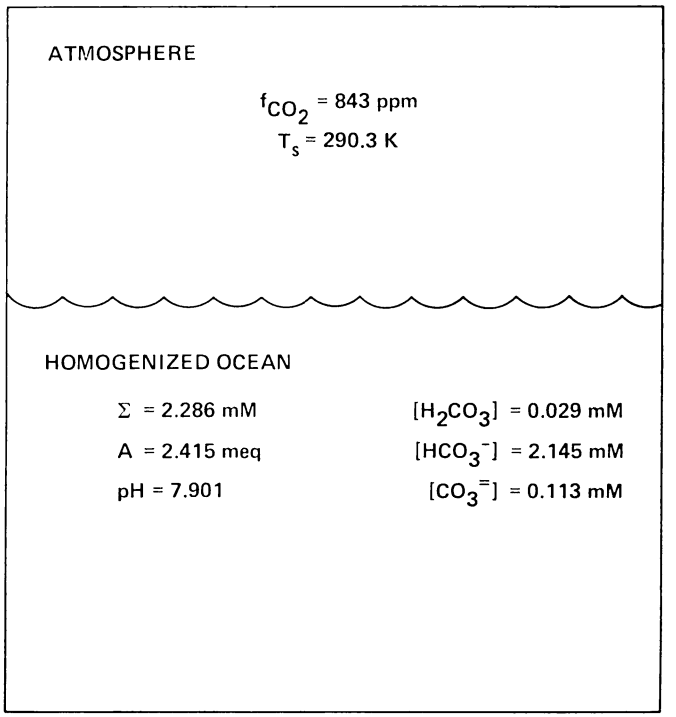

Fig. 8. Steady-state solution obtained by allowing the preindustrial surface and deep oceans to mix thoroughly and to equilibrate with the atmosphere.

in surface water would decrease from 0.23 mmoles l^{-1} to 0.11 mmoles l^{-1}, leaving the surface ocean still supersaturated with respect to calcite by a factor of about two.

The effect of homogenizing our Cretaceous ocean model is quite similar (fig. 9). The CO_2 level jumps from 1424 to 3571 ppm (again corresponding to a 3.6 K temperature increase), and $[CO_3^=]$ drops from 0.243 mmoles l^{-1} to 0.115 mmoles l^{-1}. The temperature increase is consistent with the observed decrease in $\delta^{18}O$ 5 cm above the K/T boundary (Hsu and others, 1982a,b) and is of interest because of the possibility that heat may have played a role in the extinction of the dinosaurs (Emiliani, Kraus, and Shoemaker, 1981). However, neither this model nor any of the modified Cretaceous models listed in table 1 yield an undersaturated surface ocean when subjected to this procedure. The reason is the strong dependence of the calcite dissolution flux on S, which precludes any large variations in the degree of saturation of the deep ocean (see section III). Aragonite, which is 1.6 times more soluble than calcite (Broecker and Peng, 1982) would be closer to its saturation limit, but the extinction of aragonitic organisms could not by itself account for the almost complete disappearance of calcium carbonate from marine sediments. Thus, we are forced to abandon the idea that upward mixing of deep water was the

primary cause of extinctions of calcareous organisms. Apparently, this mechanism could only work in conjunction with other short-term additions of acid as described above.

We conclude that the impact of a large bolide at the end of the Cretaceous could have resulted in a relatively short-lived dissolution event, which might help to explain the catastrophic extinction of calcareous plankton. This hypothesis cannot be discounted by the argument of Thierstein (1982), who concluded that a CO_2-induced dissolution event could be ruled out because of the observed improvement in the degree of preservation of calcareous nanofossils above the boundary. His argument is only applicable to perturbations affecting the deep ocean, which would have been largely unaffected by the surface ocean changes discussed here.

B. *Long-term effects*—Although our model is capable of simulating possible short-term perturbations to the marine carbon cycle, it fails to explain the observed 15,000 to 30,000 yr hiatus in the burial rate of calcium carbonate (sec. I). Any pH excursions caused by the addition of nitric acid or biospheric CO_2 would vanish in 20 yrs or less, as acidic surface water was replaced with deep water from below. Only changes resulting from ocean mixing itself could conceivably have lasted for more than this relatively short period of time. Since such changes would apparently have

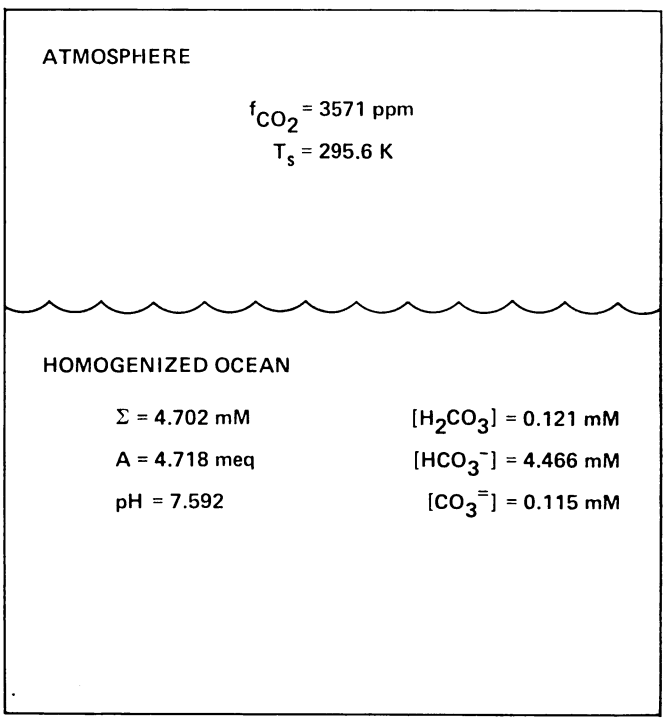

Fig. 9. Same as figure 8 for the Cretaceous ocean.

been insufficient to dissolve calcite (see above), it seems likely that the long recovery time for calcareous plankton was caused by biological difficulties in repopulating the surface ocean, rather than by a prolonged deterioration of the physical environment. This conclusion is dissatisfying, because the doubling time for plankton is typically only a few months (see sec. I). Furthermore, we continue to find it very suggestive that the amount of time required for the calcareous organisms to reestablish themselves is just what one would expect if the surface ocean had remained undersaturated for an extended period, and if the mechanism that eventually restored the stability of calcite was the slow-acting rock cycle. Given the complexity of the system we have attempted to model, it is possible that we have overlooked something that would make this type of long-lived dissolution event appear more tractable. We hope that our work will stimulate further interest in studying impact-induced perturbations to the CO_2 cycle.

References

Alvarez, L. W., Alvarez, W., Asaro, F., and Michel, H. V., 1980, Extraterrestrial cause for the Cretaceous-Tertiary extinction: Science, v. 208, p. 1095-1108.

Barron, E. J., Sloan, J. L. II, and Harrison, C. G. A., 1980, Potential significance of land-sea distribution and surface albedo variations as a climatic forcing factor: 180 my to the present: Paleography, Paleoclimatology, Paleoecology, v. 30, p. 17-40.

Barron, E. J., and Washington, W. M., 1985, Warm Cretaceous climates: High atmospheric CO_2 as a plausible mechanism, *in* Sundquist, E. T. and Broecker, W. S., eds., The Carbon Cycle and Atmospheric CO_2: Natural Variations Archean to Present: Am. Geophys. Union, Geophys. Mon. Ser., v. 32, p. 546-553.

Berner, R. A., 1977, Sedimentation and dissolution of pteropods in the ocean, *in* Andersen, N. R. and Malahoff, A., eds., The Fate of Fossil Fuel CO_2 in the Oceans: New York, Plenum Publishing Corp., p. 243-260.

Berner, R. A., Lasaga, A. C., and Garrels, R. M., 1983, The carbonate-silicate geochemical cycle and its effect on atmospheric carbon dioxide over the past 100 million years: Am. Jour. Sci., v. 283, p. 641-683.

Berner, W., Oeschger, H., and Stauffer, B., 1980, Information on the CO_2 cycle from ice core studies: Radiocarbon, v. 22, p. 227-235.

Berner, W., Stauffer, B., and Oeschger, H., 1979, Past atmospheric composition and climate: Gas parameters measured on ice cores: Nature, v. 275, p. 53-55.

Betzer, P. R., Byrne, R. H., Acker, J. G., Lewis, C. S., Jolley, R. R., and Feely, R. A., 1984, The oceanic carbonate system: A reassessment of biogenic controls: Science, v. 226, p. 1074-1077.

Bohor, B. F., Foord, E. E., Modreski, P. J., and Triplehorn, D. M., 1984, Mineralogic evidence for an impact event at the Cretaceous-Tertiary boundary: Science, v. 224, p. 867-869.

Bralower, T. J., and Thierstein, H. R., 1984, Low productivity and slow deep water circulation in mid-Cretaceous oceans: Geology, v. 12, p. 614-618.

Bramlette, M. N., and Martini, E., 1964, The great change in calcareous nannoplankton fossils between Maastrichtian and Danian: Micropaleontology, v. 10, p. 291-322.

Broecker, W. S., 1982, Glacial to interglacial changes in ocean chemistry: Prog. Oceanography, v. 11, p. 151-197.

Broecker, W. S., and Peng, T. H., 1982, Tracers in the Sea: Palisades, N.Y. Eldigio Press (Lamont-Doherty Geol. Obs.), 690 p.

Brooks, R. R., Reeves, R. D., Yang, X., Ryan, D. E., Holzbecher, J., Collen, J. D., Neall, V. E., and Lee, J., 1984, Elemental anomalies at the Cretaceous-Tertiary boundary, Woodside Creek, New Zealand: Science, v. 226, p. 539-542.

Budyko, M. I., and Ronov, A. B., 1979, Chemical evolution of the atmosphere in the Phanerozoic: Geochemistry Internat., p. 1-9.

Byrne, R. H., Acker, J. G., Betzer, P. R., Feely, R. A., and Cates, M. H., 1984, Water column dissolution of aragonite in the Pacific Ocean: Nature, v. 312, p. 321-326.

Emiliani, C., Kraus, E. B., and Shoemaker, E. M., 1981, Sudden death at the end of the Mesozoic: Earth Planetary Sci. Letters, v. 55, p. 318-334.

Fischer, A. G., 1984, The two Phanerozoic supercycles, *in* Berggren, W. A., and van Couvering, J., eds., Catastrophes and Earth History: The New Uniformitarianism: Princeton, N.J., Princeton Univ. Press, p. 129-150.

Frakes, L. A., 1979, Climates Throughout Geologic Time: New York, Elsevier Pub. Co., 375 p.

Ganapathy, R. A., 1980, Major meteorite impact on the earth 65 million years ago: Evidence from the Cretaceous-Tertiary boundary clay: Science, v. 209, p. 921-923.

Gault, D. E., and Sonett, C. P., 1982, Laboratory simulation of pelagic asteroidal impact: Atmospheric injection, benthic topography, and the surface wave radiation field, *in* Silver, L. T. and Schultz, P. H., eds., Geological Implications of Impacts of Large Asteroids and Comets on the Earth: Geol. Soc. America Spec. Paper 190, p. 69-92.

Gear, C. W., 1971, Numerical Initial Value Problems in Ordinary Differential Equations: Englewood Cliffs, N.J., Prentice-Hall, Inc., 253 p.

Harmon, R. S., White, W. B., Drake, J. J., and Hess, J. W., 1975, Regional hydrochemistry of North America carbonate terrains: Water Resources Research, v. 11, p. 963-967.

Holland, H. D., 1978, The Chemistry of the Atmosphere and Oceans: New York, Wiley Intersci., 351 p.

Hsu, K. J., 1980, Terrestrial catastrophe caused by cometary impact at the end of the Cretaceous: Nature, v. 285, p. 201-203.

———— 1985, Strangelove ocean at the beginning of the Tertiary, *in* Sundquist, E. T. and Broecker, W. S., eds., The Carbon Cycle and Atmospheric CO_2: Natural Variations Archean to Present: Am. Geophys. Union, Geophys. Mon. Ser., v. 32, p. 487-492.

Hsu, K. J., He, Q., McKenzie, J. A., Weissert, H., Perch-Nielson, K., Oberhansli, H., Kelts, K., LeBrecque, J., Tauxe, L., Krahenbuhl, U., Percival, S. F. Jr., Wright, R., Karpoff, A. M., Petersen, N., Tucker, P., Poore, R. Z., Gombos, A. M., Pisciotto, K., Carman, M. F. Jr., and Schreiber, E., 1982a, Mass mortality and its environmental and evolutionary consequences: Science, v. 216, p. 249-256.

Hsu, K. J., McKenzie, J. A., and He, Q. X., 1982b, Terminal Cretaceous environmental and evolutionary changes, *in* Silver, L. T. and Schultz, P. H., eds., Geological Implications of Impacts of Large Asteroids and Comets on the Earth: Geol. Soc. America Spec. Paper 190, p. 317-328.

Kasting, J. F., 1984, Comments on the BLAG model: The carbonate-silicate geochemical cycle and its effect on atmospheric carbon dioxide over the past 100 million years: Am. Jour. Sci., v. 284, p. 1175-1182.

Kasting, J. F., and Ackerman, T. P., 1985, High atmospheric NO_x levels and multiple photochemical steady states: Jour. Atmos. Chemistry, in press.

Kasting, J. F., Pollack, J. B., and Ackerman, T. P., 1984a, Response of Earth's atmosphere to increases in solar flux and implications for loss of water from Venus: Icarus, v. 57, p. 335-355.

Kasting, J. F., Pollack, J. B., and Crisp, D., 1984b, Effects of high CO_2 levels on surface temperature and atmospheric oxidation state on the early earth: Jour. Atmos. Chemistry, v. 1, p. 403-428.

Keir, R. S., and Berger, W. H., 1983, Atmospheric CO_2 content in the last 120,000 years: The phosphate-extraction model: Jour. Geophys. Research, v. 88, p. 6027-6038.

———— 1985, Late Holocene carbonate dissolution in the equatorial Pacific: Reef growth or neoglaciation?, *in* Sundquist, E. T. and Broecker, W. S., eds.: The Carbon Cycle and Atmospheric CO_2: Natural Variations Archean to Present: Am. Geophys. Union, Geophys. Mon. Ser., v. 32, p. 208-220.

Knox, F., and McElroy, M. B., 1985, Changes in atmospheric CO_2: Influence of the marine biota at high latitudes, *in* Sundquist, E. T. and Broecker, W. S., eds.: The Carbon Cycle and Atmospheric CO_2: Natural Variations Archean to Present: Am. Geophys. Union, Geophys. Mon. Ser., v. 32, p. 154-162.

Lasaga, A. C., Berner, R. A., and Garrels, R. M., 1985, An improved model of atmospheric CO_2 fluctuations over the past 100 million years, *in* Sundquist, E. T. and Broecker, W. S., eds., The Carbon Cycle and Atmospheric CO_2: Natural Variations Archean to Present: Am. Geophys. Union, Geophys. Mon. Ser., v. 32, p. 397-411.

Lee, Y.-N., and Schwartz, S. E., 1981, Evaluation of the rate of uptake of nitrogen dioxide by atmospheric and surface liquid water: Jour. Geophys. Research, v. 86, p. 11971-11983.

Lewis, J. S., Watkins, G. H., Hartman, H., and Prinn, R. G., 1982, Chemical consequences of major impact events on Earth, *in* Silver, L. T. and Schultz, P. H., eds., Geological Implications of Impacts of Large Asteroids and Comets on the Earth: Geol. Soc. America Spec. Paper 190, p. 215-221.

Luck, J. M., and Turekian, K. K., 1983, Osmium-187/Osmium-186 in manganese nodules and the Cretaceous-Tertiary boundary: Science, v. 222, p. 613-615.

Mackenzie, F. T., and Pigotte, J. P., 1981, Tectonic controls of Phanerozoic sedimentary rock cycling: Geol. Soc. (London) Jour., v. 138, p. 183-191.

Manabe, S., and Stouffer, R. J., 1980, Sensitivity of a global climate model to an increase in CO_2 concentration in the atmosphere: Jour. Geophys. Research, v. 85, p. 5529-5554.

McLean, D. M., 1978, A terminal Mesozoic "greenhouse": Lessons from the past: Science, v. 201, p. 401-406.

Milliman, J. D., 1974, Marine Carbonates: New York, Springer-Verlag, 375 p.

Milne, D. H., and McKay, C. P., 1982, Response of marine plankton communities to a global atmospheric darkening, *in* Silver, L. T. and Schultz, P. H., eds., Geological Implications of Impacts of Large Asteroids and Comets on the Earth: Geol. Soc. America Spec. Paper 190, p. 297-303.

Oeschger, H., Stauffer, B., Kinkel, R., and Langway, C. C. Jr., 1985, Variations of the CO_2 concentration of occluded air and of anions and dust in polar ice cores, *in* Sundquist, E. T. and Broecker, W. S., eds., The Carbon Cycle and Atmospheric CO_2: Natural Variations Archean to Present: Am. Geophys. Union, Geophys. Mon. Ser., v. 32, p. 132-142.

O'Keefe, J. D., and Ahrens, T. J., 1982, The interaction of the Cretaceous/Tertiary Extinction Bolide with the atmosphere, ocean, and solid Earth, *in* Silver, L. T. and Schultz, P. H., eds., Geological Implications of Impacts of Large Asteroids and Comets on the Earth: Geol. Soc. America Spec. Paper 190, p. 103-120.

Oorth, C. J., Gilmore, J. S., Knight, J. D., Pillmore, C. L., Tschudy, R. H., and Fassett, J. E., 1981, An iridium abundance anomaly at the palynological Cretaceous-Tertiary boundary in northern New Mexico: Science, v. 214, p. 1341-1343.

———— 1982, Iridium abundance measurements across the Cretaceous/Tertiary boundary in the San Juan and Raton basins of northern New Mexico, *in* Silver, L. T. and Schultz, P. H., eds., Geological Implications of Impacts of Large Asteroids and Comets on the Earth: Geol. Soc. America Spec. Paper 190, p. 423-433.

Perch-Nielson, K., McKenzie, J., and He, Q., 1982, Biostratigraphy and isotope stratigraphy and the 'catastrophic' extinction of calcareous nannoplankton at the Cretaceous/Tertiary boundary, *in* Silver, L. T. and Schultz, P. H., eds., Geological Implications of Impacts of Large Asteroids and Comets on the Earth: Geol. Soc. America Spec. Paper 190, p. 353-371.

Pollack, J. B., Toon, O. B., Ackerman, T. P., McKay, C. P., and Turco, R. P., 1983, Environmental effects of an impact-generated dust cloud: Implications for the Cretaceous-Tertiary extinctions: Science, v. 219, p. 287-289.

Pitman, W. C., 1978, Relationship between eustacy and stratigraphic sequences of passive margins: Geol. Soc. America Bull., v. 89, p. 1289-1403.

Rodgers, C. D., and Walshaw, C. D., 1966, The computation of infra-red cooling rate in planetary atmospheres: Royal Meteorol. Soc. Quart. Jour., v. 92, p. 67-92.

Schidlowski, M., Eichmann, R., and Junge, C. E., 1975, Precambrian sedimentary carbonates: Carbon and oxygen isotope geochemistry and implications for the terrestrial oxygen budget: Precambrian Research, v. 2, p. 1-69.

Smit, J., 1982, Extinction and evolution of planktonic foraminifera after a major impact at the Cretaceous/Tertiary boundary, *in* Silver, L. T. and Schultz, P. H., eds., Geological Implications of Impacts of Large Asteroids and Comets on the Earth: Geol. Soc. America Spec. Paper 190, p. 329-352.

Smit, J., and Hertogen, J., 1980, An extraterrestrial event at the Cretaceous Tertiary boundary: Nature, v. 285, p. 198-200.

Smit, J., and Klaver, G., 1981, Sanidine spherules at the Cretaceous-Tertiary boundary indicate a large impact event: Nature, v. 292, p. 47-49.

Smit, J., and ten Kate, W. G. H. Z., 1982, Trace element patterns at the Cretaceous-Tertiary boundary: Consequences of a large impact: Cretaceous Research, v. 3, p. 307-332.

Southham, J. R., and Hay, W. W., 1977, Time scales and dynamic models of deep sea sedimentation: Jour. Geophys. Research, v. 82, p. 3825-3842.

Southam, J. R., Peterson, W. H., and Brass, G. W., 1982, Dynamics of anoxia: Paleogeography, Paleoclimatology, Paleoccology, v. 40, p. 183-198.

Tappan, H., 1968, Primary production, isotopes, extinctions, and the atmosphere: Palaeogeography, Palaeoclimatology, Palaeoccology, v. 4, p. 187-210.

Thierstein, H. R., 1981, Late Cretaceous nannoplankton and the change at the Cretaceous-Tertiary boundary, *in* Warme, J. and others (eds): The Deep Sea Drilling Project: A Decade of Progress: Soc. Econ. Paleontologists Mineralogists, Spec. Pub. 32, p. 355-394.

———— 1982, Terminal Cretaceous plankton extinctions: A critical assessment, *in* Silver, L. T. and Schultz, P. H., eds., Geological Implications of Impacts of Large Asteroids and Comets on the Earth: Geol. Soc. America Spec. Paper 190, p. 385-399.

Toon, O. B., Pollack, J. B., Ackerman, T. P., Turco, R. P., McKay, C. P., and Liu, M. S., 1982, Evolution of an impact-generated dust cloud and its effects on the atmosphere, *in* Silver, L. T. and Schultz, P. H., eds., Geological Implications of Impacts of Large Asteroids and Comets on the Earth: Geol. Soc. America Spec. Paper 190, p. 187-200.

Turco, R. P., Toon, O. B., Park, C., Whitten, R. C., Pollack, J. B., and Noerdlinger, P., 1981, Tunguska meteor fall of 1908: Effects on stratospheric ozone: Science, v. 214, p. 19-23.

Worsley, T., 1974, The Cretaceous-Tertiary boundary event in the ocean, *in* Hay, W. W., ed., Studies in Paleo-oceanography: Soc. Econ. Paleontologists Mineralogists, Spec. Pub. 20, p. 94-125.